Asymmetric Fluoro-alkynyl Mercurials: The Synthesis and Solid State Structures of $RHgC{\equiv}CCF_3$ (R = Ph, Fc)

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Summary: The fluoro-alkynyl mercurials $RHgC{\equiv}CCF_3$ *(R = Ph, Fc) have been prepared, from the respective organomercurihalides and* $LiC{\equiv}CCF_3$*, and are the first examples of such materials to be studied crystallographically. These studies have revealed the presence of appreciable mercury-centered intermolecular interactions in the extended structures, including an apparent mercurophilic interaction.*

Introduction

Despite their inherent toxicity, organomercurials are among the most widely studied of organometallic compounds, in part because of their synthetic utility as convenient and efficient organo-transfer reagents, and more recently for their potential to exhibit closed-shell "mercurophilic" interactions in the solid state.[1] The latter is also one of several factors contributing to the recent proliferation of research into heavily fluorinated organomercury compounds,[2] which seeks to exploit the synergy between the inherently Lewis-acidic mercury(II) center and the potently σ-withdrawing perfluorocarbon moiety. There remains, however, a dearth of compounds containing small, unsaturated organofluorine fragments bound to mercury. Most significantly, there is currently just a single example of a fluorinated alkynyl-mercurial: $Hg(C{\equiv}CCF_3)_2$. Indeed, alkynyl-mercurials per se have been little explored;[3] the structures of only 20 such materials are recorded by Cambridge Crystallographic Data Center (CCDC), none of which are fluorinated.

In view of this clear deficiency, and the recent renaissance in trifluoropropynyl ($C{\equiv}CCF_3$) chemistry,[4] in which we are involved,[5] we have sought to obtain and structurally characterize for the first time a series of trifluoropropynyl-mercurials. We report herein the synthesis and structural investigation of the asymmetric mercury(II) trifluoropropynyl compounds $PhHgC{\equiv}CCF_3$ and $FcHgC{\equiv}CCF_3$.

Results and Discussion

We sought to synthesize a "family" of mercurials by the reactions of the organomercurihalides RHgCl (R = Me, *n*-Bu, *t*-Bu, Ph, $(C_5H_5)Fe(C_5H_4-)$ [Fc]) with an excess of trifluoropropynyllithium ($LiC{\equiv}CCF_3$), generated in situ as we have previously described.[5] This met with limited success; the alkyl derivatives were formed, as evident from ^{19}F NMR studies,[6] but in admixture with intractable byproducts, and it proved impossible to effect complete separation due to their appreciable thermal and photolytic sensitivity. In contrast, the compounds $PhHgC{\equiv}CCF_3$ (**1**) and $FcHgC{\equiv}CCF_3$ (**2**) were each obtained as crystalline solids in high yield and purity, as determined from spectroscopic (^{19}F, ^{1}H, ^{13}C NMR) and microanalytical data.

The properties of compounds **1** and **2** allowed for the isolation of X-ray quality single crystals, thus enabling a structural study to be undertaken. Compounds **1** and **2** represent the first examples of trifluoropropynyl derivatives of mercury to be crystallographically characterized; indeed, only four structural studies of trifluoropropynyl compounds have previously been reported, viz., $Ph_3EC{\equiv}CCF_3$ (E = C, Si, Ge)[5b] and $In(C{\equiv}CCF_3)_3(THF)_2$.[7] In common with these systems, compounds **1** and **2** exhibit largely typical internal geometries (Figures 1 and 2), with the C≡C, C−CF$_3$, and C−F linkages each lying within 2σ of the mean values for Csp≡Csp [1.183 Å], Csp−*C*sp^3 [1.466 Å], and Csp^3−F [1.322 Å],[8] respectively. The ancillary R groups (Ph, Fc) are also largely unremarkable.

Potentially greater interest resides with the extended structures of these compounds, and their apparent influence upon the geometry about mercury. Both **1** and

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[6] In each case the mercury-bound $C{\equiv}CCF_3$ group is apparent from a singlet resonance in the ^{19}F NMR spectrum, in the characteristic alkynyl CF$_3$ region (ca −50 ppm), exhibiting mercury-satellite coupling (^{199}Hg, $I = 1/2$, 16.8%, 15−30 Hz). This is supported by three quartet-based resonances in the $^{13}C\{^1H\}$ NMR spectrum, in the region 145−88 ppm.

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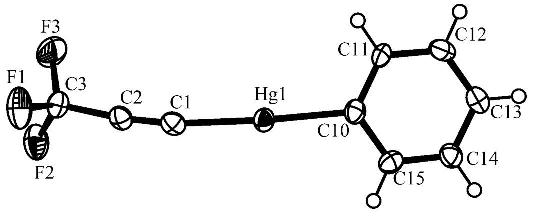

Figure 1. Representation of the molecular structure of PhHgC≡CCF$_3$ (**1**) (30% thermal ellipsoids). Selected bond distance (Å) and angles (deg): Hg1−C1 2.029(9), Hg1−C10 2.052(9), C1−C2 1.192(13), C2−C3 1.465(13), C3−F1 1.327(11), C3−F2 1.344(12), C3−F3 1.336(11), Hg1−C1−C2 170.2(7), C10−Hg1−C1 175.3(3), C1−C2−C3 174.2(9), C2−C3−F1 114.7(7), C2−C3−F2 111.5(8), C2−C3−F3 112.2(8).

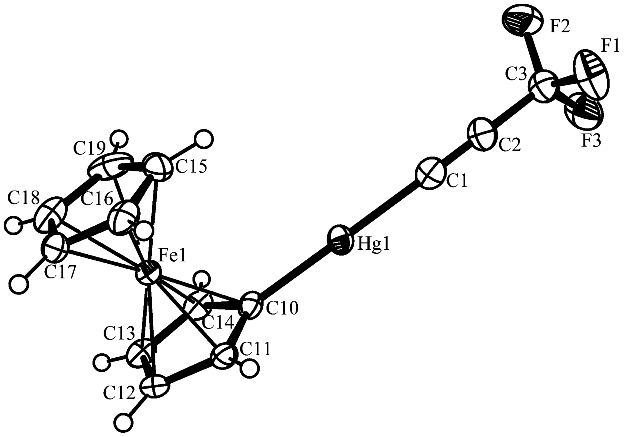

Figure 2. Representation of the molecular structure of FcHgC≡CCF$_3$ (**2**) (30% thermal ellipsoids). Selected bond distances (Å) and angles (deg): Hg1−C1 2.050(6), Hg1−C10 2.039(6), C1−C2 1.183(9), C2−C3 1.450(9), C3−F1 1.335(8), C3−F2 1.344(8), C3−F3 1.341(8), Hg1−C1−C2 178.1(6), C10−Hg−C1 179.4(2), C1−C2−C3 175.9(7), C2−C3−F1 112.9(6), C2−C3−F2 112.5(6), C2−C3−F3 112.7(5).

2 exhibit appreciable deviation from linearity of the alkynyl function [∠C≡C−C 174.2(9)° **1**; 175.9(7)° **2**], with **1** also exhibiting a significantly "bent" geometry about the Hg(II) center [∠C−Hg−C 175.3(3)°, ∠Hg−C≡C 170.2(7)°]. This latter effect is also present in **2** but is somewhat less pronounced [179.4(2)° and 178.1(6)°, respectively]. Although there is only a limited range of structurally characterized alkynyl-mercurials, such distortions are common among them, particularly in the cases of Hg(C≡CPh)$_2$ [∠(Hg−C≡C) 170.4(17)°; ∠(C≡C−C$_{Ph}$) 174(2)°][9] and PhHgC≡CPh [∠Hg−C≡C 171.9(15)°; ∠(C−Hg−C) 176.6(7)°],[10] the closest available analogue of **1**, although other examples have been recorded.[11]

The origin of these effects has, however, been little discussed, although it is believed to arise from intermolecular π(C≡C)→Hg interactions, which result in distortion of the coordination geometry at mercury, with concomitant reduction of the C≡C bond order. The significance of this argument has on occasion been questioned,[12] and it should be noted that while both **1** and **2** exhibit nonlinear geometry, in neither case is there significant supporting evidence for a reduction of the C≡C bond order, i.e., from a comparison of vibrational data for the C≡C stretching mode in solution (ν_{max} 2185 cm^{-1}) and the solid state (ν_{max} 2181 cm^{-1}).

Notwithstanding, a secondary Hg−η^2-C$_2$ interaction is clearly apparent in the extended structure of **2** [*d*(Hg···C1) 3.359(6) Å; *d*(Hg···C2) 3.487(6) Å], the Hg···C distances being below the classically accepted sum of the van der Waals radii [3.4−3.7 Å][13] and being comparable to literature precedent.[2d] The analogous interaction in compound **1** is weaker and asymmetric in nature, being localized to C2 [*d*(Hg···C2) 3.582(9), *d*(Hg···C1) 3.910(8) Å] with the Hg···C1 distance apparently exceeding the sum of van der Waals radii. However, several recent reports have advocated latitude in the interpretation of the mercury radius,[13a,14] with values of up to 2.2 Å being proposed.[15] Using such a value both of the Hg···C distances of **1** are indicative of interactions, albeit that Hg···C1 is very weak in nature.

Both **1** and **2** exhibit further secondary interactions that are within the sum of the van der Waals radii, such that the effective coordination number at each mercury center is six. Thus, the noted Hg−η^2-C$_2$ interactions are each augmented by a *trans* π(C=C)→Hg interaction with a cyclopentadiene [**2** *d*(Hg···C10) 3.531(6), *d*(Hg···C14) 3.363(6) Å] or phenyl [**1** C12, C13, C14; *d*(Hg···C) 3.376(9)−3.517(9) Å] ring of an adjacent molecule. The significance of these interactions may be contextualized by comparison with the shortest examples relevant to each case [3.20−3.24 Å for Hg···C$_{cp}$;[16] 3.24−3.36 for Hg···C$_{arene}$[17]]; those in excess of 3.4 Å must thus be deemed weak. It is noteworthy that complex **1** also exhibits a strong secondary Hg···F interaction [*d*(Hg···F1) 3.199(7) Å].

The structure of **2** also exhibits evidence of mercurophilic interactions that are strongly implicated in the arrangement of the molecules through the crystal. When viewed along the *c* direction, adjacent molecules align in a criss-cross fashion in such a way as to form a linear arrangement of successive Hg···Hg interactions [*d*(Hg···Hg) 4.0882(3) Å], as shown in Figure 3. The significance of these interactions is, however, dependent upon the chosen value of the mercury radius (vide supra). Thus, if a classical value of 1.73−2.00 Å[13b] is applied, then the distance is more than twice the van der Waals radius and therefore may be deemed largely superficial. However, adopting a value in excess of 2.00 Å would render the interaction much more significant. Indeed, interactions at similar distances have previously been

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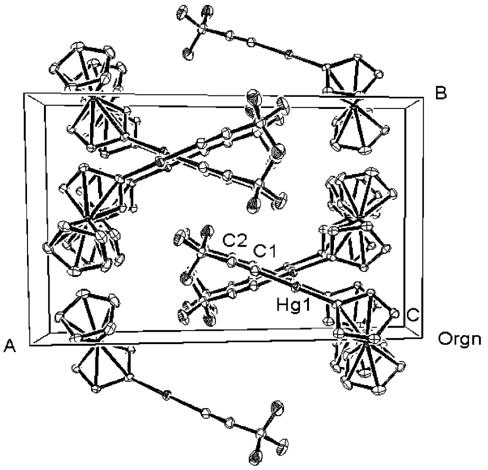

Figure 3. View of the packing of FcHgC≡CCF_3 (**2**) along the *c* axis. Thermal ellipsoids are set at the 30% probability level, and hydrogen atoms are omitted for clarity.

ascribed to mercurophilicity; for example, a distance of 4.077 Å is calculated for the Hg···Hg separation in the extended structure of HgH_2,[18] while distances of 3.811–4.093 Å are reported for trimeric perfluoro *ortho*-phenylene mercury.[3d] It is an assumed fact that interactions close to, or in excess of, 4 Å are weak—cf. the shortest reported example of 3.1463(6) Å in Hg-$(SiMe_3)_2$[19]—however, given the literature precedent, and the apparent significance to the crystal packing adopted by **2**, these interactions would, in this case, seem appropriately classified as a manifestation of mercurophilicity.

Conclusion

The first attempt to prepare asymmetric mercurials of the type RHgC≡CCF_3 has revealed that, as with many alkynyl mercurials, where R = alkyl instability precludes effective isolation. Where R = Ph or Fc, the compounds are stable and have been isolated and fully characterized. These compounds are amenable to crystallographic characterization, thus allowing the first structural study of any RHgC≡CCF_3 compounds: a significant development given the dearth of structurally characterized alkynyl-mercurials. This has revealed largely typical intramolecular geometries, though with appreciable distortion of the alkynyl unit and mercury(II) center from linearity, attributed to intermolecular Hg–η^2-C_2 association. A network of intermolecular Hg···C and Hg···F interactions is elucidated, including, for the ferrocenyl compound **2**, an apparent mercurophilic interaction. Taken together these observations offer further experimental support for the current debate as to the most appropriate van der Waals radius of mercury, for which a value of at least 2.00 Å has been suggested.

Experimental Section

General Methods. *CAUTION! Organomercurials are highly toxic and prone to disproportionation; fluorinated derivatives are potentially volatile—extreme care is necessary when handling such materials and their solutions.* Reactions were performed in well-ventilated fume hoods, using standard inert atmosphere techniques. Diethyl ether was dried over sodium wire for ca. 1 day prior to use. The compounds RHgCl (R = Me, *n*-Bu, *t*-Bu) were prepared by metathesis between $HgCl_2$ and RLi (MeLi, 1.6 M in ether; *n*-BuLi, 2.5 M in hexane; *t*-BuLi, 1.7 M in pentane (Across)); $CF_3CH_2CF_2H$ (HFC-245fa, Honeywell), FcHgCl and PhHgCl (Aldrich) were used as supplied. NMR spectra ($CDCl_3$) were recorded on Bruker DPX200 (^{19}F, 188.310 MHz with respect to $CFCl_3$) or DPX400 (^{13}C, Dept-135, 100.555 MHz; ^{1}H 400.4 MHz, with respect to $SiMe_4$) spectrometers. Infrared ($CHCl_3$, KBr plates) and Raman spectra were recorded on a Nicolet Nexus FTIR/Raman spectrometer. Elemental analyses were performed by the UMIST microanalytical service.

General Synthetic Procedure. With the exclusion of light, under N_2, a stirred ethereal solution (100 cm^3) of HFC-245fa (0.45 cm^3, 4.43 mmol) was treated with *n*-BuLi (4.80 cm^3, 12.00 mmol), at −10 °C, then after 20 min. RHgCl (3.20 mmol) in ether (20 cm^3) was added. After stirring overnight at 0 °C the reaction was allowed to attain ambient temperature, then hexane (200 cm^3) added to precipitate the inorganic salts; the settled mixture was filtered through Celite and the solvent removed in vacuo. For R = Me, Bu see Supporting Information.

PhHgC≡CCF_3 (1). From HFC-245fa (0.30 cm^3, 2.96 mmol), *n*-BuLi (3.25 cm^3, 8.13 mmol), PhHgCl (0.640 g, 2.04 mmol). Yield: 0.634 g, 84%. Anal. Calcd for $C_9H_5F_3Hg$: C, 29.2; H, 1.4; F, 15.4. Found: C, 31.0; H, 1.2; F, 15.6. δ_F −50.1 ($^4J_{HgF}$ 26.0 Hz). δ_C 132.8 [q, 7.3, $^1J_{HgC}$ 1458.3, *C*≡CCF_3], 111.6 [q, 257.2, $^3J_{HgC}$ 37.1 *C*F_3], 90.2 [q, 50.1, $^2J_{HgC}$ 405.5 C≡*C*CF_3], 155.3 [s, C, J_{HgC} 1828.9 Hz], 136.4 [s, CH, J_{HgC} 94.5 Hz], 128.5 [s, CH, J_{HgC} 24.7 Hz]. δ_H 7.6–7.2 (m). ν_{max}/cm^{-1} 2185 (C≡C str), 1247, 1139 (C–F str).

FcHgC≡CCF_3 (2). From HFC-245fa (0.50 cm^3, 4.82 mmol), *n*-BuLi (5.70 cm^3, 14.25 mmol), FcHgCl (1.000 g, 2.37 mmol). Yield: 0.995 g, 88%. Anal. Calcd for $C_{13}H_9F_3FeHg$: C, 32.6; H, 1.9; F, 11.9. Found: C, 32.8; H, 1.9; F, 11.6. δ_F −50.1 ($^4J_{HgF}$ 27.1 Hz). δ_C 136.1 [q, 6.8, *C*≡CCF_3], 111.7 [q, 257.0, *C*F_3], 90.1 [q, 50.2, C≡*C*CF_3], 83.7 [q, C, J_{CF} 1.0 Hz], 74.6 [s, CH, J_{HgC} 163.2 Hz], 71.2 [s, CH, J_{HgC} 137.1 Hz], 68.4 [s, CH]. δ_H 4.4 (br m, J_{HgH} 20.8 Hz, 2H), 4.3 (br m, J_{HgH} 21.1 Hz, 5H), 4.1 (br m, J_{HgH} 39.7 Hz, 2H). ν_{max}/cm^{-1} 2185 (C≡C str), 1247, 1141 (C–F str).

X-ray Crystallography. Data were recorded on a Nonius κ-CCD four-circle diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 120(2) K, solved using direct methods, and subject to full-matrix least-squares refinement on F^2 using SHELX-97.[20] Absorption correction was by the multiscan method. Non-hydrogen atoms were refined with anisotropic thermal parameters, while hydrogen atoms were included in idealized positions and refined isotropically. Geometric analyses were performed using Platon,[21] and figures generated with ORTEP 3 for Windows.[22] Data for **1**: $C_9H_5F_3Hg$, $M = 370.72$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 5.8459(1)$ Å, $b = 8.4130(2)$ Å, $c = 18.2492(5)$ Å, $V = 897.52(4)$ Å^3, $z = 4$, $D_c = 2.744$ g cm^{-3}, $\mu = 17.141$ mm^{-1}, $\theta = 3.66–27.46°$, 2045 unique reflections, 119 parameters, $R = 0.0443$, wR_2 0.1096. Data for **2**: $C_{13}H_9F_3FeHg$, $M = 478.64$, monoclinic, $P2_1/c$ (no. 14), $a = 16.0728(6)$ Å, $b = 9.7449(3)$ Å, $c = 8.1183(3)$ Å, $\beta = 100.8620(10)°$, $V = 1248.77(8)$ Å^3, $z = 4$, $D_c = 2.546$ g cm^{-3}, $\mu = 13.453$ mm^{-1}, $\theta = 3.30–27.39°$, 2840 unique reflections, 164 parameters, $R = 0.0366$, wR_2 0.0924.

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Supporting Information Available: For the single-crystal structure determinations, tables of crystal data and structure refinement, atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and an X-ray crystallographic file, in CIF format. Synthetic procedures and spectroscopic data for $RHgC{\equiv}CCF_3$ (R = Me, *t*-Bu, *n*-Bu). This material is available free of charge via the Internet at http://pubs.acs.org.

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