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Pentafluoropropenyl Complexes of Mercury, Germanium, Tin, and Lead Derived from (*Z*)-$CFH{=}CFCF_3$ and Their Use as Transfer Reagents

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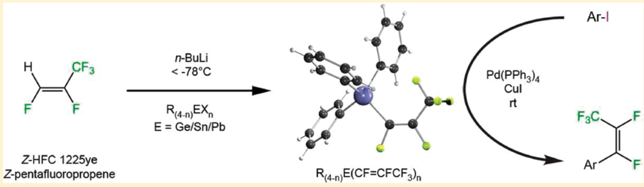
Supporting Information

ABSTRACT: A series of new (*E*)-pentafluoropropenyl complexes of Hg, Ge, Sn, and Pb are reported derived from $CFH{=}CFCF_3$ ((*Z*)-HFC-1225ye). Unequivocal assignment of the geometry of the products was achieved via a multinuclear (^1H, ^{13}C, ^{19}F, ^{119}Sn, and ^{199}Hg) NMR study. These conclusions are confirmed in the single-crystal X-ray structures of $Ph_3Ge(CF{=}CFCF_3)$ and $Ph_3Sn(CF{=}CFCF_3)$. In the solid-state structures of both molecules, short contacts are observed between one of the fluorine atoms of the CF_3 group and the metal center. The $Bu_3Sn(CF{=}CFCF_3)$ compound acts as an effective source of the pentafluoropropenyl group in a series of palladium-catalyzed Stille–Liebeskind reactions to generate new aryl–pentafluoropropenyl systems.



■ INTRODUCTION

Main-group organometallic complexes find a wide range of applications, one of which is in synthetic chemistry as transfer reagents, under either stoichiometric or catalytic conditions.[1] While there are a large number of organometallic complexes bearing hydrocarbon fragments, with the exception of Me_3SiCF_3 (Ruppert's reagent), which is used as a nucleophilic source of CF_3,[2] there are relatively few examples of this type of chemistry involving fluorocarbon organometallic systems. This is unfortunate, since they are, in comparison with their lithium or Grignard equivalents, often significantly more stable and so can be used for the site-specific introduction of fluorine and fluorinated groups, which is highly sought after in the pharmaceuticals, agrochemicals, and materials areas in order to prepare compounds with novel properties and modes of action.[3] There has been a considerable recent increase in activity in the organometallic chemistry of fluorinated substrates, with much of this centered on the CF_3 group;[4] however, from a materials standpoint unsaturated systems are often preferred, either as precursors for polymerizations[5] or in electronics materials.[6] A case in point is the perfluoropropenyl system, for which few organometallic complexes are known, which is in stark contrast with the fact that over 4800 compounds containing that group are described in patents with applications ranging from herbicides and fungicides to liquid crystals, electrooptical, and battery membanes.[7] There is therefore a need for reagents to introduce this group.

Initially, pentafluoropropenyl systems were prepared by the reaction of hexafluoropropene with an organolithium reagent;[8] however, these routes have been reported to result in explosions.[9] In 1971 the dehydrofluorination of 1,1,1,2,3,3-hexafluoropropane was described as giving a 1:1 mixture of (*Z*)- and (*E*)-1*H*-pentafluoropropenes, from which pentafluoropropenyllithium was generated by reaction with butyllithium.[10] However, when the lithium reagent was utilized in synthesis, such as in the reaction with Me_3SiCl, the product was determined to be the *Z* derivative, from which it was suggested that an *E* to *Z* isomerization of the lithium reagent occurred in solution at low temperature. Subsequent studies by Hahnfeld and Burton were unable to repeat these observations, finding instead that a mixture of (*E*)- and (*Z*)-fluoropropenes resulted in (*E*)- and (*Z*)-perfluoropropenyl-containing products in similar proportions.[11]

The trimethylsilyl (*E*)- and (*Z*)-$CF{=}CF(CF_3)$ derivatives have also been obtained from the reaction of bis(trimethylsilyl)mercury with pentafluoropropene[12] and by the electrochemical silylation of perfluoropropene in the presence of Me_3SiCl.[13] There are, however, no reports of germanium- or lead-containing compounds, while for tin just $Bu_3Sn(CF{=}CFCF_3)$ has been described before, obtained either by transmetalation from the zinc or cadmium analogues[14] or by Barbier-type coupling of Bu_3SnCl and (*Z*)-CF_3CFCFI in the presence of Zn or Cd metals.[15]

Transition-metal pentafluoropropenyl complexes have been known since the work of Stone et al. in the early 1960s, initially formed by the reaction of carbonylate anions with perfluoroacyl halides to form metal carbonyl perfluoroacyl derivatives that decarbonylated on heating.[16] More recently, rhodium perfluoropropenyl complexes, obtained by the C–F activation of hexafluoropropene, have been used to catalytically prepare $R_3SiCH_2CH_2CF_3$ from CF_2CFCF_3.[17]

In an extension of earlier work based on the two-step dehydrofluorination of 1*H*,1*H*-hydrofluorocarbons, CH_2FCF_2X (X = F, Cl),[18] a series of perfluoroalkenyl zinc complexes of the type (*E*)-$R_fCF{=}CFZnI$ have been prepared from the reaction of longer chain $R_fCF_2CFH_2$ fluoroalkanes with LDA and $ZnCl_2$.[19]

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Table 1. Selected Spectroscopic Data for (*E*)-Pentafluoropropenyl Systems

	$\delta_F(CF_3)$ ($\lvert J_{FF}\rvert$/Hz) [$\lvert J_{EF}\rvert$/Hz]	$\delta_F(CF_{gem})$ ($\lvert J_{FF}\rvert$/Hz) [$\lvert J_{EF}\rvert$/Hz]	$\delta_F(CF_{trans})$ ($\lvert J_{FF}\rvert$/Hz) [$\lvert J_{EF}\rvert$/Hz]	δ_E
$Hg(CF{=}CFCF_3)_2$ (**2**)	−69.5 (dd, 15.2, 9.0) [17.8][a]	−130.4 (m) [862.2][a]	−141.3 (dq, 15.0, 1.74) [276.2][a]	−1145.7
$PhHg(CF{=}CFCF_3)$ (**3**)	−68.8 (dd, 15.7, 8.9) [45.3][a]	−129.6 (qd, 8.9, 1.7) [650.9][a]	−144.2 (qd, 15.7, 1.8) [170.1][a]	*d*
$Ph_3Sn(CF{=}CFCF_3)$ (**4**)	−67.99 (dd, 14.3, 6.1)	−131.6 (dd, 6.3, 3.9) [207.2][b]	−138.7 (qd, 14.5, 3.9)	−148.9
$Ph_2Sn(CF{=}CFCF_3)_2$ (**5**)	−68.6 (ddd, 14.5, 5.4, 2.6)	−133.7 (m) [242.3][b]	−136.7 (qd, 14.7, 3.1)	
$PhSn(CF{=}CFCF_3)_3$ (**6**)	−69.4 (ddt, 14.3, 4.9, 2.4)	−136.4 (m) [286.8][b]	−134.4 (qd, 14.7, 3.1)	
$Sn(CF{=}CFCF_3)_4$ (**7**)	−69.6 (d, 14.2)	−139.4 (m) [369.4][b]	−131.5 (qd, 14.3, 3.1)	
$Bu_3Sn(CF{=}CFCF_3)$ (**8**)	−68.7 (dd, 14.8, 6.6)	−132.2 (qd, 6.5, 3.2) [147.0][b]	−142.5 (qd, 14.9, 3.2) [15.1][b]	−25.1
$Bu_2Sn(CF{=}CFCF_3)_2$ (**9**)	−69.2 (ddd, 14.7, 5.6, 2.2)	−134.0 (m) [189.4][b]	−139.2 (14.6, 3.4)	−78.4
$Ph_3Ge(CF{=}CFCF_3)$ (**10**)	−67.3 (dd, 13.6, 5.9)	−130.4 (overlapping m, 6.2)	−139.0 (qd, 13.7, 6.8)	
$Ph_3Pb(CF{=}CFCF_3)$ (**11**)	−67.8 (dd, 14.6, 6.8) [21.5]	−123.7 (qd, 6.8, 3.5) [225.8][c]	−141.3 (qd, 14.5, 3.6) [41.2][c]	

[a] E = Hg. [b] E = Sn. [c] E = Pb. [d] Insufficiently soluble to obtain satisfactory data.

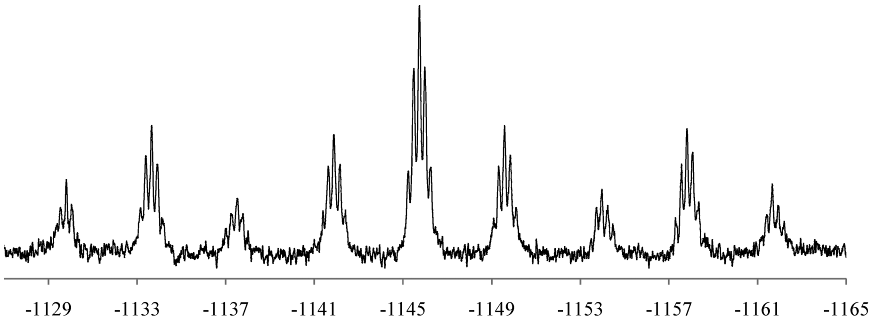


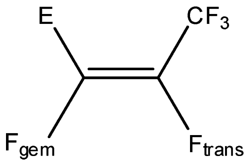
Figure 1. $^{199}Hg\{^1H\}$ NMR spectrum of $Hg((E)\text{-}CF{=}CFCF_3)_2$.

Subsequent cross-coupling with ArI under $Pd(PPh_3)_4$-catalyzed conditions were effective in generating 1-arylperfluoroprop-1-enes predominantly (87−90%) as the *Z* isomer. On the basis of our previous work involving the formation of group-14 trifluorovinyl compounds from available hydrofluorocarbon (HFC) sources[20] and the transfer of a fluorovinyl group from a tin center into organic substrates under palladium-catalyzed conditions[21] we were interested in extending this work to the pentafluoropropenyl system.

■ RESULTS AND DISCUSSION

Because of the potential to generate both (*E*)- and (*Z*)-pentafluoropropenyl isomers from other systems, as described above, our starting point for this work was (*Z*)-$CFH{=}CFCF_3$ ((*Z*)-HFC-1225ye). This compound can be successfully deprotonated by reaction with 1 equiv of butyllithium at −78 °C in diethyl ether solution to yield (*Z*)-$LiCF{=}CFCF_3$ (**1**). We have found **1** to be stable under these conditions for many hours; however, increasing the temperature results in a darkening of the solution, which ultimately results in the decomposition of **1** to generate lithium fluoride and a black solution. This decomposition is exothermic but so far has proven to be a nonviolent process. Reaction of **1** with a range of main-group electrophiles, $HgCl_2$, PhHgCl, Ph_3SnCl, Ph_2SnCl_2, $PhSnCl_3$, Bu_3SnCl, Bu_2SnCl_2, $SnCl_4$, Ph_3GeBr, and Ph_3PbCl, was undertaken, which resulted in the formation of the perfluoropropenyl-containing compounds **2**−**11** (Table 1) in good yields as air- and moisture-stable solids or liquids, which have been characterized by multinuclear (^1H, ^{13}C, ^{19}F, and ^{119}Sn or ^{199}Hg) NMR spectroscopy. While $Bu_3Sn(CF{=}CFCF_3)$ (**8**) has been prepared before, as described above, all other compounds are new. However, in the case of **8** there are apparent inconsistencies in the assignment of some of the spectroscopic data, which warranted further investigation.

The ^{19}F NMR spectra of all compounds displayed three signals consistent with an ABX_3 spin system in the relative intensity ratio 1:1:3, making assignment of the CF_3 signal (at ca. −69 ppm) trivial. The two CF signals exhibit a small mutual coupling of ca. 3 Hz, indicating that the C−F groups are cis to each other, and so confirming that the geometry of the perfluoropropenyl fragment is the same as that of the starting material and exclusively *E* isomer products are formed. Assignment of the two CF signals is less clear-cut; however, with the exception of compound **10**, the presence of satellites due to coupling to the low-abundance, spin-active metal centers (**2** and **3**, ^{199}Hg, $I = {}^1/_2$, 16.8%; **4**−**9**, ^{119}Sn, $I = {}^1/_2$, 8.59%; **11**, ^{207}Pb, $I = {}^1/_2$, 22.1%) may be used to aid assignment in comparison with previous work on the trifluorovinylmercury and -tin analogues by us[22] and others.[18] Thus, in $Hg(CF{=}CFCF_3)_2$ (**2**) coupling is observed between mercury and all three fluorine environments, resulting in the observation of a triplet of triplets of septets in the mercury NMR spectrum, as shown in Figure 1, with the magnitudes of the Hg−F coupling constants being 862.2, 276.6, and 17.8 Hz. On the basis of the assignment of the NMR data for the related compound $Hg(CF{=}CF_2)_2$ in which $^2J(HgF) = 814.3$ and $^3J(HgF) = 224.0$ Hz, we assign the fluorine resonance centered at −130.4 ppm, which exhibits the largest Hg−F coupling constant, as F_{gem} (geminal with respect to the metal) and therefore the signal at −141.3 arises from the fluorine nucleus trans to the metal center, F_{trans}.



The $^{13}C\{^{1}H\}$ NMR spectrum of **2** consists of three signals, a widely spaced quartet at 118.2 ppm ($^{1}J(CF)$ = 270.5 Hz) assigned to the CF_3 group, a doublet of quartets of doublets at 146.3 ppm ($^{1}J(CF)$ = 276.6 Hz, $^{2}J(CCF_3)$ = 35.6 Hz, $^{2}J(CCF)$ = 12.5 Hz) with attendant mercury satellites, $^{2}J(HgC)$ = 670.2 Hz, and a doublet of multiplets at 181.1 ppm ($^{1}J(CF)$ = 320.9 Hz) with ^{199}Hg satellites, $^{1}J(HgC)$ = 2132.8 Hz. The last of these signals is assigned to the carbon directly bound to the mercury center, on the basis of the large Hg−C carbon coupling constant. The $^{1}J(CF)$ coupling constant associated with that signal is also visible on the resonance at −130.4 ppm in the fluorine NMR spectrum, which provides additional confirmation of the assignment of the two CF signals. Unfortunately, the monosubstituted perfluoropropenyl derivative $PhHg(CF{=}CFCF_3)$ (**3**) was insufficiently soluble to obtain satisfactory ^{199}Hg NMR data; however, the ^{19}F NMR data could be assigned on the basis of the Hg−F coupling constants, and the identity of the compound was confirmed by elemental analysis data.

The spectra of the group 14 derivatives were assigned in a similar way, based on the magnitude of the tin coupling with both fluorine and carbon nuclei. For example, the $^{119}Sn\{^{1}H\}$ NMR spectrum of $Bu_3Sn(CF{=}CFCF_3)$ shows a doublet of doublets with SnF coupling constants of 147 and 15 Hz. The corresponding tin satellites are observed for the signals at −132 and −142 ppm, respectively, in the fluorine NMR spectrum. The signal at −132 ppm exhibits carbon satellites (J = 321 Hz), which corresponds to coupling observed on the signal at 162 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum ($J(CF)$ = 321 Hz and $J(SnC)$ = 208 Hz). On the basis of the magnitude of all these coupling constants, we assign these data to CF_{gem}. This is directly comparable to the data for the trifluorovinyl analogues, $R_3Sn(CF{=}CF_2)$ (R = Me, Ph, Bu), where F_{gem} is also found to resonate at lowest frequency and possess the larger Sn−F coupling constant: $^{2}J(SnF)$ = 134−164 Hz, cf. $^{3}J(SnF)$ = 22−28 Hz. We note that this assignment is also consistent with that previously reported for related organic systems containing the $CF{=}CF(CF_3)$ group[23] but differs in the assignment of F_{gem} and F_{trans} from that reported for $Bu_3Sn((E)\text{-}CF{=}CFCF_3)$ previously.[15]

Increasing the degree of substitution around the tin center results in fluorine NMR spectra of similar general appearance. Across the series of compounds $Ph_{4-n}Sn(CF{=}CFCF_3)_n$ (n = 1−4) and $Bu_{4-n}Sn(CF{=}CFCF_3)_n$ (n = 1, 2), they display a shift to lower frequency for the CF_3 and F_{gem} signals, and a concomitant increase in the frequency of the F_{trans} resonance, such that for compounds **6** and **7** the ordering of F_{gem} and F_{trans} is reversed. The magnitude of the $^{2}J(SnF)$ coupling constant also increases with n. Significantly, in the ^{19}F NMR spectra an additional small coupling is observed on the CF_3 signal, resulting in an additional doublet (J = 2.6 Hz) and triplet coupling (J = 2.4 Hz) being seen in the bis- and tris-substituted compounds. However, in the fully substituted tin compound **9** the anticipated quartet coupling cannot be fully resolved. These additional couplings are assigned to those between the CF_3 and F_{gem} nuclei of adjacent pentafluoropropenyl groups and could either arise through bonds, corresponding to $^{6}J(F_{gem}CF_3)$ or could be due to through-space coupling. We were able to obtain good-quality ^{119}Sn NMR data for compounds **4**, **8**, and **9**, all of which display a large Sn−F coupling of ca. 150−210 Hz to F_{gem} of the pentafluoropropenyl group, resulting in clearly recognizable patterns which confirmed the degree of substitution around the tin center.

The ^{19}F NMR spectra for the germane **10** and plumbane **11** were assigned in a similar fashion; for **11**, Pb−F coupling was observed on all signals, which aided in assignment, while the data for **10** were assigned in a consistent fashion. We did not attempt to obtain ^{209}Pb NMR data for **11**.

Crystallographic Results. By slow evaporation of a chloroform solution we were able to obtain single crystals of the phenyl derivatives **4** and **10**. Both compounds crystallize in the space group $P\overline{1}$, with two unique molecules in the unit cell of **4** and one in **10**. Selected X-ray-derived data for these compounds are given in Table 2, and their molecular structures are shown in Figures 2 and 3. Because of artifacts in the data set for **4**, the data were truncated at 95% of completeness; the level of precision in the parameters determined for the tin compound will therefore be lower than those of the germanium compound **10**. However, it is noteworthy that these constitute the first crystallographic studies of any main-group pentafluoropropenyl-containing compounds; indeed, only one σ-bound pentafluoropropenyl organometallic compound has been reported to date, namely $[(Et_3P)_3Rh(CF{=}CFCF_3)]$, which contains the Z isomer of the fluoroalkene.[17a]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Ph_3ECF{=}CFCF_3$ (E = Sn, 4; E = Ge, 10) with Estimated Standard Deviations in Parentheses

$Ph_3SnCF{=}CFCF_3$ (**4**)				$Ph_3GeCF{=}CFCF_3$ (**10**)	
molecule 1		molecule 2			
E−C1	2.177(12)	E2−C22	2.183(12)	E−C1	1.993(5)
E−C4	2.127(13)	E2−C25	2.113(12)	E−C4	1.933(5)
E−C10	2.128(12)	E2−C31	2.099(14)	E−C10	1.940(5)
E−C16	2.132(12)	E2−C37	2.110(12)	E−C16	1.950(5)
C1−C2	1.313(19)	C22−C23	1.316(17)	C1−C2	1.321(8)
C2−C3	1.43(2)	C23−C24	1.498(19)	C2−C3	1.488(8)
C1−F1	1.402(14)	C22−F6	1.355(13)	C1−F1	1.357(6)
C2−F2	1.384(16)	C23−F7	1.375(15)	C2−F2	1.355(7)
C3−F3	1.321(17)	C24−F8	1.319(17)	C3−F3	1.332(7)
C3−F4	1.337(16)	C24−F9	1.338(17)	C3−F4	1.337(8)
C3−F5	1.333(17)	C24−F10	1.312(17)	C3−F5	1.334(6)
C1−E−C4	104.8(5)	C22−E2−C25	104.2(4)	C1−E−C4	109.1(2)
C4−E−C10	107.7(4)	C22−E2−C31	107.6(5)	C4−E−C10	104.4(2)
C10−E−C16	112.5(5)	C31−E2−C37	115.2(5)	C10−E−C16	110.9(2)
C16−E−C1	111.1(5)	C37−E2−C22	113.5(4)	C16−E−C1	112.7(2)
E−C1−C2	134.8(10)	E2−C22−C23	132.2(9)	E−C1−C2	132.2(4)
C1−C2−F2	121.0(12)	C22−C23−F7	121.1(11)	C1−C2−F2	120.6(5)
F1−C1−C2	115.5(11)	F6−C22−C23	115.8(10)	F1−C1−C2	115.1(5)
C1−C2−C3	126.8(13)	C22−C23−C24	129.9(12)	C1−C2−C3	129.0(5)

In both cases the anticipated pseudotetrahedral geometry about the group 14 atom was observed, and the E geometric assignment of the pentafluoropropenyl group, made on the basis of the NMR data, is confirmed. The internal geometries of the pentafluoropropenyl group are largely as anticipated, the

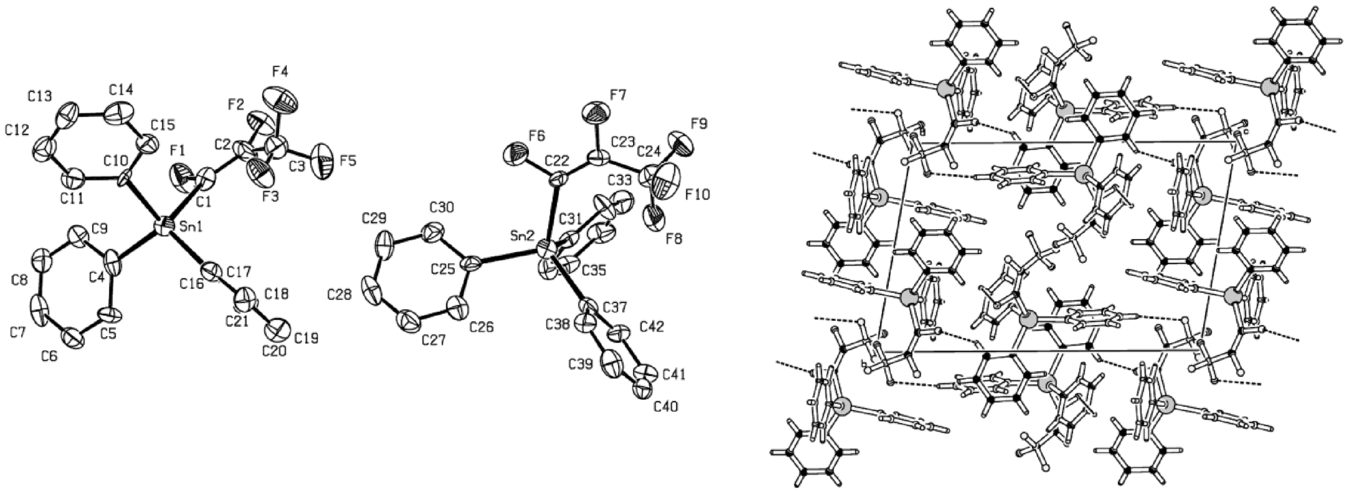


Figure 2. View of the molecular structure and packing (viewed down the *a* axis) of $Ph_3SnCF{=}CFCF_3$ (**4**), with thermal ellipsoids set at the 50% probability level.

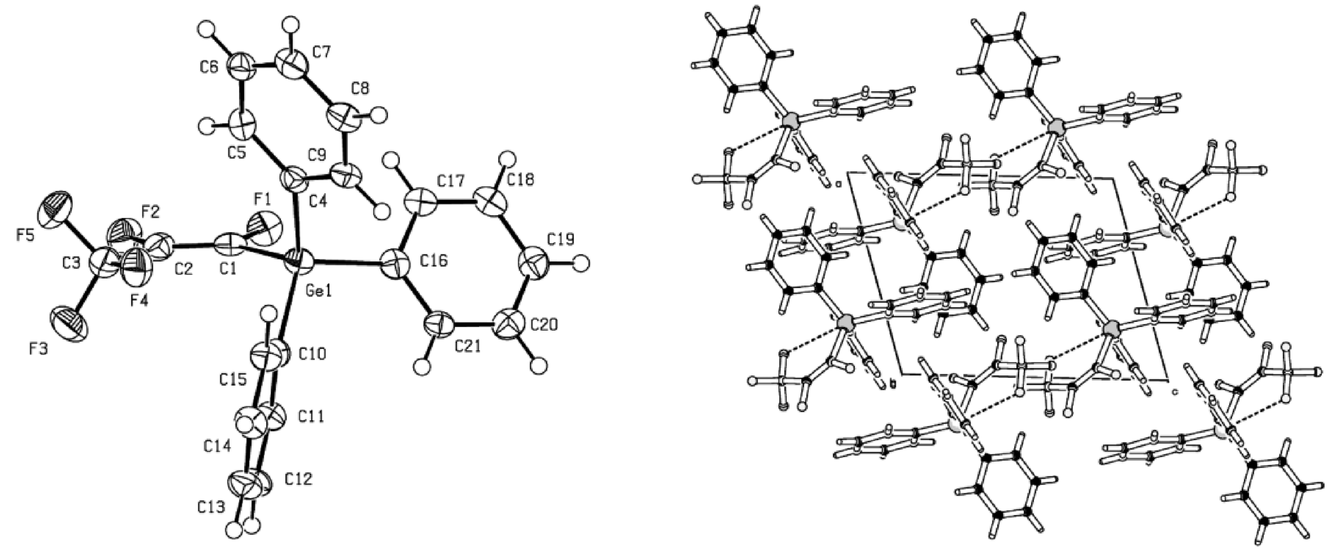


Figure 3. View of the molecular structure and packing (viewed down the *b* axis) of $Ph_3GeCF{=}CFCF_3$ (**10**), with thermal ellipsoids set at the 50% probability level.

C=C and $C-CF_3$ distances being typical of $C(sp^2){=}C(sp^2)$ (ca. 1.32 Å) and $C(sp^3)-F$ (1.322 Å), respectively,[24] and are comparable with those previously reported for the rhodium complex,[16] $CF_2{=}CF(CF_3)$,[25] and pentafluoropropenyl derivatives of uracil.[26]

Interestingly, both **4** and **10** exhibit short intramolecular contacts between one of the fluorines of the CF_3 group and the group 14 element. In each case the trifluoromethyl group is oriented such that one fluorine points directly toward the metal center; in **10** the Ge···F(4) distance of 3.073(3) Å is 0.37 Å less than the sum of the relevant van der Waals radii, while in the two molecules of **4** distances of Sn(1)···F(3) = 3.122(7) Å and Sn(2)···F(8) = 3.154(7) Å are observed, which are ca. 0.5 Å less than the sum of the van der Waals radii.

The packing diagrams of both **4** and **10** show that the fluorinated parts of the molecules tend to aggregate to form fluorous domains. In the germanium compound **10**, stacks of molecules aligned in the *c* direction are linked by intermolecular nonclassical hydrogen bonds which are formed between F(2) and two neighboring aryl C−H bonds (d(F(2)···H(5)) = 2.454 Å, d(F(2)···H20) = 2.545 Å). By comparison, in the solid-state structure of compound **4** there are no particularly short interactions or intermolecular hydrogen bonds formed, although the F(6)−H(9) distance is just less than the sum of the relevant van der Waals radii.

Chemistry of the Pentafluoropropenyl Stannanes.

Previously we have shown that derivatization of trifluorovinylsilanes and -germanes can be undertaken. For example, reaction of $R_3Ge(CF{=}CF_2)$ with alkyllithium reagents resulted in an addition−elimination reaction and formation of the corresponding $R_3Ge(XCF{=}CFR')$ compound, and a similar reaction with $LiAlH_4$ produces $R_3Ge(XCF{=}CFH)$. In both cases the predominant isomer formed was that in which the fluorine trans to the metal center was replaced.[20] However, for the trifluorovinylstannanes the $Sn-R_f$ bond is replaced under these conditions. Investigation of the pentafluoropropenyl systems under similar conditions indicated a similar reactivity trend: for example, reaction of $Ph_3Sn(CF{=}CFCF_3)$ with PhLi resulted in Ph_4Sn as the only detectable metal-containing compound. However, heating $Ph_3Sn(CF{=}CFCF_3)$ resulted in a redistribution reaction and the formation of Ph_4Sn and $Ph_2Sn(CF{=}CFCF_3)_2$.

Significantly, the tin compounds could be used as transfer reagents, in a fashion similar to that shown before for the trifluorovinyl analogues.[21] We therefore investigated the transfer of the pentafluoropropenyl fragment from some of the stannane systems to aryl substrates under Stille–Liebeskind conditions[27] (Table 3 and Scheme 1). Thus, when $Bu_3Sn(CF{=}CFCF_3)$ is reacted with iodobenzene in the presence of CuI and $Pd(PPh_3)_4$ at room temperature, the three fluorine NMR signals due to $Bu_3Sn(CF{=}CFCF_3)$ are replaced with resonances at −65.6, −109.1, and −155.6 ppm, which are characteristic of (*Z*)-$PhCF{=}CFCF_3$, which has been reported previously.[9] Similarly, in the proton NMR spectrum, new signals are observed at 7.56, 7.38, and 7.45 ppm corresponding to the product, along with signals for the ortho, meta, and para protons of PhI (at 7.63, 7.03, and 7.26 ppm). The relative intensities of these signals were used to determine the conversion of PhI to (*Z*)-$PhCF{=}CFCF_3$, which was estimated to be 27%. Use of the triphenyl analogue instead was found to be even less effective: for example, the reaction of iodobenzene with $Ph_3Sn(CF{=}CFCF_3)$ resulted in a conversion of just 10% (entry 2). We also investigated the use of the bis-substituted derivatives in order to determine whether more than one group could be transferred to a suitable substrate. On the basis of NMR data it was found that 1 equiv of $Bu_2Sn(CF{=}CFCF_3)_2$ was effective in transferring more than 1 equiv of the pentafluoropropenyl group, but it was not clear if this arose sequentially or whether a redistribution reaction was also occurring.

Table 3. **Stille–Liebeskind Coupling of Some Aryl Iodides with Pentafluoropropenyl–Tin Systems**[a]

entry	substrate	stannane	product (NMR conversn, %)
1	PhI	$Bu_3Sn(CF{=}CFCF_3)$	$Ph(CF{=}CFCF_3)$ (27)
2	PhI	$Ph_3Sn(CF{=}CFCF_3)$	$Ph(CF{=}CFCF_3)$ (10)
3	PhI	$Bu_2Sn(CF{=}CFCF_3)_2$	$Ph(CF{=}CFCF_3)$
4	*p*-$NO_2C_6H_4I$	$Bu_3Sn(CF{=}CFCF_3)$	*p*-$NO_2C_6H_4(CF{=}CFCF_3)$ (86)
5	*p*-$CH_3C_6H_4I$	$Bu_3Sn(CF{=}CFCF_3)$	*p*-$CH_3C_6H_4(CF{=}CFCF_3)$ (83)
6	*p*-$CH_3OC_6H_4I$	$Bu_3Sn(CF{=}CFCF_3)$	*p*-$CH_3OC_6H_4(CF{=}CFCF_3)$ (>97)
7	$PhCH_2Br$	$Bu_3Sn(CF{=}CFCF_3)$	$PhCH_2(CF{=}CFCF_3)$ (42)
8	(*p*−I-$C_6H_4OCH_2)_2$	$Bu_3Sn(CF{=}CFCF_3)$	$(CH_2OC_6H_4(CF{=}CFCF_3)_2$ (>97)

[a] Reactions carried out in THF solvent at room temperature.

However, while the transfer reactions to phenyl iodide were relatively poorly yielding, we were much more successful with other substituted aryl electrophiles, as given in Table 3. There appears to be little difference in the ultimate conversion of aromatic iodides with either activating or deactivating substituents, with the most successful outcomes being observed for the methoxy-substituted system and bis-ether, entries 6 and 8, for which effectively complete conversion was observed. Workup of the reaction mixtures was undertaken either by vacuum distillation, in the case of *p*-$CH_3C_6H_4(CF{=}CFCF_3)$, or by column chromatography for $CH_2OC_6H_4(CF{=}CFCF_3)_2$; in both cases the isolated yields were ca. 50% (see the Experimental Section). While some of the organic products have been reported before,[9] a number are new. For example, $PhCH_2((E)\text{-}CF{=}CFCF_3)$ has been prepared from the Cu(I) salt obtained by methathesis with Cd or Zn pentafluoropropenyl reagent,[28] but the *Z* analogue reported here is new. However, the bis-substituted compound (entry 8) was chosen because it is an analogue of a number of existing trifluorovinyl compounds used in battery membranes and liquid crystal mixtures.[29]

■ CONCLUSIONS

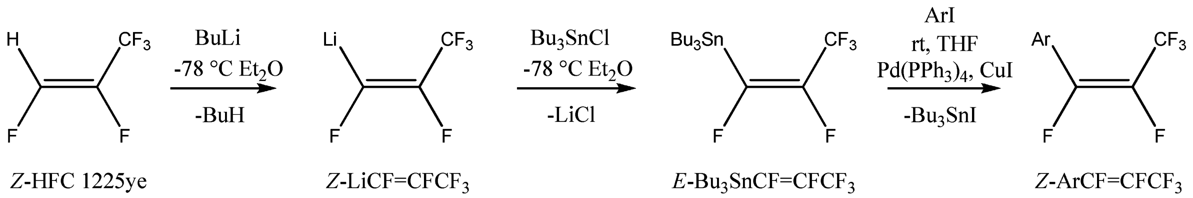
A series of organometallic pentafluoropropenyl derivatives are reported of mercury and the metallic elements of group 14. The crystal structures of two of these compounds, $Ph_3Ge(CF{=}CFCF_3)$ and $Ph_3Sn(CF{=}CFCF_3)$, and multinuclear NMR studies are described which confirm the stereochemistry within the fluorocarbon fragment as being exclusively *E* geometry. The stannane derivatives have been investigated as transfer reagents for the pentafluoropropenyl group under Stille–Liebeskind catalytic conditions. $Bu_3Sn(CF{=}CFCF_3)$ proved to be the most effective of the transfer reagents, and using this we were able to prepare a number of (*Z*)-pentafluoropropenyl–aryl systems in high conversions and with good stereocontrol under mild conditions.

■ EXPERIMENTAL SECTION

Caution! Mercury-containing compounds are potentially highly toxic materials. All reactions and handling should be carried out in a well-ventilated hood or glovebox or using vacuum-line manipulation.

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, U.K.). Diethyl ether, hexane, and THF were dried over sodium wire for ca. 1 day prior to use. All compounds were purchased from commercial suppliers and used without further purification, except for $Pd(PPh_3)_4$, which was prepared prior to use.[30] The compound (*Z*)-$CF_3CF{=}CFH$ was donated by INEOS Fluor. NMR spectra were recorded of $CDCl_3$ solutions on Bruker Avance III (^1H at 400.40 MHz and ^{13}C at 100.555 MHz, referenced to external $SiMe_4$; ^{19}F at 188.310 MHz, referenced to external $CFCl_3$) or Varian INOVA (^{119}Sn at 149.160 MHz, ^{199}Hg at 100.580 MHz, using $HgCl_2$ in DMSO as a secondary reference) spectrometers. All resonances are reported using the high frequency positive convention. Elemental analyses were performed by the School's microanalytical service.

Scheme 1



Z-HFC 1225ye

Z-$LiCF{=}CFCF_3$
1

E-$Bu_3SnCF{=}CFCF_3$
8

Z-$ArCF{=}CFCF_3$

Preparation of Hg(CF=CFCF$_3$)$_2$. In a three-necked round-bottom flask under a positive pressure of nitrogen cooled to −80 °C were added diethyl ether (200 cm^3) and (*Z*)-HFC-1225ye (1 cm^3, 0.01 mol). *n*-BuLi (2.5 M, 3.5 cm^3, 0.009 mol) was added slowly to maintain the temperature at least below −78 °C. The solution was stirred for 90 min to ensure complete deprotonation and formation of pentafluoropropenyllithium (**1**). HgCl$_2$ (0.583 g, 0.002 mol) in diethyl ether (100 cm^3) was added slowly, with the temperature maintained below −78 °C, and the mixture stirred and warmed to room temperature overnight. Hexane (250 cm^3) was added and the solution filtered through Celite. The solvents were removed using a rotary evaporator to afford a light yellow liquid which was purified using column chromatography on silica with 1/1 dichloromethane/hexane eluent to give a yellow liquid. Yield: 0.68 g, 68%. δ_F: −69.5 (dd, $^3J(\mathrm{CF_3F_{trans}}) = 15.2$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 9.0$ Hz), −130.4 (m, $^2J(\mathrm{HgF_{gem}}) = 862.2$ Hz), −141.3 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 15.0$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 1.7$ Hz, $^3J(\mathrm{HgF_{trans}}) = 276.2$ Hz). δ_C: 181.1 (dm, $^1J(\mathrm{C_{gem}F_{gem}}) = 320.9$ Hz, C$_{gem}$), 146.3 (dqd, $^1J(\mathrm{C_{trans}F_{trans}}) = 276.6$ Hz, $^2J(\mathrm{C_{trans}CF_3}) = 35.6$ Hz, $^2J(\mathrm{C_{trans}F_{gem}}) = 12.5$ Hz, C$_{trans}$), 118.2 (qdd, $^1J(\mathrm{CF_3}) = 270.5$ Hz, $^2J(\mathrm{CF_3F_{trans}}) = 36.5$ Hz, $^3J(\mathrm{CF_3F_{gem}}) = 11.1$ Hz, CF$_3$). δ_{Hg}: −1145.7 (ttsept, $^2J(\mathrm{HgF_{gem}}) = 864.1$ Hz, $^3J(\mathrm{HgF_{trans}}) = 275.9$ Hz, $^4J(\mathrm{HgCF_3}) = 17.8$ Hz).

Preparation of PhHg(CF=CFCF$_3$). (*Z*)-HFC-1225ye (0.5 cm^3, 0.005 mol), *n*-BuLi (2.5 M, 2.0 cm^3, 0.005 mol), and PhHgCl (0.795 g, 0.0025 mol) resulted in an off-white waxy solid. Yield: 0.55 g, 54%. Anal. Calcd for C$_9$H$_5$F$_5$Hg: C, 26.43; H, 1.23. Found: C, 26.78; H, 2.01. δ_F: −68.8 (dd, $^3J(\mathrm{CF_3F_{trans}}) = 15.7$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 8.9$ Hz, $^4J(\mathrm{HgCF_3}) = 45.3$ Hz), −129.6 (qd, $^4J(\mathrm{F_{gem}CF_3}) = 8.9$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 1.7$ Hz, $^2J(\mathrm{HgF_{gem}}) = 650.9$ Hz), −144.2 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 15.7$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 1.8$ Hz, $^3J(\mathrm{HgF_{trans}}) = 170.1$ Hz). δ_H: 7.0−7.5 (m, C$_6$H$_5$). δ_C: 127−137 (m, C$_6$H$_5$).

Preparation of Ph$_3$Sn(CF=CFCF$_3$). Using a similar method, (*Z*)-HFC-1225ye (4 cm^3, 0.04 mol) and *n*-BuLi (2.5 M, 16 cm^3, 0.04 mol) in diethyl ether (400 cm^3) followed by addition of Ph$_3$SnCl (13.36 g, 0.035 mol) dissolved in diethyl ether (100 cm^3) resulted in 13.86 g (82%) of the pure product as a light yellow crystalline solid. Mp: 63 °C. Anal. Calcd for C$_{21}$H$_{15}$F$_5$Sn: C, 52.41; H, 3.14. Found: C, 52.54; H, 3.14. δ_F: −67.99 (dd, $^3J(\mathrm{CF_3F_{trans}}) = 14.3$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 6.1$ Hz), −131.60 (qd, $^4J(\mathrm{F_{gem}CF_3}) = 6.3$ Hz, $^3J(\mathrm{F_{gem}F_{trans}}) = 3.9$ Hz, $^2J(\mathrm{SnF_{gem}}) = 207.2$ Hz), −138.65 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 14.5$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 3.9$ Hz). δ_H: 7.2−7.6 (m, C$_6$H$_5$). δ_C: 160.8 (dqd, $^1J(\mathrm{C_{gem}F_{gem}}) = 320$ Hz, $^3J(\mathrm{C_{gem}CF_3}) = 7.25$ Hz, $^2J(\mathrm{C_{gem}F_{trans}}) = 4.83$ Hz, $^1J(\mathrm{C_{gem}Sn}) = 386$ Hz, C$_{gem}$), 146.5 (dqd, $^1J(\mathrm{C_{trans}F_{trans}}) = 278.3$ Hz, $^2J(\mathrm{C_{trans}CF_3}) = 38.3$ Hz, $^2J(\mathrm{C_{trans}F_{gem}}) = 14.7$ Hz, C$_{trans}$), 119.9 (qdd, $^1J(\mathrm{CF_3}) = 271$ Hz, $^2J(\mathrm{CF_3F_{trans}}) = 37.1$ Hz, $^3J(\mathrm{CF_3F_{gem}}) = 11.5$ Hz, CF$_3$), 135.2 (s, $^1J(\mathrm{SnC}) = 295$ Hz, C1), 129.4 (s, $^2J(\mathrm{SnC}) = 58.5$ Hz, C2), 137.1 (s, $^3J(\mathrm{SnC}) = 42.0$ Hz, C3), 130.4 (s, $^4J(\mathrm{SnC}) = 12.8$ Hz, C4). δ_{Sn}: −148.9 (ddq $^2J(\mathrm{SnF_{gem}}) = 211.4$ Hz, $^3J(\mathrm{SnF_{trans}}) = 7.6$ Hz, $^4J(\mathrm{SnCF_3}) = 2.5$ Hz).

Preparation of Ph$_2$Sn(CF=CFCF$_3$)$_2$. In a similar fashion, (*Z*)-HFC-1225ye (1.5 cm^3, 0.015 mol) and *n*-BuLi (2.5 M, 4 cm^3, 0.010 mol) were reacted with Ph$_2$SnCl$_2$ (1.044 g, 0.003 mol) to afford a white pastelike solid after workup. Yield: 0.87 g, 54%. δ_F: −68.6 (ddd, $^3J(\mathrm{CF_3F_{trans}}) = 14.5$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 5.4$ Hz, $^6J(\mathrm{CF_3F_{gem}}) = 2.6$ Hz), −133.7 (m, $^2J(\mathrm{SnF_{gem}}) = 242.3$ Hz), −136.7 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 14.7$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 3.1$ Hz). δ_H: 7.3−7.4 (m, C$_6$H$_5$). δ_C: 156.4 (d $^1J(\mathrm{C_{gem}F_{gem}}) = 317$ Hz, C$_{gem}$), 145 (d, $^1J(\mathrm{C_{trans}F_{trans}}) = 281.0$ Hz, C$_{trans}$), 118.0 (qdd, $^1J(\mathrm{CF_3}) = 270.6$ Hz, $^2J(\mathrm{CF_3F_{trans}}) = 36.5$ Hz, $^3J(\mathrm{CF_3F_{gem}}) = 10.6$ Hz, CF$_3$), 130.8 (s, C1), 129.5 (s, $^2J(\mathrm{SnC}) = 68.3$ Hz, C2), 135.2 (s, $^3J(\mathrm{SnC}) = 48.1$ Hz, C3), 130.0 (s, $^4J(\mathrm{SnC}) = 14.6$ Hz, C4).

Preparation of PhSn(CF=CFCF$_3$)$_3$. (*Z*)-HFC-1225ye (1.5 cm^3, 0.015 mol) and *n*-BuLi (2.5 M, 4 cm^3, 0.010 mol) were reacted with PhSnCl$_3$ (0.27 cm^3, 0.0016 mol), to give a yellow oil after workup. Yield: 0.209 g, 42%. δ_F: −69.4 (ddt, $^3J(\mathrm{CF_3F_{trans}}) = 14.3$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 4.9$ Hz, $^6J(\mathrm{CF_3F_{gem}}) = 2.4$ Hz), −136.4 (m, $^2J(\mathrm{SnF_{gem}}) = 286.8$ Hz), −134.4 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 14.7$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 3.1$ Hz). δ_H: 7.1−7.5 (m, C$_6$H$_5$).

Preparation of Sn(CF=CFCF$_3$)$_4$. (*Z*)-HFC-1225ye (4 cm^3, 0.04 mol), *n*-BuLi (2.5 M, 12 cm^3, 0.03 mol), and SnCl$_4$ (0.2 cm^3, 0.0017 mol) resulted in a yellow oil after workup. Yield: 0.16 g, 15%. δ_F: −69.6 (d, $^3J(\mathrm{CF_3F_{trans}}) = 14.2$ Hz), −139.4 (m, $^2J(\mathrm{SnF_{gem}}) = 369.4$ Hz), −131.5 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 14.3$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 3.1$ Hz).

Preparation of *n*-Bu$_3$Sn(CF=CFCF$_3$). (*Z*)-HFC-1225ye (4.5 cm^3, 0.045 mol), *n*-BuLi (2.5 M, 16 cm^3, 0.04 mol), and *n*-Bu$_3$SnCl (9.50 cm^3, 0.035 mol) gave a light yellow oil after workup. Yield: 13.45 g, 91%. Anal. Calcd for C$_{15}$H$_{27}$F$_5$Sn: C, 42.76; H, 6.46. Found: C, 42.72; H, 6.43. δ_F: −68.74 (dd, $^3J(\mathrm{CF_3F_{trans}}) = 14.8$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 6.6$ Hz), −132.2 (qd, $^4J(\mathrm{F_{gem}CF_3}) = 6.5$ Hz, $^3J(\mathrm{F_{gem}F_{trans}}) = 3.2$ Hz, $^2J(\mathrm{SnF_{gem}}) = 147$ Hz), −142.5 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 14.9$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 3.2$ Hz, $^3J(\mathrm{SnF_{trans}}) = 15.1$ Hz). δ_H: 0.84 (t, $^1J(\mathrm{HH}) = 7.29$, CH$_3$), 1.06 (m, CH$_2$), 1.26 (m, CH$_2$), 1.46 (m, CH$_2$). δ_C: 162.2 (dqd, $^1J(\mathrm{C_{gem}F_{gem}}) = 321.0$ Hz, $^3J(\mathrm{C_{gem}CF_3})/^2J(\mathrm{C_{gem}F_{trans}})$ = overlapping 7.6 Hz, $^1J(\mathrm{C_{gem}Sn}) = 208$ Hz, C$_{gem}$), 144.0 (dqd $^1J(\mathrm{C_{trans}F_{trans}}) = 276$ Hz, $^2J(\mathrm{C_{trans}CF_3}) = 37.9$ Hz, $^2J(\mathrm{C_{trans}F_{gem}}) = 16$ Hz, C$_{trans}$), 120.0 (qdd $^1J(\mathrm{CF_3}) = 270$ Hz, $^2J(\mathrm{CF_3F_{trans}}) = 37.7$ Hz, $^3J(\mathrm{CF_3F_{gem}}) = 12$ Hz, CF$_3$), 10.7 (s, $^1J(\mathrm{SnC}) = 355.4$ Hz, C1), 26.9 (s, $^2J(\mathrm{SnC}) = 62.3$ Hz, C2), 28.4 (s, $^3J(\mathrm{SnC}) = 21.3$ Hz, C3), 13.0 (s, CH$_3$). δ_{Sn}: −25.1 (dd, $^2J(\mathrm{SnF_{gem}}) = 152.1$ Hz, $^3J(\mathrm{SnF_{trans}}) = 14.9$ Hz).

Preparation of *n*-Bu$_2$Sn(CF=CFCF$_3$)$_2$. Reaction of (*Z*)-HFC-1225ye (2.0 cm^3, 0.02 mol), *n*-BuLi (2.5 M, 6 cm^3, 0.015 mol), and *n*-Bu$_2$SnCl$_2$ (1.507 g, 0.005 mol) produced a light yellow liquid after workup. Anal. Calcd for C$_{14}$H$_{18}$F$_{10}$Sn: C, 33.95; H, 3.67. Found: C, 34.45; H, 3.46. δ_F: −69.2 (ddd, $^3J(\mathrm{CF_3F_{trans}}) = 14.7$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 5.6$ Hz, $^6J(\mathrm{CF_3F_{gem}}) = 2.2$ Hz), −134.0 (m, $^2J(\mathrm{SnF_{gem}}) = 189.4$ Hz), −139.2 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 14.6$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 3.4$ Hz). δ_H: 0.85 (t, $^1J(\mathrm{HH}) = 7.36$, CH$_3$), 1.29 (m, CH$_2$), 1.38 (m, CH$_2$), 1.52 (m, CH$_2$). δ_C: 158.3 (dm $^1J(\mathrm{C_{gem}F_{gem}}) = 319.9$ Hz, $^1J(\mathrm{C_{gem}Sn}) = 338$ Hz, C$_{gem}$), 144.8 (dqd $^1J(\mathrm{C_{trans}F_{trans}}) = 278.4$ Hz, $^2J(\mathrm{C_{trans}CF_3}) = 37.5$ Hz, $^2J(\mathrm{C_{trans}F_{gem}}) = 14.6$ Hz, C$_{trans}$), 119.1 (qdd $^1J(\mathrm{CF_3}) = 270.3$ Hz, $^2J(\mathrm{CF_3F_{trans}}) = 36.9$ Hz, $^3J(\mathrm{CF_3F_{gem}}) = 11.3$ Hz, CF$_3$), 12.7 (s, $^1J(\mathrm{SnC}) = 423$ Hz, C1), 26.1 (s, $^2J(\mathrm{SnC}) = 76.7$ Hz, C2), 27.2 (s, $^3J(\mathrm{SnC}) = 25.7$ Hz, C3), 12.1 (s, CH$_3$). δ_{Sn}: −78.4(t, $J(\mathrm{SnF}) = 192.8$ Hz).

Preparation of Ph$_3$Ge(CF=CFCF$_3$). From (*Z*)-HFC-1225ye (0.5 cm^3, 0.005 mol), *n*-BuLi (2.5 M, 1.5 cm^3, 0.0038 mol), and Ph$_3$GeBr (0.504 g, 0.0013 mol), a light yellow crystalline solid was obtained, which was purified using column chromatography on silica with a 1/1 dichloromethane/hexane eluent. Yield: 0.381 g, 67%. Anal. Calcd for C$_{21}$H$_{15}$F$_5$Ge: C, 57.96; H, 3.48. Found: C, 57.91; H, 3.35. δ_F: −67.3 (dd, $^3J(\mathrm{CF_3F_{trans}}) = 13.6$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 5.9$ Hz), −130.4 (qd, $^4J(\mathrm{F_{gem}CF_3})$ / $^3J(\mathrm{F_{gem}F_{trans}})$ = overlapping 6.2 Hz), −139.0 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 13.7$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 6.8$ Hz). δ_C: 156.7 (dq $^1J(\mathrm{C_{gem}F_{gem}}) = 304$ Hz, $^3J(\mathrm{C_{gem}CF_3}) = 5.1$ Hz, C$_{gem}$), 146.0 (dqd, $^1J(\mathrm{C_{trans}F_{trans}}) = 273$ Hz, $^2J(\mathrm{C_{trans}F_{gem}}) = 39.6$ Hz, $^2J(\mathrm{C_{trans}F_{gem}}) = 17.3$ Hz, C$_{trans}$), 119 (qdd, $^1J(\mathrm{CF_3}) = 271$ Hz, $^2J(\mathrm{CF_3F_{trans}}) = 36.8$ Hz, $^3J(\mathrm{CF_3F_{gem}}) = 10.1$ Hz, CF$_3$), 135.2 (s, C1), 128.7 (s, C2), 134.9 (s, C3), 130.1 (s, C4). δ_H: 7.2−7.5 (m, C$_6$H$_5$).

Preparation of Ph$_3$Pb(CF=CFCF$_3$). (*Z*)-HFC-1225ye (0.5 cm^3, 0.005 mol), *n*-BuLi (2.5 M, 0.5 cm^3, 0.0013 mol), and Ph$_3$PbCl (0.114 g, 0.0002 mol) resulted in a white solid. Yield: 0.074 g, 65%. δ_F: −67.8 (dd, $^3J(\mathrm{CF_3F_{trans}}) = 14.6$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 6.8$ Hz, $^4J(\mathrm{PbCF_3}) = 21.5$ Hz), −123.7 (qd, $^4J(\mathrm{F_{gem}CF_3}) = 6.8$ Hz, $^3J(\mathrm{F_{gem}F_{trans}}) = 3.5$ Hz, $^2J(\mathrm{PbF_{gem}}) = 225.8$ Hz), −141.3 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 14.51$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 3.6$ Hz, $^3J(\mathrm{PbF_{trans}}) = 41.2$ Hz). δ_H: 7.1−7.7 (m, C$_6$H$_5$).

Transfer Reactions under Stille−Liebeskind Conditions. *Preparation of Ph(CF=CFCF$_3$).* *n*-Bu$_3$Sn(CF=CFCF$_3$) (1.0 cm^3, 1.36 g, 3.2 mmol) was added to THF (100 cm^3) in a darkened flask under a positive pressure of nitrogen. PhI (0.157 cm^3, 1.4 mmol), CuI (0.175 g, 0.9 mmol), and Pd(PPh$_3$)$_4$ (0.08 g, 0.07 mmol) were added to the solution, which was stirred at room temperature overnight. δ_F: −65.6 (dd, $^3J(\mathrm{CF_3F_{trans}}) = 12.96$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 8.04$ Hz), −109.1 (dq, $^4J(\mathrm{F_{gem}CF_3}) = 8.12$ Hz, $^3J(\mathrm{F_{gem}F_{trans}}) = 9.37$ Hz), −155.6 (qd, $^3J(\mathrm{F_{trans}CF_3}) = 12.99$ Hz, $^3J(\mathrm{F_{trans}F_{gem}}) = 9.31$ Hz). δ_H: 7.56 (m, ArH), 7.45 (m, ArH), 7.28 (m, ArH) (lit.[9] δ_F −66 (J = 13.2, 8.0 Hz), −110 (J = 8.0, 8.0 Hz), −154.8 (J = 13.2, 8.0 Hz)).

Preparation of p-NO$_2$C$_6$H$_4$(CF=CFCF$_3$). In a similar way, *n*-Bu$_3$Sn(CF=CF(CF$_3$)) (2.23 cm^3, 2.95 g, 0.0070 mol), NO$_2$PhI (1.50 g, 0.0060 mol), CuI (1.079 g), and Pd(PPh$_3$)$_4$ (0.250 g) were reacted in THF (100 cm^3). δ_F: −65.8 (dd, $^3J(\mathrm{CF_3F_{trans}}) = 12.66$ Hz, $^4J(\mathrm{CF_3F_{gem}}) = 7.72$ Hz),

−112.1 (qd, $^4J(F_{gem}CF_3)$ = 7.79 Hz, $^3J(F_{gem}F_{trans})$ = 6.67 Hz), −150.3 (qd, $^3J(F_{trans}CF_3)$ = 12.76 Hz, $^3J(F_{trans}F_{gem})$ = 6.68 Hz). δ_H: 7.62 (d, 8.45 Hz), 8.24 (d, 8.52 Hz).

Preparation of p-MeC$_6$H$_4$(CF=CFCF$_3$). In a similar way, *n*-$Bu_3SnCF{=}CF(CF_3)$ (1.051 g, 0.00250 mol), MePhI (0.438 g, 0.00201 mol), CuI (0.651 g), and $Pd(PPh_3)_4$ (0.066 g) were reacted in THF (100 cm^3). δ_F: −65.7 (dd, $^3J(CF_3F_{trans})$ = 13.03 Hz, $^4J(CF_3F_{gem})$ = 8.20 Hz), −108.7 (dq, $^4J(F_{gem}CF_3)$ = 8.14 Hz, $^3J(F_{gem}F_{trans})$ = 9.96 Hz), −155.3 (qd, $^3J(F_{trans}CF_3)$ = 13.07 Hz, $^3J(F_{trans}F_{gem})$ = 9.97 Hz). δ_H: 2.32 (d, 1.85 Hz), 7.16 (d, 7.81 Hz), 7.27 (d, 7.98 Hz) (lit.[9] δ_F −65.8 (J = 13.2, 8.1 Hz), −108.0 (J = 8.1, 9.4 Hz), −155.0 (J = 13.2, 9.4 Hz)). The product was isolated by distillation (70−73 °C) under reduced pressure to yield 0.205 g (46%).

Preparation of p-MeOC$_6$H$_4$(CF=CFCF$_3$). In a similar way, *n*-$Bu_3Sn(CF{=}CFCF_3)$ (0.938 g, 0.0022 mol), MeOPhI (0.351 g, 0.0015 mol), CuI (0.554 g), and $Pd(PPh_3)_4$ (0.088 g) were reacted in THF (100 cm^3). δ_F: −65.5 (dd, $^3J(CF_3F_{trans})$ = 13.23 Hz, $^4J(CF_3F_{gem})$ = 8.32 Hz), −107.7 (dq, $^4J(F_{gem}CF_3)$ = 8.26 Hz, $^3J(F_{gem}F_{trans})$ = 11.18 Hz), −155.5 (qd, $^3J(F_{trans}CF_3)$ = 13.14 Hz, $^3J(F_{trans}F_{gem})$ = 11.17 Hz). δ_H: 3.78 (s, CH$_3$), 6.88 (d, 8.66 Hz), 7.33 (d, 8.64 Hz). (lit.[9] δ_F −65.8 (J = 13.2, 10.8 Hz), −108.0 (J = 8.2, 10.8 Hz), −155.0 (J = 13.2, 8.2 Hz)).

Preparation of PhCH$_2$CF=CFCF$_3$. In a similar way, *n*-$Bu_3Sn(CF{=}CFCF_3)$ (0.983 g, 0.00234 mol), $PhCH_2Br$ (0.22 cm^3, 0.00184 mol), CuI (1.185 g), and $Pd(PPh_3)_4$ (0.153 g) were reacted in THF (100 cm^3). δ_F: −65.7 (dd, $^3J(CF_3F_{trans})$ = 12.03 Hz, $^4J(CF_3F_{gem})$ = 8.86 Hz), −118.5 (qd, $^4J(F_{gem}CF_3)$ = 8.85 Hz, $^3J(F_{gem}F_{trans})$ = 4.87 Hz), −157.7 (qd, $^3J(F_{trans}CF_3)$ = 12.02 Hz, $^3J(F_{trans}F_{gem})$ = 4.81 Hz). δ_H: 3.62 (s), 3.69 (s), 6.8−7.8 (m, −C$_6$H$_5$).

Preparation of (CF$_3$CF=CFC$_6$H$_4$OCH$_2$)$_2$. In a similar way, *n*-$Bu_3Sn(CF{=}CFCF_3)$ (1.365 g, 0.00324 mol), $(IC_6H_4OCH_2)_2$ (0.511 g, 0.00109 mol), CuI (0.603 g), and $Pd(PPh_3)_4$ (0.094 g) were reacted in THF (100 cm^3). δ_F: −65.6 (dd, $^3J(CF_3F_{trans})$ = 13.17 Hz, $^4J(CF_3F_{gem})$ = 8.24 Hz), −107.9 (dq, $^4J(F_{gem}CF_3)$ = 8.22 Hz, $^3J(F_{gem}F_{trans})$ = 10.78 Hz), −155.2 (qd, $^3J(F_{trans}CF_3)$ = 13.15 Hz, $^3J(F_{trans}F_{gem})$ = 10.87 Hz). δ_H: 4.31 (s, CH$_2$−), 6.93 (broad/m d, 8.78 Hz), 7.34 (broad/m d, 8.30 Hz). The product was isolated by column chromatography (hexane/DCM 4/1) to give $(CF_3CF{=}CFC_6H_4OCH_2)_2$ as an off-white solid. (0.270 g, 52%).

X-ray Crystallography. Single crystals of compounds **4** and **10** were obtained by slow evaporation of the solvent from chloroform solutions. Diffraction data was recorded on a Nonius κ-CCD four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data collections were performed at 150(2) K. The data were solved by direct methods and subjected to full-matrix least-squares refinement on F^2 using the SHELX-97[31] program. All non-hydrogen atoms were refined with anisotropic thermal parameters, while aromatic hydrogen atoms were included in idealized positions and refined isotropically. The computer packages PLUTON[32] and MERCURY[33] were used to investigate the extended structures and to produce the graphical representations used in the figures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving the NMR spectra of the complexes and CIF files and tables giving data for the single-crystal structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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