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# Cross-coupling through Ag(I)/Ag(III) redox manifold

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In memory of Prof. Dr. Kilian Muñoz, a pioneer in high-valent chemistry.

**Abstract:** In ample variety of transformations, the presence of silver as an additive or co-catalyst is believed to be innocuous for the efficiency of the operating metal catalyst. Even though Ag additives are required often as coupling partners, oxidants or halide scavengers, its role as a catalytically competent species is widely neglected in cross-coupling reactions. Most likely, this is due to the erroneously assumed incapacity of Ag to undergo  $2e^\ominus$  redox steps. Definite proof is herein provided for the required elementary steps to accomplish the oxidative trifluoromethylation of arenes through Ag<sup>I</sup>/Ag<sup>III</sup> redox catalysis (*i.e.* CEL coupling), namely: *i*) easy Ag<sup>I</sup>/Ag<sup>III</sup>  $2e^\ominus$  oxidation mediated by air; *ii*) bpy/phen ligation to Ag<sup>III</sup>; *iii*) boron-to-Ag<sup>III</sup> aryl transfer; and *iv*) ulterior reductive elimination of benzotrifluorides from an [aryl Ag<sup>III</sup> CF<sub>3</sub>] fragment. More precisely, an ultimate entry and full characterization of organosilver(III) compounds [K]<sup>+</sup>[Ag<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>]<sup>6-</sup> (**K-1**), [(bpy)Ag<sup>III</sup>(CF<sub>3</sub>)<sub>3</sub>] (**2**) and [(phen)Ag<sup>III</sup>(CF<sub>3</sub>)<sub>3</sub>] (**3**), is described. The

utility of **3** in cross-coupling has been showcased unambiguously, and a large variety of arylboron compounds was trifluoromethylated *via*  $[\text{Ag}^{\text{III}}(\text{aryl})(\text{CF}_3)_3]^{\delta}$  intermediates. This work breaks with old stereotypes and misconceptions regarding the disability of Ag to undergo cross-coupling by itself.

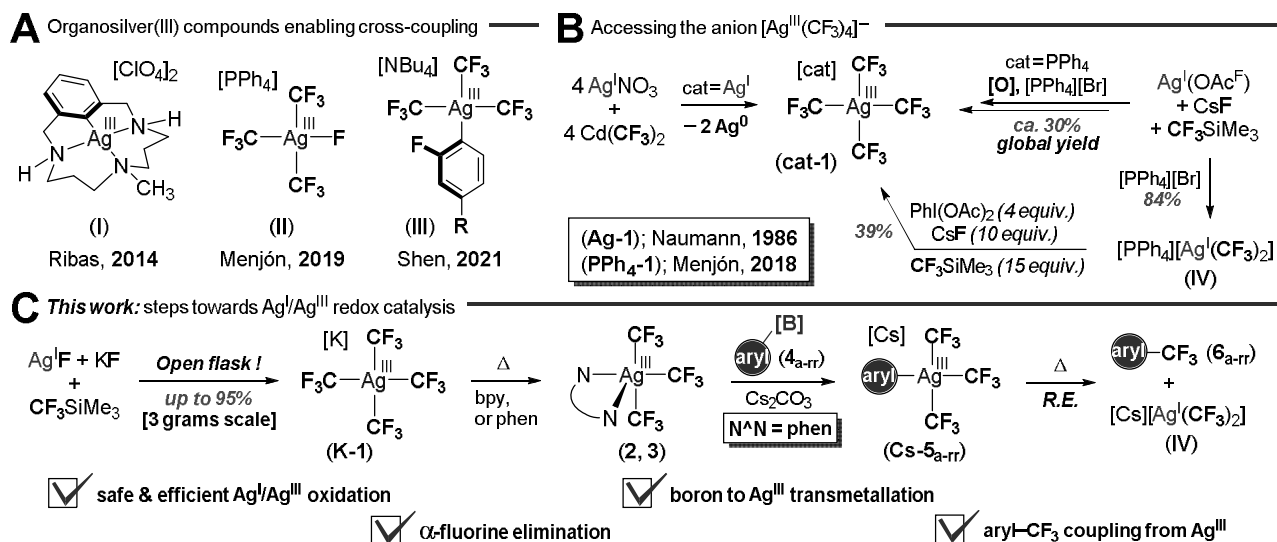
## Introduction

Going down the group often ensures the capturing of key intermediates and helps to decipher how a certain transformation proceeds, whilst the majority of 2<sup>nd</sup> row metals display middle properties between those of their group counterparts. A singular deviation is represented by coinage metals. As reflected by the authentication of organocopper(III) being active in cross-coupling,<sup>[1-3]</sup> or the outstanding discovery of Au<sup>I</sup>/Au<sup>III</sup> redox catalysis,<sup>[4,5]</sup> the uniqueness of copper and gold is steadily flourishing. In turn, the molecular chemistry of silver features a diametrically opposed panoramic, and keeps being governed by: *i*) its role as an halide scavenger, chemical oxidant or transmetallating/coupling partner; *ii*) predominant low oxidation state of +1; and *iii*) weak M L bonding interactions and high propensity to undergo  $1e^{\delta}$  redox transitions, more typical of 3d block elements.<sup>[6]</sup> These drawbacks make silver highly unpredictable, yet simultaneously attractive and challenging. This is the case of Ag<sup>III</sup> chemistry,<sup>[7]</sup> that in opposite to copper and gold, remains scarcely explored in cross-coupling.<sup>[8]</sup> Pioneering work by Ritter, Li, Hartwig and Sarpong allowed for the fluorination of distinct skeletons and pointed to the capital role of elusive Ag<sup>II</sup>F or Ag<sup>III</sup>F compounds.<sup>[9,10]</sup> Most astonishing, organosilver(III) species effecting cross-coupling were authenticated by Ribas,<sup>[11]</sup> Menjón<sup>[12]</sup> and Shen<sup>[13]</sup> who accomplished C C and C heteroatom bond formations nurtured by aryl Ag<sup>III</sup> catalyst **I**,<sup>[11]</sup> or the trifluoromethylation of thiols and arenes enabled by the anions  $[\text{Ag}^{\text{III}}(\text{F})(\text{CF}_3)_3]^{\delta}$  **II**<sup>[12]</sup> and  $[\text{Ag}^{\text{III}}(\text{aryl})(\text{CF}_3)_3]^{\delta}$  **III**,<sup>[13]</sup> respectively (Fig. 1A).<sup>[14]</sup>

From another standpoint, the fluoro-complex **II** is reminiscent of the long-known homoleptic anion  $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  **1**<sup>[15]</sup> that pertains to the intriguing coinage metalate(III) series  $[\text{M}^{\text{III}}(\text{CF}_3)_4]^\ominus$ .<sup>[16-18]</sup> They all show ligand-field inversion<sup>[19]</sup> due to  $\delta$ -non-innocence of the  $\text{CF}_3$  ligands,<sup>[20]</sup> and found applications as: *i*) organometallic synthons for cross-coupling;<sup>[4]</sup> and *ii*) non-coordinating anions in material science.<sup>[21]</sup> The mixed-valence salt  $[\text{Ag}^{\text{I}}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  **Ag-1** was synthesized back in 1986 by Naumann using toxic and potentially explosive  $\text{Cd}(\text{CF}_3)_2$  (Fig. 1B, left).<sup>[15]</sup> At best, and according to the reaction stoichiometry, only a quarter of  $\text{AgNO}_3$  is converted to  $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  **1**. Similar yield was found by Menjón for the two-step synthesis of  $[\text{PPh}_4]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  **PPh<sub>4</sub>-1** through initial formation of  $[\text{PPh}_4]^+[\text{Ag}^{\text{I}}(\text{CF}_3)_2]^\ominus$  **IV** and subsequent  $2e^\ominus$  oxidation using  $\text{PhI}(\text{OAc})_2$  (Fig. 1B, right).<sup>[22]</sup> The Menjón procedure was reinvestigated by Shen<sup>[13]</sup> leading to  $[\text{NBu}_4]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  **NBu<sub>4</sub>-1** in multigram scale, yet nearly one half of  $\text{AgF}$  is wasted and costly hypervalent iodine is required. Strikingly, and after *ca.* 35 years, a safer and high-yielding entry to the remarkable anion  $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  **1** is still lacking. As a matter of fact, whether it might be useful in coordination chemistry<sup>[23]</sup> and trifluoromethylation reactions,<sup>[13]</sup> remains poorly studied. These long-awaited accomplishments, namely, the merging of a reliable and exceedingly facile synthesis of the homoleptic anion  $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  **1** alongside its net income as an organometallic synthon for trifluoromethylation,<sup>[24]</sup> are herein reported (Fig. 1C).

We wish to report an ultimate entry to  $[\text{K}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  (**K-1**) in nearly quantitative yield from  $\text{AgF}$ ,  $\text{KF}$  and  $\text{CF}_3\text{TMS}$  upon aerobic oxidation. **K-1** was fully characterized and proved useful in coordination chemistry by adding *bpy* or *phen* in warm acetic acid or aqueous media, thus furnishing the neutral complexes  $[(\text{bpy})\text{Ag}^{\text{III}}(\text{CF}_3)_3]$  (**2**) and  $[(\text{phen})\text{Ag}^{\text{III}}(\text{CF}_3)_3]$  (**3**). The *phen*- $\text{Ag}^{\text{III}}$  complex **3** underwent efficient trifluoromethylation of arylboron derivatives **4<sub>a-rr</sub>** capitalizing on the transient formation of aryl[tris(trifluoromethyl)]argentate(III) species  $[\text{Ag}^{\text{III}}(\text{aryl})(\text{CF}_3)_3]^\ominus$  (**5<sub>a-rr</sub>**) and subsequent aryl  $\text{CF}_3$  coupling under mild conditions. This reactivity pattern (*i.e.* oxidative coupling),<sup>[25]</sup> typically conducted using  $\text{Cu}^{\text{III}}$ , high-valent  $\text{Pd}$  and  $\text{Ni}$ , or  $\text{Bi}^{\text{V}}$  intermediates,<sup>[26-29]</sup>

unlocks unequivocally the capacity of  $\text{Ag}^{\text{III}}\text{CF}_3$  species to be engaged in cross-coupling, and more specifically in aromatic trifluoromethylation. DFT analysis, coupled to experimental investigations, have corroborated the  $\alpha$ -fluorine elimination mechanism enabled by the potassium cation from **K-1** furnishing the coupling efficient  $\text{Ag}^{\text{III}}$  organometallics **2** and **3**.



**Fig. 1. State of the art and focus of this work.** (A) Structures of  $\text{Ag}^{\text{III}}$  species **I–III** determined through X-ray crystallography being engaged in cross-coupling. (B) Previous approaches to homoleptic anion  $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^-$  (**1**). (C) Easy access to  $[\text{K}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^-$  (**K-1**) and its utility in organometallic synthesis and fluorine chemistry. Aromatic trifluoromethylation enabled by  $\text{Ag}^{\text{I}}/\text{Ag}^{\text{III}}$  redox shuttles.

## Results and Discussions

Making use of valuable data for accessing  $[\text{Ag}^{\text{I}}(\text{CF}_3)_2]^{\ominus}$  **IV** from commercially available silver salts, metallic fluoride and Ruppertø silane,<sup>[30]</sup> and getting inspired by Grushinø synthesis of  $[\text{Cu}^{\text{III}}(\text{CF}_3)_4]^{\ominus}$  from  $\text{CuCl}$  employing  $\text{KF}/\text{CF}_3\text{SiMe}_3$  as a  $\text{CF}_3$ -group supplier and air as an environmentally friendly oxidant,<sup>[17]</sup> we wondered whether or not complex **IV** would be an appropriate precursor of  $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^{\ominus}$  **1** upon open-flask conditions. The difficult access to the anion  $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^{\ominus}$  (**1**) using a hazardous-free strategy was thus tackled (see Table 1).

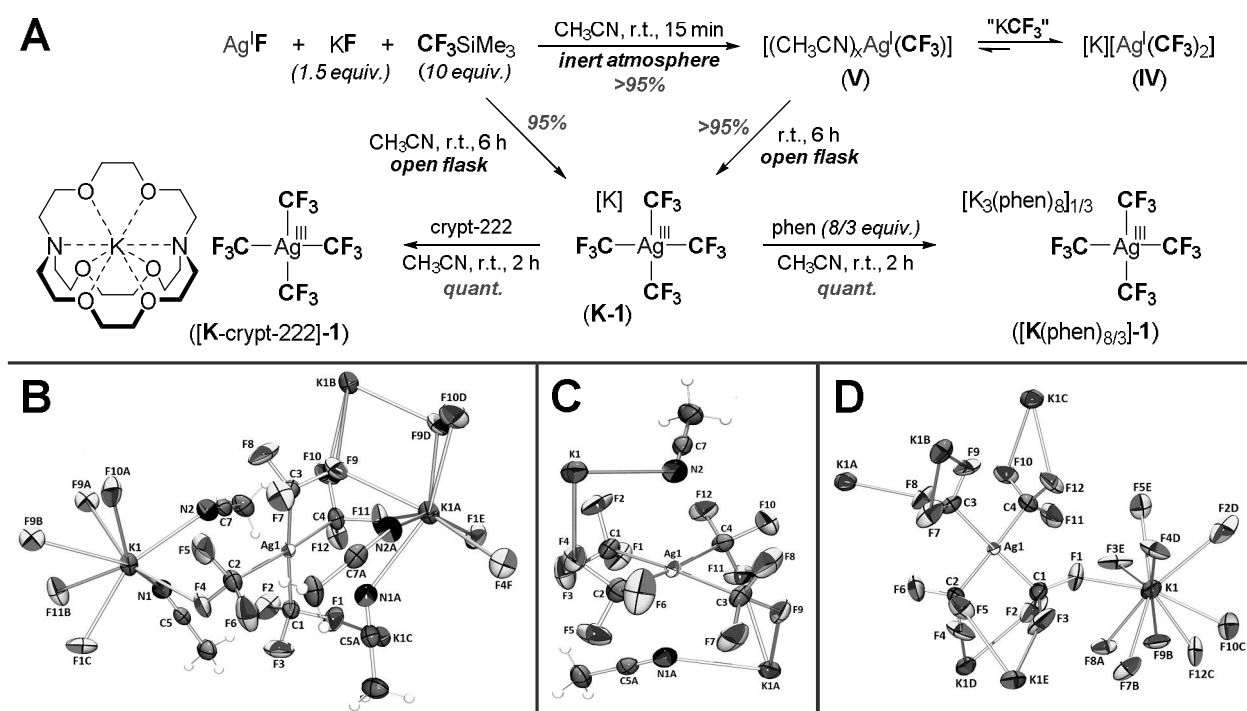
**Table 1.** Synthesis of homoleptic anion  $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  (**1**).

Entry <sup>a</sup>	solvent	MF	<i>n</i>	<i>m</i>	t (h) <sup>b</sup>	Yield (%) <sup>c</sup>
1	DMF	CsF	1	20	3	56
2	DMF	CsF	1	10	3	55
3	DMF	CsF	2.5	10	3	0
4	DMF	KF	1	20	3	58
5	DMF	KF	2.5	20	3	44
6	DMF	KF	10	20	3	1
7 <sup>d</sup>	DMF	KF	1	20	3	58
8 <sup>e</sup>	DMF	KF	1	20	3	43
9 <sup>f</sup>	DMF	KF	1	20	3	56
10	THF	KF	1	10	3	0
11	CH <sub>3</sub> CN	KF	1	10	2	92
12	CH <sub>3</sub> CN	KF	1.2	10	6	92
13	CH <sub>3</sub> CN	KF	1.5	10	6	>99 (95)

<sup>a</sup> In a drybox, AgF (0.4 mmol), MF (0.4–4.0 mmol), CF<sub>3</sub>SiMe<sub>3</sub> (4.0–8.0 mmol) and dried solvent (2 mL) were stirred at r.t. in the dark. Once  $[\text{Ag}^{\text{I}}(\text{CF}_3)_2]^\ominus$  **IV** was formed (*ca.* 20 min), the Schlenk flask was brought outside the drybox and the cap removed. <sup>b</sup> Time of exposure to air. <sup>c</sup> Yield determined through <sup>19</sup>F NMR using 4,4'-difluorobiphenyl (0.4 mmol) as an internal standard. Isolated yields are shown in brackets. <sup>d</sup> Reaction performed at 0°C. <sup>e</sup> Experiment performed at -40°C. <sup>f</sup> Pure oxygen was used as an oxidant.

In a non-optimized experiment, AgF and CF<sub>3</sub>SiMe<sub>3</sub> (excess) were reacted in *N,N*-dimethylformamide (DMF) under inert atmosphere giving rise to Ag<sup>I</sup>CF<sub>3</sub> species within minutes (*ca.* 96% yield, Fig. S3). Addition of CsF (1 equiv.) drove to instantaneous formation of the homoleptic anion  $[\text{Ag}^{\text{I}}(\text{CF}_3)_2]^\ominus$  **IV** in nearly quantitative yield (>92%). Exposed to air, **IV** underwent 2e<sup>⊖</sup> oxidation process affording  $[\text{Cs}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  (**Cs-1**) in considerable amounts (*ca.* 55%, entries 1 and 2). Similar behavior was found upon replacement of CsF by KF (entry 4) or air by pure oxygen (entry 9), the Ag<sup>III</sup> anion **1** being produced in 58% yield at best. Unlike copper,<sup>[17]</sup> the use of higher amounts of CsF proved detrimental, preventing more efficient oxidation of  $[\text{Ag}^{\text{I}}(\text{CF}_3)_2]^\ominus$  **IV** (entry 3). Although less pronounced, same trend was achieved using elevated charges of KF (10 equiv.), thereby fully inhibiting the Ag<sup>I</sup>/Ag<sup>III</sup> oxidation (entry 6). Most likely, an equilibrium between the neutral  $[(\text{solvent})_x\text{Ag}^{\text{I}}(\text{CF}_3)]$  species **V** and the homoleptic anion **IV** is

required, and the  $\text{Ag}^{\text{I}}/\text{Ag}^{\text{III}}$  oxidation enabled by oxygen occurs from  $\text{Ag}^{\text{I}}\text{CF}_3$  species of type **V** (Fig. 2A). Attempts to improve selectivity and prevent  $\text{CF}_3\text{SiMe}_3$  consumption through rigorous control of temperature at either  $0^\circ\text{C}$  or  $40^\circ\text{C}$  proved unfruitful (entries 7 and 8). The nature of solvent was revealed of utmost importance, as complete drop of reactivity was encountered in tetrahydrofuran (THF), whereas nearly quantitative formation of **1** was reached using acetonitrile (entries 10 and 11, resp.). Nevertheless, and despite the excellent yield (92%), minor impurities (*ca.* 5%) of unwanted  $[\text{Ag}^{\text{I}}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  (**Ag-1**) were consistently encountered in the isolated bulk material. Satisfyingly, this inconvenience was circumvented by adding KF in slight excess, and the synthesis of  $[\text{K}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  (**K-1**) was quantitatively accomplished (entry 13). Strikingly, **K-1** was isolated as a white powder in excellent 95% yield, proved to be bench stable (in absence of daylight), and was fully characterized using multinuclear NMR, EA and X-ray crystallography (see ESI). It is worth mentioning that the herein reported procedure was conveniently scaled up to 3 grams of analytically pure **K-1** without significant prejudice in the isolated yield (85%).



**Fig. 2. Synthesis and crystallographic studies of  $\text{Ag}^{\text{III}}\text{CF}_3$  species **1**.** (A) Synthesis of potassium salts  $[\text{K}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  (**K-1**),  $[\text{K-crypt-222}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  (**[K-crypt-222]-1**), and  $[\text{K(phen)}_{8/3}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\ominus$  (**[K(phen)<sub>8/3</sub>]-1**). Molecular views (ellipsoid drawing at 50% probability) of **[K(CH<sub>3</sub>CN)<sub>2</sub>]-1** (**B**) and **K-1** (**D**). (**C**) Closer look at  $\text{Ag}^{\text{III}}$ -coordination environment in **[K(CH<sub>3</sub>CN)<sub>2</sub>]-1**. Most significant distances [Å] and angles [°] of **[K(CH<sub>3</sub>CN)<sub>2</sub>]-1**:

Ag1 C1 2.089(4), Ag1 C2 2.092(4), Ag1 C3 2.094(4), Ag1 C4 2.103(4), Ag1 N1A 2.960(3), Ag1 N2 3.098(3), K1 N1 2.849(4), K1 N2 2.867(4); C1 Ag1 C2 88.8(2), C2 Ag1 C3 92.0(2), C3 Ag1 C4 88.8(2), C1 Ag1 C4 90.8(2), N1A Ag1 N2 175.7(1), K1A N1A C5A 136.9(3), K1 N2 C7 127.0(3). Most significant distances [Å] and angles [°] of **K-1**: Ag1 C1 2.097(6), Ag1 C2 2.092(5), Ag1 C3 2.097(5), Ag1 C4 2.091(5); C1 Ag1 C2 89.3(2), C2 Ag1 C3 90.2(2), C3 Ag1 C4 89.5(2), C1 Ag1 C4 91.5(2).

Kept at 40°C for days, single crystals of **[K(CH<sub>3</sub>CN)<sub>2</sub>]-1** were grown from a concentrated solution of **K-1** in a CH<sub>3</sub>CN/toluene mixture. At first sight, the crystallographic studies confirmed the square planar (SP) arrangement of four CF<sub>3</sub>-ligands around the Ag<sup>III</sup> center having an average Ag1 C bond length of 2.095 Å and multiple K<sup>I</sup> F interactions with the surrounding K cations (K F bond lengths ranging from 2.734(3) to 3.010(3) Å; Fig. 2B). Accordingly, a three-dimensional polymeric assembly results from the binding of the [Ag<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>]<sup>δ</sup> anion **1** to four potassium atoms: K1A and K1B bridge two contiguous CF<sub>3</sub>-groups (either through F9 and F10 or F9 and F11, respectively), whereas K1C and K1 are exclusively connected to F1 and F4, in nearly parallel (K1C) and orthogonal (K1) directions to the SP [Ag<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>]<sup>δ</sup> anion **1**. On their side, the coordination sphere of each potassium is completed by six fluorine atoms of four different [Ag<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>]<sup>δ</sup> units, and two acetonitrile ligands displaying bent coordination. Although far away (*d*<sub>(Ag1 N)</sub> of 2.960 and 3.098 Å), two acetonitrile ligands are located at apical positions of each Ag<sup>III</sup> center forming a N2 Ag1 N1A angle of 175.7(1)°, close to linearity (Fig. 2C). Taken together, this might be seen as a rare, axially distorted octahedral (Oh) silver featuring a three-center two-electron bonding of nitriles to two distinct metals (*i.e.* Ag<sup>III</sup> and K).<sup>[31]</sup> In absence of solvent, the colorless single crystals of **[K(CH<sub>3</sub>CN)<sub>2</sub>]-1** proved unstable and melted at room temperature enabling serendipitous growing of single crystals corresponding to **K-1** upon evaporation of acetonitrile. Most remarkable features found in **K-1** are as follows (Fig. 2D): *i*) **K-1** forms a three-dimensional polymer network as a consequence of multiple K<sup>I</sup> F interactions; *ii*) **1** crystallizes in SP geometry with average Ag1 C bond length of 2.094 Å; *iii*) the lack of acetonitrile allows an enhancement of the potassium coordination number up to ten fluorides pertaining to six different [Ag<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>]<sup>δ</sup> fragments; and *iv*) each [Ag<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>]<sup>δ</sup> anion **1** binds to six potassium atoms, with K1

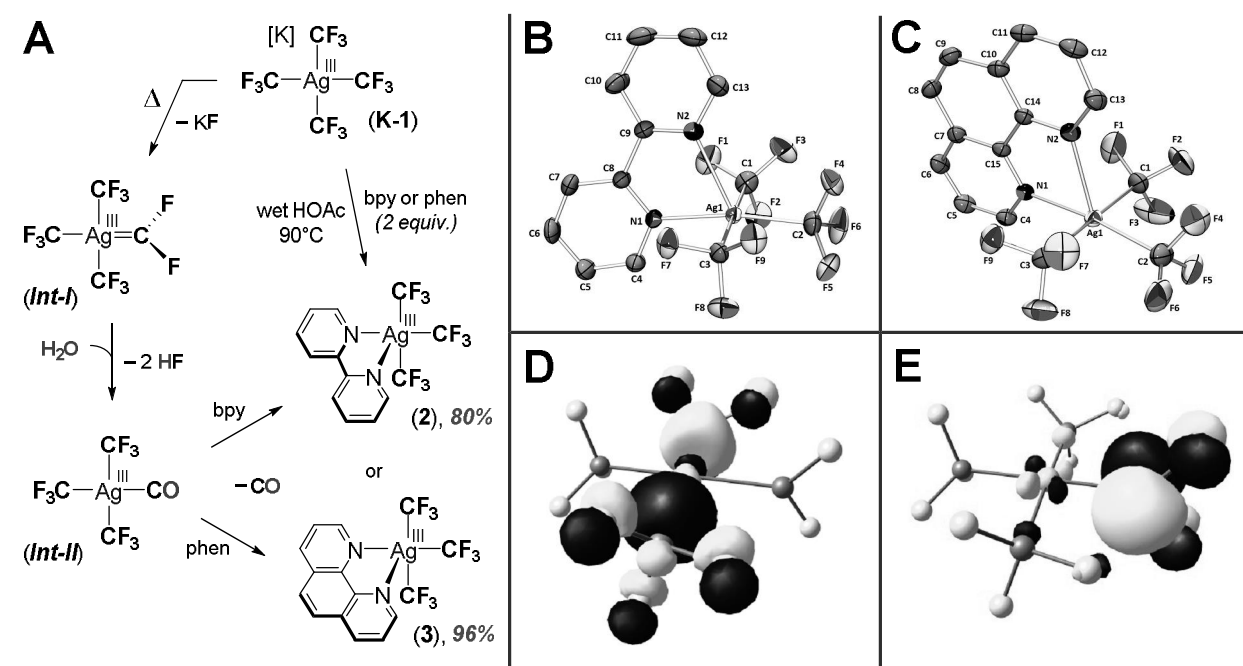


and K1A being bonded to F1 and F8 respectively, whereas the other four potassium cations are linked to two fluorine atoms of either identical (K1B, K1C) or contiguous (K1D, K1E) CF<sub>3</sub> groups. Adding 222-cryptand or phen to **K-1** lends access to [**K**-crypt-222]-**1** and [**K**(phen)<sub>8/3</sub>]-**1** in quantitative yield (Fig. 2A), and XRD analyses revealed the absence of K<sup>i</sup> F interactions and cation sequestration (Fig. S168 and S167).

Beyond the difficult isolation and striking crystallographic intricacies displayed by **K-1**, a more stable and easier-to-handle salt of [Ag<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>]<sup>6-</sup> (**1**) may be convenient for synthetic purposes. **PPh<sub>4</sub>-1**, **PPN-1** and **NBu<sub>4</sub>-1** were quantitatively achieved through salt metathesis of isolated **K-1** and [PPh<sub>4</sub>]Br, [PPN]Cl or [NBu<sub>4</sub>]Cl, and the salts were appropriately characterized using NMR spectroscopy, EA, and XRD analysis for **PPN-1** and **NBu<sub>4</sub>-1** (Fig. S166 and S165, respectively). Having in hand the homoleptic Ag<sup>III</sup> anion **1** in large amounts, its employ as an organometallic synthon to build novel Ag<sup>III</sup>CF<sub>3</sub> platforms was envisioned. Grushin reported the synthesis of [(bpy)Cu<sup>III</sup>(CF<sub>3</sub>)<sub>3</sub>] in *ca.* 50% yield from bipyridine (bpy; 2 equiv.) and [NBu<sub>4</sub>]<sup>+</sup>[Cu<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>]<sup>6-</sup> in warm acetic acid.<sup>[17]</sup> Using these conditions, bpy and **PPh<sub>4</sub>-1** (or **NBu<sub>4</sub>-1**) gave rise to the neutral complex [(bpy)Ag<sup>III</sup>(CF<sub>3</sub>)<sub>3</sub>] (**2**) in quantitative NMR yield. Nevertheless, unfortunately, prolonged heating (10-12 days) and tedious work-up was required, thereby precluding its isolation in analytically pure form and good yield.

In view of the multiple K<sup>i</sup> F interactions available within the structures of [**K**(CH<sub>3</sub>CN)<sub>2</sub>]-**1** and **K-1** (Fig. 2B and 2D, resp.), it was reasoned that the enhanced Lewis acidity of potassium (*vs.* organic cations) may be rewarding to enable easier -fluorine elimination (*i.e.* the rate determining step). We thus turned back our attention to the inorganic salt **K-1**, which may provide **2** accompanied by KF and HF side-products, easily removable upon aqueous extraction. The feasibility of the -fluorine elimination pathway mediated by potassium was first screened using DFT methods (see ESI). The computed salt [K(bpy)<sub>2</sub>]<sup>+</sup>[Ag<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>]<sup>6-</sup> ([**K**(bpy)<sub>2</sub>]-**1**) exhibited an uncommon out-of-plane coordination of the two bpy to potassium with remarkably long K N bond

distances of 2.9 Å, albeit close to the K1 N bond distances measured in  $[\mathbf{K}(\text{phen})_{8/3}]\mathbf{-1}$  (ranging from 2.875(2) to 3.026(2) Å; see Fig. S167 and Table S11). As evidenced by the energetic scan of the C F bond elongation (see ESI), the C F bond breaking event benefits from the persistent  $\text{K}^{\text{I}}$  F interactions in  $[\mathbf{K}(\text{bpy})_2]\mathbf{-1}$ , as well as from developing  $\text{Ag}^{\text{III}}$  F interaction. Not surprisingly in light of the thermal stability of  $[\mathbf{K}(\text{CH}_3\text{CN})_2]\mathbf{-1}$ , the formation of the high-energy complex  $[\text{Ag}^{\text{III}}(\text{CF}_2)(\text{CF}_3)_3]$  (*Int-I* in Fig. 3A) and  $[\mathbf{K}(\text{bpy})_2]\mathbf{F}$  is a highly endothermic reaction, which requires subsequent reaction to occur (*vide infra*). As apparent from the frontier orbitals depicted in Fig. S177, the instability and highly electrophilic nature of *Int-I* is due to a negligible  $\pi$ -back donation from the  $\text{Ag}^{\text{III}}$  to the  $\text{CF}_2$  fragment. As a result, *Int-I* would be prone to undergo instantaneous hydrolysis with adventitious water driving to the carbonyl complex *Int-II*, which allows easy bpy coordination and CO extrusion.



**Fig. 3. Synthesis and characterization of neutral  $\text{Ag}^{\text{III}}\text{CF}_3$  species **2** and **3**.** (A) Access to  $[(\text{bpy})\text{Ag}^{\text{III}}(\text{CF}_3)_3]$  (**2**) or  $[(\text{phen})\text{Ag}^{\text{III}}(\text{CF}_3)_3]$  (**3**) and mechanistic depiction *via* alpha-fluorine elimination. Ellipsoid drawing (50% probability) for the molecular structures of  $[(\text{bpy})\text{Ag}^{\text{III}}(\text{CF}_3)_3]$  (**B**) and  $[(\text{phen})\text{Ag}^{\text{III}}(\text{CF}_3)_3]$  (**C**). For clarity, hydrogen atoms are omitted. Representation of the computed Kohn-Sham HOMO (**D**) and LUMO (**E**) of the  $\text{Ag}^{\text{III}}$  carbene complex  $[\text{Ag}^{\text{III}}(\text{CF}_2)(\text{CF}_3)_3]$  (*Int-I*). Most significant distances [Å] and angles [ $^\circ$ ] of **2**: Ag1 C1 2.072(5), Ag1 C2 2.053(4), Ag1 C3 2.117(4), Ag1 N1 2.143(3), Ag1 N2 2.454(3); C1 Ag1 C2 90.9(2), C2 Ag1 C3 88.8(2), C3 Ag1 N1 93.6(2), C1 Ag1 N2 87.5(2), N1 Ag1 N2 72.2(1), C2 Ag1 N2 117.2(2); N1 C8 C9 N2 15.5(6). Most significant distances [Å] and angles [ $^\circ$ ] of **3**: Ag1 C1 2.100(3), Ag1 C2 2.055(11), Ag1 C3 2.099(2), Ag1 N1 2.139(2), Ag1 N2 2.490(2); C1 Ag1 C2 89.8(12), C2 Ag1 C3 89.4(12), C3 Ag1 N1 90.3(1), C1 Ag1 N1 90.6(1), N1 Ag1 N2 72.6(1), C2 Ag1 N2 116.0(4); N1 C15 C14 N2 0.8(3).

In agreement with theoretical predictions, our initial hypothesis proved right and the **K-1**/phen couple yields **3** quantitatively in 84 h when submitted to optimal conditions (*i.e.* ratio **K-1**/phen equal to 1:2, and warming up to 90°C in wet acetic acid). Once taken to dryness, the residual phen and inorganic waste were easily removed upon acidic treatment thereby granting the solitary extraction of **3** to dichloromethane, being garnered as a white and analytically pure powder after evaporation (96% yield). In spite of a marginal lower yield (80%), the replacement of phen by bpy permits the quantitative formation of the analogous complex [(bpy)Ag<sup>III</sup>(CF<sub>3</sub>)<sub>3</sub>] (**2**) in only 24 h under otherwise identical conditions. The observed distinct kinetics arise from the inherent flexibility of bpy *vs.* phen, this fact also influencing the solid state structure, stability and reactivity of the Ag<sup>III</sup> platform (*vide infra*). Likewise, this is consistent with the required twisted conformation of bpy to bind potassium in the computed [**K**(bpy)<sub>2</sub>]-**1**, and the energy cost imparted by the planarity of phen. In analogy to its reminiscent Cu<sup>III</sup> species [(bpy)Cu<sup>III</sup>(CF<sub>3</sub>)<sub>3</sub>],<sup>[17]</sup> complexes **2** and **3** proved fluxional in a d<sub>2</sub>-dichloromethane solution as only two distinct signals resonate in <sup>19</sup>F NMR within the typical δMCF<sub>3</sub> region ( ppm for **2**, 21.5 (app. ddsept, <sup>2</sup>J(<sup>109</sup>Ag,F) = 79.4 Hz, <sup>2</sup>J(<sup>107</sup>Ag,F) = 68.8 Hz, <sup>4</sup>J(F,F) = 8.8 Hz, 3F) and 33.9 (app. ddq, <sup>2</sup>J(<sup>109</sup>Ag,F) = 24.6 Hz, <sup>2</sup>J(<sup>107</sup>Ag,F) = 21.5 Hz, <sup>4</sup>J(F,F) = 8.7 Hz, 6F); ppm for **3**, 21.6 (app. ddsept, <sup>2</sup>J(<sup>109</sup>Ag,F) = 79.1 Hz, <sup>2</sup>J(<sup>107</sup>Ag,F) = 68.6 Hz, <sup>4</sup>J(F,F) = 8.7 Hz, 3F) and 33.8 (app. ddq, <sup>2</sup>J(<sup>109</sup>Ag,F) = 24.9 Hz, <sup>2</sup>J(<sup>107</sup>Ag,F) = 21.6 Hz, <sup>4</sup>J(F,F) = 8.8 Hz, 6F); Fig. S16 and S20, resp.). This spectroscopic signature denotes unequivocally the presence of one δAg<sup>III</sup>(CF<sub>3</sub>)<sub>3</sub> motif having two chemically equivalent CF<sub>3</sub> ligands. The identity of **2** and **3** was definitely established through Single-crystal X-ray Diffraction analysis (Sc-XRD) (Fig. 3B and 3C, resp.). In both cases, the Ag<sup>III</sup> center adopts a highly distorted square pyramidal geometry featuring three CF<sub>3</sub> ligands in equatorial positions, and constitutes the first family of Ag<sup>III</sup> compounds displaying other than SP geometry. Their structures unveiled lengthened Ag1 N2 bond distances (apical pyridyl moieties) exceeding the Ag1 N1 ones (equatorial pyridyl rings) by *ca.* 31.1 (in **2**) and 35.1 (in **3**) pm, and averaged Ag1 C bond lengths

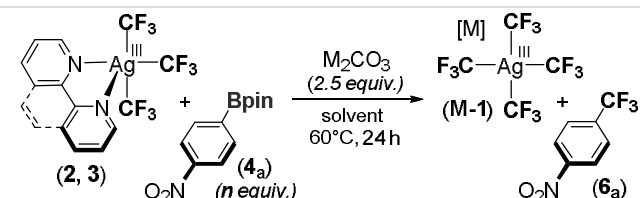
of 2.081 (in **2**) and 2.085 (in **3**) Å. The more rigid phen vs. bpy backbone was herein translated into a noticeable N1 C8 C9 N2 torsion angle of 15.5(6)° in **2** opposing the negligible N1 C15 C14 N2 torsion angle of 0.8(3)° measured in **3**. Accordingly, **3** exhibits nearly planar symmetry and almost identical Ag1 C1 and Ag1 C3 bond distances (*ca.* 2.100(3) Å), while the notorious torsion angle arranged by the two pyridyl planes in **2** originates a significant dissymmetry and triggers the simultaneous shortening/elongation of the Ag1 C1/Ag1 C3 bonds (2.072(5) Å vs. 2.117(4) Å).

To shed some light on the role of potassium throughout the  $\beta$ -fluorine elimination step from **K-1**, the isolated [**K-crypt-222**]-**1** and bpy were subjected to optimal conditions to build **2**. As might be anticipated, the potassium sequestration by 2,2,2-cryptand impedes facile  $\beta$ -fluorine abstraction and leads to **2** in nearly quantitative yield after *ca.* 5 days. The kinetics observed for the synthesis of **2** from [**K-crypt-222**]-**1** are comprised between those observed starting from **K-1** (24 h) and **PPh<sub>4</sub>-1** or **NBu<sub>4</sub>-1** (10 days), lending additional support for the potassium-enabled  $\beta$ -fluorine elimination pathway. Satisfyingly, a clearer hint for the key participation of potassium and negligible contribution of AcOH was supplied by an alternative synthesis of **3** in aqueous media, being furnished quantitatively from a mixture H<sub>2</sub>O/CH<sub>3</sub>CN (ratio 10:1) after 5 days of heating (see ESI).

Apart from the crystallographic distinctness of **2** and **3**, the reactivity of the Ag<sup>III</sup> platform is inherently governed by the nature of the chosen ancillary ligand. This is well illustrated in Table 2 by the comparative behavior of **2** and **3** vs. aryl Bpin derivatives under coupling conditions (*i.e.* basic media and mild heat). The disfavored transmetallation of electron-poor arenes from boron to metal represents a delicate bottleneck in cross-coupling, typically boosting unwanted protodeborylation.<sup>[32]</sup> To overcome this limitation and ensure broad applicability, appropriate conditions for the Ag<sup>III</sup>-mediated trifluoromethylation of arylboron compounds were explored using a gentle excess of pinacol boronate **4<sub>a</sub>**, which bears an EWG, and Cs<sub>2</sub>CO<sub>3</sub> (2.0 and 2.5 equiv., resp.). We initially screened the influence of solvent, and the cocktail constituted by **3**, **4<sub>a</sub>** and

Cs<sub>2</sub>CO<sub>3</sub> was subjected to mild warming (60°C) in a variety of well-dried polar solvents including DMF, DMAC, DMSO, CH<sub>3</sub>CN and THF (entries 1-5). With no exception, the overnight heating produced **6a** in 59-69% yield accompanied by variable amounts (14-26%) of unanticipated [Cs]<sup>+</sup>[Ag<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub>] (**Cs-1**).

**Table 2.** Optimization of the reaction conditions for the Ag<sup>III</sup>-mediated trifluoromethylation of boronic acid surrogates.



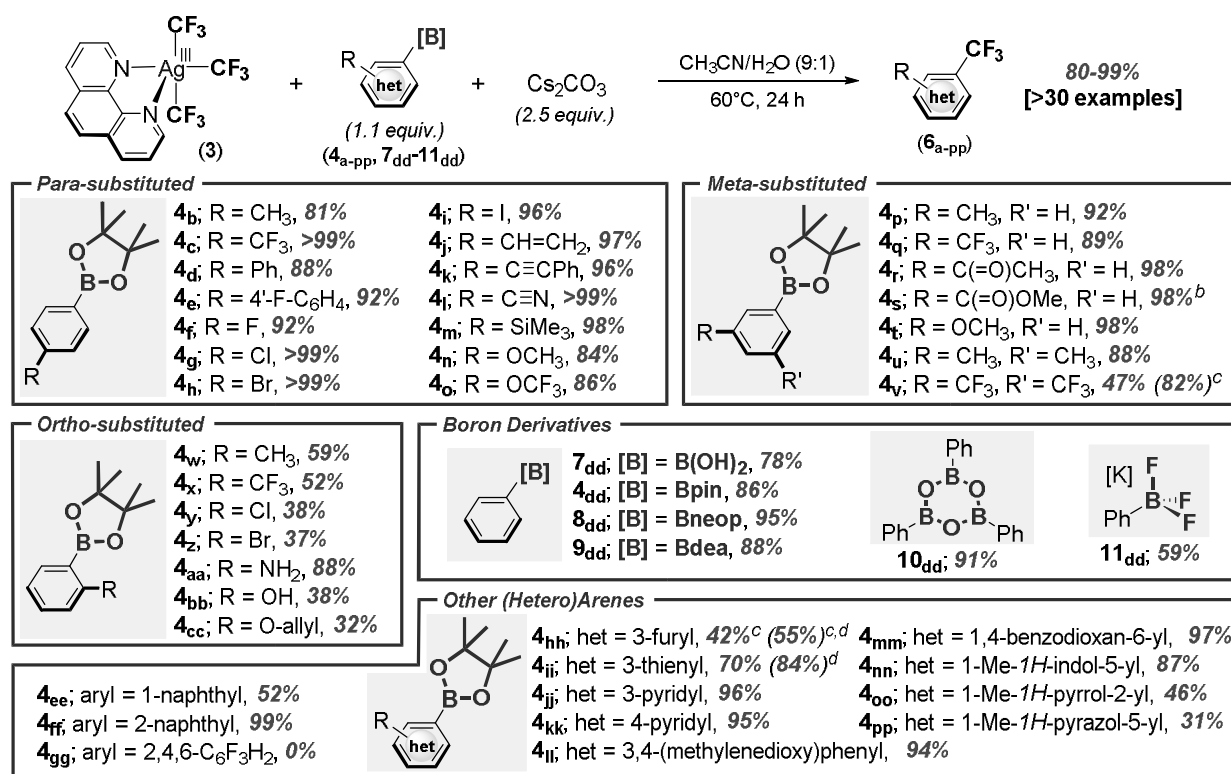
Entry <sup>a</sup>	solvent	[Ag <sup>III</sup> ]	<i>n</i>	<b>6a</b> (%) <sup>d</sup>	<b>M-1</b> (%) <sup>d</sup>
1 <sup>b</sup>	DMF	<b>3</b>	2.0	69	15
2 <sup>c</sup>	DMAC	<b>3</b>	2.0	67	14
3 <sup>b</sup>	DMSO	<b>3</b>	2.0	63	26
4 <sup>b</sup>	THF	<b>3</b>	2.0	62	22
5 <sup>b</sup>	CH <sub>3</sub> CN	<b>3</b>	2.0	59	22
6 <sup>b,e</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>3</b>	2.0	90	3
7 <sup>b,f</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>3</b>	2.0	>99	3
8 <sup>c,f</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>3</b>	2.0	>99	1
9 <sup>b,g</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>3</b>	2.0	73	2
10 <sup>b,f</sup>	DMF/H <sub>2</sub> O	<b>3</b>	2.0	76	7
11 <sup>c,f</sup>	DMAC/H <sub>2</sub> O	<b>3</b>	2.0	77	8
12 <sup>b,f</sup>	DMSO/H <sub>2</sub> O	<b>3</b>	2.0	67	8
13 <sup>b,f</sup>	THF/H <sub>2</sub> O	<b>3</b>	2.0	68	6
14 <sup>c,f</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>2</b>	2.0	95	6
15 <sup>b,f,h</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>K-1</b>	2.0	0	>99
16 <sup>b,f,i</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>K-1</b>	2.0	0	>99
17 <sup>b,f</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>3</b>	1.0	97	7
18 <sup>b,f</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>3</b>	1.1	>99	5
19 <sup>b,f,j</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	<b>3</b>	1.1	>99	10

<sup>a</sup> Experiments carried out in inert atmosphere and light-protected using Ag<sup>III</sup> complex (**2** or **3**; 0.030 mmol), **4a** (0.033–0.061 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.076 mmol) and dried solvent (1 mL). <sup>b</sup> Experiment performed in a regular NMR tube capped with a rubber septa and tightly sealed with parafilm®. <sup>c</sup> Experiment performed in a J.Young NMR tube. <sup>d</sup> Yield determined through <sup>19</sup>F NMR using 4,4'-difluorobiphenyl (0.03 mmol) as an internal standard. <sup>e</sup> Reaction performed using 5% H<sub>2</sub>O (v/v). <sup>f</sup> Reaction performed using 10% H<sub>2</sub>O (v/v). <sup>g</sup> Reaction performed using 20% H<sub>2</sub>O (v/v). <sup>h</sup> **K-1** is used instead **2** or **3**. <sup>i</sup> **K-1** associated to phen (1 equiv.) is used as a trifluoromethylating agent. <sup>j</sup> Na<sub>2</sub>CO<sub>3</sub> (2.5 equiv.) is used instead Cs<sub>2</sub>CO<sub>3</sub>.

The unforeseen formation of **Cs-1** arises from thermal decomposition of **3** driven by caesium cations, as evidenced by independent experiments. In fact, despite **3** proved stable in pure CH<sub>3</sub>CN solutions for days, it underwent partial decay in presence of Cs<sub>2</sub>CO<sub>3</sub> and smoothly delivered **Cs-1** at room temperature (Fig. S4). The addition of degassed water warranted the homogeneity of the resulting solution and hampered the formation of **Cs-1**. We thus investigated the efficiency of **3** in CH<sub>3</sub>CN/water mixtures (entries 6-9), and found that the use of 10% water brings to quantitative the yield of **6<sub>a</sub>** whereas the content of **Cs-1** becomes restrained to minute quantities (<3%, entry 8). Replacing CH<sub>3</sub>CN by alternative polar solvents (entries 10-13) or higher water proportions (entry 9) proved detrimental, while harnessing a more labile ancillary ligand (bpy in **2**) instead phen caused slightly increased amounts of **Cs-1** and slightly lesser yield of **6<sub>a</sub>** (95%, entry 14). In line with the deleterious effect of **Cs-1** on the coupling process, **K-1** was revealed completely inactive. Most likely, this points to the absolute requirement of a potentially available vacant site at Ag<sup>III</sup> rendering the aryl-group transfer and subsequent Ag<sup>III</sup>/Ag<sup>I</sup> reductive elimination step feasible. Accordingly, the participation of CF<sub>3</sub> radicals or palladium impurities might be discarded by now (*vide infra*). Remarkably, the impressive capacity of **3** to trigger the aromatic trifluoromethylation of **4<sub>a</sub>** allowed the employ of nearly equimolar boron charges without significant loss of yield or selectivity (entries 17 and 18). With optimal conditions in hand [*i.e.* ratio Ag<sup>III</sup>/arylboron compound/Cs<sub>2</sub>CO<sub>3</sub> equal to 1:1.1:2.5, and warming up to 60°C in a mixture CH<sub>3</sub>CN/H<sub>2</sub>O 9:1 (v/v)], the aromatic trifluoromethylation of a large panel of boron derivatives mediated by **3** was evaluated.

As illustrated in Fig. 4, this procedure performs better for phenylboronic esters **4<sub>dd</sub>** (86%), **8<sub>dd</sub>** (95%), **9<sub>dd</sub>** (88%) and triphenylboroxin **10<sub>dd</sub>** (91%) compared to phenylboronic acid **7<sub>dd</sub>** (78%) or its surrogate **11<sub>dd</sub>** (59%). The reaction scope was then studied for an ample variety of (hetero)aryl Bpin esters **5<sub>a-rr</sub>**. Besides substrates **5<sub>gg,qq</sub>** containing two fluorine atoms in *ortho*-position, the corresponding coupled products were afforded in yields ranging from 25% to quantitative. Remarkably, while **3** demonstrated effective for the trifluoromethylation of *para*- and

*meta*-substituted arenes, acute *ortho*-effect was attained and certain drop in the reaction yield was observed (compare **4**<sub>b,c</sub> vs. **4**<sub>p,q</sub> vs. **4**<sub>w,x</sub>). This is most likely due to difficult boron-to-Ag<sup>III</sup> aryl transfer owing to an enhanced steric hindrance of the aryl ring. Our Ag<sup>III</sup>-reagent **3** displayed high functional group tolerance and proved compatible with carbonyls (**4**<sub>r,s</sub>), double and triple unsaturations [olefins (**4**<sub>j</sub>), alkynes (**4**<sub>k</sub>) and nitriles (**4**<sub>l</sub>)], or the amino (**4**<sub>aa</sub>) function. In terms of skeleton diversity, relevant heterocycles (**4**<sub>hh-pp</sub>) were trifluoromethylated in modest to good yields using this methodology, comprising the prevailing furyl, thienyl, pyridyl, indolyl or pyrrolyl scaffolds that are commonly featured within the core of commercialized drugs. Regarding the electronic nature of the arene, the observed reactivity trend opposes the prevalent higher efficiency displayed in Pd-mediated functionalization of electronically enriched (vs. electron poor) boron compounds.<sup>[32,33]</sup> In turn, this is consistent with previous reports illustrating a reverse reactivity pattern of coinage metals compared to palladium.<sup>[34]</sup>



**Fig. 4. Aromatic trifluoromethylation of boron compounds enabled by the high-valent Ag<sup>III</sup>CF<sub>3</sub> species **3**.** <sup>a</sup> Unless otherwise stated, the coupling experiments were effected as follows: in a glovebox and light-protected, a regular NMR tube is replenished with **3** (0.030 mmol), the boron compound (0.033 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.076 mmol), and degassed CH<sub>3</sub>CN (0.9 mL). The NMR tube is capped with a rubber septa and immediately brought outside the

glovebox. After addition of degassed water (0.1 mL), the tube is tightly sealed with parafilm® and reacted overnight upon mild heating (60°C). Yields determined through <sup>19</sup>F NMR using 4,4'-difluorobiphenyl (0.030 mmol) as an internal standard (average of two runs). <sup>b</sup> Yield provided after 7 h. Heated overnight, **6s** underwent hydrolysis of the ester moiety rendering the corresponding carboxylic acid as the main product. <sup>c</sup> Yield provided after 72 h. <sup>d</sup> Reaction performed using 2 equiv. of boron derivative.

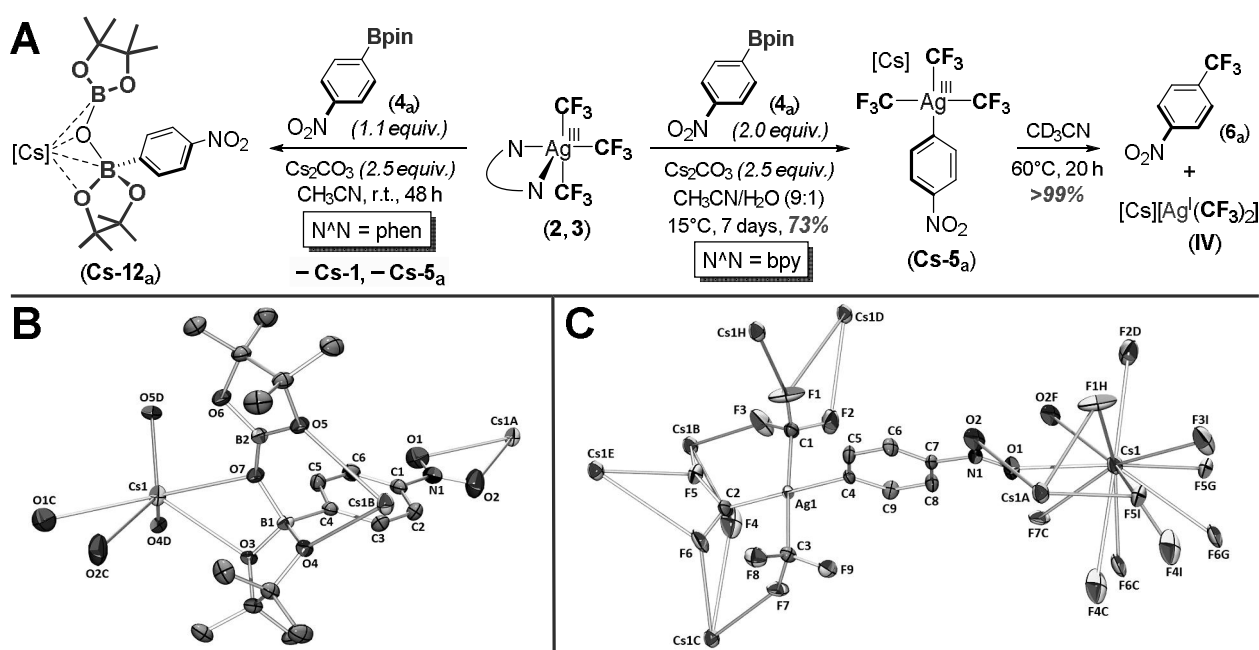
An important mechanistic insight was disclosed by radical clock experiments. Although proceeding in low yield (32%) due to the oxyallyl-group encumbrance, the trifluoromethylation of pinacol 2-oxyallylphenylboronate **4cc** was accomplished without appreciation of radical cyclization. This certainly suggests that the aryl CF<sub>3</sub> bond formation occurs through a concerted reductive elimination step from an assumed [aryl Ag<sup>III</sup> CF<sub>3</sub>] fragment, and competitive pathways involving radicals were definitively ruled out by control experiments using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or *N*-tert-butyl-phenylnitron (PBN) as radical scavengers (see ESI).

On the other hand, the capacity of silver to undergo cross-coupling events through *2e<sup>o</sup>* redox cycles is controversial. In his essay referring to unusual palladium-free catalysts for Sonogashira coupling,<sup>[35]</sup> Plenio underlined that *ōí it is hard to imagine silver shuttling between the Ag<sup>I</sup> and Ag<sup>III</sup> states, as Ag<sup>III</sup> is a strong oxidantö. Nonetheless, the viability of Ag<sup>I</sup>/Ag<sup>III</sup> oxidations harnessing a tetradentate ligand containing an aryl halide moiety was unveiled by Ribas, the resulting aryl Ag<sup>III</sup> species **I** being accommodated by its macrocyclic structure.<sup>[8,11,14a]</sup> Conversely, mechanistic studies focusing on the crucial transmetallation and reductive elimination steps are underexplored. Back in 1997, early investigations by Eujen noticed the facile decomposition of [Ag<sup>III</sup>(CN)<sub>x</sub>(CF<sub>3</sub>)<sub>4-x</sub>] anions giving rise to trifluoroacetonitrile (x × 2).<sup>[36]</sup>*

In 2020, four thiolate Ag<sup>III</sup> intermediates [Ag<sup>III</sup>(SR)(CF<sub>3</sub>)<sub>3</sub>], built from the fluorido Ag<sup>III</sup> complex **II** and thiols, were characterized *in situ* by Menjón using NMR spectroscopy and mass spectrometry before RS CF<sub>3</sub> coupling and fluoroform (HCF<sub>3</sub>) release.<sup>[12]</sup> OñHair, Ogle and Koszinowski examined the reductive elimination step from tetraorganylargentate(III) complexes [Ag<sup>III</sup>(R)(CH<sub>3</sub>)<sub>3</sub>] through gas phase fragmentations (ESI-MS) coupled to DFT calculations and highlighted the ability of Ag<sup>III</sup> to undergo cross-coupling<sup>[37,38]</sup> overpassing the activity of parent



[Cu<sup>III</sup>(R)(CH<sub>3</sub>)<sub>3</sub>] species.<sup>[39]</sup> Nevertheless, a precise study taking place from an isolable, fully characterized aryl Ag<sup>III</sup> X fragment (with X being any coupling partner) was lacking until very recently.<sup>[13]</sup> Using carefully designed fluoro-arenes, known to prevent reductive elimination from aryl M X fragments,<sup>[40]</sup> Shen succeeded to isolate the hitherto elusive aryl[tris(trifluoromethyl)]argentate(III) species **III**. Anions of type **III** were accessed from **3** and *ortho*-fluorophenylboron derivatives in presence of Cs<sub>2</sub>CO<sub>3</sub> and mild warming in pure DMSO, followed by cation exchange using [NBu<sub>4</sub>]Br. Heated at 90°C in pure chloroform, **III** underwent aryl CF<sub>3</sub> coupling thereby manifesting the capacity of Ag<sup>III</sup> to effect aromatic trifluoromethylation across a two-step procedure.

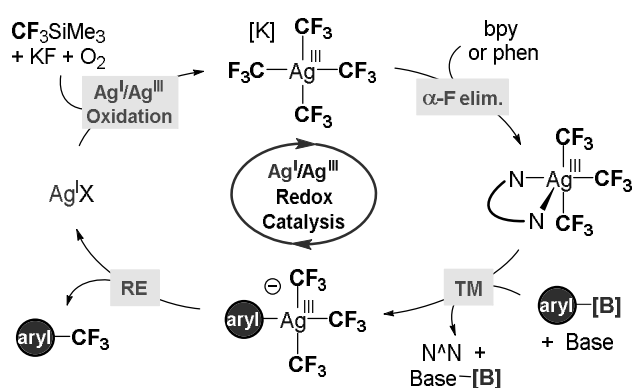


**Fig. 5. Mechanistic insight on the trifluoromethylation of aryl Bpin compounds enabled by 2 and 3.** (A) Transmetallation experiments using Ag<sup>III</sup> (**2**, **3**), **4<sub>a</sub>** and Cs<sub>2</sub>CO<sub>3</sub>: side-reactivity of **4<sub>a</sub>** (left) and key role of water contents allowing for an efficient isolation of the aryl Ag<sup>III</sup> intermediate **Cs-5<sub>a</sub>** (right). Ellipsoid drawing (50% probability) for the molecular structures of [Cs]<sup>+</sup>[(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)B(pin)(OBpin)]<sup>-</sup> (**B**) and [Cs]<sup>+</sup>[Ag<sup>III</sup>(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)<sub>3</sub>]<sup>-</sup> (**C**). For a shake of clarity, hydrogen atoms are not shown.

The herein reported trifluoromethylation of boron compounds mediated by **3** demands significantly differing conditions (*i.e.* *one-pot* procedure, mild heating, and most remarkably, presence of water). It was thus our aim to provide a deeper mechanistic picture on the decisive boron-to-Ag<sup>III</sup> transmetallation of the aryl fragment and the ensuing aryl CF<sub>3</sub> bond formation using

aqueous media. Attempts to isolate, characterize and figure out the thermal behavior of the aryl Ag<sup>III</sup> intermediates [Cs]<sup>+</sup>[Ag<sup>III</sup>(aryl)(CF<sub>3</sub>)<sub>3</sub>]<sup>6-</sup> were fruitfully undertaken (Fig. 5A). We first performed boron-to-Ag<sup>III</sup> transmetallation experiments of the aryl fragment in pure CH<sub>3</sub>CN. <sup>19</sup>F NMR monitoring indicates slow conversion of **3** at room temperature into a complex mixture of compounds resonating within the δAg<sup>III</sup>CF<sub>3</sub> region (Fig. 5A left; see Fig. S7), namely: **3** (ca. 50%), unwanted **Cs-1** (15%), and a novel Ag<sup>III</sup>(CF<sub>3</sub>)<sub>3</sub> species (ca. 25%) exhibiting two types of CF<sub>3</sub> ligands [ ppm 30.2 (app. ddq, <sup>2</sup>J(<sup>109</sup>Ag,F) = 48.3 Hz, <sup>2</sup>J(<sup>107</sup>Ag,F) = 40.3 Hz, <sup>4</sup>J(F,F) = 4.2 Hz, 6F) and 33.1 (br. multiplet, 3F)]. This very diagnostic <sup>19</sup>F NMR signature exhibiting two chemically equivalent CF<sub>3</sub>-groups shifted downfield by ca. 2.9 ppm compared to the trifluoromethyl ligand *trans* to the aryl fragment is reminiscent of the one reported by Shen for the organocuprate(III) salts [NBu<sub>4</sub>]<sup>+</sup>[Cu<sup>III</sup>(aryl)(CF<sub>3</sub>)<sub>3</sub>]<sup>3d</sup> and close to the analogous salts [NBu<sub>4</sub>]<sup>+</sup>[Ag<sup>III</sup>(aryl)(CF<sub>3</sub>)<sub>3</sub>] reported by the same group.<sup>13</sup> Accordingly, the novel Ag<sup>III</sup> species was tentatively assigned to the corresponding [Ag<sup>III</sup>(aryl)(CF<sub>3</sub>)<sub>3</sub>]<sup>-</sup> anion **5<sub>a</sub>** forged upon transmetallation. After 2 days, generous growing of single crystals corresponding to [Cs]<sup>+</sup>[(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)B(pin)(OBpin)] (**Cs-12<sub>a</sub>**) took place, and the reaction equilibrates in consequence of the aryl-group transfer disruption provoked by the bulkiness and insolubility of **Cs-12<sub>a</sub>** in CH<sub>3</sub>CN (ORTEP representation is shown in Fig. 5B). In perfect harmony with the reaction conditions optimized in Table 2, the addition of degassed water warranted the homogeneity of the resulting solution and converted the remains of **3** and **4<sub>a</sub>** into **6<sub>a</sub>** upon mild warming (60°C), also hampering further growing of **Cs-1**. The lack of selectivity towards the formation of the aryl Ag<sup>III</sup> intermediate **5<sub>a</sub>** in pure organic solvents prompted us to investigate the elementary steps in aqueous solutions. Initial trials using **3** and the boron derivative **4<sub>a</sub>** in CH<sub>3</sub>CN/H<sub>2</sub>O mixtures (9:1) denoted the need of mild heating to reach the boron-to-Ag<sup>III</sup> transmetallation, which in return also conducts to aromatic trifluoromethylation. We then turned back our attention to the analogous Ag<sup>III</sup> complex **2** bearing a more weakly coordinated bpy ligand. To our delight, fixing the reaction temperature at 15°C precluded the aryl CF<sub>3</sub> coupling and led to

the desired aryl  $\text{Ag}^{\text{III}}$  intermediate **5<sub>a</sub>** after seven days, although partially contaminated by minute amounts of **Cs-1** (*ca.* 5%), 4-nitrobenzotrifluoride (**6<sub>a</sub>**; *ca.* 5%) and  $\text{Ag}^{\text{I}}\text{CF}_3$  species (*ca.* 5%). Fortunately, **Cs-5<sub>a</sub>** was isolated in pure form as a white powder after evaporation and successive washings with water and  $\text{CH}_2\text{Cl}_2$  (73% yield, see ESI). Along with the aforementioned  $^{19}\text{F}$  NMR pattern, the forging of the aryl  $\text{Ag}^{\text{III}}$  bond and the square planar geometry having an  $\delta\text{Ag}^{\text{III}}(\text{CF}_3)_3\delta$  motif was attested by  $^{13}\text{C}$  NMR [ $\text{ppm}$  170.0 (br. signal,  $\text{C}_{\text{ipso}}$ )] and  $^{109}\text{Ag}\{^{19}\text{F}\}$  NMR that resonates at 2192.3 ppm as a triplet signal due to spatial proximity of the two *ortho*-protons and silver ( $^3J(^{109}\text{Ag},\text{H}) = 2.8$  Hz). Crystallographic studies confirmed the structure and atom connectivity in the aryl  $\text{Ag}^{\text{III}}$  complex **Cs-5<sub>a</sub>** (Fig. 5C). It is worth noting that the chemical shifts found in  $^{109}\text{Ag}$  NMR for the formally  $\text{Ag}^{\text{III}}$  species [ $\text{ppm}$  2234.6 (**K-1**), 2192.3 (**2**), 2416.4 (**3**), and 2192.3 (**Cs-5<sub>a</sub>**)] are considerably shifted from the one reported for the  $[\text{Ag}^{\text{I}}(\text{CF}_3)_2]$  anion **IV** [ $\text{ppm}$  565.5],<sup>[36]</sup> this observation being indicative of a highly oxidized metal center. Heated at 60°C in dry  $\text{CD}_3\text{CN}$  for 20 h, the authenticated  $[\text{aryl } \text{Ag}^{\text{III}}(\text{CF}_3)_3]^\delta$  fragment **5<sub>a</sub>** gave rise to 4-nitrobenzotrifluoride (**6<sub>a</sub>**) with concomitant formation of the homoleptic  $\text{Ag}^{\text{I}}$  anion  $[\text{Ag}^{\text{I}}(\text{CF}_3)_2]$  (**IV**) (Fig. S6), thereby confirming the ability of  $\text{Ag}^{\text{III}}$  to effect reductive elimination. As depicted below in Scheme 1, this study reveals the potential viability of a catalytic  $\text{Ag}^{\text{I}}/\text{Ag}^{\text{III}}$  redox scenario in aromatic trifluoromethylation including all elementary steps herein tackled.



**Scheme 1.** Mechanistic depiction for the oxidative trifluoromethylation of arylboron derivatives *via*  $\text{Ag}^{\text{I}}/\text{Ag}^{\text{III}}$  redox shuttles.

## Conclusion

A safe and ultimate synthesis of  $[\text{K}]^+[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^\delta$  (**K-1**) is herein disclosed using air as an oxidant and affording **K-1** in multigram scale and nearly quantitative yield (>90%). This finding grants easy access to  $\text{Ag}^{\text{III}}\text{CF}_3$  compounds and opens up new vistas in cross-coupling using high-valent silver. The importance of supporting ligands to enable the isolation of unprecedented  $\text{Ag}^{\text{III}}\text{CF}_3$  species along with their utility in aryl  $\text{CF}_3$  coupling is also highlighted. The facile boron-to- $\text{Ag}^{\text{III}}$  transmetallation at 15°C leads to  $[\text{aryl Ag}^{\text{III}}(\text{CF}_3)_3]^\delta$  intermediates that underwent aromatic trifluoromethylation *via*  $2e^\delta$  reduction process upon mild heating. Despite preliminary experiments resulted unfruitful, investigations to implement the oxidative trifluoromethylation of arylboron compounds using  $\text{Ag}^{\text{III}}\text{CF}_3$  catalysts are currently undergoing in our laboratories.

Compared to  $\text{Cu}^{\text{III}}\text{CF}_3$  analogs,<sup>[3,16,17]</sup> the  $\text{Ag}^{\text{III}}\text{CF}_3$  species have shown enhanced reactivity and sensitivity to ambient light. We thus anticipate broad applicability of these novel  $\text{Ag}^{\text{III}}\text{CF}_3$  compounds in trifluoromethylation reactions enabled by light irradiation, presumably overpassing the activity of copper mediators or displaying complementary selectivity.<sup>[3f,g,j,k]</sup>

In short, key elementary steps towards  $\text{Ag}^{\text{I}}/\text{Ag}^{\text{III}}$  redox catalysis were investigated and definite proof is herein provided for: *i*) easy  $\text{Ag}^{\text{I}}/\text{Ag}^{\text{III}}$   $2e^\delta$  oxidation mediated by oxygen; *ii*) bpy/phen ligation to  $\text{Ag}^{\text{III}}$ ; *iii*) boron-to- $\text{Ag}^{\text{III}}$  aryl transfer; and *iv*) reductive elimination of benzotrifluorides from  $[\text{aryl Ag}^{\text{III}} \text{CF}_3]$  intermediates. Accordingly, and most strikingly, these findings have demonstrated the capacity of high-valent  $\text{Ag}^{\text{III}}$  to grant a given cross-coupling reaction by itself, thereby ruling out old stereotypes and misconceptions regarding the assumed chemical inertness of silver compounds when dealing with C-C or C-heteroatom bond formations.

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