Preparation and Functionalization of a Range of Main-Group Trifluoropropynyl Organometallic Compounds: The Application of Metalloid-Directed Carbolithiation to the Selective Synthesis of Novel Fluorocarbon Fragments

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The reaction of 1,1,1,3,3-pentafluoropropane ($CF_3CH_2CF_2H$, HFC-245fa) with 3 equiv of *n*-butyllithium at −10 °C leads to the generation of trifluoropropynyllithium in excellent yields. This reagent reacts readily with a range of group 14 electrophiles $R_{4-n}EX_n$ (R = Ph, Et; E = C, Si, Ge, Sn, Pb; X = Cl, Br) to yield the organometalloid trifluoropropynyl compounds $R_{4-n}E(C{\equiv}CCF_3)_n$. Three of these compounds, $Ph_3EC{\equiv}CCF_3$ (E = C, Si, Ge), have been crystallographically characterized, representing the first such study of these materials. The silane $Ph_3SiC{\equiv}CCF_3$ has been derivatized by reaction with $LiAlH_4$ and a range of organolithium reagents (RLi, R = *n*-Bu, Ph, *t*-Bu) to afford a new series of β-CF_3-substituted vinylsilanes of the type $Ph_3SiCH{=}C(CF_3)R$, with predominantly *E* geometry at the double bond. In the cases R = *n*-Bu, *t*-Bu, and Ph, these materials have been crystallographically characterized. Additionally, a remarkably facile cyclization pathway for $Ph_3SiC{\equiv}CCF_3$, initiated by *t*-BuLi, that yields the respective *gem*-difluorocyclopropene has been explored and is described in detail, along with its extension to a number of other systems.

Introduction

The importance of fluorinated compounds is becoming paramount, particularly with regard to their pharmaceutical, agrochemical, and materials applications.[1,2] Consequently, the identification of new synthetic routes to such materials and subsequent exploration of their reactivity continue to be areas of intense research. In particular, the growing need for methods of selectively introducing small, fluorinated functions is an area of great current interest,[3] which has led to a strong impetus for the development and study of organometallic systems, given the extensive applications of their hydrocarbon counterparts.

We have been exploring organometallic trifluorovinyl compounds, derived from readily available hydrofluorocarbon precursors,[4] to this end. More recently, we have reported for the first time that trifluoropropynyl compounds ($-C{\equiv}CCF_3$) can be similarly obtained, via the respective lithium reagent, generated under mild conditions from the commercially available hydrofluorocarbon 245fa (1,1,1,3,3-pentafluoropropane, CF_3CH_2-CF_2H).[5] This constitutes the most convenient synthetic route yet developed for these materials, previous work having utilized gaseous reagents and much lower temperatures.[6−9] Indeed, these materials are now more readily available than ever before, potentially even on an industrial scale.

Despite the unique biological and physical properties imparted by the CF_3 group, and the obvious versatility of alkynes as building blocks for more functional molecules, trifluoropropynyl compounds have received relatively little study to date. Where these materials have been explored, work has been largely restricted to organic derivatives,[10] despite the existence of a significant, though small, range of organometallic systems. In particular, it is noted that while a number of silicon and

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germanium derivatives have been prepared previously ($R_nE(C{\equiv}CCF_3)_{4-n}$, R = H/D, n = 3; R = Me, n = 1−3; R = Et, n = 3),[6,11] their obvious potential as precursors to more functional organo-transfer reagents seems overlooked, few reports having described conversion of the trifluoropropynyl unit to more elaborate functionalities.[11a,d,12]

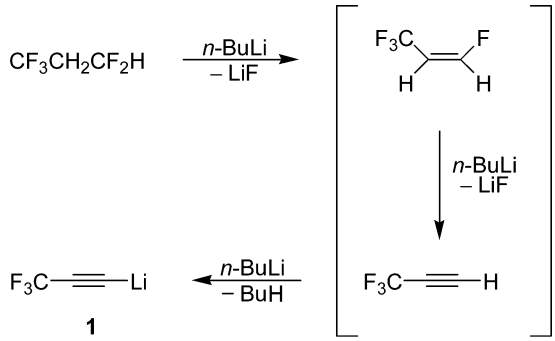
With this in mind, we have undertaken to prepare and investigate a range of novel group 14 trifluoropropynyl organometalloids, with a view to developing functional building blocks. Herein, we detail the synthesis of the parent trifluoropropynyls, and report for the first time the structural facets of these materials. We also describe subsequent investigation of the potential for selective reduction and carbolithiation at the triple bond, as a means of generating β-CF_3-substituted alkenic systems. Moreover, we expand upon our recently communicated discovery of a remarkable cyclization pathway for these materials.[13]

Results and Discussion

Generation of Trifluoropropynyllithium from HFC-245fa. The addition of 3 equiv of *n*-butyllithium to an ethereal solution of HFC-245fa (1,1,1,3,3-pentafluoropropane, $CF_3CH_2CF_2H$) at −10 °C results in formation of the trifluoropropynyllithium reagent $CF_3C{\equiv}C^-Li^+$ (**1**) in high yields. We have found **1** to be stable under these conditions for extended periods of up to 24 h, after which time slow decomposition to lithium fluoride and intractable organic material becomes significant. The stability is only marginally affected on raising the temperature to 0 °C; however above this temperature the onset of decomposition is visibly more rapid, darkening of the initially deep-orange solution to black occurring within minutes. Nonetheless, decomposition has, thus far, proven to be a nonviolent process, though exothermic.

The generation of **1** is presumed to occur via the process outlined in Scheme 1. Thus, in the presence of *n*-BuLi, HFC-245fa is deprotonated, with subsequent elimination of lithium fluoride, to afford 1,3,3,3-tetrafluoropropene, which undergoes a second deprotonation−elimination step to generate 3,3,3-trifluoropropyne in situ. Subsequent deprotonation to afford **1** is, as might be anticipated, rapid, this being apparent from the near quantitative generation of **1** from HFC-245fa, despite the volatility of 3,3,3-trifluoropropyne (bp −48 °C). Indeed, the rate-determining step would seem to be initial deprotonation of the HFC, with successive steps being considerably more facile, and this is supported by several investigations. Notably, when the HFC and *n*-BuLi are present in equimolar amounts, subsequent addition of an electrophile traps only the trifluoropropynyl moiety, with no evidence of the alkenyl

Scheme 1. Formation of Trifluoropropynyllithium from HFC-245fa and *n*-BuLi[a]



[a] Conditions: diethyl ether, −10 °C.

intermediate. Attempts to intercept the intermediate, by generating it in the presence of an electrophile, were unsuccessful, the noncoordinating bases necessary for this experiment proving ineffective in initiating the reaction.

Additional information was obtained by quenching the HFC/*n*-BuLi mixture with D_2O at progressive stages of mixing, which revealed in every case the presence of a predominant concentration of **1**, as determined by the characteristic position of the alkynic CF_3 resonance in the ^{19}F NMR spectrum. An appreciable amount of unreacted HFC-245fa (δ_F −64.3 (m), −116.8 (m)) was also consistently observed.

Synthesis and Characterization of Trifluoropropynyl Compounds. Under the conditions outlined, **1** reacts readily with a range of electrophilic centers to afford the respective trifluoropropynyl compounds, typically in good to excellent yields. In our initial communication, we reported that upon the addition of the electrophile, the mixture should be allowed to warm to ambient temperature over approximately 12 h. However, we have since discovered that if the mixture is held at or below 0 °C over that period, thus extending the lifetime of **1**, yields can be increased by up to 20%. In this way, the organic trifluoropropynyl **2**, group 14 organometalloids **3**−**6**, and organometallic analogues **7**−**9** (Table 1) have now been prepared and isolated as air- and moisture-stable solids or liquids. Compounds **2**, **3**, and **7** can be prepared in analytically pure form, while purification of all materials is conveniently effected by chromatography on silica, eluting with 1:1 dichloromethane/hexane, or by distillation.

In each case, the presence of the trifluoropropynyl moiety is supported by the observation of a singlet resonance in the ^{19}F NMR spectrum in the region of −50 ppm (with respect to $CFCl_3$), characteristic of an alkynic CF_3 function. With the exception of compounds **2** and **6**, this resonance displays satellites due to coupling to the low-abundance, spin-active group 14 centers (**3**−**5** ^{29}Si, $I = {}^1/_2$, 4.67%; **7**,**8** ^{119}Sn, $I = {}^1/_2$, 8.59%; **9** ^{207}Pb, $I = {}^1/_2$, 22.1%), the small magnitudes of these coupling constants being consistent with considerable separation of the metalloid and fluorine nuclei. Additional confirmation of the trifluoropropynyl unit is obtained by ^{13}C NMR spectroscopy, the CF_3 group being clearly resolved as a quartet resonance in the region 120−110 ppm (J_{CF} 250−280 Hz). Two further quartet resonances are observed in the range 100−70 ppm, corresponding to

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Table 1. Selected Spectroscopic Data for Group 14 Trifluoropropynyl Compounds

	δ_F (J_{EF}/Hz)	δ_C (J_{CF}/Hz)	$\nu_{C\equiv C}$/cm^{-1}
$Ph_3CC\equiv CCF_3$ (**2**)	−50.0	114.8 (q, 256.9, CF_3), 93.9 (q, 6.7, $C\equiv CCF_3$), 72.6 (q, 52.2, $C\equiv CCF_3$)	2256
$Ph_3SiC\equiv CCF_3$ (**3**)	−50.4 (3.0)	113.3 (q, 258.7, CF_3), 93.8 (q, 51.6, $C\equiv CCF_3$), 90.3 (q, 5.8, $C\equiv CCF_3$)	2204
$Ph_2Si(C\equiv CCF_3)_2$ (**4**)	−52.2 (unres.)	112.3 (q, 259.0, CF_3), 94.1 (q, 52.0, $C\equiv CCF_3$), 85.9 (q, 5.7, $C\equiv CCF_3$)	2210
$Et_3SiC\equiv CCF_3$ (**5**)	−51.1 (4.0)	112.0 (q, 258.8, CF_3), 92.3 (q, 51.2, $C\equiv CCF_3$), 88.8 (q, 5.8, $C\equiv CCF_3$)	2200
$Ph_3GeC\equiv CCF_3$ (**6**)	−51.0	111.1 (q, 258.0, CF_3), 90.6 (q, 51.2, $C\equiv CCF_3$), 88.8 (q, 6.0, $C\equiv CCF_3$)	2200
$Ph_3SnC\equiv CCF_3$ (**7**)	−50.8 (12.0)	111.5 (q, 260.0, CF_3), 94.5 (q, 50.0, $C\equiv CCF_3$), 91.8 (q, 6.0, $C\equiv CCF_3$)	2183
$Bu_3SnC\equiv CCF_3$ (**8**)	−50.4 (11.7)	111.7 (q, 257.2, CF_3), 94.7 (q, 6.0, $C\equiv CCF_3$), 93.5 (q, 50.0, $C\equiv CCF_3$)	2175
$Ph_3PbC\equiv CCF_3$ (**9**)	−50.0 (7.9)	111.5 (q, 257.9, CF_3), 104.3 (q, 7.3, $C\equiv CCF_3$), 94.2 (q, 50.0, $C\equiv CCF_3$)	2169

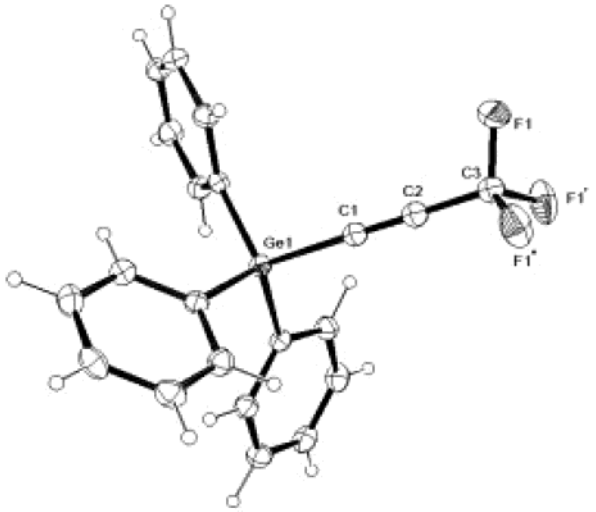

Figure 1. View of the molecular structure of $Ph_3GeC\equiv CCF_3$ (**6**) with thermal ellipsoids set at the 30% probability level. The numbering scheme of the trifluoropropynyl function is directly transposable to the structures of **2** and **3**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Ph_3EC\equiv CCF_3$ (E = C 2, Si 3, Ge 6) with Estimated Standard Deviations in Parentheses

	$Ph_3CC\equiv CCF_3$ (**2**)	$Ph_3SiC\equiv CCF_3$ (**3**)	$Ph_3GeC\equiv CCF_3$ (**6**)
E1′−C1	1.475(2)	1.860(3)	1.933(3)
C1−C2	1.186(3)	1.190(4)	1.186(4)
C2−C3	1.444(3)	1.469(4)	1.466(4)
C3−F1	1.314(2)	1.323(3)	1.318(3)
C3−F2	1.325(3)	1.323(3)	1.318(3)
C3−F3	1.324(3)	1.323(3)	1.318(3)
E1′−C1−C2	179.32(17)	180.0(3)	180.0(3)
C1−C2−C3	178.6(2)	180.0(4)	180.0(4)
C2−C3−F1	113.21(17)	112.1(2)	112.5(2)
C2−C3−F2	112.42(17)	112.1(2)	112.5(2)
C2−C3−F3	112.05(17)	112.1(2)	112.5(2)
F1−C3−F2	106.77(17)	106.7(2)	106.3(2)
F2−C3−F3	104.99(18)	106.7(2)	106.3(2)
F3−C3−F1	106.85(17)	106.7(2)	106.3(2)

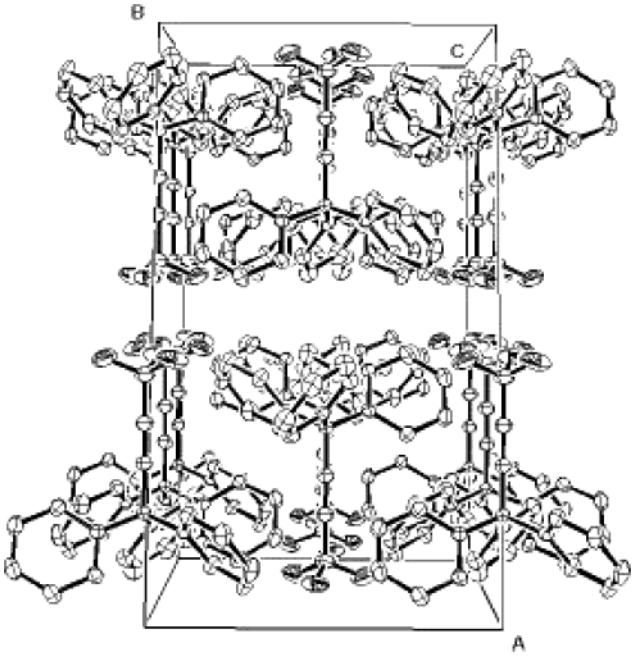

Figure 2. Packing diagram of $Ph_3CC\equiv CCF_3$ (**2**) projected along the *c* direction.

the centers α (J_{CF} 5−10 Hz) and β (J_{CF} 50−55 Hz) to the metalloid. The alkyne function is also apparent from a strong infrared absorption around 2200 cm^{-1}, the frequency of which decreases upon descending the group, consistent with the increased mass of the metalloid fragment. In all cases, satisfactory microanalytical data were obtained.

For the phenyl-substituted derivatives **2**, **3**, and **6**, additional information was acquired from single-crystal X-ray diffraction studies. In each case, the anticipated pseudotetrahedral geometry about the group 14 atom was observed, as illustrated in Figure 1. Selected bond distances and angles for these compounds are summarized in Table 2. It is noteworthy that these constitute the first crystallographic study of any main group trifluoropropynyl compounds; indeed, only one σ-trifluoropropynyl has been so characterized previously, namely, $In(C\equiv CCF_3)_3(THF)_2$.[14] In common with this indane, the internal geometries of the group 14 systems are largely as anticipated, the C≡C and C−CF_3 distances being typical of Csp≡Csp [1.183 Å] and Csp−Csp^3 [1.466 Å],[15] respectively, with near perfect linearity of the alkyne function. Similarly, the C−F distances are typical of Csp^3−F [1.322 Å][15] and are consistent with those of other, crystallographically characterized, alkyne-bound CF_3 moieties recorded in the Cambridge Crystallographic Database. It is noteworthy that the E−C1 distances for **3** and **6** exhibit no appreciable shortening to indicate delocalization of the π-system to the metalloid d orbitals. This supports the earlier assertion that the decreasing frequency of the alkyne stretch on descending the group reflects the increased mass of the element E.

The extended structure of **2** is remarkable (Figure 2) and differs from those of **3** and **6**, the individual molecules aligning in single file along the *c* direction, with adjacent files stacking head-to-tail. The resulting sheets in the *ac* plane stack in a manner that maximizes congregation of the fluorinated functions into domains,

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which propagate through the crystal in the *c* direction. In contrast, the extended structures of **3** and **6** exhibit less well-defined 3-D order. In all three cases there is a notable absence of any, classically, short intermolecular interactions, the structures apparently being determined by an extensive network of weak H···F interactions lying in the range 2.70−2.80 Å, which are just beyond the sum of the van der Waals radii [2.67 Å].[16]

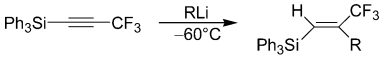
Derivatization of the Trifluoropropynyls. Among the most versatile aspects of alkyne reactivity are their interactions with strongly nucleophilic species, resulting in either reduction or carbolithiation of the triple bond. In this way, a wealth of alkene derivatives can be prepared, often with remarkable levels of stereocontrol.[17] Notwithstanding, few reports describe the application of these methods to trifluoropropynyl systems, a fact that contributes significantly to the dearth of reagents for introducing β-CF_3-substituted vinylic functions. Indeed, only a handful of silanes of the type $R_3SiCH{=}C(CF_3)R'$ have been reported, typically where R = Me and R′ = $-(CH_2)_3Ph$, −Ph, $-OCH_2Cy$, $-OCH_2Ph$, −OCy, $-N(C_2H_4)_2O$, $-NEt(CH_2Ph)$, or −S-*n*-hexyl.[18] In all cases, the silanes were obtained by olefination of the respective carbonyl compound, $(CF_3)RC{=}O$, with $CpTi(SiMe_3)_3$. One further example (R′ = H) was obtained by the Ru/Rh-catalyzed addition of Me_3SiH to 3,3,3-trifluoromethylpropene, the product arising in admixture with $Me_3SiCH_2CH_2CF_3$.[19] It is noteworthy that for all of the above materials, a *trans* arrangement of the CF_3 and Me_3Si groups is observed.

Given that trifluoropropynyl compounds are now more readily available than ever before, it would seem appropriate that they begin to serve as precursors to these potentially useful vinylic systems. With this in mind, and in view of the utility of silanes as organotransfer reagents,[20] and in fluoro/hydro-desilylation chemistry,[21] the chemistry of the silicon derivatives was investigated further.

Stereospecific Reduction by $LiAlH_4$. It has been previously documented that, upon extended reflux with $LiAlH_4$ (THF/diglyme, 150 °C, 5 h), alkynes such as $Et_3SiC{\equiv}CCH_3$ undergo stereospecific reduction to afford the respective *trans*-alkenes.[22] Given the enhanced electrophilicity imparted to trifluoropropynyl analogues by the CF_3 function, milder conditions were sought to effect a similar transformation of **5**. Thus, **5** was treated, in THF, with a slight excess of $LiAlH_4$ and the mixture brought to reflux for 4 h. Upon completion, the reaction mixture was hydrolyzed and extracted into ether, evaporation of the solvent affording a small amount of colorless oil.

The presence of the alkene $Et_3SiCH{=}CHCF_3$ (**10**) was confirmed by multinuclear (^{19}F, ^1H) NMR spectroscopy.

Scheme 2. Carbolithiation of $Ph_3SiC{\equiv}CCF_3$[a]



12 R = *n*-Bu
13 R = Ph
14 R = *t*-Bu

[a] Conditions: (i) Et_2O, −60 °C, (ii) RLi, 6 h, (iii) rt, (iv) MeOH/hexane.

The ^{19}F NMR spectrum indicated consumption of **5**, the singlet resonance at δ_F −51.1 having been replaced by a doublet of doublets at δ_F −66.8 (J_{FH} 5.2, 2.0 Hz), characteristic of an alkenic CF_3 function. This was verified by observation of the corresponding alkenic proton resonances at 6.6 and 6.1 ppm, with a mutual $^1H-^1H$ coupling constant of 18 Hz suggesting a *trans* arrangement, thus identifying **10** as *E*-$Et_3SiCH{=}CHCF_3$. However, **10** constitutes a minor component of the mixture and is not readily separated from the bulk, which apparently results from defluorination of the substrate. Moreover, the crude mass yield was poor (<20%), presumably due to loss of the volatile substrate during the reaction and/or workup.

In view of these difficulties, further investigations were restricted to the more robust, and considerably less volatile, silane **3** ($Ph_3SiC{\equiv}CCF_3$). A comparable reaction again resulted in defluorination of the substrate, alongside formation of small amounts of the alkene *E*-$Ph_3SiCH{=}CH(CF_3)$ (**11**); hence less harsh conditions were explored. It was thus determined that the reduction is best effected when **3** and $LiAlH_4$ are mixed at −60 °C in THF, then stirred together while warming to ambient temperature, over no more than 3 h. In this way, **11** is obtained as the major product, in admixture with small amounts of the *Z* isomer (*E*:*Z* 97:3 by ^{19}F NMR), but no evidence of defluorinated material. Formation of the *Z* isomer is completely inhibited if the reaction is conducted entirely at −60 °C; however, under these conditions less than 10% of **11** is isolated.

Carbolithiation of the Trifluoropropynyl Compounds. The interaction of **3** with a range of organolithium reagents has also been explored (Scheme 2). Thus, it was found that when RLi (R = *n*-Bu, Ph) were added to ethereal solutions of **3** at −60 °C, then stirred together while warming to ambient temperature, nonaqueous workup afforded isomeric mixtures of the respective alkenes $Ph_3SiCH{=}C(CF_3)R$. As with the dihydroalkenes **10** and **11**, the ^{19}F NMR spectra each exhibit two vinylic CF_3 resonances (R = *n*-Bu δ_F −63.9 and −67.4 ppm; Ph δ_F −59.8 and −67.5 ppm), the lower frequency of which was assigned, by comparison to **10** and **11**, as *E*-$Ph_3SiCH{=}CHR$ (R = *n*-Bu **12**, Ph **13**). Indeed, as with the dihydroalkenes, when the reaction is conducted entirely at low temperature (−60 °C), the single isomers **12** and **13** are obtained, neither of which exhibit NOE interactions between the R group and alkenic protons, and both of which have been crystallographically characterized with the *E* geometry (vide infra). In contrast, when the reaction with *n*-BuLi is preformed at ambient temperature, an appreciable amount of the *Z* isomer is obtained, which clearly exhibits a NOE interaction with the proximate butyl-CH_2 unit.

Crystallographic Characterization of *E*-$Ph_3SiCH{=}C(CF_3)R$. The solid-state structures of **12** and **13**

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(20) See for example: (a) Li, G. L.; Chen, Y. H.; Missert, J. R.; Rungta, A.; Dougherty, T. J.; Grossman, Z. D.; Pandey, R. K. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1785. (b) Xue, L.; Lu, S. D.; Pedersen, Q.; Liu, R. M.; Narske, D. J.; Burton, *J. Org. Chem.* **1997**, *62*, 1064.
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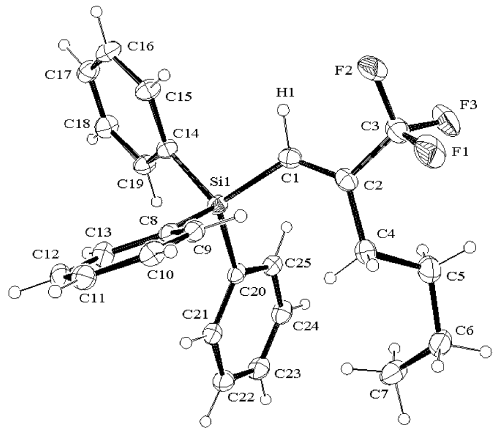


Figure 3. View of the molecular structure of $Ph_3SiCH{=}C(CF_3)$*n*-Bu (**12**) with thermal ellipsoids set at the 30% probability level.

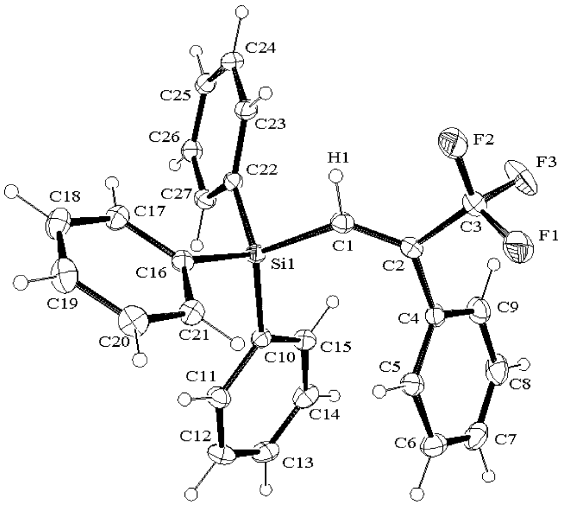


Figure 4. View of the molecular structure of *E*-$Ph_3SiCH{=}C(CF_3)Ph$ (**13**) with thermal ellipsoids set at the 30% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Ph_3SiCH{=}C(CF_3)$*n*-Bu (12) with Estimated Standard Deviations in Parentheses

Si1−C1	1.876(2)	C5−C6	1.526(3)
C1−H1	0.98(2)	C6−C7	1.501(3)
C1−C2	1.331(3)	C3−F1	1.344(2)
C2−C3	1.501(3)	C3−F2	1.340(2)
C2−C4	1.507(3)	C3−F3	1.341(2)
C4−C5	1.531(3)		
Si1−C1−C2	129.13(16)	C2−C1−H1	117.3(12)
Si1−C1−H1	113.0(12)	C2−C3−F1	111.72(17)
C1−C2−C3	119.69(18)	C2−C3−F2	113.86(18)
C1−C2−C4	125.54(18)	C2−C3−F3	113.15(17)
C3−C2−C4	114.75(17)		

are illustrated in Figures 3 and 4, respectively, with selected geometric parameters summarized in Tables 3 and 4. Along with the structure of *E*-$Ph_3SiCH{=}C(CF_3)$*t*-Bu (**14**), which we have previously reported,[13] these are the first examples of β-CF_3-substituted vinylic compounds to be crystallographically characterized. As with the parent alkyne, the anticipated pseudotetrahedral geometry is adopted about silicon, and the internal distances of the vinylic unit are largely typical. Indeed, the $C_\alpha{=}C_\beta$ and $C_\beta{-}C_\gamma$ distances compare well with the average values for $Csp^2{=}Csp^2$ [1.326 Å] and $Csp^2{-}Csp^3$ [1.503 Å], respectively, though a slight foreshortening of C2−C4 is apparent in **13**, presumably due to partial overlap of the alkenic and aromatic π-systems. All C−F distances are close to idealized values [1.322 Å].[15]

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Ph_3SiCH{=}C(CF_3)Ph$ (13) with Estimated Standard Deviations in Parentheses

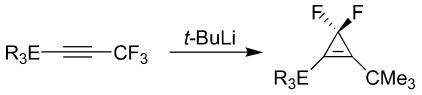
Si1−C1	1.8814(14)	C5−C6	1.393(3)
C1−H1	0.983(19)	C6−C7	1.378(3)
C1−C2	1.3324(19)	C7−C8	1.380(3)
C2−C3	1.508(2)	C8−C9	1.383(3)
C2−C4	1.491(2)	C3−F1	1.336(2)
C4−C5	1.387(2)	C3−F2	1.330(2)
C4−C9	1.395(2)	C3−F3	1.337(2)
Si1−C1−C2	133.19(13)	C2−C1−H1	114.6(9)
Si1−C1−H1	112.1(9)	C2−C3−F1	111.96(14)
C1−C2−C3	119.46(14)	C2−C3−F2	114.38(12)
C1−C2−C4	126.18(14)	C2−C3−F3	112.35(14)
C3−C2−C4	114.36(12)		

In common with **14**, however, the internal geometries of **12** and **13** are subject to notable distortion, due to the *cis* arrangement of sterically demanding substituents. Thus, the angles Si1−C1−C2 and C1−C2−C4 are "opened-out" relative to ideality, while ∠Si1−C1−H1 are contracted. These effects are, however, somewhat less severe than for **14** [∠Si1−C1−C2 139.37(18)°; ∠C1−C2−C4 127.4(2)°], the *n*-Bu and Ph substituents adopting conformations that minimize unfavorable interactions with the triphenylsilyl fragment. Thus, in **12** [∠Si1−C1−C2 129.13(16)°; ∠C1−C2−C4 125.54(18)°] the *n*-Bu group bends away from silicon, while in **13** [∠Si1−C1−C2 133.19(13)°; ∠C1−C2−C4 126.18(14)°] the phenyl unit staggers the alkene π-system with a torsion of 64°, an orientation enforced by a significant, intramolecular π-stacking interaction with the ring C10−C15 [*d*(Cg−Cg) 3.8772(9) Å, ∠18.82°]. Consequently, the close approach of alkenic proton and eclipsing fluorine atom previously noted of **14** [*d*(H···F) 2.13(2) Å] is somewhat diminished in both cases [*d*(H···F) **12** 2.35(2) Å; **13** 2.266(16) Å].

Carbolithiation with *t*-BuLi. When **3** is treated with *t*-BuLi at −60 °C, as described above, three distinct species are observed in the ^{19}F NMR spectrum, characterized by two alkenic resonances [δ_F −56.7 (∼2.5%) and −60.7 (>95%)] and one further signal at appreciably lower frequency [δ_F −103.1 (∼2.5%), vide infra]. The corresponding proton resonances for the major product are clearly identified (δ_H 6.9, $C_\alpha H$; 1.06 $C(CH_3)_3$) and exhibit a discernible NOE interaction, which previously led us to assign this material as *Z*-$Ph_3SiCH{=}C(CF_3)$*t*-Bu.[13] This contrasts the more recently explored reactions with *n*-BuLi and PhLi, though it was again the *E* isomer (**14**) that was crystallographically characterized.

In light of the more recent results, carbolithiation with *t*-BuLi has now been reexamined. Fortuitously, in one instance, upon mixing **3** and *t*-BuLi at ambient temperature, the anticipated ^{19}F NMR resonances at 103.1 (52%) and −60.7 (19%) ppm were accompanied by a significant proportion of the previously trace component observed at −56.7 ppm (29%). This finally allowed unequivocal assignment of the corresponding proton resonances [δ_H 6.7 (1H), 1.1 (9H)], which were found to exhibit a strong NOE interaction. Significantly, the original NOESY cross-peak was again observed, though with a considerably lower intensity; this would

Scheme 3. Cyclization of Group 14 Trifluoropropynyls, Initiated by Addition of *tert*-Butylithium[a]



2 R = Ph, E= C
3 R = Ph, E = Si
5 R = Et, E = Si

90 - 95 %

[a] Conditions: (i) THF reflux, 20 h, (ii) rt, hexane.

suggest that relative concentrations had previously biased the data. The bulk product from the low-temperature reaction of **3** and *t*-BuLi is thus reassigned as *E*-$Ph_3SiCH{=}C(CF_3)$*t*-Bu (**14**).

Cyclization of Trifluoropropynyls via *tert*-Butyllithium Carbolithiation. The carbolithiation of **3** with *t*-BuLi routinely affords, in addition to *E* and *Z* alkenes, a species exhibiting a singlet ^{19}F NMR resonance at −103.1 ppm (**15**), characteristic of a *gem*-difluorocyclopropenyl compound.[23] This component becomes increasingly important as the reaction temperature is increased, such that at ambient temperature it typically constitutes up to 80% of the product mixture, which also contains **14** (∼20%) and a trace of the *Z* isomer. While **15** cannot be separated from the mixture either chromatographically, due to limited stability upon the column, or by recrystallization, its identity has been unequivocally established as $Ph_3SiC{=}C(CF_2)$*t*-Bu on the basis of ^{13}C NMR spectroscopic studies, which reveal the presence of three quaternary centers, each one appearing as a triplet resonance. The CF_2 unit is clearly observed at δ_C 108.2 (J_{CF} 271 Hz), with C_α (δ_C 124.6, J_{CF} 13.1 Hz) and C_β (δ_C 157.9, J_{CF} 8.3 Hz) resonating at higher frequency; characteristic resonances for the Ph_3Si and *t*-Bu functions are also clearly resolved. Moreover, as we have previously communicated,[13] **15** preferentially crystallizes when a dichloromethane/hexane solution is allowed to evaporate slowly; thus its solid-state structure has been determined and found to be consistent with the spectroscopic data.

While **15** cannot be prepared in complete isolation of **14**, it has proven possible to maximize the proportion of cyclization by operating at elevated temperatures, for extended periods. Thus, when **3** and *t*-BuLi are held at THF reflux for 20 h (Scheme 3), **15** accounts for over 95% of the isolated products, with yields in excess of 80% after purification, eluting from a short column with 1:1 DCM/hexane affording **15** as an air/moisture-stable yellow solid. This methodology thus holds considerable advantage over more traditional difluorocyclopropene syntheses, based upon heavy-metal difluorocarbene sources, which have been recently reviewed.[24]

Significantly, the reduced proportion of **14** in samples obtained via these conditions has a considerable effect upon the solution stability of **15**. Indeed, it has been observed that when mixtures containing over 15% of **14** are left in solution over a period of days, complete defluorination of **15** results. This process has been noted in a range of solvents, and the lifetime of **15** is temperature dependent, ranging from 7 days at 20 °C to less than 1 h at 50 °C. However, with less than 5% of **14** present, apparently infinite solution stability is observed, samples remaining unchanged after several weeks at 70 °C. Moreover, while defluorination had been previously accelerated by the presence of an electrophile (e.g., Ph_3SiCl, Ph_3CCl), no such effect is now observed.

Interestingly, such instability toward defluorination has been previously reported for *gem*-difluorocyclopropenes, such as $PhC{=}C(CF_2)H$, and the somewhat more stable $PhC{=}C(CF_2)I$, both of which decompose in this manner upon prolonged exposure to air at room temperature.[25] Moreover, a range of such materials, notably $CH_3(CH_2)_5C{=}C(CF_2)H$ and $PhC{=}C(CF_2)Ph$, are reportedly moisture sensitive and hydrolyze rapidly to the respective cyclopropenones.[26] That **15** is indefinitely stable in the absence of solvent, and even in solution when in a pure state, is thus a significant feature. Moreover, the extended exposure of **15**, as solution, to water affords no indication of hydrolysis.

Mechanistic Considerations. The formation of exclusively *E*-$Ph_3SiCH{=}C(CF_3)R$ at low temperature would seem largely consistent with reaction proceeding under kinetic control, a classical nucleophilic mechanism resulting in *anti* addition of the organolithium reagent. Indeed, evidence in support of this has been obtained by the addition of tetramethylethylenediamine (TMEDA) under these conditions, resulting, for *n*-BuLi and Ph, in the exclusive generation of **12** and **13**, respectively. Surprisingly, in the case of *t*-BuLi, this results in an approximately equimolar mixture of **14** and *Z*-$Ph_3SiCH{=}C(CF_3)$*t*-Bu, which had previously seemed consistent with the preferential formation of *Z*-$Ph_3SiCH{=}C(CF_3)$*t*-Bu under these conditions, the product mixture being presumed to reflect inhibition of a precursor lithium-alkyne π-complex.[13] However, the data do, in fact, support the preferential formation of **14** at low temperature, there being precedent for the apparently anomalous behavior of *t*-BuLi in the presence of TMEDA. Indeed, the reactions of RLi/TMEDA (R = *n*-Bu, Et, Ph) with diphenylacetylene have been reported to proceed with exclusively *anti* addition, the exception being where R = *t*-Bu, in which case a mixture of *syn* (80%) and *anti* (20%) products was obtained.[27] This was presumed to illustrate thermodynamic preference, driven by the greater steric footprint of *t*-Bu.

Competition between kinetic and thermodynamic control is similarly consistent with the enhanced generation of *Z*-$Ph_3SiCH{=}C(CF_3)R$ observed at higher reaction temperatures. Indeed, ab initio studies of the trimethylsilyl analogues *E*/*Z*-$Me_3SiCH{=}C(CF_3)$*t*-Bu at the B3LYP/6-311+G* level suggest a slight thermodynamic preference for the *Z* isomer of 19.5 kJ mol^{-1} (4.66 kcal mol^{-1}). However, the necessity for preassociation of the alkyne and organolithium reagent, to effect *syn* addition, renders formation of the *Z* isomer inherently slow, relative to *anti* addition; thus the *E* isomer still predominates.

The remarkably facile cyclization observed with *t*-BuLi at ambient and elevated temperature is presum-

(23) Eujen, R.; Hoge, B. *J. Organomet. Chem.* **1995**, *503*, C51.
(24) Dolbier, W. R., Jr.; Battiste, M. A. *Chem. Rev.* **2003**, *103*, 1071.
(25) Xu, W.; Chen, Q.-Y. *J. Org. Chem.* **2002**, *67*, 9421.
(26) Bessard, Y.; Schlosser, M. *Tetrahedron* **1991**, *47*, 7323.
(27) Mulvaney, J. E.; Newton, D. J. *J. Org. Chem.* **1969**, *34*, 1936.

ably driven by the thermodynamically favorable elimination of LiF from the lithio-alkene intermediate *E*-$Ph_3SiC(Li)=C(CF_3)$*t*-Bu (**16**). Indeed, this is supported by the fact that, while carbolithiation at −60 °C affords exclusively *E*-$Ph_3SiCH=C(CF_3)$*t*-Bu, allowing the reaction to attain ambient temperature prior to workup results in formation of an appreciable amount of the cyclized product.

This mechanism is presumably enabled by the severely distorted geometry imposed in accommodating the *cis* arrangement of sterically demanding substituents. As noted previously (vide supra), the protonated alkene **14** exhibits an extremely short H···F contact [2.13(2) Å] in the solid state, which would seem to support the likelihood of an appreciable Li···F interaction within **16**, thus predisposing it to LiF elimination. In contrast, the somewhat longer H···F distances observed in **12** [2.35(2) Å] and **13** [2.266(16) Å] offer some insight into the reluctance of these systems to undergo cyclization and support the notion of a sterically driven mechanism. Indeed, these data also concur with earlier DFT studies, at the B3LYP/6-311+G* level, of *E*-$Me_3SiCH=C(CF_3)$*t*-Bu [*d*(H···F) 2.119 Å] and *E*-$Me_3SiCH=C(CF_3)H$ [*d*(H···F) 2.407 Å], which led us to a similar conclusion.[13] Significantly, it would appear that the *E*-alkenes represent valuable models by which to assess the potential for cyclization of a given substrate, thus availing the possibility of theoretical screening. However, current data do not yet allow for determination of the limiting H···F separation for cyclization.

Verification of a sterically driven process, as opposed to one mediated by silicon d orbitals, arises from the efficiency by which the trityl-trifluoropropynyl **2** can be similarly cyclized to $Ph_3CC=C(CF_2)$*t*-Bu, which accounts for 90% of the isolated products. However, the required level of steric bulk to initiate cyclization remains unclear, the ab initio studies suggesting substituents smaller than Ph_3Si- might prove equally effective. Indeed, analytical scale investigations reveal that $Et_3SiC\equiv CCF_3$ (**5**) reacts readily with *t*-BuLi to afford over 80% of the respective cyclopropene, which was identified by a combination of ^{19}F and ^{13}C NMR spectroscopy. We continue to explore an increasing range of substrates.

Conclusions

Hydrofluorocarbon 245fa serves as an effective source of the trifluoropropynyl moiety for the development of metalloid-based systems, the first homologous series of which has been prepared and fully characterized. For the first time, the single-crystal X-ray structures of a series of these compounds have been determined, and these constitute the first series of σ-trifluoropropynyl derivatives to be so characterized. The trifluoropropynyl silane $Ph_3SiC\equiv CCF_3$ has proven to be readily converted into a range of β-CF_3 vinyl derivatives, through its low-temperature reactions with nucleophiles; the products of these reactions constitute the first β-CF_3 vinylic systems to be crystallographically characterized. Moreover, trifluoropropynyl compounds of the type $R_3EC\equiv CCF_3$ (E = C, Si) constitute convenient precursors to the versatile *gem*-difluorocyclopropenyl compounds, which can be generated under mild conditions, via a sterically assisted process initiated by *t*-BuLi, and driven by elimination of LiF from the carbolithiation product. The susceptibility of a given trifluoropropynyl toward this process would seem to be conveniently modeled by consideration of the respective *E*-$R_3ECH=C(CF_3)$*t*-Bu system, a *syn* H···F contact of ≤2.12 Å indicating a likely cyclization candidate. This affords the potential of more widespread applicability for this methodology than has yet been elucidated.

Experimental Section

General Methods. Reactions were carried out under anaerobic conditions in flame-dried glassware, with moisture-sensitive reagents being handled under an argon atmosphere in a drybox (Belle Technologies, UK). Diethyl ether and THF were dried over sodium wire for ca. 1 day prior to use. The compounds $CF_3CH_2CF_2H$ (Honeywell), *n*-BuLi (2.5 M in hexane), *t*-BuLi (1.5 M in pentane) (Acros), PhLi (1.8 M in ether/pentane), Ph_3CCl, Ph_3GeBr, Bu_3SnCl (Aldrich), Et_3SiCl, Ph_2SiCl_2, Ph_3SiCl, Ph_3SnCl, $LiAlH_4$, TMEDA (Lancaster), and methanol (BDH) were used as supplied after spectroscopic verification of purity. All NMR spectra were recorded of $CDCl_3$ solutions on Bruker DPX200 (^{19}F, 188.310 MHz, referenced to external $CFCl_3$) or DPX400 (^1H, NOESY, 400.4 MHz; ^{13}C, Dept-135, 100.555 MHz referenced to external $SiMe_4$) spectrometers. All resonances are reported using the high-frequency positive convention. Infrared spectra were recorded of chloroform solutions or neat liquids, between KBr plates on a Nicolet Nexus FTIR spectrometer. Elemental analyses were performed by the departmental microanalytical service.

Preparation of $Ph_3CC\equiv CCF_3$ (2). Typically, a stirred ethereal solution (200 cm^3) of HFC-245fa (1.8 cm^3, 17.73 mmol) was treated, under N_2, with *n*-BuLi (21.0 cm^3, 52.50 mmol), at −10 °C. After 15 min, Ph_3CCl (3.264 g, 11.71 mmol) in ether (40 cm^3) was added, while maintaining −10 °C. Then the mixture was held at 0 °C and stirred overnight. The reaction was allowed to attain ambient temperature, then hexane (160 cm^3) was added to precipitate the inorganics; the settled mixture was filtered through Celite and the filtrate concentrated in vacuo. Purification on a silica column, eluting with 50:50 DCM/hexane, afforded **2** as a pale brown solid. Yield: 2.431 g, 62%. Mp: 150 °C. Anal. Calcd for $C_{22}H_{15}F_3$: C, 78.6; H, 4.5; F, 16.9. Found: C, 78.8; H, 4.3; F, 16.6. ^{13}C NMR: δ 135.4 [CH, s], 131.6 [C, s], 131.1 [CH, s], 128.8 [CH, s], see Table 1. ^1H NMR: δ 7.7−7.4 (m). IR: ν_{max}/cm^{-1} 2256 (C≡C str.), 1276, 1145 (C−F str.).

$Ph_3SiC\equiv CCF_3$ (3). HFC-245fa (2.16 cm^3, 21.28 mmol), *n*-BuLi (25.5 cm^3, 63.75 mmol), Ph_3SiCl (4.150 g, 14.07 mmol) were used. **3** was obtained as a pale yellow solid. Yield: 4.520 g, 90%. Mp: 110 °C. Anal. Calcd for $C_{21}H_{15}F_3Si$: C, 71.6; H, 4.3; F, 16.2. Found: C, 71.9; H, 4.5; F, 16.0. ^{13}C NMR: δ 135.4 [CH, s], 131.6 [C, s], 131.1 [CH, s], 128.8 [CH, s], see Table 1. ^1H NMR: δ 7.7−7.4 (m). IR: ν_{max}/cm^{-1} 2204 (C≡C str.), 1245, 1151 (C−F str.).

$Ph_2Si(C\equiv CCF_3)_2$ (4). HFC-245fa (1.80 cm^3, 17.73 mmol), *n*-BuLi (21.0 cm^3, 52.50 mmol), and Ph_2SiCl_2 (1.20 cm^3, 5.71 mmol) were used. Crude product was distilled at 124 °C/9 mmHg. Yield: 1.460 g, 69%. Anal. Calcd for $C_{18}H_{10}F_6Si$: C, 58.7; H, 2.7; F, 30.9. Found: C, 58.4; H, 2.4; F, 30.6. ^{13}C NMR: δ 135.4 [CH, s], 132.3 [CH, s], 129.2 [CH, s], 127.5 [C, s], see Table 1. ^1H NMR: δ 7.7−7.4 (m). IR: ν_{max}/cm^{-1} 2210 (C≡C str.), 1241, 1149 (C−F str.).

$Et_3SiC\equiv CCF_3$ (5). HFC-245fa (1.50 cm^3, 14.77 mmol), *n*-BuLi (17.4 cm^3, 43.50 mmol), and Et_3SiCl (1.60 cm^3, 9.54 mmol) were used. Crude product was distilled at 30 °C/10 mmHg. Yield: 1.006 g, 51%. ^{13}C NMR: δ 6.1 [CH_3, s, J_{SiC} 31.8 Hz], 3.9 [CH_2, s, J_{SiC} 57.0 Hz], see Table 1. ^1H NMR: δ 1.0 (t, J_{HH} 8 Hz) 0.7 (q, J_{HH} 8 Hz). IR: ν_{max}/cm^{-1} 2200 (C≡C str.), 1253, 1143 (C−F str.).

$Ph_3GeC\equiv CCF_3$ (6). HFC-245fa (0.55 cm^3, 5.42 mmol), *n*-BuLi (6.25 cm^3, 15.63 mmol), and Ph_3GeBr (1.006 g, 2.62

Table 5. Crystal Data and Structure Refinement for $Ph_3CC{\equiv}CCF_3$ (2), $Ph_3SiC{\equiv}CCF_3$ (3), $Ph_3GeC{\equiv}CCF_3$ (6), *E*-$Ph_3SiCH{=}C(CF_3)$*n*-Bu (12), and *E*-$Ph_3SiCH{=}C(CF_3)Ph$ (13)

	2	3	6	12	13
formula	$C_{22}H_{15}F_3$	$C_{21}H_{15}F_3Si$	$C_{21}H_{15}F_3Ge$	$C_{25}H_{25}F_3Si$	$C_{27}H_{21}F_3Si$
mol wt	336.34	352.42	396.92	410.54	430.53
cryst syst	monoclinic	cubic	cubic	triclinic	triclinic
space group	*C*2/*c* (No. 15)	$Pa\bar{3}$ (No. 205)	$Pa\bar{3}$ (No. 205)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cryst dimens, mm	0.07 × 0.10 × 0.25	0.15 × 0.13 × 0.08	0.15 × 0.13 × 0.08	0.20 × 0.20 × 0.10	0.15 × 0.25 × 0.25
habit	plate	prism	prism	plate	prism
color	colorless	colorless	colorless	colorless	colorless
a, Å	19.1078(7)	15.1654(7)	15.2629(7)	10.2298(4)	9.2663(2)
b, Å	10.6047(4)	15.1654(7)	15.2629(7)	10.2607(4)	11.1733(2)
c, Å	18.0521(8)	15.1654(7)	15.2629(7)	12.3244(6)	12.7350(3)
α, deg	90	90	90	93.092(2)	105.3040(10)
β, deg	106.251(2)	90	90	105.670(2)	98.6910(10)
γ, deg	90	90	90	116.434(2)	114.0070(10)
V, Å^3	3511.8(2)	3487.9(3)	3555.6(2)	1092.33(8)	1110.63(4)
Z	8	8	8	2	2
D_{calc}, g cm^{-3}	1.272	1.342	1.483	1.248	1.287
μ mm^{-1}	0.095	0.164	1.752	0.141	0.142
θ range, deg	2.22 to 27.44	3.00 to 26.33	2.98 to 28.69	1.75 to 24.91	2.50 to 27.50
no. of data collected, unique reflns	9814, 3922	21 893, 1188	19 041, 1213	10 774, 3777	22 312, 5044
no. of params refined	286	96	96	362	364
F(000)	1392	1456	1600	432	448
R1 ($I > 2\sigma(I)$)[a]	0.0539	0.0584	0.0344	0.0403	0.0374
wR2 (all data)[b]	0.1483	0.0963	0.0784	0.0970	0.0929
max. and min./e Å^{-3}	0.295, −0.241	0.186, −0.177	0.355, −0.355	0.223, −0.247	0.250, −0.250

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

mmol) were used. **6** was obtained as a pale yellow solid. Yield: 0.968 g, 93%. Mp: 108 °C. Anal. Calcd for $C_{21}H_{15}F_3Ge$: C, 63.5; H, 3.8; F, 14.8. Found: C, 63.8; H, 3.6; F, 14.4. ^{13}C NMR: δ 133.4 [CH, s], 131.6 [C, s], 129.2 [CH, s], 127.7 [CH, s], see Table 1. ^1H NMR: δ 7.7−7.4 (m). IR: ν_{max}/cm^{-1} 2200 (C≡C str.), 1247, 1149 (C−F str.).

$Ph_3SnC{\equiv}CCF_3$ (7). HFC-245fa (1.30 cm^3, 12.81 mmol), *n*-BuLi (14.6 cm^3, 36.50 mmol), and Ph_3SnCl (3.154 g, 8.18 mmol) were used. **7** was obtained as a pale yellow solid. Yield: 3.186 g, 88%. Mp: 90 °C. Anal. Calcd for $C_{21}H_{15}F_3Sn$: C, 57.0; H, 3.4; F, 12.8. Found: C, 57.1; H, 3.6; F, 12.6. ^{13}C NMR: δ 135.6 [CH, s, J_{SnC} 44 Hz], 133.6 [C, s], 129.2 [CH, s, J_{SnC} 12.5 Hz], 128.1 [CH, s, J_{SnC} 61 Hz], see Table 1. ^1H NMR: δ 7.7−7.4 (m). IR: ν_{max}/cm^{-1} 2184 (C≡C str.), 1244, 1175 (C−F str.).

$Bu_3SnC{\equiv}CCF_3$ (8). HFC-245fa (1.60 cm^3, 15.76 mmol), *n*-BuLi (18.6 cm^3, 46.50 mmol), and Bu_3SnCl (2.20 cm^3, 8.11 mmol) were used. Crude product was distilled at 113 °C/15 mmHg. Yield: 1.976 g, 63%. Anal. Calcd for $C_{15}H_{27}F_3Sn$: C, 47.0; H, 7.1; F, 14.9. Found: C, 47.1; H, 7.1; F, 14.7. ^{13}C NMR: δ 29.0 [CH_2, s, J_{SnC} 24 Hz], 27.3 [CH_2, s, J_{SnC} 60 Hz], 13.9 [CH_3, s, J_{SnC} 2.5 Hz], 11.7 [CH_2, s, J_{SnC} 377 Hz], see Table 1. ^1H NMR: δ 1.6 (m, 2H), 1.4 (m, 2H), 1.1 (m, 2H), 0.9 (m, 3H). IR: ν_{max}/cm^{-1} 2175 (C≡C str.), 1243, 1139 (C−F str.).

$Ph_3PbC{\equiv}CCF_3$ (9). HFC-245fa (0.22 cm^3, 2.17 mmol), *n*-BuLi (2.5 cm^3, 6.25 mmol), and Ph_3PbCl (0.498 g, 1.05 mmol) were used. **9** was obtained as a beige solid. Yield: 0.212 g, 38%. Mp: 94 °C. Anal. Calcd for $C_{21}H_{15}F_3Pb$: C, 47.5; H, 2.8; F, 10.7. Found: C, 47.1; H, 3.0; F, 9.5. ^{13}C NMR: δ 147.2 [C, s, J_{PbC} 661.5 Hz], 135.9 [CH, s, J_{PbC} 84.0 Hz], 129.1 [CH, s, J_{PbC} 104.0 Hz], 128.6 [CH, s, J_{PbC} 23.2 Hz], see Table 1. ^1H NMR: δ 7.7−7.3 (m). IR: ν_{max}/cm^{-1} 2169 (C≡C str.), 1241, 1141 (C−F str.).

Synthesis of *E*-$Ph_3SiCH{=}CHCF_3$ (11). To a suspension of $LiAlH_4$ (0.113 g, 2.98 mmol) in THF (10 cm^3) cooled to −60 °C was added dropwise a THF solution (5 cm^3) of **3** (1.001 g, 2.84 mmol). After complete addition, the mixture was allowed to attain ambient temperature while stirring over 2.5 h. The reaction was quenched at −30 °C by addition of 5 cm^3 H_2O, then allowed to reattain ambient temperature and extracted with diethyl ether (2 × 10 cm^3). The organics were combined, washed with water (2 × 10 cm^3), and dried over $MgSO_4$. The filtered solution was concentrated in vacuo and purified on a silica column eluting with 50:50 DCM/hexane to afford **12** as a pale yellow solid. Yield: 0.694 g, 69%. Anal. Calcd for $C_{21}H_{17}F_3Si$: C, 71.2; H, 4.8; F, 16.1. Found: C, 72.0; H, 6.1; F, 16.7. ^{19}F NMR: δ −66.8 (dd, J_{HF} 5.8, 1.5 Hz). ^{13}C NMR: δ 134.9 [CH, s], 131.1 [C, s], 129.2 [CH, s], 127.2 [CH, s], 136.3 [C_αH, m], 134.3 [CH, q, J_{CF} 5.0 Hz C_β], 121.1 [C, q, J_{CF} 271.2 Hz, CF_3]. ^1H NMR: δ 7.2 (dq, J_{HH} 18.6, J_{HF} 1.5 Hz), 6.1 (dq, J_{HH} 18.6, J_{HF} 5.8 Hz). IR: ν_{max}/cm^{-1} 1280, 1130 (C−F str.).

Synthesis of *E*-$Ph_3SiCH{=}C(CF_3)R$ (R = *n*-Bu) (12). To an ethereal solution (15 cm^3) of **3** (0.503 g, 1.43 mmol), held at −60 °C, was added dropwise *n*-BuLi (1.0 cm^3, 2.5 mmol); then the mixture was stirred for 5 h, before being quenched by addition of methanol (~3 cm^3). Having attained ambient temperature, hexane was added to precipitate the inorganic salts, and the mixture filtered through Celite. Concentration in vacuo afforded the crude product as an oil, which was purified by passing down a short silica column (50:50 DCM/hexane), affording analytically pure **13** as an off-white material. Yield: 0.382 g, 65%. Anal. Calcd for $C_{25}H_{25}F_3Si$: C, 72.2; H, 6.2; F, 13.9. Found: C, 73.4; H, 6.4; F, 13.5. ^{19}F NMR: δ −67.4 (d, J_{HF} 1.3 Hz). ^{13}C NMR: δ 136.2 [CH, s], 134.1 [C, s], 130.3 [CH, s], 128.5 [CH, s], 149.5 [C, q, J_{CF} 27.6 Hz, C_β], 127.9 [CH, q, J_{CF} 4.0 Hz C_α], 123.8 [C, q, J_{CF} 276.8 Hz, CF_3], 31.8 [CH_2, s, $C_\gamma H_2$*n*-Pr], 31.2 [CH_2, s, $C_\gamma H_2CH_2$Et], 23.1 [CH_2, s, $C_\gamma H_2CH_2CH_2$Me], 13.9 [CH_3, s]. ^1H NMR: δ 6.8 (q, J_{HF} 1.3 Hz), 2.1 (m, 2H), 1.1 (m, 2H), 0.7 (m, 2H), 0.6 (m, 3H). IR: ν_{max}/cm^{-1} 1589 (C=C str.), 1168, 1118 (C−F str.).

(R = Ph) (13). $Ph_3SiC{\equiv}CCF_3$ (**3**) (0.503 g, 1.43 mmol) and PhLi (1.0 cm^3, 1.80 mmol) were used at −30 °C for 5 h. The product was isolated as an off-white solid. Yield: 0.397 g, 65%. Anal. Calcd for $C_{27}H_{21}F_3Si$: C, 75.3; H, 4.9; F, 13.2. Found: C, 75.5; H, 4.9; F, 13.2. ^{19}F NMR: δ −67.5 (br m). ^{13}C NMR: δ 135.8 [CH, s, Ph_3Si], 133.3 [C, s, Ph_3Si], 129.7 [CH, s, Ph_3-Si], 127.9 [CH, s, Ph_3Si]; 148.2 [C, q, J_{CF} 29.9 Hz, C_β], 131.1 [CH, q, J_{CF} 3.4 Hz C_α], 122.6 [C, q, J_{CF} 276.0 Hz, CF_3], 129.3 [CH, s, *Ph*], 128.4 [CH, s, *Ph*], 127.6 [CH, s, *Ph*]. ^1H NMR: δ 7.4−7.1 (m), 6.9 (br m). IR: ν_{max}/cm^{-1} 1494 (C=C str.), 1249, 1172 (C−F str.).

(R = *t*-Bu) (14). $Ph_3SiC{\equiv}CCF_3$ (**3**) (0.503 g, 1.43 mmol) and *t*-BuLi (1.1 cm^3, 1.65 mmol) were used at −60 °C for 5 h. The product was isolated as an off-white solid. Yield: 0.480 g, 82%.

Mp: 89 °C. Anal. Calcd for $C_{25}H_{25}F_3Si$: C, 73.2; H, 6.1; F, 13.9. Found: C, 73.4; H, 6.1; F, 13.5. ^{19}F NMR δ −60.7 [d, J_{HF} 1.5 Hz]. ^{13}C NMR: δ 134.7 [CH, s], 134.1 [C, s], 128.6 [CH, s], 127.0 [CH, s], 155.7 [C, q, J_{CF} 23.7 Hz, C_β], 126.2 [CH, q, J_{CF} 4.8 Hz, C_α], 123.2 [C, q, J_{CF} 279 Hz, CF_3], 35.3 [C, s CMe_3], 29.7 [CH_3, s, $C(CH_3)_3$]. ^{1}H NMR: δ 7.7−7.4 (m), 6.9 [q, J_{HF} 1.5 Hz. 1H] 1.06 [s, 9H]. IR: ν_{max}/cm^{-1} 1429 (C═C str.), 1251, 1157 (C−F str.).

Preparation of $Ph_3SiC{=}C(CF_2)t$-Bu (15). In a typical reaction, a THF solution (15 cm^3) of **3** (0.501 g, 1.42 mmol) was warmed to 40 °C, prior to the dropwise addition of *t*-BuLi (1.1 cm^3, 1.65 mmol); the mixture was then brought to reflux for 20 h. The cooled mixture was then quenched by addition of methanol (∼3 cm^3). Then hexane (50 cm^3) was added to precipitate the inorganic salts. Filtration through Celite and concentration in vacuo afforded the crude product, which was purified by passing down a short silica column (50:50 DCM/hexane), resulting in a yellow solid. Yield: 0.470 g, 85%. Anal. Calcd for $C_{25}H_{24}F_2Si$: C, 76.9; H, 6.2; F, 9.7. Found: C, 76.5; H, 6.1; F, 10.0. ^{19}F NMR: δ −103.1 [s]. ^{13}C NMR: δ 134.6 [CH, s], 130.9 [C, s], 129.3 [CH, s], 127.2 [CH, s], 157.9 [C, t, J_{CF} 8.3 Hz, C_β], 124.6 [C, t, J_{CF} 13.1 Hz, C_α], 108.2 [C, t, J_{CF} 271 Hz, CF_2], 29.7 [C, s, CMe_3], 27.4 [CH_3, s, $C(CH_3)_3$]. ^{1}H NMR: δ 7.7−7.4 (m), 1.1 [s, 9H]. IR: ν_{max}/cm^{-1} 1729 (C═C str.), 1261, 1149 (C−F str.).

X-ray Crystallography. Single crystals of compounds **2**, **3**, **6**, **12**, and **13** were obtained by slow evaporation of the solvents from dichloromethane/hexane solutions. Diffraction data were recorded on a Nonius κ-CCD 4-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collections were performed at 150(2) K in all cases. The data for all structures were solved by direct methods and subjected to full-matrix least-squares refinement on F^2 using the SHELX-97[28] program. Structures were corrected for absorption by the multiscan method using the SORTAV program. All non-hydrogen atoms were refined with anisotropic thermal parameters. For compounds **2**−**5** the aromatic hydrogen atoms were included in idealized positions and refined isotropically, while in all other cases hydrogen atoms were located. Data collection and refinement parameters are summarized in Table 5. Molecular representations shown in the figures were generated using ORTEP 3 for Windows.[29]

Ab Initio Calculations. Calculations were performed with the Gaussian 98 package, Revision A.7,[30] running on a Sun Enterprise HPC 4500 workstation. Geometries were optimized at the B3LYP/6-311+G* level and characterized as minima by frequency calculations. Thermally corrected free energies were calculated at 298 K and used comparatively without further scaling.

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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, and bond angles and an X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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