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Alkali metal trifluoroacetates for the nucleophilic trifluoromethylation of fullerenes

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Graphical Abstract



Highlights:

- Facile and rapid method for nucleophilic fullerene trifluoromethylation by thermolysis of trifluoroacetates was developed.
- *ortho*-C₆₀(CF₃)H was obtained with 30% yield and unambiguously characterized.
- Reactivities of CF₃CO₂M are increased within the row of Li<Na<K≈Cs in agreement with the thermal stability drop.
- CF₃⁻ addition mode for K/Cs salts switches over to :CF₂ addition for Na/Li salts in good accordance with HSAB theory.
- Proposed synthetic route can be adopted for trifluoromethylation of electron-deficient fullerenes and related compounds.

Abstract

Fullerene C₆₀ readily reacts with potassium and cesium trifluoroacetates yielding C₆₀(CF₃)⁻M⁺ salts, and subsequent acid hydrolysis gives $ortho-C_{60}(CF_3)H$. The reaction rate and the probability of the alternative reaction pathways strongly depend on the particular metal cation. Thus, the reactivity increases in the order Li<Na<K≈Cs, in correlation with the decreasing thermal stability. Furthermore, the sodium and, especially, lithium salts tend to effect CF₂- rather than CF₃-functionalization of the fullerene, in good accordance with the hard/soft acids and bases theory. The nucleophilic trifluoromethylation is found to be applicable to other pristine fullerenes like C_{70} as well as to fullerene derivatives like p^7mp - $C_{70}(CF_3)_{10}$. It enables selective trifluoromethylated preparation of low fullerenes via regioselective consecutive trifluoromethylation under accurately controlled solution-phase conditions.

1. Introduction

In the past decade, the most common methods for fullerene trifluoromethylation were based on the thermolysis of CF₃I or silver trifluoroacetate [1–3]. Typically, radical trifluoromethylation of fullerenes yields a complex mixture of products with broad compositional and isomeric distribution, but normally only a few compounds are available in isolable amounts. To selectively obtain particular trifluoromethylated products, one needs a specifically tailored synthetic approach, but so far such approaches are known only for two derivatives of C₆₀, *para*-C₆₀(CF₃)₂[4] and S₆-C₆₀(CF₃)₁₂[5].

Surprisingly, nucleophilic trifluoromethylation of fullerenes or their derivatives has not been yet reported. Moreover, while silver trifluoroacetate is extensively used in fullerene trifluoromethylation, the reaction of fullerenes with alkali metal trifluoroacetates has not yet been investigated, even though several related successful reactions have been reported. Thus, C₆₀ and C₇₀ are known to undergo nucleophilic trichloromethylation under gentle heating with alkali metal trichloroacetates, and the thermally labile C_{60/70}(CCl₃)⁻ anionic intermediates can give C_{60/70}(CCl₂) under refluxing at 80–110 °C [6,7]. Analogously, refluxing of alkali metal chlorodifluoroacetates at 160–180 °C with fullerenes in *ortho*-dichlorobenzene in the presence of 18-crown-6 as a phase transfer catalyst [8,9] (inspired by the analogous treatment of alkenes in diglyme or triglyme [10,11]) yields C_{60/70}(CF₂) derivatives, though this reaction is presently believed to be [2+1]-cycloaddition of the pre-formed :CF₂ carbenes, since no C_{60/70}(CF₂Cl)⁻ intermediates have been detected. Also to be mentioned is the treatment of C_s -C₆₀Cl₆ with C₂F₅Li to give C_s-C₆₀(C₂F₅)H upon the subsequent protonation [12].

Thermolysis of the alkali metal halodifluoroacetates is known to proceed via decarboxylation, leaving CF_2X^- anions. In some cases, X^- is then abstracted to give : CF_2 carbenes [11,13–15]. Recently, a CF_3^- intermediate was isolated and spectroscopically

characterized as a $[K(18\text{-}crown-6)]^+CF_3^-$ complex that is stable at -78 °C but is prone to a slow α -defluorination at -35 °C, also to give :CF₂, as a side process to deprotonation of the THF medium [16]. CF₃⁻ generation by means of thermolysis can be employed for the nucleophilic trifluoromethylation of aryl halides, aldehydes, ketones, diaryldisulfides, as well as for gemdifluorocyclopropanation of alkenes via further decomposition of CF₃⁻ to :CF₂ [17–22]. In particular, aryl halides and carbonyl compounds undergo nucleophilic trifluoromethylation in reaction with alkali metal trifluoroacetates [19,20,23]. The reaction is typically carried out in dipolar aprotic solvents in the presence of copper(I) iodide as a catalyst and stabilizer under several hours of refluxing.

In this work, we report the first nucleophilic trifluoromethylation of the pristine fullerenes C_{60} and C_{70} and of the exohedral derivative p^7mp - $C_{70}(CF_3)_{10}$ with alkali metal trifluoroacetates in solution. In contrast to most of the other substrates, fullerenes rapidly attach a CF_3^- anion without a need for stabilizers or activators. The present approach afforded selective preparation and the first comprehensive characterization of *ortho*- $C_{60}(CF_3)H$ (Fig. 1). Previously, preparation of $C_{60}(CF_3)H$ and the related $C_{60}(CF_2Br)H$ and $C_{60}(CF_2Cl)H$ was reported in some early works [24,25], but treatment of C_{60} with di(trifluoroacetyl) peroxide or perfluoroalkyl halides under the radical functionalization conditions and subsequently with Bu₃SnH gave only moderate yields of the target product, and no spectroscopic data for $C_{60}(CF_3)H$ has ever been reported, except for the mass spectra [26,27]. We have also obtained two major isomeric compounds of $C_{70}(CF_3)H$ and four isomers of $C_{70}(CF_3)_{11}H$ obtained from p^7mp - $C_{70}(CF_3)_{10}$.

2. Results and discussion

Lithium, sodium, potassium, and cesium trifluoroacetates were prepared by treatment of the respective carbonates with CF₃COOH followed by freeze-drying. Their composition was verified by means of the ATR–IR spectroscopy (see Fig *S*1 in ESI). Intense symmetric and asymmetric stretching bands of the carboxylate group (1670–1653, 1472–1425 cm⁻¹), C–F stretching bands (1200–1110 cm⁻¹), carboxylate scissoring bands and C–C stretching bands (860–720 cm⁻¹) were in a good agreement with the reference data [28–30]. The CF₃COOLi sample also demonstrated a broad absorption band at 3200–3600 cm⁻¹ due to the absorbed water, a sign of higher hygroscopicity compared to the other trifluoroacetates.

The decomposition temperatures of the solid CF₃COOM salts are known to show a decreasing trend from 250 °C for Li to 210 °C (Na), 150 °C (K), and 154 °C (Cs) [31], i.e., their lability increases with the size of the alkali metal cation. Cesium salts usually being better

soluble in organic solvents, we started from a systematic study of the reaction of C_{60} with cesium trifluoroacetate. The conditions of the series of experiments with CF₃COOCs are listed in Table 1. *Ortho*-dichlorobenzene, benzonitrile (PhCN) and *o*DCB:PhCN 8:2 v/v mixtures were used as solvents due to a combination of high boiling point (ca 180 °C) with relatively high fullerene solubility (ca 25 mg of C_{60} per ml in *o*DCB and 0.4 mg/ml in PhCN at 25 °C) [32]. Rapid color change of the reaction mixture from purple (pristine fullerene) to black (dark green on dilution), which is known to indicate the formation of the anionic monoadducts $C_{60}R^-$ [33,34], occurred within 2 min of refluxing. Attribution of the color change to $C_{60}(CF_3)^-$ is further supported by the UV/Vis/NIR spectrum of the reaction media (Fig. 2b) with its broad bands at 620 and 930 nm that are characteristic of the $C_{60}R^-$ anions [35,36] while being absent from the spectrum of pristine fullerene (Fig. 2a). Upon acidic workup, the mixture turns brown, and the said broad bands vanish. Instead, the final spectrum features a small peak at 430 nm (Fig. 2c) typical of various *ortho*- $C_{60}R_2$ adducts [36–40]. HPLC analysis of the acidified mixture (Fig. 3a) reveals unreacted C_{60} (t_R =7.6 min) together with some weaker retained major reaction product (t_R = 6.9 min).

The HPLC-purified reaction product was identified by means of high-resolution mass spectrometry (Fig S3 in ESI) as $C_{60}(CF_3)H$, a compound that, as of yet, remained without spectroscopic and structural characterization. The UV/Vis absorption data of $C_{60}(CF_3)H$ (Fig S2 in ESI) strongly resemble those for the *ortho*- $C_{60}(CCl_3)H$ and other *ortho*- $C_{60}R_2$ compounds [6,38], and the ¹H, ¹³C, and ¹H–¹³C HMBC NMR spectra further provide a clear and unequivocal support of the *ortho*-addition pattern (Figs. 2 and S4, S5). The ¹H and ¹⁹F NMR spectra feature singlets at 6.88 ppm and -72.32 ppm, respectively, confirming the presence of only a single type of both hydrogen and fluorine atoms. In the proton-decoupled ¹³C NMR spectrum we observed 25 resonances of sp^2 -C atoms (130 – 155 ppm; theory predicts 30 signals for C_s-symmetric ortho-C₆₀XY, some likely being overlapped) and three quartets at 54.7 ($J_{CF} = 2.20$ Hz), 67.7 (J_{CF} = 29.71 Hz), and 127.8 ppm (J_{CF} = 280.60 Hz) due to the sp^3 -C atoms. The magnitude of the J_{CF} coupling constants dictates assignment of the sp³-C resonances to the C-C-CF₃, C-CF₃, and CF₃ carbon atoms, respectively, thus suggesting, in further agreement with the ¹H–¹³C HMBC data, adjacent location of the H and CF3 addends. Finally, the DFT calculations reveal that the orthoprotonation of $C_{60}(CF_3)^-$ is favored by both the thermodynamic and kinetic factors. Firstly, this is the *ortho*-position along the [6,6]-bond that shows the largest effective negative charge; secondly, protonation at the *ortho*-position is 28 kJ mol⁻¹ more favorable than at the *para*position and even more so than the rest of the alternatives.

The optimal synthetic conditions with respect to the solvent composition, amount of the substrate, reaction atmosphere, and reaction time were achieved in the experiments nos. 8 and 9

of Table 1. It was found, that the 8:2 v/v mixture of *o*DCB:PhCN likely provides the optimally balanced solubility of both C_{60} and CF₃COOCs and that the reaction time needs to be limited to 6–10 min, possibly in order to obtain the maximum amount of the labile $C_{60}(CF_3)^-$ intermediate.

The inertness of the reaction atmosphere turns out to crucially affect the yield of the product and the selectivity. Thus, the HPLC analyses of the ambient atmosphere reaction revealed several by-products with high retention times ($t_R = 15-18 \text{ min}$) typical of double-caged fullerene dimers [41,42]. Instead of the molecular ions $C_{60}(CF_3)H^+$ that prevail in the mass-spectra of $C_{60}(CF_3)H$, LC-APPI-MS analysis revealed the fragment $C_{60}(CF_3)^+$ ions which likely originated from the [$C_{60}(CF_3)$]₂ precursor. One can hypothesize that the $C_{60}(CF_3)^-$ intermediates can be oxidated with the molecular oxygen to the respective neutral radical species and further recombine into [$C_{60}(CF_3)$]₂, similarly to the formation of the ($C_{60}CH_2Ph$)₂ and ($C_{60}H$)₂ dimers upon electrochemical oxidation of $C_{60}(CH_2Ph)^-$ and $C_{60}H^-$, respectively. [43,44].

The above-optimized reaction conditions were used in a comparative reactivity study of all four alkali metal trifluoroacetates (Table 2 and Fig 3a). HPLC monitoring of the reaction mixture reveals that reactivity increases in the order Li<Na<K≈Cs, which correlates with the order of thermal stability of the trifluoroacetates [31]. While potassium and cesium trifluoroacetates rapidly decompose at 180 °C and selectively yield $C_{60}(CF_3)H$ via $C_{60}(CF_3)^-$, sodium trifluoroacetate thermolyzes considerably slower and gives both $C_{60}(CF_3)H$ and $C_{60}(CF_2)$. Finally, lithium salt decomposes even slower to produce $C_{60}(CF_2)$.

Initially, it was necessary to find out, whether any less substantial synthetic conditions would make any significant difference. Firstly, we tested different phase transfer catalysts (PTC), namely 15-crown-5 and 12-crown-4, that are complementary to the Na⁺ and Li⁺ ions, respectively (Table 2). It turned out that 18-crown-6 is still advantageous due to stronger binding to the respective cations [45,46], the yield of $C_{60}(CF_3)H$ being slightly reduced when using with 12-crown-4 and 15-crown-5. However, no qualitative differences have been observed (see the HPLC traces for CF₃COONa and CF₃COOLi with varied crown ethers in the Fig S7 of the ESI). Likewise, additional experiments with trace amounts of water intended to simulate hygroscopicity of the trifluoroacetates did not reveal any qualitative effect on the composition of the products. One can only find a need to increase the reaction time and the excess of the trifluoroacetate in order to compensate for the possible rapid protonation of the intermediate CF_3^- anion.

Turning to the principal effect of the alkali metal cation as revealed by the data of Table 2, there is a switch of reaction pathways when going from the larger Cs and K to the smaller Na and Li cations. While with the K⁺ and Cs⁺ cations the lifetime of the CF₃⁻ anion is long enough to react with C₆₀ (see Fig 3b), with Na⁺ and, especially, with Li⁺ there is a much increased rate of decomposition toward the singlet :CF₂ carbene (MCF₃ \rightarrow :CF₂+MF) and, accordingly, C₆₀(CF₂) becomes the major product. Those differences are in line with the concept of hard/soft acids and bases (HSAB theory) [47,48]. Indeed, CF₃Li is known to readily decompose, apparently to :CF₂, even when formed at low temperature in the presence of a suitable electrophile, but the other metal cations are capable of stabilizing the CF₃⁻ anion. For example, CF₃MgI is stable enough to react with various electrophiles at low temperature [49], copper(I) iodide can be used to stabilize the CF₃⁻ anion for the purpose of decarboxylative nucleophilic trifluoromethylation of aryl halides and carbonyl compounds [19,50]. One can expect the Gibbs energy of α -defluorination of CF₃M to correlate with the lattice energy of MF that equal –1045, –924, –822, and –737 kJ mol⁻¹ for M=Li, Na, K, and Cs, respectively [51], so that the decomposition to the :CF₂ carbene becomes the principal pathway in the lithium trifluoroacetate case.

The nucleophilic trifluoromethylation route looks perfectly applicable not only to the pristine fullerenes but also to their derivatives. We further tested our synthetic methodology with the pristine C_{70} and with its exohedral derivative p^7mp - $C_{70}(CF_3)_{10}$ [52]. The HPLC-APPI-MS data revealed the formation of at least two isomers of $C_{70}(CF_3)$ H and at least of four isomers of $C_{70}(CF_3)_{11}$ H (Fig. 4, *S*8 and *S*9). Comparison of the UV/Vis data for the major $C_{70}(CF_3)$ H isomers (t_R =10.8 and 11.9 min, see Fig *S*9) against the previously characterized $C_{70}(CCl_3)$ H isomers [6] makes possible to identify them as the C_1 - and C_s -symmetric *ortho*-adducts at the pole of the C_{70} cage, namely 7,22- $C_{70}(CF_3)$ H and 8,25- $C_{70}(CF_3)$ H (locant indexes are given according to IUPAC recommendation [53]). While 7,22- $C_{70}(CF_3)$ H should be a mixture of the two equivalent stereoisomers, 8,25- $C_{70}(CF_3)$ H allows for the two possible isomers depending on the position of each of the addends. In view of higher reactivity of the atoms in the polar pentagon of C_{70} toward nucleophilic addition [6,54], we expect that it is the CF₃ group that is attached at the respective position 25. A comprehensive study of the isomers of $C_{70}(CF_3)$ H and $C_{70}(CF_3)_{11}$ H will be a subject of our further publications.

3. Conclusion

Nucleophilic trifluoromethylation of the fullerene compounds can be readily carried out by means of thermolysis of the potassium and cesium trifluoroacetates. Rapid conversion of the C_{60} fullerene into $C_{60}(CF_3)^-$ and, upon subsequent protonation, into *ortho*- $C_{60}(CF_3)$ H demonstrates high efficiency of our approach. Moreover, it can be easily transferred onto other fullerene

substrates, including the already functionalized compounds, as is illustrated by trifluoromethylation of C_{70} and p^7mp - $C_{70}(CF_3)_{10}$. Importantly, our method requires milder solution-phase conditions than the common high temperature trifluoromethylation and thus can be executed in a selective and directed manner. We, therefore, believe that the nucleophilic trifluoroacetate pathway can be developed into a methodology for large-scale synthesis of many less-accessible isomers of the trifluoromethylated fullerenes including the compounds of potential interest as electron acceptors in the molecular electronics [55,56], and/or as the fluorescent materials [57].

4. Experimental

4.1. Reagents and solvents

All reagents and solvents were used as received unless otherwise noted. Fullerenes C₆₀ (99.8%) and C₇₀ (99.5%) were purchased from "Fullerene centre". CF₃COOH (99+%, Sigma Aldrich), CF₃I (P&M-Invest, 98%), 18-crown-6 (99%, Acros Organics), 15-crown-5 (98%, Sigma-Aldrich), 14-crown-4 (98%, Sigma-Aldrich), M₂CO₃ (M = Li, Na, K, Cs; 98%, Reachim, Russia), *ortho*-dichlorobenzene (99%, abcr), benzonitrile (99%, Sigma-Aldrich), and toluene (99.8%, Khimmed, Russia). Prior to usage toluene was distilled at atmospheric pressure while *o*DCB and benzonitrile were distilled at 20 mbar vacuum (68 °C and 80 °C boiling points respectively).

4.2. HPLC

HPLC analyses were performed using Agilent 1100 instrument equipped with a diodearray detector (DAD) and a temperature controlled Cosmosil Buckyprep analytical column (4.6 mm I.D. \times 25 cm, Nacalai Tesque Inc.). HPLC separation was carried out on an Cosmosil Buckyprep semi-preparative column (10 mm I.D. \times 25 cm, Nacalai Tesque Inc.) using Waters 1500 chromatographic system equipped with an isocratic pump and a dual wavelength UV/Vis detector. Toluene was used as an eluent at flow rates of 1.0 and 4.6 ml min⁻¹, HPLC traces were registered at 290 and 360 nm simultaneously.

4.3. MS and LC-MS

LC-APPI-MS data were acquired using the above mentioned HPLC instrument with Agilent 6410 triple quadrupole mass spectrometer in positive mode. APPI HRMS spectra in positive ion mode were acquired for toluene solutions using AB Sciex TripleTOF 5600+ instrument equipped with a PhotoSpray ion source.

4.4. UV/Vis/NIR spectroscopy

UV/Vis spectra of C₆₀(CF₃)H in toluene solution were obtained using the abovementioned HPLC DAD detector in the 290–900 nm range with 2 nm resolution. UV/Vis/NIR spectra were obtained in 200–1100 nm wavelength range using Avantes-2048 waveguide spectrometer equipped with a linear CCD detector (300 gr/mm grating, 50 μ m slit, 2.4 nm resolution) and an AvaLight-DHc light source. The studied samples were loaded into the 1 cm × 0.4 cm quartz cells (Quartz SUPRASIL, Hellma Analytics).

4.5. NMR spectroscopy

The ¹H, ¹⁹F, and ¹³C and 2D NMR spectra of C₆₀(CF₃)H were recorded in a chloroform-*d* using a Bruker Avance-III spectrometer operating at 600.3, 564.7 and 150.9 MHz respectively; tetramethylsilane (Me₄Si, $\delta_{\rm H}$ 0.00 ppm) and hexafluorobenzene (C₆F₆, $\delta_{\rm F}$ –162.9 ppm) were applied as an internal standard.

4.6. IR spectroscopy

IR spectra of alkali metal trifluoroacetates were registered within the wavenumber range of 500–4000 cm⁻¹ (resolution of 2 cm⁻¹) using FTIR IRAffinity-1 spectrometer (Shimadzu, Japan) and MIRacle ATR (Pike Technologies) equipped with a diamond/ZnSe crystal plate.

4.7. Quantum chemical calculations

DFT calculations of the relative energies of $C_{60}(CF_3)H$ isomers and $C_{60}(CF_3)^-$ anion were performed with the use of PRIRODA package [58]. The PBE exchange-correlation functional [59] and the built-in TZ2P-quality basis set were used.

4.8. Alkali metal trifluoroacetates preparation

Anhydrous trifluoroacetic acid (1.7 mL, 22 mmol, 10% excess) was added to water solution (50 mL) of alkali metal carbonate (10 mmol of Li₂CO₃, Na₂CO₃, K₂CO₃, or Cs₂CO₃) at room temperature and stirred for 30 min. Then the solvent was removed using rotary evaporator at 60° at 40 mbar. Obtained solid samples were further freeze-dried at room temperature and 0.2 mbar (Christ Alpha 1-2 LD plus freeze dryer) for 12 hours. White-colored products were obtained with quantitative yields and identified as respective alkaline-metal trifluoroacetates using IR data in good accordance with early reported data [28–30].

4.9. Syntheses of $C_{60}(CF_3)H$

Finely grounded sample of C_{60} fullerene (40 mg, 0.056 mmol) was dissolved in *ortho*dichlorobenzene/benzonitrile mixture (8:2 v/v, 20 mL) and placed into the three-neck flask mounted into magnetic stirrer equipped with a heater. Then 20 µl phase transfer catalyst (either

18-crown-6, 15-crown-5 or 12-crown-4) and ca 15-fold molar excess of CF₃COOM (0.84 mmol) were added and the mixture sparged with Ar for 15 minutes while stirring before heating up. Within 2 minutes upon reaching the boiling point, the reaction mixture containing K or Cs salts turned black (dark green at dilution). After reaching the boiling point the mixture was refluxed for 6 min for K and Cs, 20 min for Na, 1 hour for Li and then allowed to cool down to the room temperature and quenched with 0.5 mL of CF₃COOH. The obtained product was filtered through a silica gel column to remove inorganic residue and subjected further purification. The brown product was isolated by HPLC with 30% isolated yield (ca 50% HPLC yield) for the synthesis with CF₃COOCs.

4.10. Preparation of $p^7mp-C_{70}(CF_3)_{10}$

Trifluoromethylated fullerene p^7mp -C₇₀(CF₃)₁₀ was synthesized from C₇₀ and CF₃I using two-stage ampoule approach according to work [60]. Individual p^7mp -C₇₀(CF₃)₁₀ (99+%) was isolated by means of HPLC separation (Cosmosil Buckyprep, 10 mm I.D. × 25 cm, toluene as an eluent), MALDI MS, NMR, and UV/Vis data of obtained sample were found to be in good accordance with literature data [60].

4.10. Hydrotrifluoromethylation of C_{70} and $p^7mp-C_{70}(CF_3)_{10}$

Fine grounded sample of the fullerene substrate (20 mg, 0.023 mmol for C₇₀, 6 mg, 0.004 mmol for C₇₀(CF₃)₁₀) was dissolved in *ortho*-dichlorobenzene/benzonitrile mixture (8:2 v/v, 20 mL for C₇₀, 6 ml for C₇₀(CF₃)₁₀) and placed into the three-neck flask mounted into magnetic stirrer equipped with heater. Then 20 μ l of 18-crown-6 and ca 15-fold molar excess of CF₃COOCs (85 mg, 0.345 mmol for C₇₀, 15 mg, 0.06 mmol for C₇₀(CF₃)₁₀) were added and the mixture sparged with Ar for 15 minutes while stirring before heating up. Within 2 minutes upon reaching the boiling point, the reaction mixture turned dark green. After reaching the boiling point, the room temperature and quenched with 0.5 mL of CF₃COOH. The obtained mixture was filtered through a silica gel column to remove inorganic residue and subjected to LC-APPI-MS analysis.

4.11. Compound data

Lithium trifluoroacetate: a white solid, 1.6 g, 67% yield. IR (ATR, v/cm⁻¹) 1663, 1472, 1198, 1141, 859, 802, 729.

Sodium trifluoroacetate: a white solid, 1.8 g, 66% yield. IR (ATR, *v*/cm⁻¹): 1717, 1669, 1448, 1182, 1140, 840, 801, 725.

Potassium trifluoroacetate: a white solid, 2.2 g, 72% yield. IR (ATR, *v*/cm⁻¹): 1709, 1653, 1436, 1172, 1133, 837, 805, 722.

Cesium trifluoroacetate: a white solid, 4.2 g, 84% yield. IR (ATR, *v*/cm⁻¹): 1689, 1665, 1425, 1417, 1199, 1158, 1108, 828, 799, 719.

1-trifluoromethyl-1,9-dihydro[C₆₀-*I*_h]fullerene: a brown solid, 30% isolated yield (52 % HPLC yield, 92% HPLC yield based on converted C₆₀). HPLC (*Cosmosil Buckyprep* 4.6 mm ID × 25 cm, toluene, 1 ml/min) $t_{\rm R}$ 7.0 min. UV/vis (toluene, $\lambda_{\rm max}$ / nm): 326, 432, 694. HRMS (APPI, positive ion mode), m/z calculated for [C₆₁F₃H]⁺: 790.0025, found: 790.0029. ¹H NMR (600.3 MHz, CDCl₃, 25°C, TMS): 6.88 (1H, *s*, HC_{cage}). ¹⁹F NMR (564.7 MHz, CDCl₃, 25°C, C₆F₆, $\delta_{\rm F}$ = -162.90): -72.32 (3F, *s*, F₃C). ¹³C NMR (150.9 MHz, CDCl₃, 25°C, TMS): 54.66 (*q*, ³*J*_{CF} = 2.2 Hz, HC_{cage}), 67.73 (*q*, ²*J*_{CF} = 28.7 Hz, F₃CC_{cage}), 127.82 (*q*, ¹*J*_{CF} = 280.6 Hz, F₃C), {135.77, 137.94, 139.96, 140.78, 141.10, 141.85, 142.22, 142.25, 142.31, 142.76, 142.86, 143.25, 144.35, 144.78, 145.25, 145.45, 145.73, 146.23, 146.33, 146.42, 146.51, 146.63, 146.75, 147.02, 150.79} (total 25 signals, *sp*²-C_{cage}).

 $C_{70}(CF_3)H$ (isomer I, 7,22-adduct): (*Cosmosil Buckyprep* 4.6 mm ID× 25 cm, toluene, 1 ml/min) t_R 10.8 min. UV/vis (toluene, λ_{max} / nm): 363, 400, 443, 690. APPI MS (positive ion mode), m/z (rel. int.): 840 (8) [M-CF₃H]⁺, 910 (100) [M]⁺, 911 (98) [M+H]⁺, [M]⁺ (second isotopomer).

C₇₀(CF₃)H (isomer II), 25-trifluoromethyl-8,25-dihydro[C₇₀- D_{5h}]fullerene: (*Cosmosil Buckyprep* 4.6 mm ID × 25 cm, toluene, 1 ml/min) $t_{\rm R}$ 11.9 min. UV/vis (toluene, $\lambda_{\rm max}$ / nm): 340, 395, 465, 670. APPI MS (positive ion mode), m/z (rel. int.): 840 (8) [M-CF₃H]⁺, 910 (90) [M]⁺, 911 (100) [M+H]⁺, [M]⁺ (second isotopomer).

 $C_{70}(CF_3)_{11}H$ (I) (*Cosmosil Buckyprep* 4.6 mm ID× 25 cm, toluene/hexane 8:2 v/v, 1 ml/min) t_R 3.2 min. UV/vis (toluene, λ_{max} / nm): 480 (absorption edge). APPI MS (positive ion mode), m/z (rel. int.): 1530 (12) [M-CF₃H]⁺, 1600 (100) [M]⁺.

 $C_{70}(CF_3)_{11}H$ (II) (*Cosmosil Buckyprep* 4.6 mm ID× 25 cm, toluene/hexane 8:2 v/v, 1 ml/min) t_R 3.5 min. UV/vis (toluene, λ_{max} / nm): 395, 480, 500. APPI MS (positive ion mode), m/z (rel. int.): 1530 (8) [M-CF_3H]^+, 1600 (100) [M]^+.

C₇₀(CF₃)₁₁H (III) (*Cosmosil Buckyprep* 4.6 mm ID× 25 cm, toluene/hexane 8:2 v/v, 1 ml/min) t_R 3.8 min. UV/vis (toluene, λ_{max} / nm): 380, 500. APPI MS (positive ion mode), m/z (rel. int.): 1530 (4) [M-CF₃H]⁺, 1600 (100) [M]⁺.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:

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Figure captions



Figure 1. Side view of ortho- $C_{60}(CF_3)H$



Figure 2. UV/Vis/NIR spectra of C_{60} (a), reaction mixture before (b) and after (c) acidic workup. ¹³C NMR spectrum (d) of $C_{60}(CF_3)H$ (the residual toluene signals are marked with asterisks, ¹H and ¹⁹F spectra are shown in the left and right insets, respectively).



Figure 3. (a) HPLC traces (290 nm) of the CF_3COOM/C_{60} reaction products (M=Li–Cs) after the acidic workup. (b) The proposed reaction scheme.



Figure 4. (a) LC-APPI-MS (positive mode) traces of the CF₃COOCs/C₇₀ reaction mixture, (toluene, 1 ml/min; BPC (base peak chromatogram) and selected ion monitoring traces) (b) LC-APPI-MS traces of the CF₃COOCs/C₇₀(CF₃)₁₀ reaction mixture (toluene/hexane 8:2 v/v, 1 ml/min)

Table

Exp. No.	C60, mg	Solvent (v/v)	Atmosphere ^[b]	Time / min	C60(CF3)H yield ^[c] / %			
1	20	oDCB	inert	20	18 (26)			
2	5	PhCN	inert	20	45 (88)			
3	20	oDCB:PhCN (8:2)	inert	20	30 (34)			
4	40	oDCB:PhCN (8:2)	inert	20	36 (39)			
5	40	oDCB:PhCN (8:2)	inert	30	21 (23)			
6	40	oDCB:PhCN (8:2)	inert	15	47 (56)			
7	40	oDCB:PhCN (8:2)	air	15	10 (11)			
8	40	oDCB:PhCN (8:2)	inert	10	50 (72)			
9	40	oDCB:PhCN (8:2)	inert	6	52 (92)			
10	40	oDCB:PhCN (8:2)	inert	4	32 (93)			
11	40	oDCB:PhCN (8:2)	inert	2	10 (95)			
[a] Solvent volume 20 mL, CF ₃ COOCs/C ₆₀ molar ratio of 15:1.[b] Argon was used								

Table 1. Trifluoromethylation of fullerene C₆₀ with CF₃COOCs. ^[a]

[a] Solvent volume 20 mL, CF₃COOCs/C₆₀ molar ratio of 15:1.[b] Argon was used for inert atmosphere. [c] The yields are according to the HPLC analysis (see ESI for details), the values in parentheses are based on the rate of conversion of C_{60} .

Salt	T _{dec} ^[b] ∕ °C	t / min	РТС	C60 conversion / - %	Yield / %	
					C60(CF3)H	C60(CF2)
CF ₃ COOLi	250	60	18CR6	12	<0.5	3
			12CR4	7	<0.1	0.5
CF ₃ COONa	210	20	18CR6	22	16	4
			15CR5	19	11	8
CF ₃ COOK	150	6	18CR6	60	35	<0.3
CF ₃ COOCs	154	6	18CR6	56	52	<0.3

Table 2. Reaction of C_{60} with alkali metal trifluoroacetates in the presence of a phase-transfer catalyst.^[a]

[a] Reaction conditions: 40 mg C₆₀, 15-fold molar excess of CF₃COOM and 20 μ l of phase transfer catalyst [PTC: 18-crown-6 (18CR6), 15-crown-5 (15CR5), or 12-crown-4 (12CR4)] were dissolved in 20 mL of mixture *o*DCB:PhCN (8:2 v/v) and refluxed (ca 180 °C) under Ar. Products were identified using HPLC, UV-Vis, and LC-MS data; C₆₀ conversion rate and product yield were estimated from the HPLC data (see ESI for details). [b] Onset of decomposition in the solid state according to the TGA data [31].