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Reactive Intermediates | **Very Important Paper**

Long-Lived Trifluoromethanide Anion: A Key Intermediate in Nucleophilic Trifluoromethylations**

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Abstract: *The trifluoromethanide anion is the postulated key intermediate in nucleophilic trifluoromethylation reactions. However, for more than six decades, the trifluoromethanide anion was widely believed to exist only as a short-lived transient species in the condensed phase. It has now been prepared in bulk for the first time in THF solution. The trifluoromethanide anion with the $[K(18\text{-crown-}6)]^+$ cation was unequivocally characterized by low-temperature ^{19}F and ^{13}C NMR spectroscopy. Its intermediacy in nucleophilic trifluoromethylation reactions was directly evident by its reaction chemistry with various electrophilic substrates. Variable-temperature NMR spectroscopy, along with quantum mechanical calculations, support the persistence of the trifluoromethanide anion.*

Because of the potential applications of fluorinated compounds in chemistry, biology, and materials science,[1–5] fluorine substitution of organic compounds has become a vibrant research area in synthetic organic chemistry.[6–10] Among various fluorinated substituents, the trifluoromethyl group (CF_3) stands out not only because of its role as the parent of other fluoroalkyl moieties, but also owing to its remarkable potential for modulating chemical, physical, and biochemical properties of molecules.[1,4,11] Over the past several decades, significant advances have been made for the synthetic incorporation of the trifluoromethyl moiety, such as cross-coupling reactions or nucleophilic and electrophilic trifluoromethylations.[8,9,12–16] Mechanistically, a vast majority of these transformations are proposed to involve, directly or indirectly, the trifluoromethanide anion (CF_3^-; Figure 1a). Despite evidence for CF_3^- in the gas phase from mass spectrometry[17] and photoelectron spectroscopy,[18] and tentatively from IR spectroscopy at 5 K in a neon matrix,[19] it was widely accepted for more than six decades that CF_3^- is an essentially transient species, which in the condensed phase can undergo swift α-defluorination to singlet difluorocarbene (Figure 1b).[5,8,15,20–27] To date, the extremely low thermal stability of CF_3^- has been frequently invoked in the mechanisms of various reactions in organofluorine chemistry. Herein, we report the generation and characterization of CF_3^-, with the $[K(18\text{-crown-}6)]^+$ cation in THF solution, as a long-lived key intermediate at subambient temperatures.

Considering the high strength of C–F bonds among carbon–halogen bonds[20a] and the relatively strong Lewis acidity of singlet difluorocarbene (CF_2), as computed by its fluoride (F^-) affinity of 46.7 kcal mol^{-1} in the gas phase[28,29] (see the Supporting Information for details), CF_3^- is expected to be a rather persistent species at low temperatures. We have estimated the adiabatic C–F bond dissociation enthalpy and free energy of CF_3^- in THF to be 25.4 kcal mol^{-1} and 16.7 kcal mol^{-1}, respectively, at the COSMO-CCSD(T)/Def2-TZVPPD//SMD-M06-2X/Def2-TZVPPD level of theory (Figure 1c; see the Supporting Information for details). Further calculations predict that the α-defluorination enthalpy and free energy can be significantly reduced to $+17.1$ kcal mol^{-1} and $+9.7$ kcal mol^{-1}, respectively, in the presence of a potassium cation (Figure 1c). On the one hand, these results indicate that CF_3^- might possess sufficient thermal stability to allow its preparation and isolation at subambient temperatures. On the other hand, to suppress possible decomposition, it is necessary to diminish the metal–trifluoromethanide interactions through efficient coordination of the metal cation.[30a]

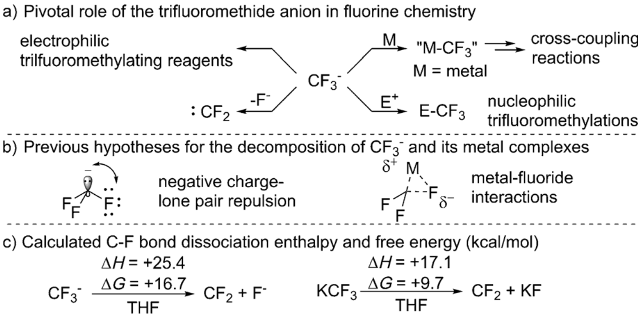

Figure 1. a) Central role of trifluoromethanide in fluoroalkylation chemistry. b) Proposed mechanisms for the decomposition of trifluoromethanide and ionic metal-CF_3 complexes. c) Calculated C–F bond dissociation enthalpies and free energies of CF_3^- and the KCF_3 ion pair (1 M concentration) in THF at 298 K. THF = tetrahydrofuran.

Based on the discussions above, the generation of CF_3^- was initially attempted by treating fluoroform (CF_3H) with

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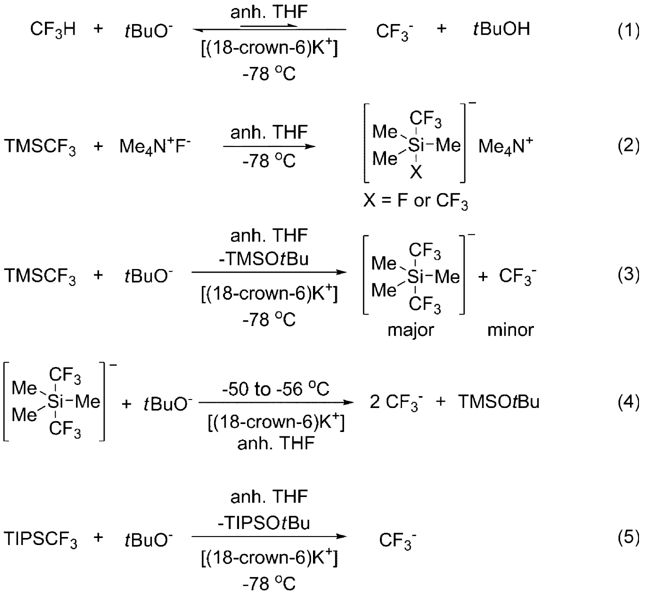


Scheme 1. Attempted preparations of CF_3^- under various reaction conditions [Eqs. (1)–(3)]. Equilibrium between CF_3^- and the pentacoordinated $[(CH_3)_3Si(CF_3)_2]^-$ anion at different temperatures in a THF solution [Eq. (4)]. Optimal reaction conditions for the synthesis of CF_3^- [Eq. (5)].

excess potassium *tert*-butoxide (*t*BuOK) in the presence of 18-crown-6 in THF at −78 °C [Scheme 1, Eq. (1); see Figure S1 in the Supporting Information]. Although CF_3^- was previously not reported as an observable species in the direct deprotonation of CF_3H using organic superbases[26,27] and potassium-based strong bases,[16,23–25,31] a weak broad signal around $\delta = -19$ ppm was found by ^{19}F NMR spectroscopy at −78 °C under the present reaction conditions.[30b] Compared with the reported ^{19}F NMR chemical shifts of transition metal–CF_3 complexes, such as $CuCF_3$[25,32] and the $[Cu(CF_3)_2]^-$ anion,[33] the observed broad signal is likely to correspond to exchange-broadened CF_3^-.

Considering that the reactions between trifluoromethyltrimethylsilane ($TMSCF_3$, the Ruppert–Prakash reagent)[34] and Lewis bases can be energetically more favorable than those using CF_3H, further investigation focused on generating CF_3^- using $TMSCF_3$. Similar to previous observations in the literature,[35,36] initial attempts to react $TMSCF_3$ with various fluoride sources exclusively led to CF_3-containing pentacoordinated silicon adducts [Scheme 1, Eq. (2)].

In spite of using a bulky *tert*-butoxy anion as a Lewis base, the pentacoordinated $[(CH_3)_3Si(CF_3)_2]^-$ anion was observed as the major product in the ^{19}F NMR spectrum (a singlet at $\delta = -65.6$ ppm), along with CF_3H (a doublet at $\delta = -81.0$ ppm) which is possibly generated by the deprotonation of the solvent or crown ether by CF_3^-, and a sharp singlet at $\delta = -18.8$ ppm implied the formation of some CF_3^- [Scheme 1, Eq. (3); see Figure S2]. Intriguingly, the $[(CH_3)_3Si(CF_3)_2]^-$ anion, dominant at −78 °C, was found to dissociate to CF_3^- and TMSO*t*Bu at −56 °C [Scheme 1, Eq. (4); Figures S15 and S16]. Although the preparation of CF_3^- can thus be achieved in relatively high conversions, complete dissociation of the $[(CH_3)_3Si(CF_3)_2]^-$ to CF_3^- can be accomplished in this manner only under strictly controlled reaction conditions.

Sterically bulky trifluoromethyltriisopropylsilane ($TIPSCF_3$)[16] was then employed to inhibit the formation of undesired pentacoordinated silicon species. By reacting a mixture of *t*BuOK and 18-crown-6 in THF at −78 °C with $TIPSCF_3$, complete conversion to CF_3^- was achieved within minutes [Scheme 1, Eq. (5); see Figure S4]. A sharp singlet was detected at $\delta = -18.7$ ppm in the ^{19}F NMR spectrum, and this chemical shift was essentially identical to those observed with either CF_3H or $TMSCF_3$ as the trifluoromethanide sources (Figure 2a). A small amount of CF_3H was also observed as a result of protonation from the solvent or crown ether by CF_3^-, along with a fairly weak singlet at $\delta = -116.1$ ppm. The latter signal can be tentatively assigned to a CF_2-containing compound, presumably arising from the singlet difluorocarbene formed by slow CF_3^- decomposition.

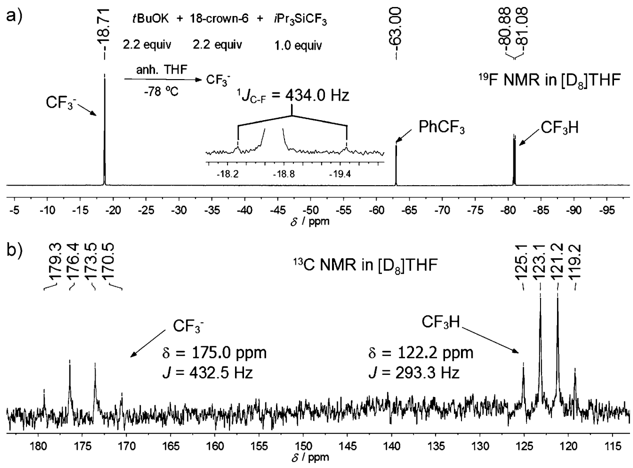


Figure 2. a) 376 MHz ^{19}F NMR spectrum of CF_3^-, generated according to Equation (5) in Scheme 1, in THF at −78 °C with $PhCF_3$ as an internal standard at $\delta = -63.0$ ppm relative to $CFCl_3$. The CF_3H is due to protonation of CF_3^- by the solvent or crown ether. b) ^{13}C NMR spectrum of CF_3^-, generated according to Equation (3) in Scheme 1, in THF at −56 °C.

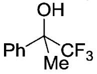
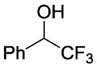
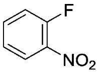
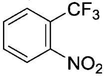
After meticulous efforts, the ^{13}C NMR spectrum of CF_3^- was obtained at −56 °C by using $TMSCF_3$ as the trifluoromethanide source. The ^{13}C NMR spectrum showed an explicit quartet at $\delta = 175.0$ ppm with a 1:2:2:1 intensity pattern, thus suggesting that the carbon atom is attached to three equivalent fluorine atoms (Figure 2b). The $^1J_{C\text{-}F}$ coupling constant was determined to be 432.5 Hz, which is among the largest $^1J_{C\text{-}F}$ coupling constants ever observed (see Figure 2b and Figure S3).[37] This value is in good agreement with the $^1J_{C\text{-}F}$ coupling constant measured by the ^{13}C satellite signals in the ^{19}F NMR spectra (429.3 Hz and 434.0 Hz with $TMSCF_3$ and $TIPSCF_3$, respectively, as CF_3^- sources). These results not only confirm the correspondence between the ^{19}F and ^{13}C NMR signals, but also provide evidence that the reactions employing $TMSCF_3$ and $TIPSCF_3$ leads to the same species, that is, CF_3^- at $\delta = -18.7$ ppm in the ^{19}F NMR spectra. The assignment of our NMR spectroscopic data to CF_3^- were validated by GIAO-PCM-B3LYP/aug-cc-pVTZ//PCM-

B3LYP/6-31+G(d,p) calculations (see the Supporting Information for details).[38,39] The ^{19}F NMR and ^{13}C NMR chemical shifts of CF_3^- were computed to be $\delta = -23.7$ and 170.3 ppm, respectively, which are in good agreement with the experimental data. Although the predicted $^1J_{C\text{-}F}$ coupling constant of 393.0 Hz for CF_3^- differs from the experimental value by 9%, possibly because of reported systematic errors,[40] the significantly larger experimental and calculated $^1J_{C\text{-}F}$ coupling constants of CF_3^- compared with that of CF_3H are consistent with the expected higher pyramidalization of anionic carbon centers.[37] Similar observations have been documented in the literature, such as those for CF_3CF_2Li[41] and $(PhSO_2)_2CF^-$.[42]

The thermal stability of CF_3^- was investigated by variable-temperature ^{19}F NMR experiments. The trifluoromethanide anion was found to have reasonable stability at −78 °C for a few days, which supports the relatively high decomposition barrier in THF, as predicted by our calculations. When samples containing $[K(18\text{-crown-6})]^+[CF_3]^-$ in a THF solution were recorded at temperatures from −50 to −35 °C, the intensity of the CF_3^- signal decreased with time while that of CF_3H increased, and the sum of the areas of the two signals remained essentially constant (see Figures S13 and S14). This observation not only demonstrates the strong basic character of CF_3^- enabling the deprotonation of either THF or 18-crown-6, but also suggests that α-defluorination of CF_3^- is a relatively slow process compared to its protonation. Upon prolonged exposure at −35 °C, the decomposition of CF_3^- was significantly accelerated as indicated by the appearance of two sets of signals, that is, a relatively simple one consisting of two singlets at $\delta = -125.7$ ppm and −129.1 ppm with an area ratio of 1.2:1.0, respectively, and a more complex one in the $\delta = -40$ to −140 ppm range with several multiplets, probably resulting from F–F coupling (Figure S13). As mentioned above, a fairly weak singlet at $\delta = -116.1$ ppm was also observed in the range characteristic for CF_2-group-containing compounds.[37] Although tetrafluoroethylene (C_2F_4, $\delta_F \sim -134$ ppm)[37] was not observed in the current reactions, an explicit interpretation of these spectral data remains difficult because of their complexity and the paucity of literature data on the condensation reactions of difluorocarbene. The relatively long life of CF_3^- at low temperature, along with the recently observed high thermal stabilities of SnF_3^- and GeF_3^-,[43] demonstrate that the widely invoked strong repulsion between the free valence electron pair on carbon and the partial negative charges on the fluorine ligands in CF_3^-[5,8,20] does not necessarily lead to its spontaneous α-defluorination. (see the Supporting Information for detailed discussions on charge distribution,[44] the lone pair of electrons in CF_3^-,[45] and its C_{3v} symmetry).

Along with the unequivocal NMR spectroscopic characterization, a series of trapping experiments was carried out to ascertain the reactivity of CF_3^- in nucleophilic trifluoromethylations (see the Supporting Information for details). The experiments were performed by mixing $TIPSCF_3$ with *t*BuOK in the presence of 18-crown-6 at −78 °C for 0.5 hours, which assured the complete conversion of $TIPSCF_3$ into CF_3^-. The reaction mixture was subsequently treated with electrophilic substrates to afford the corresponding trifluoromethylated products. As shown in Table 1, various types of trifluoromethylation reactions were achieved by the above-mentioned reaction sequence, including nucleophilic substitution reactions (entries 1–4), nucleophilic addition reactions (entries 5–7), aromatic nucleophilic substitution reaction (entry 8), and cupration (entry 9; see the Supporting Information for details). Because of the ubiquitous presence of proton sources in the trapping experiments, CF_3H can be formed and possibly participate in the trifluoromethylation reactions. As the concentration of CF_3^- was shown, by NMR experiments, to be generally higher than that of CF_3H, direct reactions between CF_3^- and the substrates most likely made a significant contribution to the overall trifluoromethylations, particularly in the high yielding reactions, shown in entries 1, 6, 7, and 9 of Table 1. Given the considerable long life of CF_3^- at low temperatures, the results from the trapping experiments mentioned above, and recent observations of trifluoromethylations in solvents other than DMF,[16,26,27] detailed mechanistic investigations may still be warranted for nucleophilic trifluoromethylations, the mechanisms of which were postulated by assuming the inherent instability of CF_3^-.[23,25,26]

Table 1: Capture of CF_3^- with various electrophiles.

Entry	Electrophile (equiv)	Product	δ [ppm][a]	Yield [%][b] (conv.)
1	PhSSPh (2.2)	$PhSCF_3$	−43.4	70 (70)
2	I_2 (2.2)	CF_3I	−16.5	48 (61)
3	MeI (11.0)	$MeCF_3$	−60.8	21 (24)
4	$(PhSO_2)_2NF$ (2.2)	$PhSO_2CF_3$	−79.5	41 (72)
5	PhCOMe (11.0)		−79.5	22 (36)
6	PhCHO (2.2)		−78.3	68 (68)
7	CO_2 (excess)	CF_3CO_2K	−75.2	76 (76)
8	 (11.0)		−60.3	7 (21)
9	CuI (11.0)	$CuCF_3$	−24.9	66 (77)

[a] ^{19}F NMR chemical shifts relative to $PhCF_3$ ($\delta = -63.0$ ppm) as an internal standard. [b] Product yields and conversion of $TIPSCF_3$, based on $TIPSCF_3$ with reference to $PhCF_3$ as an internal standard, as determined by ^{19}F NMR spectroscopy.

In conclusion, the trifluoromethanide anion with a $[K(18\text{-crown-6})]^+$ countercation has been successfully observed and characterized for the first time in solution. Its formation was confirmed by low-temperature ^{13}C and ^{19}F NMR spectroscopy in THF solution. Contrary to the previous assumption, it has now been shown that CF_3^- is not a transient species but possesses significant lifetime at subambient temperatures. The reaction chemistry of isolated CF_3^- provides direct evidence, for the first time, of the intermediacy of CF_3^- in various nucleophilic trifluoromethylation reactions. Previous failures to isolate this key intermediate can be attributed to its facile reaction with reactive acceptors, such as TMSF and $TMSCF_3$, and ready protonation to form CF_3H because of its strong basicity. Considering the central role of CF_3^- in fluoroalkylation reactions, the present results not only advance the understanding of the related chemistry, but are also expected to provide a mechanistic basis for the development of novel synthetic protocols in organofluorine chemistry.

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Keywords: carbanions · fluorine · NMR spectroscopy · reaction mechanisms · reactive intermediates

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