Exploring the role of coinage metallates in trifluorometalation: a combined experimental and theoretical study

Sara Martínez de Salinas,[a] Ángel L. Mudarra,[a],[b] Carlota Odena,[a],[b] Marta Martínez Belmonte,[a] Jordi Benet-Buchholz,[a] Feliu Maseras,* [a],[c] Mónica H. Pérez-Temprano*[a]

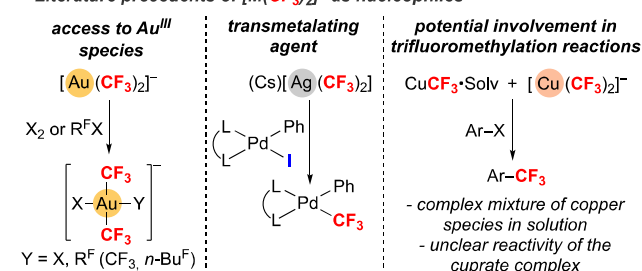**Abstract:** *Despite the known nucleophilic nature of [M(CF$_3$)$_2$]$^-$ (M = Cu, Ag, Au), their participation in trifluoromethylation reactions of aryl halides remains unexplored. Herein, we report, for the first time, the selective access to Cu(CF$_3$)$_2$$^-$ species, ubiquitous in Cu-mediated trifluoromethylations, and we rationalize its complex mechanistic scenario and its behavior compared to its silver and gold congeners through a mixture of experimental and computational approaches.*

Undoubtedly, over the past years, trifluoromethyl organometallic compounds of coinage metals have played a key role as reactive intermediates in organic synthesis.[1,2,3] In this context, fundamental studies on the reactivity of ate-type complexes as nucleophiles has received little attention since until recently, only well-defined (Cat)[Au(CF$_3$)$_2$] complexes were isolable.[4] In 2018, we reported, for the first time, not only the isolation of an unique silver salt, (Cs)[Ag(CF$_3$)$_2$], but also its high efficiency as transmetalating reagent in Pd-catalyzed trifluoromethylations.[2d] Although different literature reports have proposed the existence and involvement of nucleophilic [Cu(CF$_3$)$_2$]$^-$ species in C–CF$_3$ bond-forming reactions, their detailed chemical behavior remains obscure.[3,5] This can be attributed to challenges associated to their selective access (i) its inherent instability and (ii) the existence of different neutral and ionic species in solution that are in equilibrium (Figure 1).
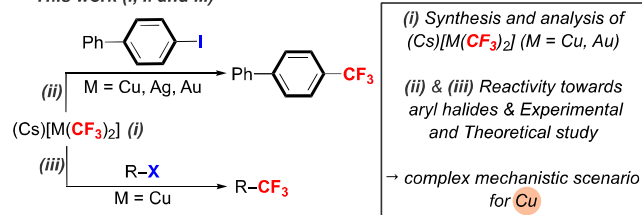
As part of our ongoing interest in the reactivity of ate-type complexes, we wondered whether it could be possible to unravel the potential of (Cat)[M(CF$_3$)$_2$] (M = Cu, Ag, Au) as reactive species in trifluoromethylation reactions and to compare/understand their performance. Herein, we explore previously inaccessible features of these rather unique [M(CF$_3$)$_2$]$^-$ species, including: 1) a direct synthetic route for accessing unprecedented (Cs)[M(CF$_3$)$_2$] (M = Cu, Au) salts and their unambiguously characterization by single crystal X-ray diffraction; 2) a comprehensive experimental and computational analysis of coinage [M(CF$_3$)$_2$]$^-$ and their relative reactivity to a benchmark aryl halide; and 3) the first experimental evidence of the participation of [Cu(CF$_3$)$_2$]$^-$ in trifluoromethylation processes.

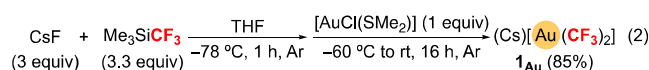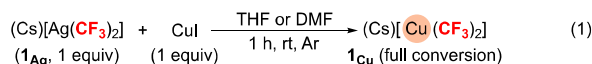**Figure 1.** Reactivity of bis-(trifluoromethyl)metallates of coinage metals.

[a]   Dr. S. Martínez de Salinas, A. L. Mudarra, C. Odena, M. Martínez Belmonte, Dr. J. Benet-Buchholz, Prof. F. Maseras, Dr. M. H. Pérez-Temprano
       Institute of Chemical Research of Catalonia (ICIQ)
       Avgda. Països Catalans 16, 43007 Tarragona (Spain)
       E-mail: mperez@iciq.es
[b]   A. L. Mudarra, C. Òdena
       Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, C/ Marcelli Domingo s/n, 43007 Tarragona (Spain)
[c]   Prof. F. Maseras
       Departament de Química
       Universitat Autònoma de Barcelona
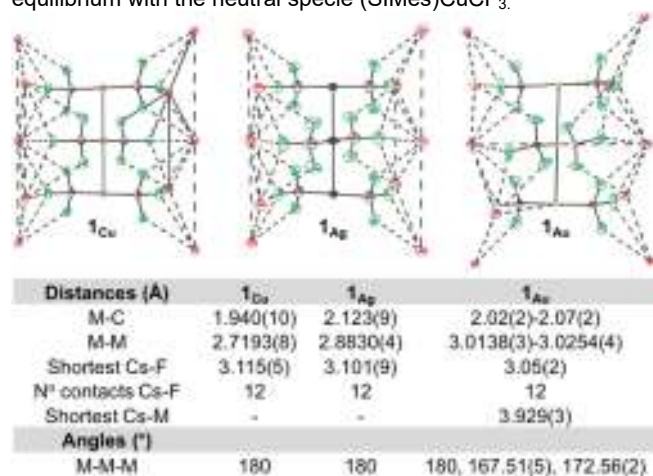   08193 Bellaterra (Spain)
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Inspired by our previous results, we started our investigations by targeting the access to (Cs)[M(CF$_3$)$_2$] (**1$_M$**, M = Cu, Au) using **1$_{Ag}$** as CF$_3$ shuttle.[2d] Gratifyingly, we were able to in situ generate **1$_{Cu}$** in quantitative yield using 1 equiv of CuI and 1 equiv of **1$_{Ag}$** in THF or DMF at rt after 1 hour (eqn. 1).[6] Although **1$_{Cu}$** is insufficiently stable for isolation,[7] we confirmed its structure by ^{19}F NMR spectroscopy, ESI-MS and single crystal X-ray

$$(Cs)[Ag(CF_3)_2] + CuI \xrightarrow[\text{1 h, rt, Ar}]{\text{THF or DMF}} (Cs)[Cu(CF_3)_2] \qquad (1)$$
$$\textbf{1}_{Ag}\text{, 1 equiv)} \quad \text{(1 equiv)} \qquad\qquad \textbf{1}_{Cu}\text{ (full conversion)}$$

$$CsF + Me_3SiCF_3 \xrightarrow[-78\,°C,\,1\,h,\,Ar]{\text{THF}} \xrightarrow[-60\,°C\,to\,rt,\,16\,h,\,Ar]{[AuCl(SMe_2)]\,(1\,equiv)} (Cs)[Au(CF_3)_2] \qquad (2)$$
$$\text{(3 equiv)} \quad \text{(3.3 equiv)} \qquad\qquad\qquad\qquad\qquad \textbf{1}_{Au}\text{ (85%)}$$

diffraction.[8] This result is certainly remarkable in view of the previously described difficulties to access to [Cu(CF$_3$)$_2$]⁻ species in a selective manner in solution. Under identical conditions, the reaction between **1$_{Ag}$** and [AuCl(SMe$_2$)] in THF afforded a complex reaction mixture. However, after some experimentation, we found that the treatment of 1 equiv of [AuCl(SMe$_2$)] with the combination Me$_3$SiCF$_3$/CsF (3.3/3) in THF afforded **1$_{Au}$**, a highly stable blue solid, in 85% isolated yield (eqn. 2). The resulting salt was fully characterized by NMR spectroscopy, ESI-MS and X-ray diffraction.

The X-ray structures of **1$_{Cu}$** and **1$_{Au}$** are shown in Figure 2, along with the most relevant parameters of the measured compounds including **1$_{Ag}$**, previously described by our group.[2d,9] In these series of Cs-salts, all the metal atoms are forming linear chains with metal-metal contacts, differing from the other previously described [M(CF$_3$)$_2$]⁻ anions,[1a,2e,3c,4] showing **1$_{Au}$** a zigzag pattern every three Au-atoms. Regarding the M–C bonds lengths, the Ag–C is the longest distance (2.12 Å), while the Cu–C the shortest with 1.94 Å. The Au–C distances, in the range of 2.04–2.07 Å due to the relativistic gold contraction effect,[10] are comparable with previously described (cat)[Au(CF$_3$)$_2$] salts.[1a,4] Regarding the Cu–C bond distance, it is shorter than the only (cat)[Cu(CF$_3$)$_2$] characterized by X-ray diffraction, [(SIMes)$_2$Cu][Cu(CF$_3$)$_2$] (1.94 vs 1.97 Å), which in solution is in equilibrium with the neutral specie (SIMes)CuCF$_3$.[3c]

Distances (Å)	1$_{Cu}$	1$_{Ag}$	1$_{Au}$
M-C	1.940(10)	2.123(9)	2.02(2)-2.07(2)
M-M	2.7193(8)	2.8830(4)	3.0138(3)-3.0254(4)
Shortest Cs-F	3.115(5)	3.101(9)	3.05(2)
N° contacts Cs-F	12	12	12
Shortest Cs-M	-	-	3.929(3)
Angles (°)			
M-M-M	180	180	180, 167.51(5), 172.56(2)

Figure 2. ORTEP structures of **1$_{Cu}$**, **1$_{Ag}$** and **1$_{Au}$** are shown with thermal ellipsoids set at 50% probability. Red (Cs), Grey (Carbon), Green (Fluorine), Orange (Copper), Black (Silver) and Yellow (gold). Most relevant parameters of the structures are shown in the table.

With a reliable route in hand for accessing the target **1$_M$** (M = Cu, Au), we next aimed to unravel the participation of these species, along with **1$_{Ag}$**, in the activation of aryl halides using as benchmark a common model system in trifluoromethylation reactions, 4-iodobiphenyl (**2**) (Scheme 1).[11] The reaction of **1$_{Ag}$** or **1$_{Au}$** with **2** in DMF at 50 °C during 24 hours did not provide the desired product, observing by ¹⁹F NMR the starting materials and/or decomposition products.[12] Delightfully, the reaction of **1$_{Cu}$** with 1.6 equivalents of **2** under the same reaction conditions led to an excellent yield of 4-trifluoromethylbiphenyl (**2$_{CF3}$**, 93%) by

¹⁹F NMR spectroscopy, along with the formation of [Cu(CF$_3$)I]⁻ (**3$_{Cu}$**) (Scheme 1b). These preliminary results confirm, for the first time, the involvement of **1$_{Cu}$** in the activation of **2**, its capability to transfer the two trifluoromethyl groups, and highlights its remarkable performance compared to previously described Cu-mediated systems under analogous reaction conditions.[3g]
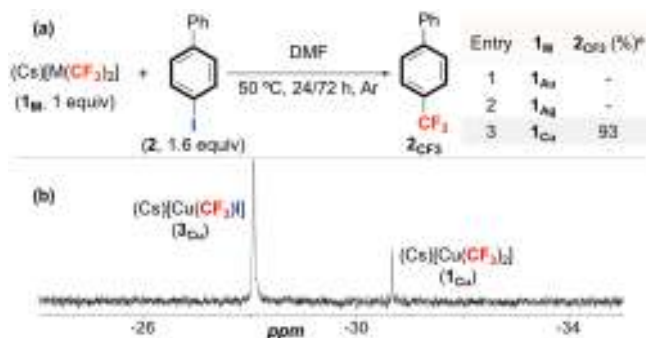
Scheme 1. a)Trifluoromethylation of **2** with **1$_{Cu}$**, **1$_{Ag}$**, **1$_{Au}$**. [a] Yield obtained by ¹⁹F NMR analysis using 4,4′-difluorobiphenyl as internal standard. b) ¹⁹F NMR spectrum in the region of CuCF$_3$ species after the trifluoromethylation reaction.

We next explore the reactivity of **1$_{Cu}$** towards different representative organic electrophiles such as 10-iodobenzo[h]quinoline (**4**), benzyl bromide (**5**), methyl-6-bromopyridine-2-carboxylate (**6**) and 1-(allyloxy)-2-iodobenzene (**7**). In all the cases, the yields were from moderate to excellent, pointing out the capability of these bis-(trifluoromethyl)cuprate species activating a variety of bonds such as Csp²–I, Csp²–Br and Csp³–Br (Scheme 2). The selection of 1-(allyloxy)-2-iodobenzene (**7**) as representative substrate was not adventitious since it is used to evaluate the presence of radical species.[3d,f] Under our standard conditions, we exclusively observed **7$_{CF3}$**, discarding the participation of Cu^{II} radical intermediates during the reaction.
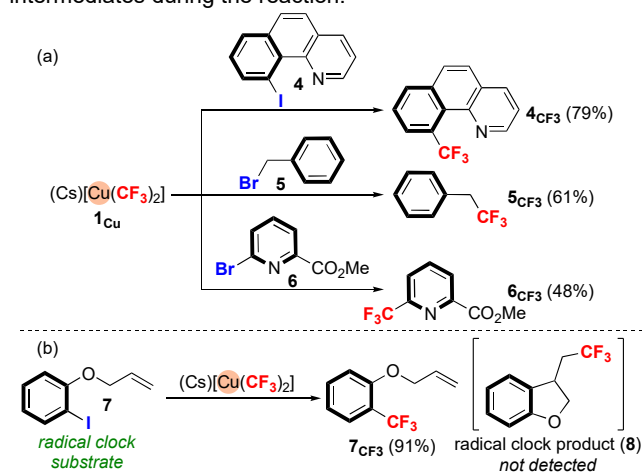
Scheme 2. Trifluoromethylation reactions. [a]Reaction conditions: **1** (0.016 mmol), substrate (0.0256 mmol), DMF (0.6 mL), 50 °C (**4**, **5** and **7**) or 80 °C (**6**), 24 h under Ar. [b] Yield obtained by ¹⁹F NMR analysis using 4,4′-difluorobiphenyl as internal standard.

Intrigued by spectacular performance of 1_{Cu} compared to its silver and gold congeners, and the experimental observation of other potentially reactive species such as 3_{Cu} (Scheme 1b), we decided to examine these intricacies through a computational study. There are a limited number of theoretical mechanistic studies on copper-catalyzed/mediated trifluoromethylation reactions of aryl halides and they are not directly related to our system.[3d,f,5d,13] DFT calculations were carried out with the M06 functional with a double-ζ plus polarization basis set in a DMF continuum solvent. A data set collection of computational results is available in the ioChem-BD repository.[14] We used as model reagent phenyl iodide, and we did not include the countercation of 1_M in the calculations.[15] In alignment with the experimental results when using **7** as substrate, preliminary calculations allowed us to rule out radical mechanisms with involvement of Cu^{II} intermediates.[16] Our favored mechanism involves oxidative addition (OA) through a concerted transition state to form Cu^{III} intermediates, as shown in Figures 3 and 4. We first analyzed the direct involvement of species $[Cu(CF_3)_2]^-$, labeled as $I1^{Cu}$, as trifluoromethylating agent. The free energy profile, shown in Figure 3, shows a quite high barrier of 29.2 kcal/mol, which would lead to a too slow trifluoromethylation process at the experimental conditions.
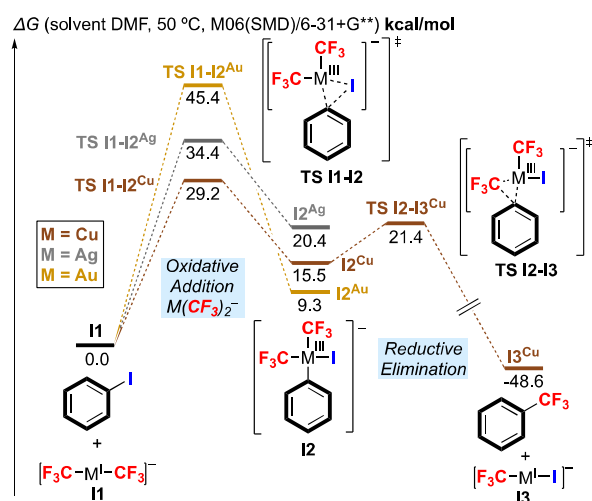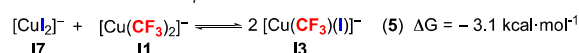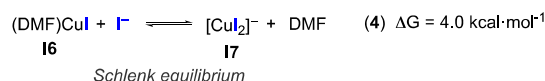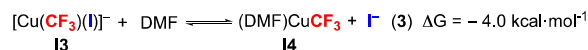

Figure 3. Computed energy profile for the oxidative addition and reductive elimination sequence of different $[M(CF_3)_2]^-$ complexes. Free energies in kcal/mol.
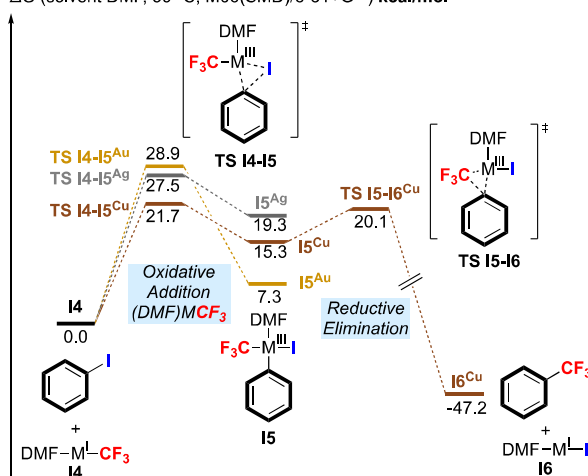
In view of this result, we investigated other potential reactive species. Interestingly, the situation changes if the trifluoromethylating agent is $(DMF)CuCF_3$ ($I4^{Cu}$). This copper species is not among the initial species in solution, but it can be generated efficiently through the nearly thermoneutral equilibria outlined in equations 3 to 5. The initial generation of $I4^{Cu}$ will come from ligand substitution in $I3^{Cu}$, which is the side product in the first, slow, trifluoromethylation process, shown in Figure 3.[17] Once a critical concentration of $I4^{Cu}$ is reached, the second, faster, trifluoromethylation starts with an affordable barrier of 21.7 kcal/mol (Figure 4), and this generates as side-product $I6^{Cu}$, which through the equilibria in equations 4 and 5 can regenerate $I4^{Cu}$ and restarts the process.[18] The validity of this DFT description was confirmed by microkinetic modeling,[19] where the evolution of concentrations through time is estimated from initial concentrations and theoretically computed rate constants. This microkinetic modeling (see Figure S15) results in a reaction time compatible with experiment in spite of the high barrier of 29.2 kcal/mol for the first reaction (Figure 3). An induction period, required for the generation of $(DMF)CuCF_3$ is also predicted.

■ Speciation of copper complexes in solution

$[Cu(CF_3)(I)]^-$ + DMF $\rightleftharpoons$ $(DMF)CuCF_3$ + I^- (3) $\Delta G = -4.0$ kcal·mol^{-1}
   I3   I4

$(DMF)CuI$ + I^- $\rightleftharpoons$ $[CuI_2]^-$ + DMF   (4) $\Delta G = 4.0$ kcal·mol^{-1}
   I6   I7
           Schlenk equilibrium

$[CuI_2]^-$ + $[Cu(CF_3)_2]^-$ $\rightleftharpoons$ 2 $[Cu(CF_3)(I)]^-$ (5) $\Delta G = -3.1$ kcal·mol^{-1}
   I7   I1   I3

**Figure 4.** Computed energy profile for the oxidative addition and reductive elimination sequence of different $(DMF)MCF_3$ complexes and speciation of copper in reaction conditions. Free energies in kcal/mol.

It is noteworthy to mention that for silver and gold analogous systems, also in Figures 3 and 4, we found that the paucity of reactivity towards the trifluoromethylation of aryl halides is related to a sluggish oxidative addition event. The increased barrier when going from copper to gold correlates with the nucleophilic character of the different metallates as can be seen in Table S3.

Although to a certain extent it is counterintuitive that the neutral $I4^{Cu}$ species is a better trifluoromethylating agent than the anionic complex $I1^{Cu}$, this can be explained considering the lability of the DMF–Cu bond, which favors the approach of PhI to the metal center (see Scheme S4). This mechanism explains also the convenience of using coordinating solvents, such as DMF for the reaction to take place.[20] Under our reaction conditions, 1_{Cu} acts as CF_3 reservoir, being $(DMF)CuCF_3$ the most active species.[3f]

We then aimed to experimentally corroborate this theoretical mechanistic scenario, with these two concatenated pathways. To do so, we monitored by ^{19}F NMR spectroscopy the trifluoromethylation reaction of **2**, first forming a mixture of 1_{Cu} and 1_{Ag} (83:17) using substoichiometric amounts of CuI respect to 1_{Ag}, and next adding excess of CuI. Our goal was to ensure

that, initially, all the copper was speciated as 1_{Cu}, since an excess of CuI (5 equiv) generates a mixture containing 1_{Cu} along with $[Cu(CF_3)I]^-$ (3_{Cu}) (65:35). Based on eqn. 3-5, in the absence of excess of I^-, 3_{Cu} would not be formed, hindering the most facile route shown in Figure 4 and observing a delay in the formation of 2_{CF3} due to the proposed induction period. Under these substoichiometric conditions, after 20 h at 50 ºC, we only observed the trifluoromethylated product in 4% yield.[21] As predicted by DFT, when we added the excess of CuI to the reaction mixture, we observed a dramatic increase in yield of 2_{CF3} (55% after 4 hours). Moreover, we detected the appearance not only of (Cs)[Cu(CF$_3$)I] (s, δ = –27.44 ppm)[22] but also of (DMF)CuCF$_3$ (broad signal, δ = –25.75 ppm), the reactive species based on our DFT calculations (Figure 5b).[23]
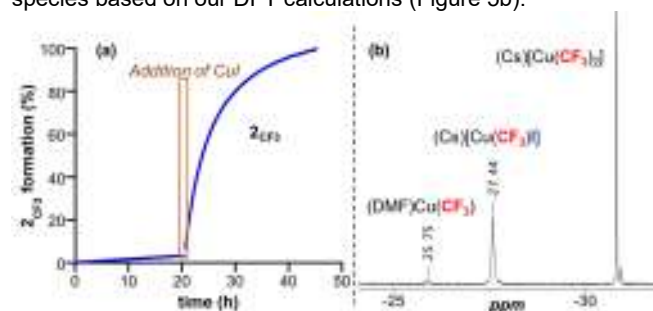
Figure 5. a) Kinetic experiment using 1_{Cu} before and after the addition of excess of CuI; b) ^{19}F NMR spectrum showing the Cu species present in the trifluoromethylation reaction of **2**, 4 hours after the addition of CuI.

In summary, we report the synthesis and structural characterization of (Cs)[M(CF$_3$)$_2$] (M = Cu (1_{Cu}), Au (1_{Au})) and compare their reactivity, along with 1_{Ag}, in the trifluoromethylation of a benchmark aryl halide from an experimental and computational point of view. The selective synthesis of 1_{Cu} allowed us not only to unravel the potential of 1_{Cu} in Cu-mediated trifluoromethylation reactions but also to disclose the complex underlying Cu$^{I/III}$ reaction mechanism due to the generation of more reactive species such as (DMF)CuCF$_3$.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

[1]   For representative examples on the synthesis and reactivity of AuCF₃ complexes, see: a) S. Martínez-Salvador, L. R. Falvello, A. Martín, B. Menjón, *Chem. Eur. J.* **2013**, *19*, 14540; b) M. S. Winston, W. J. Wolf, F. D. Toste, *J. Am. Chem. Soc.* **2014**, *136,* 7777; c) J. Gil-Rubio, J. Vicente, *Dalton Trans.* **2015**, *44*, 19432; d) A. Pérez-Bitrián, S. Martínez-Salvador, M. Baya, J. M. Casas, A. Martín, B. Menjón, J. Orduna, *Chem. Eur. J.* **2017**, *23*, 6919; e) M. D. Levin, T. Q. Chen, M. E. Neubig, C. M. Hong, C. A. Theulier, I. J. Kobylianskii, M. Janabi, J. P. O'Neil, F. D. Toste, *Science* **2017**, *356*, 1272; f) A. Pérez-Bitrián, M. Baya, J. M. Casas, A. Martín, B. Menjón, J. Orduna, *Angew. Chem. Int. Ed.* **2018**, *57*, 6517; *Angew. Chem.* **2018**, *130*, 6627.

[2]   For representative examples on the synthesis and reactivity of AgCF₃ complexes, see: a) W. Tyrra, D. Naumann, *J. Fluorine Chem.* **2004**, *125*, 823; b) Z. Weng, R. Lee, W. Jia, Y. Yuan, W. Wang, X. Feng, K.-W. Huang, *Organometallics* **2011**, *30*, 3229; c) A. Hafner, N. Jung, S. Bräse, *Synthesis* **2014**, *46*, 1440; d) S. Martínez de Salinas, A. L. Mudarra, J. Benet-Buchholz , T. Parella, F. Maseras, M. H. Pérez-Temprano, *Chem. Eur. J.* **2018**, *24*, 11895; e) D. Joven-Sancho, M. Baya, A. Martín, B. Menjón, *Chem. Eur. J.* **2018**, *24*,13098.

[3]   For representative examples on the synthesis and reactivity of CuCF₃ complexes, see: a) D. M. Wiemers, D. J. Burton, *J. Am. Chem. Soc.* **1986**, *108*, 832; b) G. G. Dubinina, H. Furutachi, D. A. Vicic, *J. Am. Chem. Soc.* **2008**, *130*, 8600; c) G. G. Dubinina, J. Ogikubo, D. A. Vicic, *Organometallics* **2008**, *27*, 6233; d) H. Morimoto, T. Tsubogo, N. D. Litvinas, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2011**, *50*, 3793; *Angew. Chem.* **2011**, *123*, 3877; e) O. A. Tomashenko, E. C. Escudero-Adán, M. Martínez-Belmonte, V. V. Grushin, *Angew. Chem. Int. Ed.* **2011**, *50*, 7655; *Angew. Chem.* **2011**, *123*, 7797; f) A. I. Konovalov, A. Lishchynskyi, V. V. Grushin, *J. Am. Chem. Soc.* **2014**, *136*, 13410; g) P. T. Kaplan, J. A. Lloyd, M. T. Chin, D. A. Vicic, *Beilstein J. Org. Chem.* **2017**, *13,* 2297.

[4]   a) D. Zopes, S. Kremer, H. Scherer, L. Belkoura, I. Pantenburg, W. Tyrra, S. Mathur, *Eur. J. Inorg. Chem.* **2011**, 273; b) D. Zopes, C. Hegemann, J. Schläfer, W. Tyrra, S. Mathur, *Inorg. Chem.* **2015**, *54*, 3781.

[5]   a) M. A. Willert-Porada, D. J. Burton, N. C. Baenzig, *J. Chem. Soc., Chem. Comm.* **1989**, *21*, 1633; b) A. Kütt, V. Movchun, T. Rodima, T. Dansauer, E. B. Rusanov, I. Leito, I. Kaljurand, J. Koppel, V. Pihl, I. Koppel, G. Ovsjannikov, L. Toom, M. Mishima, M. Medebielle, E. Lork, G.-V. Röschenthaler, I. A. Koppel, A. A. Kolomeitsev, *J. Org. Chem.*

2008, *73*, 26070; c) I. Popov, S. Lindeman, O. Daugulis, *J. Am. Chem. Soc.* **2011**, *133*, 9286; d) I. A. Sanhueza, M. C. Nielsen, M. Ottiger, F. Schoenebeck, *Helvetica Chimica Acta*, **2012**, *95*, 2231; e) M. Hu, C. Ni, J. Hu, *J. Am. Chem. Soc.* **2012**, *134*, 15257; f) K. Aikawa, Y. Nakamura, Y. Yokota, W. Toya, K. Mikami, *Chem. Eur. J.* **2015**, *21*, 96.

[6]   It is crucial that the amount of CuI is accurately measured when performing the reaction in DMF since an excess of CuI generates a mixture of 1_{Cu} and $[Cu(CF_3)I]^-$ (3_{Cu}) in different proportions.

[7]   In THF, the compound decomposes less than 10% after 15 days stored in the glovebox at –30 ºC. At rt, overnight, 1_{Cu} decomposes around 18%. See SI for further details.

[8]   CCDC 1891323 (1_{Cu}), CCDC 1891324 (1_{Au}) and CCDC 1891325 (**S1**) contain the supplementary crystallographic data for these structures. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[9]   The solid-state structures of the ionic compounds 1_{Cu} and 1_{Au} have been established by single crystal X-ray structure analysis at 100 K. The structure of 1_{Cu} is isostructural to the previously reported structure of 1_{Ag} (see ref 2d) while complex 1_{Au} crystallizes in a new unit cell within the space group $P2_1$/m, but showing a very similar packing as 1_{Cu}.

[10]   A. Bayler, A. Schier, G. A. Bowmaker, H. Schmidbaur, *J. Am. Chem. Soc.* **1996**, *118*, 7006.

[11]   We selected analogous reaction conditions to those reported previously by Vicic and co-workers. See ref 3g for further details.

[12]   It is worth mentioning that for 1_{Au}, the presence of the cesium as cation does not impact its reactivity towards I₂, obtaining a Au(III) complex (**S1**), analogous to the one previously described by Menjón and co-workers. See pag S7 of the SI and ref 1a for further details.

[13]   a) G. E. Carr, R. D. Chambers, T. F. Holmes, D. G. Parker, *J. Chem. Soc., Perkin Trans. 1* **1988**, 921; b) Q.-Y. Chen, S.-W. Wu, *J. Chem. Soc., Perkin Trans. 1* **1989**, 2385; c) M. Chen, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2013**, *125*, 11842; *Angew. Chem.* **2013**, *125*, 4341.   d) J. Jover, F. Maseras, *Chem. Commun.* **2013**, *49*, 10486.

[14]   M. Alvarez-Moreno, C. de Graaf, N. Lopez, F. Maseras, J. M. Poblet, C. Bo, *J. Chem. Inf. Model.* **2015**, *55*, 95.

[15]   Previous experimental and theoretical data for 1_{Ag} suggest no contribution of ion pairs in DMF. See SI pag S17 for further details.

[16]   See SI pag S19-S20 for further details.

[17] The displacement of I⁻ in this species has been proposed to occur by water in similar systems: See ref 5e.

[18] We also computed the OA barrier starting from **I3^{Cu}**, being 2.4 kcal/mol higher than the one for **I4^{Cu}**. See SI page S19 for further details.

[19] M. Besora, F. Maseras, *WIREs Comput. Mol. Sci*. **2018**, *8*, 1372.

[20] When the same reaction is performed in THF as solvent, a weaker coordinating solvent, the product formation is around 12% during 5 days at 50 ºC.

[21] The different yield of **2$_{CF3}$** in comparison with the one obtained in Scheme 1a can be explained by two mains reasons: i) No stirring in the reaction media and ii) the presence of **1$_{Ag}$** that could act as scavenger of the I⁻ avoiding the formation of **3$_{Cu}$**.

[22] We observed a variation on the chemical shift of (Cs)[Cu(CF$_3$)I] (**3$_{Cu}$**) during the reaction, from –26.83 ppm to –28.00 ppm, due to the formation of [CuI$_2$]⁻. See SI pag S39-40 for further details.

[23] A. Zanardi, M. A. Novikov, E. Martin, J. Benet-Buchholz, V. V. Grushin, *J. Am. Chem. Soc.* **2011**, *133*, 20901.

Layout 1:

COMMUNICATION

Herein, we investigate the involvement of bis-(trilfuoromethyl)metallates of coinage metals in trifluoromethylation reactions. We report, for the first time, not only the selective access to a unique (Cs)[Cu(CF$_3$)$_2$] salt, but also its superior activity compared to its congeners, and a detailed mechanistic understanding, combining experimental and computational studies.

experimental and computational study
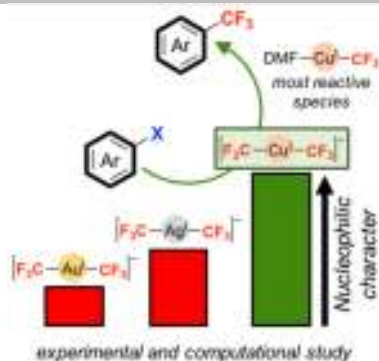
S. Martínez de Salinas, A. L. Mudarra, C. Òdena, M. Martínez Belmonte, J. Benet-Buchholz, F. Maseras*, M. H. Pérez-Temprano*

Exploring the role of coinage metallates in trifluorometalation: a combined experimental and theoretical study