

Stable and Storable $N(\text{CF}_3)_2$ Transfer Reagents

Leon N. Schneider,^[a] Eva-Maria Tanzer Krauel,^[c] Carl Deutsch,^[b] Klaus Urbahns,^[b] Tobias Bischof,^[a] Kristina A. M. Maibom,^[a] Johannes Landmann,^[a] Fabian Keppner,^[a] Christoph Kerpen,^[a] Michael Hailmann,^[a] Ludwig Zapf,^[a] Tanja Knuplez,^[a] Rüdiger Bertermann,^[a] Nikolai V. Ignat'ev,^[a] and Maik Finze*^[a]

In memory of Siegfried Hünig.

Abstract: Fluorinated groups are essential for drug design, agrochemicals, and materials science. The bis(trifluoromethyl) amino group is an example of a stable group that has a high potential. While the number of molecules containing perfluoroalkyl, perfluoroalkoxy, and other fluorinated groups is steadily increasing, examples with the $N(\text{CF}_3)_2$ group are rare. One reason is that transfer reagents are scarce and metal-based storable reagents are unknown. Herein, a set of Cu^{I} and Ag^{I} bis(trifluoromethyl)amido complexes stabilized by N- and

P-donor ligands with unprecedented stability are presented. The complexes are stable solids that can even be manipulated in air for a short time. They are bis(trifluoromethyl) amination reagents as shown by nucleophilic substitution and Sandmeyer reactions. In addition to a series of benzylbis(trifluoromethyl)amines, 2-bis(trifluoromethyl)amino acetate was obtained, which, upon hydrolysis, gives the fluorinated amino acid *N,N*-bis(trifluoromethyl)glycine.

Transition metal perfluoroalkyl complexes are highly valuable reagents for the synthesis of fluorinated biologically active molecules that are employed as pharmaceuticals or agrochemicals and in materials applications.^[1–6] Especially, copper(I) complexes are important as they enable the introduction of a broad variety of perfluoroalkyl groups into organic molecules that range from the simplest congener, trifluoromethyl, to longer linear and branched perfluoroalkyl groups such as the heptafluoroisopropyl (hfip) group.^[7–10] Although many of these complexes are used either in situ or immediately after generation, some complexes have been isolated and characterized, in

detail. These complexes are often stabilized by co-ligands that typically are pyridines or phosphanes, for example $[(\text{bpy})\text{CuC}_2\text{F}_5]$ (Figure 1)^[11] and $[(\text{Ph}_3\text{P})_2\text{Cu}\{\text{CF}(\text{CF}_3)_2\}]$ ($[(\text{Ph}_3\text{P})_2\text{Cu}(\text{hfip})]$).^[12] Silver(I) complexes have been employed as perfluoroalkylation reagents as well,^[13–14] although to a lesser extent than the related copper(I) derivatives. Because of their easy accessibility using silver(I) fluoride and the respective perfluoroalkene, for example, heptafluoropropene and tetrafluoroethylene,^[15] they

[a] L. N. Schneider, T. Bischof, K. A. M. Maibom, Dr. J. Landmann, Dr. F. Keppner, Dr. C. Kerpen, Dr. M. Hailmann, L. Zapf, T. Knuplez, Dr. R. Bertermann, Dr. N. V. Ignat'ev, Prof. Dr. M. Finze
Institut für nachhaltige Chemie & Katalyse mit Bor (ICB)
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: maik.finze@uni-wuerzburg.de
Homepage: <http://go.uniwiue.de/finze-group>

[b] Dr. C. Deutsch, Dr. K. Urbahns
Merck Healthcare KGaA
Frankfurter Straße 250, 64293 Darmstadt (Germany)

[c] Dr. E.-M. Tanzer Krauel
Insitro Inc (previously employed by Merck KGaA, Darmstadt (Germany)
where the research supporting this publication was conducted).
279 E Grand Ave., South San Francisco, CA 94080 (USA)

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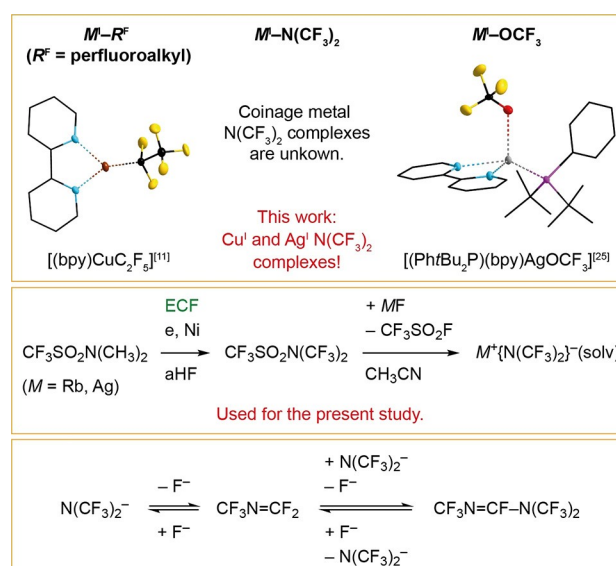


Figure 1. Top: Comparison of the availability of Cu^{I} and Ag^{I} complexes. Middle: Two-step synthesis of salts of the $N(\text{CF}_3)_2^-$ ion by electrochemical fluorination (ECF) of $\text{CF}_3\text{SO}_2\text{N}(\text{CH}_3)_2$.^[16–17] Bottom: Decomposition sequence of the $N(\text{CF}_3)_2^-$ ion via perfluoroazapropene to give $\text{CF}_3\text{N}=\text{CF}-\text{N}(\text{CF}_3)_2$.^[18]

are of increasing interest. Similarly, copper(I) and silver(I) complexes with perfluorinated ligands that are coordinated via oxygen, sulfur, or selenium to the coinage metal have recently come into focus and have been established as transfer reagents for perfluorinated groups, for example for trifluoromethoxylation,^[19–20] trifluoromethylthiolation,^[21–22] and trifluoromethylselenation reactions.^[23–24] So far, only few Cu^I and Ag^I metal complexes with the trifluoromethoxy ligand like [(Ph_tBu₂P)(bpy)AgOCF₃]^[25] are known (Figure 1).^[25–27] The small number of structurally characterized complexes is due to the low stability of the OCF₃[−] ion that easily loses F[−] while releasing carbonyl fluoride (difluorophosgene), which enabled the use of AgOCF₃ as C(O)F₂ source.^[28] This synthetic useful reaction is similar to the decomposition of perfluoroalkyl ions into perfluoroalkenes and fluoride, for example the generation of tetrafluoroethylene from the pentafluoroethyl ion.

In contrast to perfluoroalkyl and perfluoroalkoxy groups, the chemistry of related perfluoroalkyl nitrogen substituents has been studied to a much lesser extent. Some synthetic strategies towards *N*-trifluoromethylamines and related *N*-perfluoroalkyl nitrogen derivatives have been developed in recent years.^[28–38] Efficient strategies towards *N,N*-bis(perfluoroalkyl)nitrogen compounds remain scarce, presumably, because of the lack of suitable starting materials.^[18,39–40] Especially the *N,N*-bis(trifluoromethyl)amino group is of interest as its organic derivatives are known to exhibit high stability, for example against acids and bases,^[1,41] and because its potential as substituent in pharmaceuticals was demonstrated, earlier.^[42–43] *N,N*-Bis(trifluoromethyl)amino derivatives have been obtained from perfluoroazapropene CF₃N=CF₂ as initial starting compound or through tedious reaction sequences.^[18,39,44] Perfluoroazapropene is only accessible through laborious multistep

syntheses,^[45–47] it is a reactive gas that requires special equipment for handling, and its transformation into the synthetically useful bis(trifluoromethyl)amide ion N(CF₃)₂[−] is usually accompanied by dimerization giving CF₃N=CF–N(CF₃)₂ (Figure 1). *N,N*-Bis(trifluoromethyl)trifluoromethanesulfonimide CF₃SO₂N(CF₃)₂ is accessible through electrochemical fluorination (ECF) of CF₃SO₂N(CH₃)₂ in anhydrous hydrogen fluoride (aHF) according to the Simons process on a large scale.^[16,44,48] CF₃SO₂N(CF₃)₂ reacts with fluorides such as silver(I) and rubidium fluoride providing a convenient access to the N(CF₃)₂[−] ion (Figure 1).^[17,49] Some *N,N*-bis(trifluoromethyl)amides with organic cations are stable whereas metal salts can only be handled in solution to prevent decomposition. Few of these organic salts have been used in metatheses^[49–52] or for the synthesis of organic molecules with the N(CF₃)₂ group.^[39–40,53–54] So far, mercury complexes, for example [Hg{N(CF₃)₂}₂], are the sole stable metal complexes with the N(CF₃)₂ ligand, known.^[55] The salts *M*{N(CF₃)₂}·NCCH₃ (*M* = Ag, Cu) have been described as white solids.^[49] However, these salts cannot be stored because they immediately start to decompose, even at low temperature.^[56] So, they are no convenient, storable N(CF₃)₂ transfer reagents.

Herein, we present a set of stable and storable copper(I) and silver(I) complexes of the bis(trifluoromethyl)amido ligand. These complexes have been found to be promising compounds for the transfer of the bis(trifluoromethyl)amino group into organic molecules.

Copper(I) complexes with the N(CF₃)₂ ligand have been synthesized via metatheses using CH₃CN solutions of rubidium or cesium bis(trifluoromethyl)amide that were generated from CF₃SO₂N(CF₃)₂ and the respective dry alkali metal fluoride (Figure 2). The dark orange complex [(bpy)Cu{N(CF₃)₂}] (**1a**, bpy = 2,2'-bipyridine) was prepared from a solution of Rb

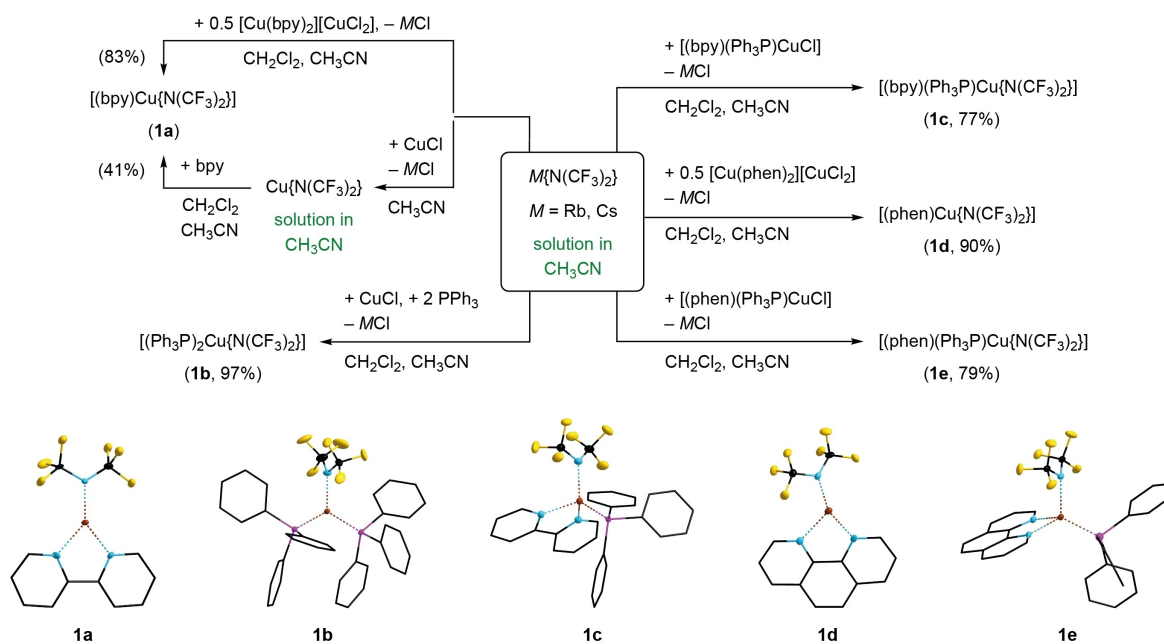


Figure 2. Synthesis and crystal structures of the copper(I) complexes **1a**–**1e** (thermal ellipsoids set at 25% probability; H atoms are omitted for clarity; C atoms of the N- and P-donor ligands are depicted as stick models).

$\{N(CF_3)_2\}$ in acetonitrile and $[Cu(bpy)_2][CuCl_2]$. The copper(I) derivative $[Cu(bpy)_2][CuCl_2]$ was either isolated and redissolved or prepared in situ from copper(I) chloride and 2,2'-bipyridine giving almost equal yields for **1a** of 83 and 82%, respectively. Alternatively, $Cu\{N(CF_3)_2\}$ was synthesized from $CuCl$ and $Rb\{N(CF_3)_2\}$ in acetonitrile, and 2,2'-bipyridine was added to give **1a** in 41% yield (Figure 2). Because of the lower yield, all further copper(I) bis(trifluoromethyl)amido complexes were synthesized from preformed copper(I) complexes and $Rb\{N(CF_3)_2\}$ or $Cs\{N(CF_3)_2\}$. In addition to **1a**, the analogous dark orange 1,10-phenanthroline (phen) complex $[(phen)Cu\{N(CF_3)_2\}]$ (**1d**) was isolated in 90% yield. The colorless triphenylphosphane complex $[(Ph_3P)_2Cu\{N(CF_3)_2\}]$ (**1b**) that was obtained in almost quantitative yield represents the third complex with a tricoordinate copper center. In contrast, the yellow-orange mixed complexes $[(bpy)(Ph_3P)Cu\{N(CF_3)_2\}]$ (**1c**) and $[(phen)(Ph_3P)Cu\{N(CF_3)_2\}]$ (**1e**) that were isolated in 77 and 79% yield, respectively, contain four coordinate Cu^I centers (Figure 2).

Acetonitrile solutions of the silver(I) salt $Ag\{N(CF_3)_2\}$ obtained from silver(I) fluoride and $CF_3SO_2N(CF_3)_2$ (Figure 1) were used for the synthesis of silver(I) bis(trifluoromethyl)amido complexes (Figure 3). In analogy to the copper(I) $N(CF_3)_2$ derivatives, three- and four-coordinate Ag^I complexes were obtained. The three colorless complexes $[(bpy)Ag\{N(CF_3)_2\}]$ (**2a**), $[(Ph_3P)_2Ag\{N(CF_3)_2\}]$ (**2b**), and $[(bpy)(Ph_3P)Ag\{N(CF_3)_2\}]$ (**2c**) were isolated in yields of 78, 89, and 90%, respectively. The 2,2':6',2''-terpyridine (terpy) derivative $[(terpy)Ag\{N(CF_3)_2\}]$ (**2f**) was obtained as a yellow crystalline material in 62% yield.

The silver(I) triphenylphosphane complex **2b** reacts with additional triphenylphosphane under formation of the complex salt $[Ag(PPh_3)_4]\{N(CF_3)_2\}$ (**3**) that is composed of the tetrahedral $[Ag(PPh_3)_4]^+$ cation and a non-coordinated $\{N(CF_3)_2\}^-$ anion. Salt **3** was selectively prepared from triphenylphosphane and $Ag\{N(CF_3)_2\}$ in 60% yield and characterized, in detail (Figure 3). In contrast to $[(Ph_3P)_2Ag\{N(CF_3)_2\}]$ (**2b**), the respective copper(I) complex $[(Ph_3P)_2Cu\{N(CF_3)_2\}]$ (**1b**) does not react with an excess of triphenylphosphane to result in a complex salt and **1b** was

obtained even in the presence of a twofold excess of PPh_3 in 78% yield.

The copper(I) and silver(I) bis(trifluoromethyl)amido complexes are thermally stable with decomposition temperatures ranging from 114 to 204 °C (onset, DSC measurements). The solid complexes can be stored in a glove box in an inert atmosphere for more than one year without noticeable decomposition and they can be manipulated in air for a short period of time enabling a convenient handling.

The coordination of the bis(trifluoromethyl)amido ligand to copper in **1a–1e** and to silver in **2a–2c** and **2f** in the solid state is evident from single-crystal X-ray diffraction (SC-XRD) analyses, which are the first examples for SC-XRD studies on $N(CF_3)_2$ coordination compounds (Figures 2 and 3 and Table S5 in the Supporting Information). The metal–nitrogen distances depend on the coordination number of the metal center. So, $d(Cu–N(CF_3)_2)$ is 1.900(9)–2.004(8) Å in the tricoordinate complexes **1a**, **1b**, and **1d** but 2.0654(16) and 2.101(2) Å in four-coordinate **1c** and **1e**, respectively. As expected from the slightly smaller covalent radius of copper (1.32 Å for Cu vs. 1.45 Å for Ag),^[57] the metal– $N(CF_3)_2$ distance is longer in the silver(I) complexes with 2.138(2) and 2.255(4) Å for tricoordinate complexes **2a** and **2b** and 2.330(5) and 2.233(3) Å for the four-coordinate derivatives **2c** and **2f**. The crystal structure of **3** proves the ionic nature of the complex salt (Figure 3). The $N(CF_3)_2^-$ ion, which was until now not characterized by SC-XRD, at all, is disordered over two positions precluding a detailed discussion of bonding parameters.

All copper(I) and silver(I) $N(CF_3)_2$ derivatives were characterized by multinuclear NMR, IR, and Raman spectroscopy, as well as by elemental analysis. The ^{19}F NMR signal of the complexes is in the range from –40.7 to –43.7 ppm, which is similar to $\delta(^{19}F)$ of $Ag\{N(CF_3)_2\}$ and $Cu\{N(CF_3)_2\}$ in CD_3CN with –42.1 and –43.4 ppm, respectively. The signal of $Rb\{N(CF_3)_2\}$ in CD_3CN is observed at a significantly lower chemical shift of –37.5 ppm (Figure S17). Thus, the interaction between the coinage metal and the $N(CF_3)_2^-$ ligand in solution is evident

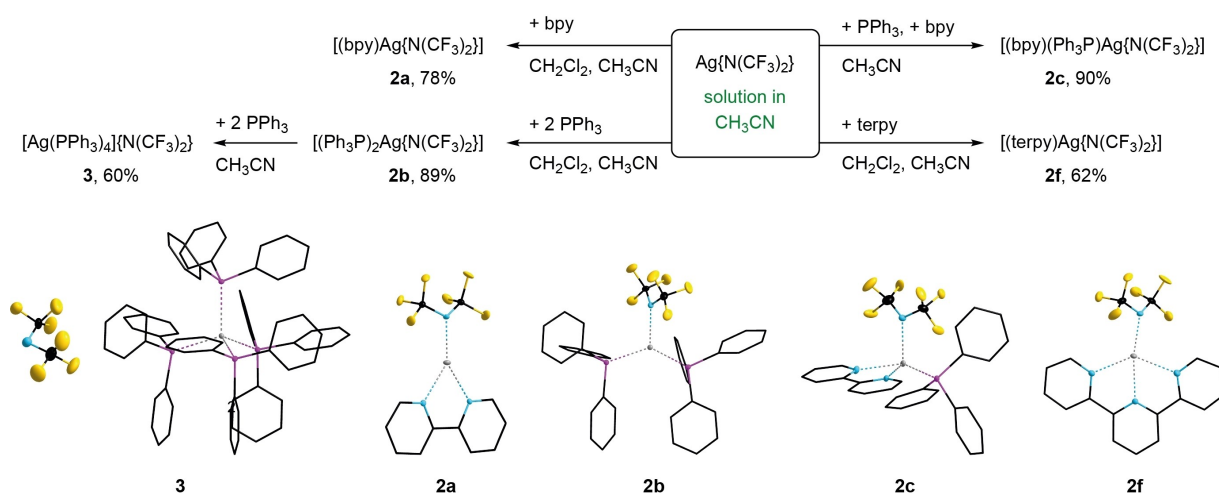


Figure 3. Synthesis and crystal structures of the silver(I) complexes **2a–2c**, **2f** and of the complex silver(I) salt **3** (thermal ellipsoids set at 25% probability; H atoms are omitted for clarity; C atoms of the N- and P-donor ligands are depicted as stick models).

from the ^{19}F NMR spectroscopic data. The signal of the complex salt $[\text{Ag}(\text{PPh}_3)_4\{\text{N}(\text{CF}_3)_2\}]$ (**3**) in CD_2Cl_2 is observed at -39.6 ppm, which, in turn, is indicative for the ionic nature that was proven by the SC-XRD study. Solid state ^{19}F NMR spectra reveal an even more pronounced difference for $\delta_{\text{iso}}(^{19}\text{F})$ with -31.6 and -34.6 ppm for the salt **3** and -40.4 and -41.4 ppm for the complexes $[(\text{Ph}_3\text{P})_2\text{Ag}\{\text{N}(\text{CF}_3)_2\}]$ (**2b**) and $[(\text{Ph}_3\text{P})_2\text{Cu}\{\text{N}(\text{CF}_3)_2\}]$ (**1b**) (Figure S19). The ^{31}P and ^{13}C solid state NMR spectra of **3** and **2b** also reveal the different bonding situations in the two related silver(I) bis(trifluoromethyl)amido complexes. Especially, the smaller $^1J(^{107/109}\text{Ag}, ^{31}\text{P})$ coupling constants observed for **3** are indicative for a four-coordinate complex whereas larger $^1J(^{107/109}\text{Ag}, ^{31}\text{P})$ hint towards a three-coordinate silver complex in case of **2b** (Figure S18).^[58]

The bis(triphenylphosphane) complexes **1b** and **2b** were studied by diffusion-ordered spectroscopy (DOSY) in CD_3CN and CD_2Cl_2 (Table S7). The diffusion constants derived from the ^1H and ^{19}F NMR measurements on samples dissolved in CD_2Cl_2 are very similar. The hydrodynamic radii of **1b** (^1H DOSY: 6.15 Å; ^{19}F DOSY: 5.97 Å) and **2b** (^1H DOSY: 6.16 Å; ^{19}F DOSY: 6.00 Å) calculated from diffusion constants using a modified Stokes-Einstein equation, are close to radii estimated from the crystal structures (**1b**: 5.07 Å; **2b**: 5.08 Å; see Supporting Information for a detailed description). Thus, it can be concluded that **1b** and **2b** remain intact in CD_2Cl_2 . In contrast, in CD_3CN the diffusion constants derived from the ^1H NMR signals of the PPh_3 ligands and from the ^{19}F NMR signal of the $\text{N}(\text{CF}_3)_2^-$ ligand are significantly different. However, the diffusion constant of the unbound $\text{N}(\text{CF}_3)_2^-$ ion ($D_t(^{19}\text{F}) = 24.04 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$) derived from a DOSY study on **3** in CD_3CN is much larger than $D_t(^{19}\text{F})$ measured for **1b** ($17.48 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$) and **2b** ($14.65 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$) in the same solvent. These data indicate an equilibrium between coordinated and free $\text{N}(\text{CF}_3)_2^-$ in solutions of **1b** and **2b** in CD_3CN as $D_t(^{19}\text{F})$ is an averaged value since $M-\text{N}(\text{CF}_3)_2$ bond formation and dissociation is too fast to be resolved on the NMR timescale. Similar to **1b** and **2b**, the bipyridine complexes **1a** and **2a** reveal partial dissociation into ions in CD_3CN solution, as well.

The novel thermally robust bis(trifluoromethyl)amido copper(I) and silver(I) complexes were used for the introduction of the $\text{N}(\text{CF}_3)_2$ group into organic molecules. The reactions studied, so far, are i) nucleophilic substitutions giving a set of benzylbis(trifluoromethyl)amines (**4–6**), 2-bis(trifluoromethyl)aminomethylnaphthalene (**7**), 2-bis(trifluoromethyl)amino acetate (**8a**), and ii) a Sandmeyer reaction leading to 1-fluoro-4-bis(trifluoromethyl)aminobenzene (**9**).

The four benzylbis(trifluoromethyl)amines **4–6** and the naphthalene derivative **7** were isolated in yields of 56–65% using the 2,2'-bipyridine and 1,10-phenanthroline complexes **1a**, **2a**, or **1d** as starting materials (Figure 4). The synthesis of the parent benzylbis(trifluoromethyl)amine **4** was reported using freshly prepared solutions of rubidium or cesium bis(trifluoromethyl)amide.^[17,59] Compounds **4** and **6** are liquids, whereas the *para*-cyano derivative **5** and the naphthalene compound **7** are solids. The four related compounds **4–7** are air and water stable and no decomposition was observed during work-up or storage. Crystals of **5** and **7** were studied by SC-XRD.

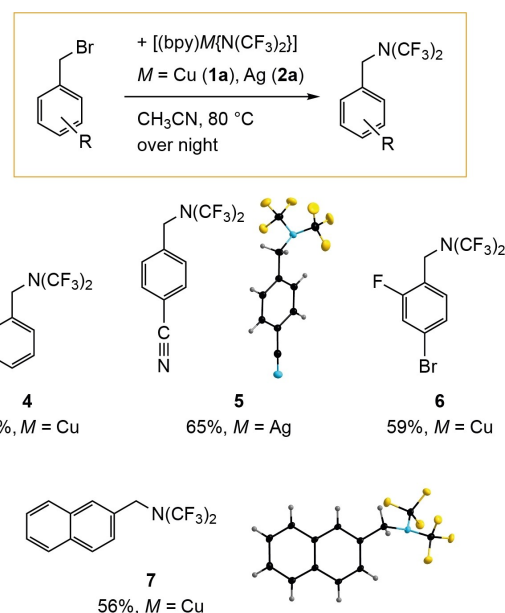


Figure 4. Synthesis of bis(trifluoromethyl)methyl arenes and crystal structures of **5** and **7**.

The $\text{N}-\text{CF}_3$ distances in **5** ($1.399(5)$ Å) and **7** ($1.409(3)$ Å) are longer than in the coinage metal(I) complexes (ca. 1.35 Å).

The reaction of 2-(bromomethyl)naphthalene with $[(\text{bpy})\text{Cu}\{\text{N}(\text{CF}_3)_2\}]$ (**1a**) was screened in acetonitrile, dichloromethane, *N,N*-dimethylacetamide (DMAC), toluene, pyridine, and THF. The highest yield for **7** was observed in CD_3CN . In dichloromethane and DMAC significantly lower yields were obtained and in toluene, pyridine, and THF almost no conversion to **7** was observed by ^{19}F NMR spectroscopy (Table S1).

2-Bis(trifluoromethyl)amino acetate (**8a**) was isolated in 56% yield (Figure 5). Its conversion into ethyl *N,N*-bis(trifluoromethyl)glycine (**8b**) was described, earlier.^[39] The synthesis of **8b** was repeated and the fluorinated amino acid was characterized by SC-XRD for the first time. Two formula units of **8b** form dimers in the solid state via a cyclic H-bond motif with $d(\text{O} \cdots \text{O}') = 2.679(3)$ Å that are located on a center of inversion (Figure 5).

The conversion of ethyl bromoacetate into **8a** using different copper(I) and silver(I) bis(trifluoromethyl)amido complexes was monitored by ^{19}F NMR spectroscopy in CD_3CN using

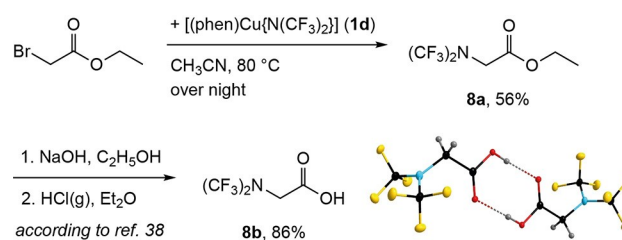


Figure 5. Synthesis of 2-bis(trifluoromethyl)amino acetate (**8a**), its conversion into *N,N*-bis(trifluoromethyl)glycine (**8b**), and the crystal structure of **8b** (thermal ellipsoids set at 30% probability; H atoms are omitted for clarity).

benzotrifluoride as internal reference (Table 1). Especially, the complexes with 2,2'-bipyridine and 1,10-phenanthroline were found to be efficient $N(\text{CF}_3)_2$ transfer reagents and the copper(I) complexes **1 a** and **1 d** were identified as most efficient reagents with internal yields of 74 and 75 %, respectively. The related silver(I) complex **2 a** gave ester **8 a** in significantly lower yield of 54 %. Triphenylphosphane complexes are less efficient $N(\text{CF}_3)_2$ transfer reagents and the amount of **8 a** formed, dropped with increasing number of PPh_3 ligands at copper(I) or silver(I). The lower yields were accompanied with an increasing amount of side products. A major side product was identified as Ph_3PF_2 that was confirmed by ^{19}F and ^{31}P NMR spectroscopy in the reaction mixtures. Most of the phosphorane formed crystallized from the CD_3CN solutions upon cooling to room temperature and a single crystal of Ph_3PF_2 was characterized by X-ray diffraction (Figure S16).

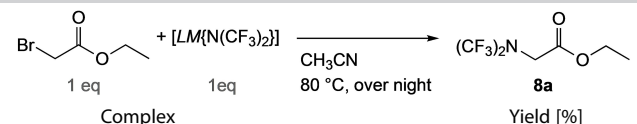
The lower yield of ester **8 a** starting from $[(\text{bpy})\text{Ag}\{\text{N}(\text{CF}_3)_2\}]$ (**2 a**) compared to $[(\text{bpy})\text{Cu}\{\text{N}(\text{CF}_3)_2\}]$ (**1 a**; Table 1), tempted us to perform a comparative study on nucleophilic substitution reactions using complexes **1 a** and **2 a** (Table S2). Similar to the syntheses of **8 a**, lower yields were observed for reactions using the silver(I) complex **2 a**. The reactions studied include the synthesis of benzylbis(trifluoromethyl)amine **4** starting from benzylbromide and benzyl iodide as well as the formation of **7** starting from the respective bromide. Furthermore, the conversion of allylbromide into allylbis(trifluoromethyl)amine (**10**)

showed a much lower yield for $(\text{CF}_3)_2\text{NCH}_2\text{CH}=\text{CH}_2$ (**10**) in case of the reaction from **2 a** (38 %) compared to **1 a** (75 %).

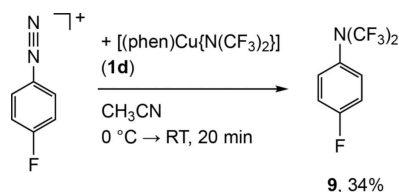
The further potential of the coinage metal(I) complexes as bis(trifluoromethyl)amination reagents was demonstrated by the conversion of 4-fluorobenzene diazonium tetrafluoroborate into 1-fluoro-4-bis(trifluoromethyl)aminobenzene (**9**) with $[(\text{bpy})\text{Cu}\{\text{N}(\text{CF}_3)_2\}]$ (**1 a**) in 34 % yield as assessed by ^{19}F NMR spectroscopy (Scheme 1). An analogous Sandmeyer reaction resulting in **9** was reported in the literature^[40] starting from the corresponding 4-fluorobenzene diazonium bis(trifluoromethyl)amide and a copper(I) salt with a yield of 43%.^[51] However, the preformation of the diazonium bis(trifluoromethyl)amide salt is inconvenient compared to a reaction with a stable and storable metal complex of the $N(\text{CF}_3)_2$ ligand. Furthermore, the addition of elemental copper was necessary to get any product. Preliminary results indicate a higher yield of **9** for the reaction of 4-fluorobenzene diazonium tetrafluoroborate with **1 a**, as well.

The first copper(I) and silver(I) bis(trifluoromethyl)amido complexes using stabilizing N- and P-donor ligands have been obtained in high yield starting from $\text{CF}_3\text{SO}_2\text{N}(\text{CF}_3)_2$, which is easily accessible by electrochemical fluorination (ECF). The complexes have unprecedented stabilities that allow for a long-term storage and easy handling. This is a prerequisite for their application as bis(trifluoromethyl)amination reagents. The potential of these complexes, especially with pyridine-type ligands, to serve as convenient $N(\text{CF}_3)_2$ transfer reagents was demonstrated by nucleophilic substitution reactions and a Sandmeyer reaction.

Table 1. Reactivity screening of copper(I) and silver(I) bis(trifluoromethyl)amido complexes with ethyl bromoacetate to give 2-bis(trifluoromethyl)amino acetate (**8 a**).^[a]

		Yield [%]
Complex		
1	$[(\text{bpy})\text{Cu}\{\text{N}(\text{CF}_3)_2\}]$ (1 a)	75
2	$[(\text{phen})\text{Cu}\{\text{N}(\text{CF}_3)_2\}]$ (1 d)	74
3	$[(\text{bpy})(\text{Ph}_3\text{P})\text{Cu}\{\text{N}(\text{CF}_3)_2\}]$ (1 c)	33
4	$[(\text{phen})(\text{Ph}_3\text{P})\text{Cu}\{\text{N}(\text{CF}_3)_2\}]$ (1 e)	39
5	$[(\text{Ph}_3\text{P})_2\text{Cu}\{\text{N}(\text{CF}_3)_2\}]$ (1 b)	8
6	$[(\text{bpy})\text{Ag}\{\text{N}(\text{CF}_3)_2\}]$ (2 a)	54
7	$[(\text{bpy})(\text{Ph}_3\text{P})\text{Ag}\{\text{N}(\text{CF}_3)_2\}]$ (2 c)	28
8	$[(\text{Ph}_3\text{P})_2\text{Ag}\{\text{N}(\text{CF}_3)_2\}]$ (2 b)	7

[a] The reactions were performed in Young NMR tubes and monitored by ^{19}F NMR spectroscopy using equimolar amounts of the coinage metal(I) complex and ethyl bromoacetate. The internal yields were determined with benzotrifluoride as standard.



Scheme 1. Sandmeyer-type reaction of **1 d** giving **9** (yield of **9** determined by ^{19}F NMR spectroscopy with benzotrifluoride as internal standard).

Experimental Section

Single-crystal X-ray diffraction

Single-crystal X-ray diffraction: Deposition Numbers 2051510-2051523, 2052134 and 2055702 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: amination · copper · fluorinated ligands · N ligands · silver

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