

How Trimethyl(trifluoromethyl)silane Reacts with Itself in the Presence of Naked Fluoride—A One-Pot Synthesis of Bis([15]crown-5)cesium 1,1,1,3,5,5,5-Heptafluoro-2,4-bis(trifluoromethyl)pentenide

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Dedicated to Professor Herbert Jacobs on the occasion of his 70th birthday

Abstract: Reactions of trimethyl(trifluoromethyl)silane in the presence of “naked” fluoride proceed up to a temperature of +5°C mainly with formation of $[\text{Me}_3\text{Si}(\text{CF}_3)_2]^-$. A further rise of temperature up to about 20°C gives evidence for the formation of a salt with the 1,1,1,2,3,6,6-octafluoro-2,4,4,5,5-pentakis(trifluoromethyl)hex-

an-3-ide anion. This intermediate decomposes at room temperature into the 1,1,1,3,5,5,5-heptafluoro-2,4-bis(trifluoromethyl)pentenide anion. The

Keywords: allenes • allylic compounds • C–C coupling • fluoride • silicates

bis([15]crown-5)cesium salt, $[\text{Cs}([15]\text{-crown-5})_2][(\text{CF}_3)_2\text{CCFC}(\text{CF}_3)_2]$ has been characterized unambiguously as the stable final product of this reaction sequence. Thermal decomposition of this salt opens a convenient nontoxic route to obtain 1,1,3,3-tetrakis(trifluoromethyl)allene, $(\text{F}_3\text{C})_2\text{C}=\text{C}=\text{C}(\text{CF}_3)_2$.

Introduction

Trimethyl(trifluoromethyl)silane is widely used in different reactions in organic and organometallic synthesis.^[1] The diversity of these reactions spreads from additions to heteromultiple bonds to nucleophilic substitutions. Also the potential of trifluoromethylsilicates^[2] intermediately formed in solution as reagents of high nucleophilicity has been utilized to abstract protons, for example, from alkynes^[3] or acetonitrile^[4] with formation of fluoroform and the corresponding alkynylsilanes and cyanomethylsilane, respectively.

In the course of our investigations mainly on halide substitutions with less-activated halides or in reactions with elemental chalcogens,^[5] we observed numerous signals, in most cases of low intensity, in the ¹⁹F NMR spectra of the reaction mixtures covering the region mainly between $\delta = -45$ and -80 ppm. These signals did not attract our attention so far and were interpreted in terms of “not further identified by-products”.

It is known that Me_3SiCF_3 reacts with MeCN in the presence of fluoride ions with formation of $\text{Me}_3\text{SiCH}_2\text{CN}$ and CF_3H ^[4] and even formally adds to the “C=O” double bond of DMF^[6] in the presence of cyanide ions, while ethers such as THF and DME (glyme, 1,2-dimethoxyethane) remain unaffected by this reagent combination.^[1] As a consequence, THF and DME became solvents of choice in fluoride-mediated reactions. But the question remained open what happens if Me_3SiCF_3 and small amounts of a fluoride source are combined in these solvents in absence of any further reagent.

Results and Discussion

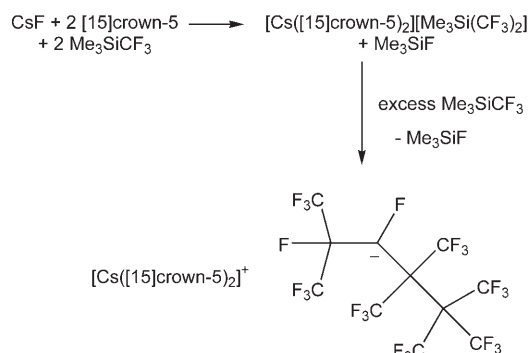
On the basis of our previous work,^[2] we found that independently from the solvent (THF, DME) and the fluoride source ($[\text{NMe}_4]\text{F}$, $[\text{Cs}([15]\text{crown-5})_2]\text{F}$), the silicate $[\text{Me}_3\text{Si}$

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$(\text{CF}_3)_2^-$ is selectively formed if the molar ratio of $\text{F}^-/\text{Me}_3\text{SiCF}_3$ is kept between 1:2 and 1:14. This anion can be detected in addition to excessive silane in ^{19}F NMR spectra up to $+5^\circ\text{C}$ (Scheme 1, Figure 1).



Scheme 1. Formation of the 1,1,1,2,3,6,6,6-octafluoro-2,4,4,5,5-pentakis(trifluoromethyl)hexan-3-ide.

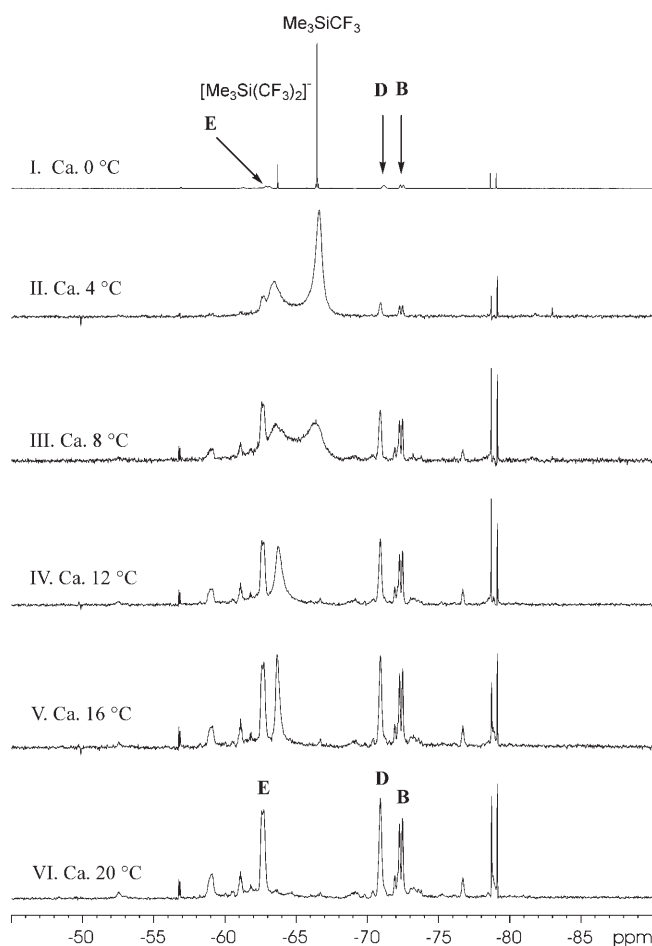


Figure 1. Series of ^{19}F NMR spectra recorded during the process of warming a sample of a mixture of Me_3SiCF_3 and $[\text{Cs}([15]\text{crown-5})_2]\text{F}$ from 0°C to 20°C (temperature of the probehead 21°C at 188.3 MHz), for labelling scheme see Figure 2.

The onset of decomposition is best monitored by recording a series of ^{19}F NMR spectra as the temperature in the NMR spectrometer is increased from 0°C to $+20^\circ\text{C}$ (Figure 1 traces I to VI, region -40 to -90 ppm; ratio $\text{F}^-/\text{Me}_3\text{SiCF}_3 = 1:12$). In experiments with a stoichiometric ratio of 1:40, all compounds mentioned can be detected in the ^{19}F NMR spectra in addition to significant quantities of unreacted Me_3SiCF_3 . Prolonged reaction times of more than 96 h at ambient temperature cause a decrease of the amount of the silane, mainly under formation of CF_3H .

While at $+4^\circ\text{C}$ mainly the significantly broadened signals of $[\text{Me}_3\text{Si}(\text{CF}_3)_2]^-$ and Me_3SiCF_3 can be detected (Figure 1, trace II), further signals at $\delta = -63$, -71 , and -73 ppm intensify upon warming to $+16^\circ\text{C}$ (Figure 1, traces III to V) and finally to ambient temperature (Figure 1, trace VI). In this temperature range, a complex reaction sequence occurs yielding an intermediate that was identified on the basis of 2D ^{19}F and ^{13}C NMR spectra by using different programs and pulse sequences to be most probably 1,1,1,2,3,6,6,6-octafluoro-2,4,4,5,5-pentakis(trifluoromethyl)hexan-3-ide (Figure 2). The ^{19}F -COSY experiment allows the identification of all fluorinated groups in the intermediate. Unfortunately, in some cases it is not possible to determine unambiguously which coupling constant is cause of a special cross-peak. Nevertheless, the proposed structure is in good agreement with the spectrum and additionally supported by the results of ^{19}F NOE experiments. It has to be noted that

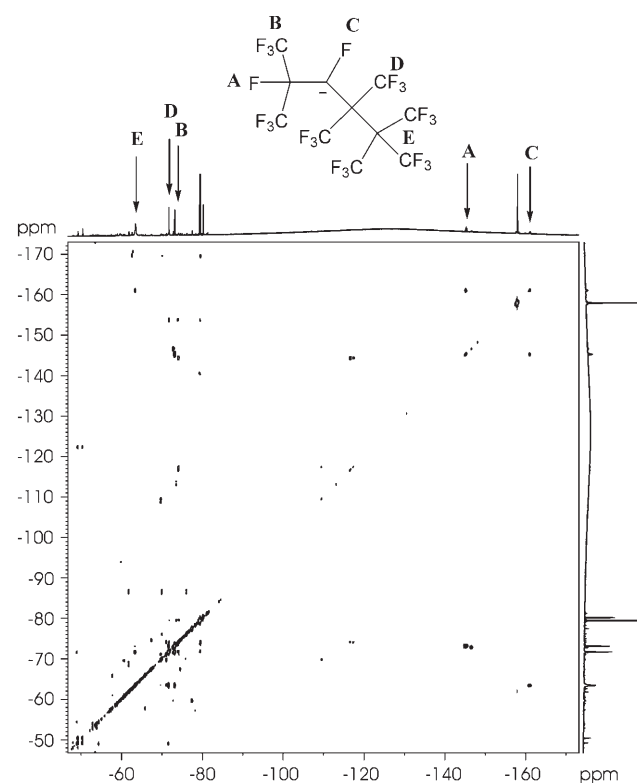
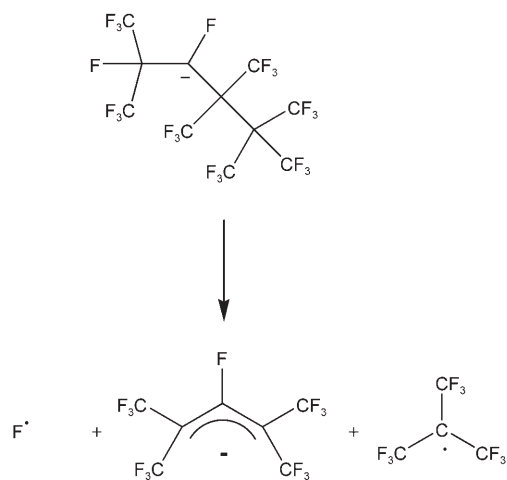


Figure 2. ^{19}F COSY spectrum of the intermediate 1,1,1,2,3,6,6,6-octafluoro-2,4,4,5,5-pentakis(trifluoromethyl)hexan-3-ide in $[\text{D}_8]\text{THF}$ recorded at -5°C .

the process of the formation of this intermediate is significantly slower in THF than in DME, while with respect to the decay the half-life time of the intermediate is significantly longer in DME than in THF.

All attempts to get a deeper insight into the process of the formation of the intermediate remained poor. Variation of temperature, the stoichiometric ratios of the reactants, use of different sources of fluoride only showed ^{19}F NMR spectroscopic evidence for products containing the C_2F_5 group, the $t\text{C}_4\text{F}_9$ group and in few cases the perfluoro-*neo*-pentyl group, $\text{R}-\text{CF}_2\text{C}(\text{CF}_3)_3$ (R: not further specified).^[7] In no case, signals for derivatives with a $i\text{C}_3\text{F}_7$ moiety were detected in the ^{19}F NMR spectra making this group suspicious to be a key substance during the formation of 1,1,1,2,3,6,6,6-octafluoro-2,4,4,5,5-pentakis(trifluoromethyl)hexan-3-ide. This result can only be explained by successive substitution of fluoride bond to sp^3 -hybridized carbon centres by perfluoroalkyl groups.

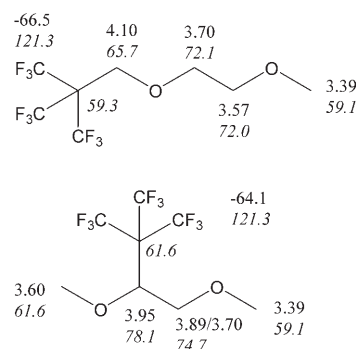
This intermediate can be stored in solution for several weeks at -78°C without any significant decomposition. Solid material obtained upon removal of all volatile components under reduced pressure at 0°C can be stored for several days at -20°C . Exposure to ambient temperature either of the solid or of solutions was accompanied by a rapid decomposition with formation of a salt with the 1,1,1,3,5,5,5-heptafluoro-2,4-bis(trifluoromethyl)pentenide (allyl) anion as the stable major product (Scheme 2).



Scheme 2. Proposed fragmentation of the 1,1,1,2,3,6,6,6-octafluoro-2,4,4,5,5-pentakis(trifluoromethyl)hexan-3-ide anion.

The decomposition involves the formation of one perfluoro-*tert*-butyl radical as well as one fluorine radical. The fluorine radical can be trapped by addition of triphenylphosphane, which is converted into the corresponding difluoride, Ph_3PF_2 (^{19}F , ^{31}P NMR spectroscopy),^[8] while without addition of Ph_3P not further specified reactions of the fluorine radical occur. Addition of Ph_3P to the reaction mixture after decomposition of the intermediate did not give any evidence for oxidation products. The fate of the perfluoro-*tert*-butyl radical may be understood as formation of the correspond-

ing anion^[9] in the presence of Ph_3P or a consecutive reaction with the solvent to give $(\text{CF}_3)_3\text{CCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ and two diastereomers of $(\text{CF}_3)_3\text{CCH}(\text{OCH}_3)\text{CH}_2\text{OCH}_3$ (Scheme 3), which were unambiguously identified by two-dimensional NMR methods.^[10] The formation of perfluoro-*tert*-butyl ethers, $(\text{CF}_3)_3\text{COR}$, can be excluded by comparison with literature data.^[11]



Scheme 3. ^1H , ^{19}F and ^{13}C NMR shifts of the ethers $(\text{CF}_3)_3\text{CCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ and $(\text{CF}_3)_3\text{CCH}(\text{OCH}_3)\text{CH}_2\text{OCH}_3$ (^{13}C NMR shifts in italics).^[10]

Bis([15]crown-5)cesium 1,1,1,3,5,5,5-heptafluoro-2,4-bis(trifluoromethyl)pentenide has been isolated from the reaction mixture as a colorless crystalline material in average yields of 60% with a visible melting point of $123\text{--}125^\circ\text{C}$. The compound, especially the anion, was characterized by ^{13}C , ^{19}F HMBC spectra (Figure 3). Cross-peaks from $^1J(^{13}\text{C}, ^{19}\text{F})$ couplings were identified by characteristic doublets splitting on the F axis (horizontal). They allow an assignment of the ^{13}C signal at $\delta=125.9$ ppm to the CF_3 (F) and of the ^{13}C resonance at $\delta=167.6$ ppm to the CF group (G) of the anion. The fluorine signals of both the CF_3 and the CF group show additional cross-peaks to the resonance of a quaternary carbon atom at $\delta=70.6$ ppm. The experimental parameters chosen prove that these cross-peaks result from $^2J(^{13}\text{C}, ^{19}\text{F})$ couplings supporting the connectivity of the molecule.

Negative ESI mass spectrometry (m/z (%): 330.91 (100) [M^-]) in solution, a single-crystal structure analysis as well as vibrational spectra of the solid prove the composition of the anion. The results of these last methods were supported by DFT calculation (B3PW91/6-311G+(2d,p)).^[12]

The salt crystallizes in the triclinic space group with $a=881.0(1)$, $b=1433.7(1)$, $c=1440.8(1)$ pm, $\alpha=88.78(1)$, $\beta=82.25(1)$, $\gamma=79.47(1)^\circ$, and $Z=2$. The structure of the anion is depicted in Figure 4 and it shows only small deviations from C_2 symmetry, which was assumed for DFT calculations, exhibiting a very good agreement between experimental and theoretical results. The C–F bonds within the trifluoromethyl groups vary between $133.6(2)$ and $136.4(2)$ pm, while that to the central fluorine atom is slightly longer ($137.9(2)$ pm). The C–C bonds to the CF_3 groups show an average value of approximately 147.4 pm and significantly differ from that within the central “allyl” unit (137.8 pm).

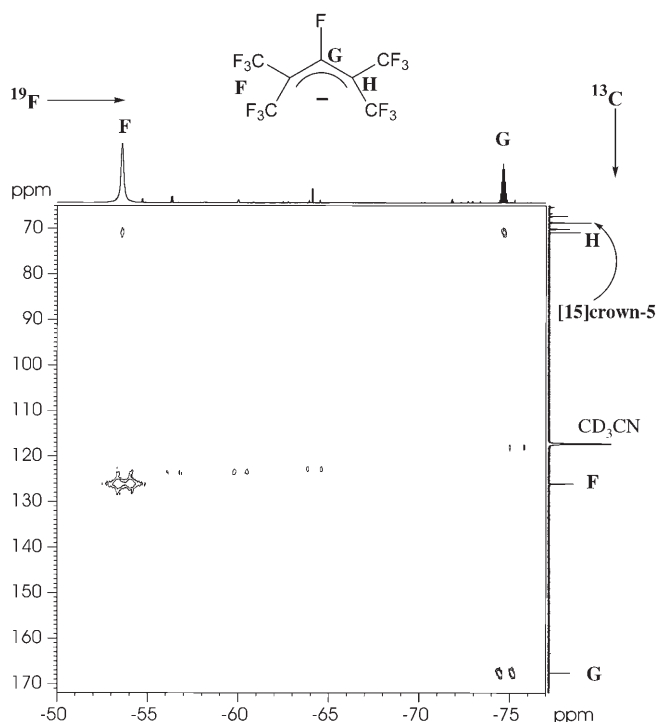


Figure 3. ^{13}C , ^{19}F HMBC spectrum of bis([15]crown-5)cesium 1,1,1,3,5,5,5-heptafluoro-2,4-bis(trifluoromethyl)pentenide in CD_3CN at 25°C .

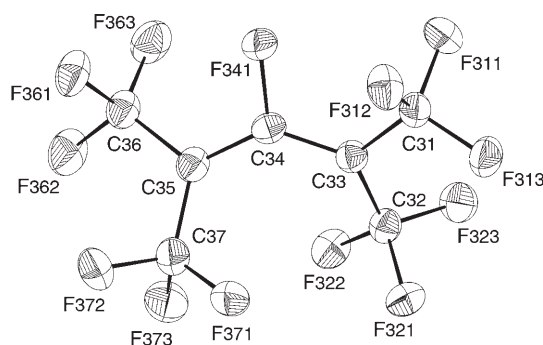
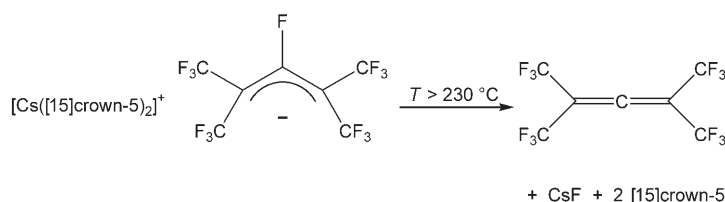


Figure 4. Molecular structure of the 1,1,1,3,5,5,5-heptafluoro-2,4-bis(trifluoromethyl)pentenide anion. Interatomic distances [pm] and angles $^\circ$; calculated values with assumption of C_2 symmetry in italics: C31–C33 147.5(3) C35–C36 147.2(3), 148.0; C32–C33 147.5(3) C35–C37 147.4(3), 147.4; C33–C34 137.8(3) C35–C34 137.7(3), 138.3; C34–F341 137.9(2), 136.7; C–F in CF_3 groups 133.6(2)–136.4(2), 135.0–136.0; C31–C33–C32 116.5(2) C36–C35–C37 116.3(2), 116.3; C31–C33–C34 120.3(2) C36–C35–C34 119.6(2), 119.1; C32–C33–C34 122.6(2) C37–C35–C34 123.8(2), 124.2; C33–C34–C35 134.4(2), 134.5; C33–C34–F341 112.7(2) C35–C34–F341 112.9(2), 112.8.

Together with the angle C33–C34–C35 of $134.4(2)^\circ$, these data appear to be representative for a $(\text{CF}_3)_2\text{CCC}(\text{CF}_3)_2$ moiety in comparison with literature values.^[13]

The process of formation of the “allyl” anion—addition of a fluoride source to tetrakis(trifluoromethyl)allene^[13–15]—appears to be reversible; $[\text{Cs}([15]\text{crown-5})_2][(\text{CF}_3)_2\text{CCFC}(\text{CF}_3)_2]$ decomposes selectively at a temperature above

230°C into 1,1,1,5,5,5-hexafluoro-2,4-bis(trifluoromethyl)penta-2,3-diene (1,1,3,3-tetrakis(trifluoromethyl)allene)^[16] and cesium fluoride with release of two equivalents of the crown ether (Scheme 4).



Scheme 4. Thermal decomposition of $[\text{Cs}([15]\text{crown-5})_2][(\text{CF}_3)_2\text{CCFC}(\text{CF}_3)_2]$.

This reaction sequence opens a new and convenient access to 1,1,3,3-tetrakis(trifluoromethyl)allene avoiding the use of highly toxic perfluoroisobutene.^[17]

Experimental Section

NMR spectra: The ^{19}F COSY and ^{19}F NOE spectra were performed on a Bruker Avance 400 spectrometer by using a triple-resonance ^1H , ^{19}F , BB inverse probehead with the ^{19}F frequency on the detection coil. The ^{13}C , ^{19}F HMBC spectrum of bis([15]crown-5)cesium 1,1,1,3,5,5,5-heptafluoro-2,4-bis(trifluoromethyl)pentenide was recorded with a triple resonance ^1H , ^{19}F , BB inverse probehead with the ^{19}F frequency on the detection coil and the decoupling coil tuned on ^{13}C . 1D-NMR spectra were run either on the Bruker spectrometer AC200 or Avance 400.

Bis([15]crown-5)cesium 1,1,1,3,5,5,5-heptafluoro-2,4-bis(trifluoromethyl)pentenide: A quantity of CsF (0.30 g, 2 mmol) was added in one portion to a well-stirred mixture of Me_3SiCF_3 (3.40 g, 24 mmol) and [15]crown-5 (0.88 g, 4 mmol) in anhydrous dimethoxyethane (4 mL) at -20°C . The mixture was slowly warmed to ambient temperature (about 3 h) and vigorously stirred for another 12 h. All volatile materials were condensed in vacuo at room temperature; the residue was washed with anhydrous benzene (2×3 mL), dried in vacuo and dissolved in diethyl ether. The solution was placed in a cold bath at -50°C , while a triple amount of *n*-hexane was condensed onto the solution over a period of 3 d. Colorless crystals suitable for XRD measurement were collected in 60.7% yield (1.10 g). Elemental analysis calcd (%) for $\text{C}_{27}\text{H}_{40}\text{F}_{15}\text{O}_{10}\text{Cs}$ (904.49): C 35.85, H 4.46; found: C 35.46, H 4.25; m.p. $123\text{--}125^\circ\text{C}$ (glass capillary), $>230^\circ\text{C}$ (decomp; DTA); ^1H NMR (400.1 MHz, CD_3CN , 21°C , TMS): $\delta = 3.56$ ppm (s); ^{19}F NMR (376.4 MHz, CD_3CN , 0°C , CCl_3F): $\delta = -53.4$ (br, 6F; CF_3), -54.1 (br, 6F; CF_3), -74.5 ppm (tridecet, $^4J(\text{F},\text{F}) = 19$ Hz, 1F; CF); ^{13}C NMR (100.6 MHz, CD_3CN , 21°C , TMS): $\delta = 167.7$ (dm, $^1J(\text{F},\text{C}) = 262$ Hz; CF), 125.9 (q, $^1J(\text{F},\text{C}) = 266$ Hz; CF_3), 70.6 (m; $\text{C}(\text{CF}_3)_2$), 68.7 ppm (tm, $^1J(\text{C},\text{H}) = 141$ Hz; OCH_2); MS (neg. ESI, MeCN): m/z (%): 330.91 (100) $[\text{M}^-]$; MS (EI, 20 eV): m/z (%): 312 (65) $[\text{M}^+ - \text{F}]$, 293 (19) $[\text{M}^+ - 2\text{F}]$, 224 (14) $[\text{M}^+ - \text{CF}_4]$, 133 (51) $[\text{C}_6\text{H}_{13}\text{O}_3^+]/[\text{Cs}^+]$, 89 (100) $[\text{C}_4\text{H}_9\text{O}_2^+]$, 45 (75) $[\text{C}_2\text{H}_5\text{O}^+]$. Fragments with intensities less than 5% were detected for 243, 205, 155. The EI mass spectrometric fragmentation (m/z from 312 to 155) was identical with that reported for $(\text{CF}_3)_2\text{C}=\text{C}=\text{C}(\text{CF}_3)_2$.^[16]

Single-crystal structure determination: The intensity data were collected on an imaging-plate diffractometer (IPDS II, Stoe & Cie) with MoK_α radiation ($\lambda = 71.073$ pm, graphite monochromator) at 130 K. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 . The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms.

ters for all of the hydrogen atoms. A numerical absorption correction was applied after optimization of the crystal shape.^[18–21]

Crystal data for bis([15]crown-5)cesium 1,1,1,3,5,5,5-heptafluoro-2,4-bis-(trifluoromethyl)pentene: C₂₇H₄₀F₁₃O₁₀Cs, triclinic space group *P* $\bar{1}$, *a* = 881.0(1), *b* = 1433.7(1), *c* = 1440.8(1) pm, α = 88.78(1), β = 82.25(1), γ = 79.47(1)°, *V* = 1772.8(2) × 10⁶ pm³, *Z* = 2, μ = 1.163 mm^{−1}, *F*(000) = 908, *R*_{int} = 0.0312, no. collected/unique/*I*₀ > 2σ(*I*₀) data = 21951/7694/7206, *R*₁/*wR*₂ (all data) = 0.0285/0.0694, *R*₁/*wR*₂ [*I*₀ > 2σ(*I*₀)] = 0.0266/0.0679, max/min electron density = 0.529/−0.915 × 10^{−6} e pm^{−3}. CCDC-265521 contains 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.

1,1,3,3-Tetrakis(trifluoromethyl)allene: Solid [Cs([15]crown-5)₂]-[(CF₃)₂CCFC(CF₃)₂] (3.52 g, 3.8 mmol) was heated to 230 °C under a weak flow of nitrogen for 2.5 h. Volatile products were collected in a cold trap at −78 °C. After distillation (CF₃)₂C=C(CF₃)₂ was obtained (0.60 g, 51% yield). B.p. 43–45 °C (41 °C (743 mm Hg)^[16]); ¹⁹F NMR (188.3 MHz, CDCl₃, 21 °C, CCl₃F): δ = −61.4 ppm (s); ¹³C NMR (50.3 MHz, CDCl₃, 21 °C, TMS): δ = 204.7 (br; =C=), 118.5 (qm, ¹J(F,C) = 277 Hz; CF₃), 106.8 ppm (septet, ²J(F,C) = 40 Hz; C(CF₃)₂).

Acknowledgements

Generous financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged (436 UKR 113/26).

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Received: July 12, 2005
Published online: August 25, 2005