Angewandte
International Edition Chemie

International Edition: DOI: 10.1002/anie.201507356
German Edition: DOI: 10.1002/ange.201507356

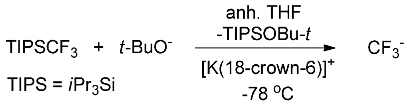
Carbanions

The Trifluoromethyl Anion

*Anton Lishchynskyi, Fedor M. Miloserdov, Eddy Martin, Jordi Benet-Buchholz, Eduardo C. Escudero-Adán, Andrey I. Konovalov, and Vladimir V. Grushin**

Abstract: *First evidence for the existence of free trifluoromethyl anion CF_3^- has been obtained. The 3D-caged potassium cation in $[K(crypt\text{-}222)]^+$ is inaccessible to CF_3^-, thus rendering it uncoordinated ("naked"). Ionic $[K(crypt\text{-}222)]^+$ CF_3^- has been characterized by single-crystal X-ray diffraction, solution NMR spectroscopy, DFT calculations, and reactivity toward electrophiles.*

We were both impressed and intrigued by the recent Communication by Prakash et al.[1] claiming the observation of "the trifluoromethanide anion with a $[K(18\text{-crown-}6)]^+$ countercation" by ^{19}F and ^{13}C NMR spectroscopy at −78 °C.[2] The Prakash group have reported[1] that the reaction of *t*BuOK-18-crown-6 in anhydrous THF with $TIPSCF_3$ (TIPS = iPr$_3$Si) at −78 °C gives rise to "CF_3^-" (Scheme 1). The resultant solutions have been shown to trifluoromethylate a variety of electrophiles.



$$\mathrm{TIPSCF_3} + t\text{-BuO}^- \xrightarrow[\text{[K(18-crown-6)]}^+,\ -78\ ^\circ\mathrm{C}]{\text{anh. THF},\ -\mathrm{TIPSOBu}\text{-}t} \mathrm{CF_3}^-$$

TIPS = iPr$_3$Si

Scheme 1. Generation of the trifluoromethyl anion as shown in Ref. [1].

Numerous organic transformations are mediated by carbanions and carbocations.[3] In most instances, however, such intermediates in solution are not free anions and cations per se, but rather their synthetic equivalents, sometimes referred to as "synthons". For example, even some highly ionic organosodium and -potassium compounds, which are often regarded as carbanion salts, comprise polymeric chains or polynuclear units containing C−Na and C−K bonds.[4] Purely ionic compounds, such as tetraalkylammonium salts in solvents of low or moderate polarity, THF included, form tight ion pairs aggregated in clusters.[5] Furthermore, the abundant literature data[6] and our own research experience[7,8] show that the potassium atom in $[K(18\text{-crown-}6)]^+$ is coordinatively unsaturated and therefore readily binds to additional ligands. The electrophilicity of the K^+ in the crown is sufficient to form bonds to a broad variety of electron pair donors, including those that are vastly weaker nucleophiles than CF_3^-, such as BF_4^- (see below). Of particular relevance is the fact that *t*BuOK and 18-crown-6 form a stable neutral complex [K(18-crown-6)(*t*BuO)] that has been characterized in solution and in the crystal state.[9] All of the above prompted us to question the notions of the $[K(18\text{-crown-}6)][CF_3]$[1] being a derivative of the naked[2a] and isolable[2b,c] trifluoromethyl anion.

We were also puzzled by the contradiction between the stoichiometry shown in Scheme 1 and the actual reagent ratio used to generate "CF_3^-" within the same report.[1] Scheme 1, which is identical with Equation (5) of the original publication,[1] indicates that $TIPSCF_3$, *t*BuOK, and 18-crown-6 react in a 1:1:1 molar ratio to give CF_3^-. Surprisingly, however, the ratio used in the actual experiments was 0.9:2:2 without any comments on this inconsistency.[1] In our hands,[10,11] the reaction of 1 equiv of $TIPSCF_3$ with 1 equiv of *t*BuOK/18-crown-6 in THF at −78 °C reproducibly gave rise to only barely detectable quantities of the "CF_3^-" (^{19}F NMR, $\delta = -18.6$ ppm; Table 1, entry 1). A variable temperature (VT) ^{19}F NMR spectroscopic study suggested the formation of $[TIPS(CF_3)_2]^-$ (two broad 1:1 peaks at $\delta = -46.5$ and $\delta = -56.0$ ppm) in 20–25 % yield and the presence of 20 % of unreacted $TIPSCF_3$ resonating at $\delta = -55.6$ ppm.[12] A small amount of CHF_3 (2–5 %) was also produced.

Table 1: Reaction of [K(18-crown-6)(*t*BuO)] with $TIPSCF_3$ in [D$_8$]THF or THF (0.3–0.6 mL) at −78 °C in the presence of $PhCF_3$ as an internal standard.

Entry	[K(18-crown-6)(*t*BuO)] [mmol]	$TIPSCF_3$ [mmol]	^{19}F NMR yield [%]	
			CF_3^-	CHF_3
1	5.0×10^{-2}	5.5×10^{-2}	<0.5	2
2	5.0×10^{-2}	2.3×10^{-2}	5	5
3	3.3×10^{-2}	1.5×10^{-2}	20	10
4	1.7×10^{-2}	7.5×10^{-3}	80	15
5	6.8×10^{-3}	7.5×10^{-3}	65	10

In contrast, the reaction of $TIPSCF_3$, *t*BuOK, and 18-crown-6 in a 1:2:2 molar ratio in THF at −78 °C proceeded as reported.[1] The yields of the "CF_3^-" species (^{19}F NMR, $\delta = -18.7$ ppm) and CHF_3, however, were only 5 % (Table 1, entry 2), appreciably lower than 34–39 % ("CF_3^-") and 26–28 % (CHF_3) obtained in the original work.[1,13] During our studies, we noticed that a solid was produced in the reaction and hypothesized that the low NMR yield dealt with this precipitation. Indeed, repeating the reaction at a threefold dilution resulted in less precipitate and a higher, 20 % yield of the "CF_3^-" (Table 1, entry 3). At a sixfold dilution, no precipitate was observed and the yield of the "CF_3^-" was

---

[*] Dr. A. Lishchynskyi, Dr. F. M. Miloserdov, Dr. E. Martin, Dr. J. Benet-Buchholz, E. C. Escudero-Adán, Dr. A. I. Konovalov, Dr. V. V. Grushin
Institute of Chemical Research of Catalonia (ICIQ)
Avgda. Països Catalans 16, 43007 Tarragona (Spain)
E-mail: vvgrushin@gmail.com

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507356.

80 % (entry 4). Finally and most importantly, reacting $TIPSCF_3$, tBuOK, and 18-crown-6 in a 1:0.9:1 molar ratio under these high-dilution conditions furnished "CF_3^-" in 65 % yield (entry 5). The addition of 1 equiv of $TIPSCF_3$ to the "CF_3^-" generated in these experiments prompted an immediate reaction leading to the formation of $[TIPS(CF_3)_2]^-$.

The experiments described above and summarized in Table 1 indicated that the stoichiometry shown in Scheme 1 is correct. However, in order to reproducibly observe the formation of the "CF_3^-" in good yield from [K(18-crown-6)(tBuO)] and $TIPSCF_3$ in a 1:1 molar ratio, the reaction should be performed at 1/6th the originally reported[1] concentration. At higher concentrations, [K(18-crown-6)-(tBuO)] precipitates out of THF where it is only moderately soluble at −78 °C.[9] Consequently, the amount of the base in the liquid phase is diminished, which makes the $TIPSCF_3$ an excess reagent that efficiently sequesters the "CF_3^-" in the form of $[TIPS(CF_3)_2]^-$.

Small quantities of CHF_3 were invariably side-produced in all of the reactions of [K(18-crown-6)(tBuO)] with $TIPSCF_3$ (Table 1).[14] Under identical conditions, the yield of CHF_3 remained roughly the same regardless of whether the reaction was performed in a dry glass NMR tube or in an FEP liner. Higher yields of CHF_3 observed at a higher dilution were commensurate with the water assay in solvent used (ca. 10 ppm). Finally, the reactions in [D$_8$]THF gave rise exclusively to CHF_3, not CDF_3. All these data indicate that the formation of fluoroform deals with the presence of residual water in [D$_8$]THF or THF used, rather than their deprotonation by CF_3^-, as previously proposed.[1]

After the reaction mixtures (Table 1) were allowed to warm up and kept at ambient temperature for several weeks, solid materials were produced. X-ray diffraction of a single crystal from one of the samples revealed the structure [K(18-crown-6)(BF_4)]·0.25 H_2O (Figure 1).[15] The source of boron for the BF_4^- was clearly the borosilicate glass of the NMR tube. The asymmetric unit contains two independent [K(18-crown-6)(BF_4)] molecules and 0.25 of a disordered molecule of water that is shared by two neighboring potassium ions. The observed interaction of the K^+ inside the crown with the BF_4^-, which is a very poor electron pair donor, is yet another persuasive argument for coordination of the much more nucleophilic CF_3^- to [K(18-crown-6)]$^+$ in media of low or moderate polarity, such as THF, especially at −78 °C.

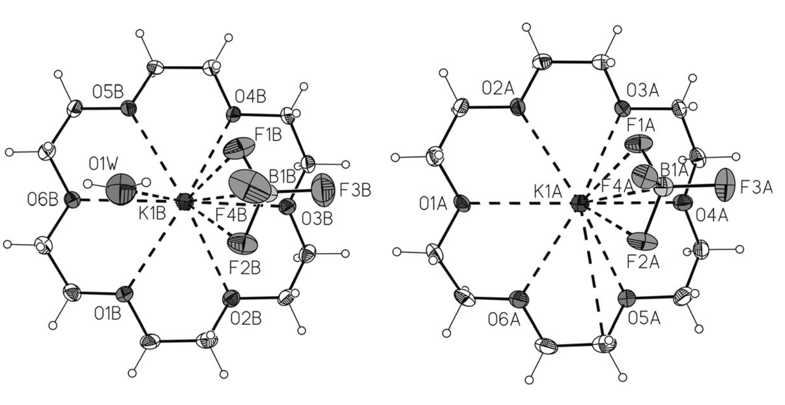


Figure 1. ORTEP drawings of [K(18-crown-6)(BF_4)] with (left) and without (right) coordinated H_2O molecule. Thermal ellipsoids set at 50 % probability.

To probe the existence of the naked[6a] CF_3^-, 18-crown-6 was replaced with its three-dimensional analogue [2.2.2]cryptand (crypt-222). Encapsulation of a potassium cation within the crypt-222 cage is known[6] to result in coordinative saturation of the K^+, thereby eliminating altogether its Lewis acidity. For instance, in the structure of [K(18-crown-6)][(tBuO)$_2$Cu], there is a chemical bond between the potassium atom and one of the oxygen atoms on the Cu, whereas the cation and anion are fully separated in [K(crypt-222)]$^+$ [(tBuO)$_2$Cu]$^-$.[7]

The fundamental difference[6a] between [K(18-crown-6)]$^+$ (Lewis acidic) and [K(crypt-222)]$^+$ (not Lewis acidic) suggested that a much stronger base would be produced upon treatment of tBuOK with crypt-222 than with 18-crown-6. As discussed above, 18-crown-6 reacts with tBuOK to give neutral [K(18-crown-6)(tBuO)][9] that is stable in THF. In sharp contrast, we found that the reaction of tBuOK with crypt-222 (1:1) in THF under similar rigorously anhydrous conditions gives rise to a species that is unstable at room temperature. A colorless solution of tBuOK in [D$_8$]THF turned yellow immediately upon addition of crypt-222 at 23 °C. After 10 min at room temperature, a weak doublet of doublets at $\delta = 6.2$ ppm ($J = 15.3$ and 8.9 Hz) along with other minor signals in the $\delta = 6.1$–7.7 ppm region of the ^{1}H NMR spectrum could be clearly seen.[10] These resonances grew in intensity over time and were likely from olefinic species that probably emerged from deprotonation of the cryptand with highly basic non-coordinated tBuO$^-$. From a similar experiment performed in THF–ether–pentane, a crystalline solid was isolated and found to be ionic [K(crypt-222)]$^+$ [(tBuO)$_2$H]$^-$ by single-crystal X-ray diffraction (Figure 2).[15] Evidently, the naked[6a] tBuO$^-$ generated upon complexation of the K^+ with crypt-222 deprotonated the ligand (and possibly the solvent) to give tBuOH that instantaneously H-bonded to the as yet unreacted *tert*-butoxide.

Deprotonation within the tBuOK-crypt-222-THF system does not occur to an observable extent within the time of mixing and can be avoided at low temperatures. Dissolving tBuOK and crypt-222 in THF within 1–2 min at 23 °C and immediately cooling the solution to −78 °C did not give rise to the products resonating at $\delta = 6.1$–7.7 ppm (see above). Instead, a white solid precipitated, apparently [K(crypt-222)]$^+$ [tBuO]$^-$. The addition of $TIPSCF_3$ (1 equiv) to this reaction mixture at −78 °C resulted in dissolution of the solid, followed by the formation of small yet well-shaped clear crystals. Extreme air and temperature sensitivity of these crystals, coupled with their poor solubility in THF, made their analysis particularly challenging. After numerous attempts, we succeeded in performing an X-ray study of this highly air-sensitive and thermally unstable material (Figure 3), pointing to an ionic structure, [K(crypt-222)]$^+$ CF_3^-.[15] The asymmetric unit contains one-third of the potassium cryptate and one-third of the CF_3 unit, both of which are located on 3-fold rotation axes. Disorder is observed in both entities.[10,15] The rotational disorder (50:50) of the fluorine atoms in the CF_3 around the 3-fold axis is

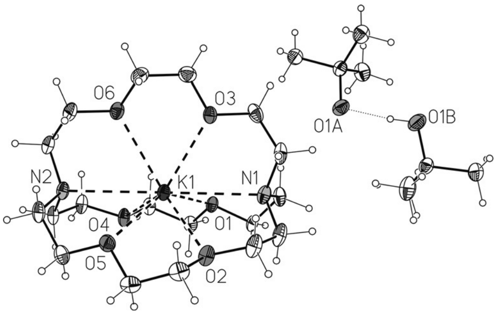


Figure 2. ORTEP drawing of $[K(crypt\text{-}222)]^+$ $[(tBuO)_2H]^-$ with thermal ellipsoids set at 50% probability.

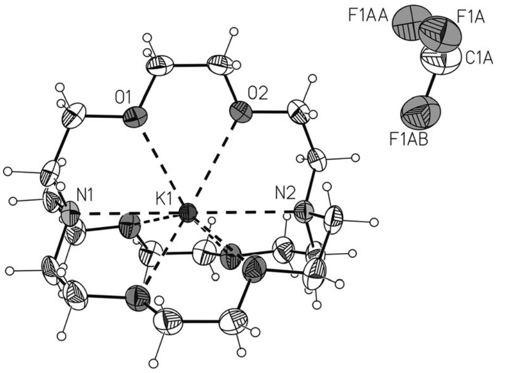
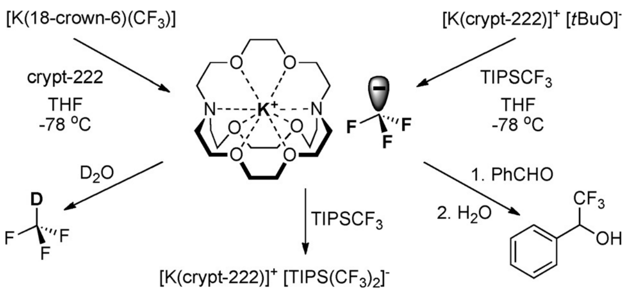


Figure 3. ORTEP drawing of $K(crypt\text{-}222)]^+$ CF_3^- with thermal ellipsoids set at 50% probability.

common for solid-state structures of CF_3 derivatives. The carbon atom bearing the fluorine atoms is located in inverted positions (70:30).

In spite of the disorder, the veracity of the structure shown in Figure 3 is manifested by the R1 value of 6.38%. However, an X-ray study performed on a single crystal cannot and does not guarantee the same structure for the bulk material. Playing devil's advocate, it could also be suggested that a highly improbable 1:1 clathrate of CHF_3 trapped in the lattice of deprotonated $[K(crypt\text{-}222)]^+$ accounts for the X-ray data. Additional observations and facts presented below, however, confirm that it is $[K(crypt\text{-}222)]^+$ CF_3^- that is produced in the reaction:

1. At -78 °C, $[K(crypt\text{-}222)]^+$ is not deprotonated by bases[16] that are over ten orders of magnitude stronger than CF_3^- (pK_a of $CHF_3 \approx 27$–31).[17,14b]
2. For self-explanatory technical difficulties, multiple crystals rather than a single one were mounted on the goniometer head for the structure determination of the CF_3^- crypt derivative. Initial data collection scans showed that all of those crystals had unit cell parameters identical with those of the structure displayed in Figure 3.
3. In a separate experiment, crypt-222 (2.5 equiv) was added at -84 °C to $[K(18\text{-}crown\text{-}6)(CF_3)]$[1] pre-generated at -78 °C in $[D_8]$THF at a sevenfold dilution to ensure full solubility (see above). The resultant solution was then studied by VT ^{1}H and ^{19}F NMR spectroscopy.[10] K^+ transfer from 18-crown-6 to crypt-222 was complete after approximately 2–3 min at -84 °C and then 30 min at -88 °C. The ^{19}F NMR signal from the thus generated $[K(crypt\text{-}222)]^+$ CF_3^- ($\delta = -17.2$ ppm) appeared ca. 2 ppm downfield from that of $[K(18\text{-}crown\text{-}6)(CF_3)]$. As the monitoring continued at -78–-48 °C, the resonances from the CF_3^- and from $[K(crypt\text{-}222)]^+$ lowered in intensity and a white solid precipitated. No CDF_3 formation was observed. However, the addition of D_2O (10 equiv) to this mixture at -88 °C resulted in the quantitative formation of CDF_3 that was unambiguously identified by its characteristic 1:1:1 triplet resonance at $\delta = -79.8$ ppm with $J(F,D) = 12$ Hz in the ^{19}F NMR spectrum. Most importantly, there was no change in the amount of CHF_3 (ca. 10%) originally produced in the generation of $[K(18\text{-}crown\text{-}6)(CF_3)]$ (see above) throughout the experiment. Alternatively, $[K(crypt\text{-}222)]^+$ CF_3^- could be generated directly from $[K(crypt\text{-}222)]^+$ $[tBuO]^-$ and $TIPSCF_3$. Both $[K(crypt\text{-}222)]^+$ $[tBuO]^-$ and $[K(crypt\text{-}222)]^+$ CF_3^- are poorly soluble in THF at -78 °C and considerably less so than their 18-crown-6 non-ionic counterparts. In the range of concentrations used, however, the precipitation was not instantaneous but rather occurred in the course of 15–30 min. The sequential addition of crypt-222 (1 equiv) and then $TIPSCF_3$ (0.4–0.5 equiv) to easily soluble tBuOK (1 equiv) in $[D_8]$THF at -78 °C produced oversaturated solutions of $[K(crypt\text{-}222)]^+$ CF_3^- (^{19}F NMR, δ: -17.1 ppm), which were amenable to study by ^{19}F and ^{1}H NMR spectroscopy for 10–20 min before most of the salt precipitated out. The treatment of the thus prepared reaction mixtures with $TIPSCF_3$, or PhCHO resulted in the formation of $[TIPS(CF_3)_2]^-$ and $PhCH(OH)CF_3$, respectively.[10] A summary of the transformations described above is presented in Scheme 2.



Scheme 2. Generation and reactions of $[K(crypt\text{-}222)]^+$ CF_3^-.

The above crystallographic, solution, and reactivity studies provided strong evidence for the ionic structure $[K(crypt\text{-}222)]^+$ CF_3^-. We then carried out a computational study of the CF_3^- anion and its ability to deprotonate crypt-222.

Selected experimental[10,15] and computed[10] geometry parameters for the CF_3^- anion are compiled in Table 2. As anticipated (VSERP), the DFT calculations show that CF_3^- has longer C–F bonds and exhibits a stronger deviation from the ideal tetrahedral geometry than CHF_3. Upon superficial consideration, the geometries around C1A and C1A′ in the crystal structure might appear consistent with those of CHF_3 and CF_3^-, respectively. This conclusion, however, cannot be

Table 2: Selected experimentally determined and computed geometry parameters for CF_3^- and CHF_3.

Parameter	X-ray[a]		DFT[b]	
	C1A	C1A′	CF_3^-	CHF_3
C-F [Å]	1.26(2) 1.35(2)	1.37(3) 1.43(3)	1.43	1.33
C-[F,F,F-centroid] [Å]	0.37 0.40	0.63 0.66	0.67	0.47
F-C-F [°]	112(2) 112(2)	99(3) 102(3)	99.6	108.4
C-F-[F,F,F-centroid] [°]	17.0 17.2	26.1 28.7	28.2	20.5
F-F-F-C [°]	−31 −32	−44 −48	−46.9	−36.8

[a] The two values presented for each parameter are related to F1A and F2A atoms, respectively. [b] M06/6-31+G*, gas phase.

drawn because of the limited accuracy of the X-ray data as a result of the above-described disorder in the crystal. Computing the thermodynamics of deprotonation of [K(crypt-222)]$^+$ by CF_3^- in THF produced positive ΔG values of 17.5, 20.3, and 16.9 kcal mol^{-1} for proton removal from the α, β, and γ positions, respectively. For the most thermodynamically acidic γ-CH, the deprotonation barrier was calculated at 24.7 and 29.1 kcal mol^{-1} at 195 and 298 K, respectively.[10] Furthermore, the DFT study pointed to a diminished affinity of CF_3^- for [K(crypt-222)]$^+$ in THF, where the tight ion pair lies 3–5 kcal mol^{-1} higher in energy than the solvent-separated ions. This result is consistent with the lack of close cation–anion contacts in the X-ray structure of [K(crypt-222)]$^+$ CF_3^- shown in Figure 3.

The whole set of the experimental and computational results obtained shows that, while deprotonation of [K(crypt-222)]$^+$ under conditions used in the current work may occur at ambient temperature, this process is not feasible at −78 °C. The literature data[16] lend additional support to this conclusion.

One more point merits comments. The polyfluorinated products of the decomposition of "CF_3^-" remained unidentified in the original work.[1] We were able to identify most of the species produced in this decomposition (Figure 4)[10] by comparison of their ^{19}F NMR spectroscopic parameters with those reported in the literature. At −20 °C, the main decomposition product is $[(CF_3CF_2)C(CF_3)_2]^-$,[18] a stable tertiary carbanion that is likely produced by a series of CF_2 insertion, α- and β-F-elimination, and trifluoromethylation reactions,[19] as proposed in Scheme S3 in the Supporting Information.[10] Thermodynamically unstable[20] $CF_2{=}CF_2$ was never detected among the decomposition products and may not be involved in these transformations.

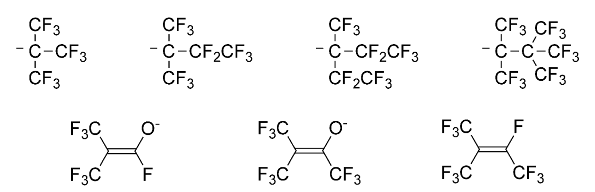


Figure 4. ^{19}F NMR spectroscopy-identified products of decomposition of "CF_3^-" generated in the reaction of TIPSCF$_3$ with *t*BuOK-18-crown-6 in various ratios in THF at −78 °C.

The seminal work of Prakash and co-workers[1] has demonstrated beyond any doubt that an anionoid CF_3 species can be spectroscopically detected at −78 °C. Although stated otherwise,[1,2] however, no evidence for this species being free CF_3^- has been presented. Numerous data suggest that while featuring a high degree of ionicity, the bonding between K(18-crown-6)$^+$ and CF_3^- in the observed[1] derivative certainly has a covalent component. In our current work, the existence of the free trifluoromethyl anion CF_3^- has been established for the first time.[21] Our combined crystallographic, solution, reactivity, and DFT study provides strong evidence for ionic [K(crypt-222)]$^+$ CF_3^-. In contrast with the potassium cation in [K(18-crown-6)]$^+$, the one in [K(crypt-222)]$^+$ is 3D-caged and thus inaccessible to CF_3^- and other anions, thereby rendering them "naked".[6a] It is believed that the results reported herein are of considerable importance to fundamental organic and general chemistry.

Acknowledgements

We thank Viacheslav (Slava) Petrov and William J. Marshall for discussions. This work was supported by the ICIQ Foundation and the Spanish Government (Grant CTQ 2011-25418 and Severo Ochoa Excellence Accreditation 2014–2018 SEV-2013-0319). F.M.M. is thankful to the Government of Spain (MINECO) for the FPI Ph.D. Scholarship (BES-2012-054922).

Keywords: carbanions · NMR spectroscopy · trifluoromethyl anion · trifluoromethylation · X-ray diffraction

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 15289–15293
Angew. Chem. **2015**, *127*, 15504–15508

[1] G. K. S. Prakash, F. Wang, Z. Zhang, R. Haiges, M. Rahm, K. O. Christe, T. Mathew, G. A. Olah, *Angew. Chem. Int. Ed.* **2014**, *53*, 11575; *Angew. Chem.* **2014**, *126*, 11759.

[2] For Highlights of the work reported in Ref. [1], see: a) N. Santschi, R. Gilmour, *Angew. Chem. Int. Ed.* **2014**, *53*, 11414; *Angew. Chem.* **2014**, *126*, 11598; b) S. K. Ritter, *Chem. Eng. News* **2014**, *92*, 4; c) T. Ritter, as cited in Ref. [2b].

[3] M. B. Smith, *March's Advanced Organic Chemistry*: *Reactions, Mechanisms, and Structure*, *7th ed.*, Wiley, New York, **2013**.

[4] See, for example: W. Clegg, B. Conway, A. R. Kennedy, J. Klett, R. E. Mulvey, L. Russo, *Eur. J. Inorg. Chem.* **2011**, 721 and references cited therein.

[5] See, for example: a) H. Mo, A. Wang, P. S. Wilkinson, T. C. Pochapsky, *J. Am. Chem. Soc.* **1997**, *119*, 11666; b) A. N. Ivashkevich, V. P. Kostynyuk, *Zh. Fiz. Khim.* **1991**, *65*, 948 and references cited therein; c) J. Everaert, A. Persoons, *J. Phys. Chem.* **1981**, *85*, 3930; d) C. Barker, J. Yarwood, *Faraday Symp. Chem. Soc.* **1977**, *11*, 136.

[6] a) "Naked Anion Effect": D. Landini, A. Maia in *Encyclopedia of Supramolecular Chemistry*, CRC, New York, **2004**, p. 939; b) M. Hiraoka, *Crown Ethers and Analogous Compounds*, Elsevier, Amsterdam, **1992**; c) G. W. Gokel, W. M. Leevy, M. E. Weber, *Chem. Rev.* **2004**, *104*, 2723.

[7] A. I. Konovalov, J. Benet-Buchholz, E. Martin, V. V. Grushin, *Angew. Chem. Int. Ed.* **2013**, *52*, 11637; *Angew. Chem.* **2013**, *125*, 11851.

[8] V. V. Grushin, C. Bensimon, H. Alper, *Inorg. Chem.* **1993**, *32*, 345.

[9] C. Kleeberg, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1790.

[10] See the Supporting Information for details.

[11] We initially experienced a problem reproducing the reaction of $TIPSCF_3$ with *t*BuOK/18-crown-6. Our attempts to add $TIPSCF_3$ to *t*BuOK/18-crown-6 in THF at −78 °C "along the inner wall of the NMR tube"[1] were unsuccessful as $TIPSCF_3$ quickly solidified on the cold glass surface before reaching the liquid phase. This problem was solved by slowly injecting a THF solution of $TIPSCF_3$ through a long syringe needle immersed in a *t*BuOK-18-crown-6-THF mixture in an NMR tube at −78 °C, while moving the needle up and down to ensure good mixing.

[12] In this and other experiments reported herein, the yields were thoroughly quantified by ^{19}F and ^{1}H NMR spectroscopy using $PhCF_3$ as an internal standard, the chemical shift of $PhCF_3$ being referenced at $\delta = -63.0$ ppm throughout.

[13] Calculated on the basis of the integral values presented in Figure S4, general procedure 4 on p. 4, and Ref. [2] of the Supporting Information of the original report.[1]

[14] a) In experiments lacking excess *t*BuOK/18-crown-6, two different CHF_3 species were detected (^{1}H, ^{19}F NMR) at −78–−88 °C.[10] With extra *t*BuOK, however, only one signal from fluoroform was always observed. If present, $t\mathrm{BuO}^-$, the strongest H-bond acceptor[14b] in the system, binds the entire small amount of CHF_3 in the form of a single species, likely $[\mathrm{K(18\text{-}crown\text{-}6)}(t\mathrm{BuO})]\cdot\mathrm{HCF_3}$. In the absence of *t*BuOK, CHF_3 is bonded to weaker H-bond acceptors present to produce less-stable adducts, possibly $[\mathrm{K(18\text{-}crown\text{-}6)TIPS(CF_3)_2}]\cdot\mathrm{HCF_3}$ and $[\mathrm{K(18\text{-}crown\text{-}6)(CF_3)}]\cdot\mathrm{HCF_3}$; b) M. L. Chabinyc, J. I. Brauman, *J. Am. Chem. Soc.* **1998**, *120*, 10863.

[15] CCDC 1417271 ($[\mathrm{K(18\text{-}crown\text{-}6)(BF_4)}]\cdot 0.25\,\mathrm{H_2O}$), 1417272 ($[\mathrm{K(crypt\text{-}222)}]^+$ $[(t\mathrm{BuO})_2\mathrm{H}]^-$), and 1417273 ($[\mathrm{K(crypt\text{-}222)}]^+$ $\mathrm{CF_3}^-$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] S. E. Landau, K. E. Groh, A. J. Lough, R. H. Morris, *Inorg. Chem.* **2002**, *41*, 2995.

[17] a) S. Andreades, *J. Am. Chem. Soc.* **1964**, *86*, 2003; b) E. A. Symons, M. J. Clermont, *J. Am. Chem. Soc.* **1981**, *103*, 3127.

[18] B. E. Smart, W. J. Middleton, W. B. Farnham, *J. Am. Chem. Soc.* **1986**, *108*, 4905.

[19] W. B. Farnham, *Chem. Rev.* **1996**, *96*, 1633.

[20] See, for example: Y. I. Babenko, Ya. A. Lisochkin, V. I. Poznyak, *Combust. Explos. Shock Waves* **1993**, *29*, 603.

[21] It has been stated[1] that in our 2011 paper on the direct cupration of fluoroform[22] "the involvement of a $\mathrm{CF_3}^-$ species is particularly discounted based on the previously assumed extreme lability of $\mathrm{CF_3}^-$."[1] In fact, the formation of the $\mathrm{CF_3}^-$ (e.g., upon deprotonation of CHF_3) is not only not questioned, but, on the contrary, recognized and acknowledged in the paper cited[22] and in our other publications.[23] Many of our reports[22,23a,b,e] contain chemical equations and schemes displaying the generation and transformations of the $\mathrm{CF_3}^-$. As for the particular reaction of direct cupration of fluoroform, the subject of the cited report,[22] the above statement[1] is also incorrect. We do not "discount"[1] the involvement of the $\mathrm{CF_3}^-$ in the cupration reaction[22] based on its "previously assumed extreme lability",[1] but rule it out on the basis of a conclusive mechanistic study[7] published in this journal one year before the Prakash report.[1]

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

[23] See, for example: a) O. A. Tomashenko, V. V. Grushin, *Chem. Rev.* **2011**, *111*, 4475; b) A. Lishchynskyi, M. A. Novikov, E. Martin, E. C. Escudero-Adán, P. Novák, V. V. Grushin, *J. Org. Chem.* **2013**, *78*, 11126; c) A. Lishchynskyi, V. V. Grushin, *J. Am. Chem. Soc.* **2013**, *135*, 12584; d) F. M. Miloserdov, V. V. Grushin, *J. Fluorine Chem.* **2014**, *167*, 105; e) V. V. Grushin, *Chim. Oggi* **2014**, *32*, 81.

Received: August 7, 2015
Published online: October 26, 2015