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Article

Spectroscopic and Structural Assignment of the Absolute Stereochemistry in a Series of 1,2-Difluorovinyl Organometalloids. The First Crystallographic Characterization and Structural Series of Group 14 Fluorovinyl Compounds

Alan K. Brisdon,* Ian R. Crossley, Robin G. Pritchard, and John E. Warren

Department of Chemistry, UMIST, P.O. Box 88, Manchester M60 1QD, U.K.

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The group 14 trifluorovinyl compounds $Ph_3ECF{=}CF_2$ (E = Ge, Sn, Pb) have been prepared in high yield by the low-temperature reaction of the triphenylelement halide with trifluorovinyllithium, generated from tetrafluoroethane (CF_3CH_2F, HFC-134a) and 2 equiv of *n*-butyllithium. The X-ray crystal structures of these materials have been obtained, so affording the first structural series for such species. Subsequent reaction of $Ph_3GeCF{=}CF_2$ with $LiAlH_4$ and a range of organolithium reagents has led to preparation of the 1,2-difluorovinylgermanes $Ph_3GeCF{=}CFR$ (R = H, Me, *n*-Bu, *t*-Bu, Ph). Multinuclear NMR spectroscopic and X-ray crystallographic studies of these compounds have been undertaken and have shown unequivocally the exclusive *trans*-geometry of the 1,2-difluorovinyl moiety.

Introduction

In recent years, there has been a surge of interest in the chemistry of fluorinated compounds, in particular those with potential pharmaceutical, agrochemical, and materials applications.[1,2] Typically, a fluorinated group is employed as an isosteric replacement for a key functionality, so imparting electronic diversity, yet minimal perturbation of the molecular geometry. Thus, it is possible to prepare compounds with unique physical and chemical properties and biological interactions, on the basis of well-understood structure−reactivity relationships.

A consequence of this has been a renewed interest in the chemistry of fluorocarbon-containing organometallic compounds, driven by their potential to serve as convenient, selective reagents for introducing small fluorocarbon moieties. One such class of compounds, of current interest, is the trifluorovinyl ($CF{=}CF_2$) derivatives, among the first examples of which were tin- and silicon-based species, prepared from trifluorovinyl Grignard reagents[3] derived from halofluoroalkenes.[4] These systems have been the subject of considerable interest for their potential utility as transfer and cross-coupling reagents.[5]

Increasingly, attention has turned to the use of these species as precursors for 1,2-difluorovinyl reagents, an area first explored by Seyferth. Thus, it was observed that trifluorovinylsilanes interact with a range of nucleophiles, via an addition−elimination mechanism, to afford predominantly a single 1,2-difluorovinylsilane species, which was assigned as the *trans* isomer on the basis of ^{19}F NMR studies.[6] Efforts to duplicate this reactivity with stannane-based systems were unsuccessful, metathesis instead being observed. However, such tin-based species have been prepared by Burton et al., by effecting the transformation of

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* To whom correspondence should be addressed. E-mail: alan.brisdon@umist.ac.uk.

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a trifluorovinylsilane and subsequently using this as a transfer reagent for the fluorocarbon moiety to a tin center.[7]

Comparison with the chemistry of group 14 vinyl compounds would suggest that germanium and lead trifluorovinyls should exhibit analogous reactivity to silicon and tin derivatives, respectively. However, these systems have been little explored. Only five trifluorovinylgermane compounds have been reported, namely $Ge(CF{=}CF_2)_4$,[8,9] $Me_2Ge(CF{=}CF_2)_2$,[9] $Me_3GeCF{=}CF_2$,[9,10] $Et_3GeCF{=}CF_2$, and $Ph_3GeCF{=}CF_2$,[11] all in low to moderate yield, while there is a single report of a trifluorovinyllead compound, namely $Pb(CF{=}CF_2)_4$.[8] There is just one report of the reactivity of such species, namely the reaction of $Me_3GeCF{=}CF_2$ with tin hydrides to yield predominantly *cis*-(1,2-difluorovinyl)trimethylgermane, in addition to smaller amounts of the *trans* and *gem* isomers and a range of dimeric species.[10]

With the progressive international phase-out of halofluorocarbons, because of their deleterious effect upon atmospheric ozone levels, the availability of precursors for trifluorovinyl Grignard, and lithium, reagents has been severely restricted, thus necessitating the development of alternative routes. To this end, it has recently been shown that trifluorovinyllithium (**1**) can be obtained in high yield through the low-temperature reaction of the commercially available CFC-replacement CF_3CH_2F (HFC-134a) with 2 equiv of butyllithium,[12] and that **1** may be subsequently used to prepare trifluorovinyl-containing species in high yields, in a one-pot procedure.[13] We have thus prepared a range of systems and have obtained the first structural characterizations of any trifluorovinyl derivatives.[14] In continuation of this work, we have now turned our attention to the group 14 systems, for which no structural data are currently available. Here, we report the synthesis and structural characterization of the compounds $Ph_3ECF{=}CF_2$ (E = Ge, Sn, Pb). Moreover, in view of a recent report where the assignment of fluorovinyl geometry cannot be unambiguously made on the basis of the conventional order of ^{19}F NMR coupling constants,[15] we have undertaken to characterize thoroughly a range of 1,2-difluorovinyls, derived from the trifluorovinylgermane, by a combination of spectroscopic and crystallographic means.

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, U.K.). Diethyl ether and THF were dried over sodium wire for ca. 1 day prior to use. The compounds CF_3CH_2F (Ineos Fluor), *n*-BuLi (2.5 M in hexane), MeLi (1.6 M in ether), PhLi (2 M in ether/pentane), *t*-BuLi (1.7 M in pentane) (Acros), Ph_3GeBr (Aldrich), Ph_3SnCl, $LiAlH_4$ (Lancaster), and methanol (BDH) were used as supplied. Fluorine NMR spectra of $CDCl_3$ solutions were recorded on a Bruker DPX200 spectrometer at 188.310 MHz and referenced to external $CFCl_3$. Carbon and proton NMR spectra were recorded on a Bruker DPX400 spectrometer at 100.555 and 400.4 MHz, respectively, as solutions in $CDCl_3$ and referenced to external $SiMe_4$. All resonances are reported using the high-frequency positive convention. Infrared spectra were recorded as mineral oil mulls or neat liquids between KBr plates on Nicolet PC-5 or Nexus FTIR spectrometers. Elemental analyses were performed by the departmental microanalytical service.

Preparation of $Ph_3GeCF{=}CF_2$ (2). To a three-necked round-bottomed flask, equipped with nitrogen inlet/outlet and magnetic stirrer, maintained at −78 °C, were added diethyl ether (150 cm^3) and CF_3CH_2F (1.09 g, 10.67 mmol). BuLi (8.5 cm^3, 21.25 mmol) was added slowly at such a rate as to maintain the low temperature. The mixture was left to stir for 2 h, to ensure complete generation of trifluorovinyllithium **1**. After this time, Ph_3GeBr (1.995 g, 5.20 mmol) dissolved in ether (50 cm^3) was added dropwise, and the reaction was left to stir overnight. Subsequently, the mixture was allowed to warm to room temperature and then worked up by addition of hexane (150 cm^3) to precipitate the inorganic salts. After filtration through a sinter, the filtrate was concentrated by rotary evaporation to afford the crude product. Purification by column chromatography on silica, with a 1:1 dichloromethane/hexane eluent, yielded 1.426 g, 71% of the pure product, as a yellow solid. Mp 79 °C. Anal. Calcd for $C_{20}H_{15}F_3Ge$: C, 62.4; H, 3.9; F, 14.8. Found: C, 62.2; H, 4.0; F, 15.0. For δ_F, see Table 2. δ_H 7.9−7.4 (m, C_6H_5). δ_C 161.5 (C, ddd, J_{CF} 310, 277, 36 Hz, CF_2), 135.4 (CH), 132.8 (C), 130.4 (CH), 129.0 (CH). ν_{max}/cm^{-1} 2000−1780 (Ar overtones), 1722.7 (C═C str), 1284.8, 1186.8, 1020.5 (C−F str), 738.9, 696.4 (C−F def).

Preparation of $Ph_3SnCF{=}CF_2$ (3). In a similar procedure to that given in the preceding paragraph, an ethereal solution of Ph_3SnCl (1.9 g, 4.64 mmol) was added to 1.05 equiv of **1**, generated in situ from 0.5 cm^3 (5.93 mmol) of HFC-134a and 3.9 cm^3 (9.75 mmol) of *n*-BuLi. Workup yielded 1.800 g, 86% of the pure, yellow product. Mp 73 °C. Anal. Calcd for $C_{20}H_{15}F_3Sn$: C, 55.7; H, 3.5; F, 13.2. Found: C, 57.0; H, 3.7; F, 12.9. For δ_F, see Table 2. δ_H 7.7−7.5 (m, C_6H_5). δ_C 160.9 (C, ddd, J_{CF} 316, 269, 33 Hz, CF_2), 137.4 (CH), 135.3 (C), 130.3 (CH), 129.4 (CH). ν_{max}/cm^{-1} 1970−1740 (Ar overtones), 1712.5 (C═C str), 1272.8, 1107.0, 1076.1 (C−F str).

Preparation of $Ph_3PbCF{=}CF_2$ (4). Analogously, Ph_3PbCl (0.995 g, 2.1 mmol) was introduced to an ethereal solution of 2 equiv of **1**, prepared from 0.4 cm^3 (4.74 mmol) of HFC-134a and 3.4 cm^3 (8.5 mmol) of *n*-BuLi. The pure product was obtained on workup as a beige-colored solid, 0.842 g, 77%. Mp 67−9 °C. Anal. Calcd for $C_{20}H_{15}F_3Pb$: C, 46.2; H, 2.9; F, 10.9. Found: C, 46.5; H, 2.9; F, 10.7. For δ_F, see Table 2. δ_H 7.8−7.5 (m, C_6H_5). δ_C 160.9 (C, ddd, J_{CF} 318, 265, 29 Hz, CF_2), 143.0 (C, ddd, J_{CF} 315, 90, 9 Hz, CF), 146.7 (C, J_{PbC} 651 Hz), 136.2 (CH, J_{PbC} 77 Hz), 128.9 (CH, J_{PbC} 97 Hz), 129.4 (CH, J_{PbC} 28 Hz). ν_{max}/cm^{-1} 2000−1780 (Ar overtones), 1711.1 (C═C str), 1263.7, 1113.1, 983.7 (C−F str), 726.4, 694.5 (C−F def).

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Synthesis of Ph$_3$GeCF=CFH (5). Synthesis was based upon literature methods.[7a] A three-necked flask, equipped with N$_2$ inlet/outlet and magnetic stirrer, was charged with LiAlH$_4$ (0.075 g, 1.98 mmol) suspended in 15 cm^3 of dry THF. The suspension was cooled to −30 °C and a solution of **2** (0.323 g, 0.8 mmol) in 10 cm^3 of THF added cautiously. The reaction was allowed to warm to room temperature and stirred for 6 h. Excess LiAlH$_4$ was quenched by the cautious addition, at −20 °C, of degassed water (40 cm^3). The mixture was extracted with diethyl ether (3 × 40 cm^3), and the organics were combined and dried over MgSO$_4$. Filtration and removal of the solvent in vacuo afforded the product as a pale yellow solid. Yield: 0.196 g, 64%. Mp 80 °C. Anal. Calcd for C$_{20}$H$_{16}$F$_2$Ge: C, 65.5; H, 4.4; F, 10.4. Found: C, 63.9; H, 5.2; F, 8.7. δ_F −169.7 (dd, J_{FF} 131 Hz, J_{FH} 78 Hz, *trans*-CF=C*F*H), −172.4 (dd, J_{FF} 131 Hz, J_{FH} 10 Hz, *trans*-C*F*=CFH). δ_H 7.9 (1H, dd, J_{FH} 78, 10 Hz), 7.6 (6H, m), 7.5 (9H, m). δ_C 158.4 (C, dd, J_{CF} 280, 58 Hz, *C*F=CFH), 152.2 (CH, dd, J_{CF} 241, 50 Hz, CF=*C*FH), 134.0 (CH), 132.1 (C), 128.7 (CH), 127.4 (CH). ν_{max}/cm^{-1} 2000−1780 (Ar overtones), 1649.4 (C=C str), 1147.8, 1026.3 (C−F str), 734.9, 696.4 (C−F def).

Synthesis of Ph$_3$GeCF=CFMe (6). A three-necked round-bottomed flask, equipped with N$_2$ inlet/outlet, magnetic stirrer, and a rubber septum, was charged with 0.3 g (0.78 mmol) of **2** in diethyl ether (20 cm^3), and the temperature was held at −78 °C during the addition of MeLi (2.5 cm^3, 4.00 mmol). The mixture was left to stir and warm slowly to room temperature over 6 h, after which time workup was effected by addition of hexane (80 cm^3), followed by filtration and solvent removal in vacuo. The product was obtained as a pale yellow solid. Yield: 0.230 g, 77%. Mp 74.5 °C. Anal. Calcd for C$_{21}$H$_{18}$F$_2$Ge: C, 66.2; H, 4.8; F, 9.9. Found: C, 66.5; H, 4.9; F, 9.7. For δ_F, see Table 5. δ_H 7.6−7.4 (15H, m, C$_6$H$_5$); see also Table 5. δ_C 162.5 (C, dd, J_{CF} 236.6, 39.5 Hz, *C*F=CFMe), 153.2 (C, dd, J_{CF} 274.3, 77.3 Hz, CF=*C*FMe), 135.6 (CH), 134.4 (C), 130.0 (CH), 128.8 (CH), 13.5 (CH$_3$, dd, J_{CF} 26.5, 2.5 Hz, Me). ν_{max}/cm^{-1} 2000−1800 (Ar overtones), 1684.1 (C=C str), 1184.4, 999.3 (C−F str), 734.9, 696.3 (C−F def).

Synthesis of Ph$_3$GeCF=CF*n*-Bu (7). In an analogous manner to that described previously, 0.3 g (0.78 mmol) of **2** was treated with 2 equiv of *n*-BuLi (0.6 cm^3, 1.50 mmol). Workup afforded the product as a pale yellow, viscous liquid. Yield: 0.293 g, 89%. Anal. Calcd for C$_{24}$H$_{24}$F$_2$Ge: C, 68.1; H, 5.7; F, 9.0. Found: C, 68.3; H, 5.9; F, 8.7. For δ_F, see Table 5. δ_H 7.7−7.4 (15H, m, C$_6$H$_5$); see also Table 5. δ_C 165.9 (C, dd, J_{CF} 239.5, 38.6 Hz, *C*F=CF*n*-Bu), 152.8 (C, dd, J_{CF} 274.3, 78.2 Hz, CF=*C*F*n*-Bu), 135.5 (CH), 134.5 (C), 130.0 (CH), 128.8 (CH), 28.6 (CH$_2$, s, CH$_2$*C*H$_2$-Et), 26.9 (CH$_2$, dd, J_{CF} 25, 1 Hz, CF=CF*C*H$_2$Pr), 22.5 (CH$_2$, s, CH$_2$CH$_2$*C*H$_2$Me), 14.2 (CH$_3$, s, Me). ν_{max}/cm^{-1} 3071.1, 3051.8 (CH$_2$ str), 2259.2−2872.4 (CH$_3$ str), 2000−1800 (Ar overtones), 1676.4 (C=C str), 1431.4 (C−H def), 1093.8, 999.3 (C−F str), 735, 698.3 (C−F def).

Synthesis of Ph$_3$GeCF=CF*t*-Bu (8). Using a method similar to that described previously, germane **2** (0.3 g, 0.78 mmol) was treated with 2.1 equiv (1.1 cm^3, 1.65 mmol) of *t*-BuLi. Workup afforded the product as a beige solid. Yield: 0.306 g, 93%. Mp 88 °C. Anal. Calcd for C$_{24}$H$_{24}$F$_2$Ge: C, 68.1; H, 5.7; F, 9.0. Found: C, 68.4; H, 5.9; F, 8.7. For δ_F, see Table 5. δ_H 7.6−7.4 (15H, m, C$_6$H$_5$); see also Table 5. δ_C 167.6 (C, dd, J_{CF} 238.5, 31 Hz, *C*F=CF*t*-Bu), 150.7 (C, dd, J_{CF} 280, 91 Hz, CF=*C*F*t*-Bu), 134.0 (CH), 133.2 (C), 128.4 (CH), 127.3 (CH), 34.7 (C, dd, 24, 2.5 Hz, *C*Me$_3$), 24.5 (CH$_3$, dd, J_{CF} 5, 3.6 Hz). ν_{max}/cm^{-1} 2880 (CH$_3$ str), 2000−1800 (Ar overtones), 1660 (C=C str), 1091.9, 1010 (C−F str), 735, 698.9 (C−F def).

Synthesis of Ph$_3$GeCF=CFPh (9). Analogous treatment of **2** (0.3 g, 0.78 mmol) with PhLi (1.2 cm^3, 2.4 mmol) and subsequent workup led to isolation of the compound as a pale brown solid. Yield: 0.297 g, 86%. Mp 122 °C. Anal. Calcd for C$_{26}$H$_{20}$F$_2$Ge: C, 70.5; H, 4.6; F, 8.6. Found: C, 70.4; H, 4.7; F, 8.3. For δ_F, see Table 5. δ_H 7.8−7.4 (m, C$_6$H$_5$). δ_C 159.5 (C, dd, J_{CF} 226, 30 Hz, *C*F=CFPh), 156.5 (C, dd, J_{CF} 289, 80 Hz, CF=*C*FPh), 135.6 (CH), 134.2 (C), 130.1 (CH), 128.9 (CH), 129.9 (C, dd, J_{CF} 27, 3 Hz, *i*-C$_6$H$_5$), 129.8 (CH, d, J_{CF} 2.5 Hz, *p*-C$_6$H$_5$), 129.2 (CH, d, J_{CF} 3.5 Hz, *m*-C$_6$H$_5$), 126.2 (CH, dd, J_{CF} 10, 7.5 Hz, *o*-C$_6$H$_5$). ν_{max}/cm^{-1} 2000−1800 (Ar overtones), 1637.8 (C=C str), 1122.5, 1074.5 (C−F str), 735, 696.4 (C−F def).

Synthesis of Ph$_3$GeCF=CFOMe (10). Under the anaerobic conditions outlined previously, germane **2** (0.215 g, 0.56 mmol) was treated with sodium methoxide (0.63 g, 11.66 mmol), freshly prepared from metallic sodium and analytical grade methanol, as a solution in methanol (2 cm^3). After 12 h, the reaction mixture was worked-up with hexane. The product was recrystallized from dichloromethane and obtained as a pale yellow solid. Yield: 0.143 g, 64%. Mp 76 °C. Anal. Calcd for C$_{21}$H$_{18}$F$_2$GeO: C, 63.5; H, 4.6; F, 9.6. Found: C, 63.7; H, 4.9; F, 9.2. For δ_F, −118.1 (d, J_{FF} 122 Hz, CF=C*F*OMe), −187.77 (d, J_{FF} 122 Hz, C*F*=CFOMe). δ_H 7.7−7.4 (15H, m, C$_6$H$_5$), 3.9 (3H, OCH$_3$). δ_C 163.4 (C, dd, J_{CF} 245, 31 Hz), 135.5 (CH), 134.2 (C), 130.0 (CH), 128.8 (CH), 59.4 (CH$_3$, dd, J_{CF} 4, 3 Hz).

X-ray Crystallography. Single crystals of compounds **2**−**5**, **8**, and **9** 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[16] 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 1. Molecular representations shown in the figures were generated using ORTEP 3 for Windows.[17]

Results and Discussion

Synthesis and Spectroscopic Characterization of Group 14 Trifluorovinyls. The reaction of trifluorovinyllithium (**1**), prepared from CF$_3$CH$_2$F (HFC-134a), in cold diethyl ether solution, with the group 14 precursors Ph$_3$EX (E = Ge, Sn, Pb; X = Cl, Br) yields the respective trifluorovinyl compounds Ph$_3$E(CF=CF$_2$) (E = Ge **2**, Sn **3**, Pb **4**) as stable materials. It is noteworthy that, while **3** is readily generated from a 1:1 equivalence of the halide and trifluorovinyllithium, **2** and **4** require a 2-fold excess of **1** to maximize conversion. Moreover, while **3** and **4** are prepared in analytically pure form, the germane forms in admixture with other, unidentified species. Notwithstanding, this product is readily purified by column chromatography on silica gel, using a 1:1 dichloromethane/hexane eluent, to yield over 70% of the desired material.

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Table 1. Crystal Data and Structure Refinement for $Ph_3GeCF{=}CF_2$ (**2**), $Ph_3SnCF{=}CF_2$ (**3**), $Ph_3PbCF{=}CF_2$ (**4**), $Ph_3GeCF{=}CFH$ (**5**), $Ph_3GeCF{=}CF$*t*-Bu (**8**), and $Ph_3GeCF{=}CFPh$ (**9**)

	2	**3**	**4**	**5**	**8**	**9**
formula	$C_{20}H_{15}F_3Ge$	$C_{20}H_{15}F_3Sn$	$C_{20}H_{15}F_3Pb$	$C_{20}H_{16}F_2Ge$	$C_{24}H_{24}F_2Ge$	$C_{26}H_{20}F_2Ge$
mol wt	384.91	431.01	519.51	366.92	423.02	443.01
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*P*21/*c* (No. 14)	*Cc* (No. 9)	*P*21/*c* (No. 14)	*P*21 (No. 4)
cryst dimens, mm^3	0.4 × 0.3 × 0.3	0.2 × 0.1 × 0.1	0.25 × 0.22 × 0.2	0.25 × 0.15 × 0.03	0.25 × 0.25 × 0.1	0.3 × 0.2 × 0.2
habit	prism	prism	prism	plate	prism	prism
color	colorless	colorless	colorless	colorless	colorless	colorless
a, Å	10.087(2)	9.6807(6)	9.6770(5)	10.2386(6)	11.4276(2)	7.5395(3)
b, Å	10.338(5)	9.9819(8)	10.0367(7)	29.170(3)	11.4998(2)	11.4621(6)
c, Å	18.704(9)	18.2114(14)	18.2499(10)	7.3196(6)	32.0449(5)	12.2168(6)
α, deg	103.05(4)	90.020(4)	90	90	90	90
β, deg	95.43(3)	85.893(4)	94.492(2)	129.109(4)	93.7970(10)	99.400(2)
γ, deg	108.91(2)	87.843(3)	90	90	90	90
V, Å^3	1767.4(12)	1754.0(2)	1767.78(18)	1696.3(2)	4201.94	1041.58(9)
Z	4	4	4	4	8	2
D_{calcd}, g cm^{-3}	1.447	1.632	1.952	1.437	1.337	1.413
μ mm^{-1}	1.759	1.483	9.570	1.821	1.480	1.497
θ range/deg	1.14−24.99	2.11−27.45	3.02−29.11	2.88−24.98	2.55−27.46	3.82−27.43
no. data collected, unique reflns	6534, 6147	10924, 7203	11516, 4288	2206, 2206	24763, 9427	7146, 4543
params refined	479	452	217	213	679	342
F(000)	776	848	976	744	1744	452
R1^a ($I > 2\sigma(I)$)	0.0648	0.087	0.0631	0.0426	0.0448	0.0284
wR2^b (all data)	0.1716	0.2460	0.1717	0.1075	0.1111	0.0656
max and min/e·Å^{-3}	0.523, −0.371	6.496, −1.879	2.088, −2.884	0.460, −0.511	0.743, −0.432	0.602, −0.432

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

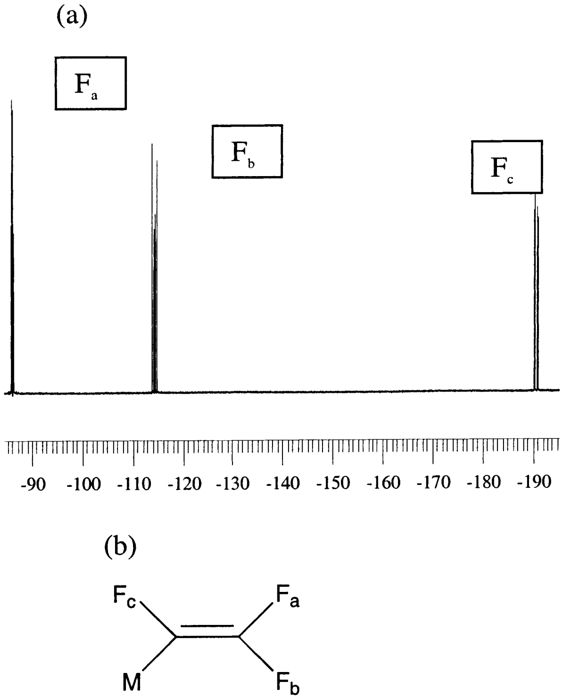

Figure 1. (a) ^{19}F NMR spectrum of $Ph_3GeCF{=}CF_2$ (**2**). (b) Labeling scheme adopted for trifluorovinyl compounds.

Table 2. ^{19}F NMR Assignments for $Ph_3ECF{=}CF_2$ (E = Ge **2**, Sn **3**, Pb **4**)

cmpd	$\delta(^{19}F)$	J/Hz
$Ph_3GeCF{=}CF_2$ (**2**)	−86.2	65 (F_a, F_b), 31 (F_a, F_c)
	−114.5	118 (F_b, F_c), 65 (F_a, F_b)
	−190.9	119 (F_b, F_c), 31 (F_a, F_c)
$Ph_3SnCF{=}CF_2$ (**3**)	−85.4	70 (F_a, F_b), 34 (F_a, F_c), J_{SnF} 23
	−118.9	117 (F_b, F_c), 70 (F_a, F_b), J_{SnF} 26
	−192.6	117 (F_b, F_c), 35 (F_a, F_c), J_{SnF} 184
$Ph_3PbCF{=}CF_2$ (**4**)	−88.5	78 (F_a, F_b), 41 (F_a, F_c), J_{PbF} 18
	−121.7	114 (F_b, F_c), 78 (F_a, F_b), J_{PbF} 32
	−184.2	114 (F_b, F_c), 41 (F_a, F_c), J_{PbF} 187

In each case, the presence of a trifluorovinyl moiety is evident from the ^{19}F NMR spectra, a doublet of doublets being observed for each of the three inequivalent fluorine environments, in distinct regions, typical of an AMX spin system (Figure 1a). The assignment of individual resonances is based upon the unique chemical shift position of nucleus F_c (Figure 1b) and the typically observed trends in the magnitude of $^{19}F-^{19}F$ coupling constants for alkenic systems, specifically that $J_{trans} > J_{gem} > J_{cis}$. Thus, resonances in the region of −85, −118, and −190 ppm are assigned to F_a, F_b, and F_c, respectively. In the cases of compounds **3** and **4**, each resonance additionally exhibits satellite structure due to coupling to the low-abundance, spin-active metalloid isotopes (**3** ^{119}Sn, $I = {}^1/_2$, 8.59%; **4** ^{207}Pb $I = {}^1/_2$, 22.1%). This coupling is observed most readily to the geminal fluorine center, the smallest interaction being observed for F_a. Full assignments are presented in Table 2.

The ^{13}C NMR spectra of **2**−**4** exhibit characteristic aromatic resonances, due to the phenyl rings, in the region 125−150 ppm, with satellite coupling also being observed for **3** and **4**. A further resonance is observed at ca. 160 ppm for all three compounds and appears as a doublet of doublet of doublets. This is assigned as the β-CF_2-carbon of the trifluorovinyl moiety, on the basis of two large (ca. 300 Hz) C−F coupling constants and one smaller coupling (ca. 30 Hz) to the α-fluorine. For compound **4**, a signal due to the α-carbon is observed at 143 ppm, resonating, as expected, at lower frequency, and appearing as a doublet of doublet of doublets, with a single large $^1J_{CF}$ coupling constant. The equivalent signal for compounds **2** and **3** cannot be fully resolved because it is coincident with the aromatic resonances.

Structural Analysis of Group 14 Trifluorovinyl Compounds. The molecular structures of compounds **2**−**4** each

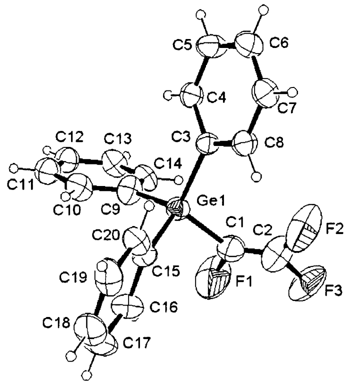

Figure 2. View of the molecular structure of $Ph_3GeCF{=}CF_2$ (**2**), with thermal ellipsoids set at the 30% probability level. The molecular geometry is comparable to that found for $Ph_3SnCF{=}CF_2$ (**3**) and $Ph_3PbCF{=}CF_2$ (**4**), and the illustrated numbering scheme is directly transposable.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Ph_3ECF{=}CF_2$ (E = Ge **2**, Sn **3**, Pb **4**) with Estimated Standard Deviations in Parentheses

	$Ph_3GeCF{=}CF_2$ (**2**)	$Ph_3SnCF{=}CF_2$ (**3**)	$Ph_3PbCF{=}CF_2$ (**4**)
E1−C1	1.969(6)	2.149(8)	2.234(13)
C1−C2	1.230(8)	1.259(12)	1.21(2)
C1−F1	1.383(7)	1.373(10)	1.372(17)
C2−F2	1.298(8)	1.339(11)	1.314(18)
C2−F3	1.345(7)	1.345(10)	1.365(16)
F1−C1−E1	114.6(4)	118.5(5)	117.5(11)
F1−C1−C2	112.1(6)	115.2(8)	115.9(13)
F2−C2−C1	121.7(6)	122.8(8)	123.7(14)
F2−C2−F3	111.0(6)	108.4(8)	107.2(14)
F3−C2−C1	127.2(7)	128.7(9)	129.1(15)

exhibit the anticipated pseudotetrahedral geometry about the metalloid, as illustrated in Figure 2. For compounds **2** and **3**, the asymmetric unit comprises two such molecules, one of which displays some disorder in the fluorovinyl moiety. In contrast, the asymmetric unit of **4** contains a single molecule. Selected bond distances and angles for the three structures are presented in Table 3.

In common with our previous work in this area, we note that for each of **2**−**4** the C=C distance is shorter than that for a typical vinyllic $C(sp^2){=}C(sp^2)$ bond [1.299 Å][18] and the C=C distances found in C_2H_4 [1.3142(3) Å][19] and C_2F_4 [1.311(3) Å].[20] Nonetheless, such distances are not without precedence; for stannane **3**, the observed distance [1.259(12) Å] is comparable to that reported for triphenylvinyltin [1.27(7) Å].[21] Indeed, even shorter C=C distances have been reported for other tin−vinyl species, for example, 1.158(10) Å as observed in $SnCl_2(CH{=}CH_2)_2(bipy)$.[22] Unfortunately, for compounds **2** and **4**, direct comparison with vinyl analogues is impossible, no structural data being available for the latter. Comparison with data for other trifluorovinyl-containing inorganic systems shows that the C=C distances are considerably shorter than has been previously observed [e.g., $Hg(CF{=}CF_2)_2$ 1.312(6) Å,[14a] $PhP(CF{=}CF_2)_2$ 1.318(4) Å,[23] $[(Ph_3P)Au(CF{=}CF_2)]$ 1.297(14) Å[24]]; however, they are comparable to those found in the 1-chloro-2,2-difluorovinyl derivatives $HgCl(CCl{=}CF_2)$ [1.23(5) Å] and *trans*-$[Pd(CCl{=}CF_2)_2(PBu_3)_2]$ [1.26(2) Å].[24]

It has previously been suggested that the shorter C=C distance [1.3130(3) Å] observed for C_2H_4 in the solid-state[19] compared with that found in the gas-phase [1.3384(10) Å][25] is due to librational effects. This too may account for the apparent short C=C distances observed for compounds **2**−**4**. However, detailed analysis of the structural data suggests that the trifluorovinyl moiety has a tendency to exhibit an oscillation about an axis which passes through the metal and a terminal fluorine, approximately bisecting the C=C bond. This would foreshorten the C=C bond, but because of the complex nature of the oscillation, it is difficult to make a reliable estimate of this effect.

We have previously noted significant variation of the internal C−F distances of the trifluorovinyl moiety, a trend that is again evident in compounds **2**−**4**. The α-CF distance has consistently proven to be the longest, a fact also reported for perfluoroalkyl systems and taken as evidence for α-CF activation. This is reflected in compounds **2**−**4**, which exhibit largely comparable α-CF distances, these being the longest yet observed for coordinated fluorovinyl systems [cf., $Hg(CF{=}CF_2)_2$ 1.362(6) Å,[14a] $PhP(CF{=}CF_2)_2$ 1.353(3) Å,[23] $[(Ph_3P)Au(CF{=}CF_2)]$ 1.350(11) Å[24]], but consistent with those reported for fluoroethylene.[20] The lengthening of the α-CF bond in metal bound fluoroalkyl systems is accompanied by a concomitant increase in the strength of the $M{-}C_\alpha$ bond. However, while the Sn−C1 distance of **3** [2.149(8) Å] is shorter than that of triphenylvinyltin [2.17(4) Å],[21] neither this, nor the E−C1 distances of **2** or **4** are significantly short. Variation in the two β-CF distances is also observed in each molecule, though this is small in both **3** and **4**. Significantly, in all three molecules, it is the C−F linkage *cis* to the metalloid (C2−F2) that is the shortest. Such consistency has not previously been observed, though it is perhaps significant that the current work represents the first structurally characterized series of trifluorovinyl homologues.

In the extended structures, the trifluorovinyl compounds **2**−**4** each align in infinite stacks and exhibit a tendency for aggregation of the fluorinated moieties in domains running through the crystal lattice. Individual molecules tend to stack in "head-to-tail" fashion, constrained by H···F interactions between the fluorovinyl moieties and aromatic hydrogen atoms of adjacent molecules [**3** *d*(F2···H11) 2.45 Å; **4** *d*(F2···H5) 2.48 Å]. These contacts are notably shorter than the sum of the atomic contact radii [2.67 Å].[26] Additional packing forces arise from intermolecular $\pi{-}H$ interactions which

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range between d(H−Cg) 2.8 and 2.9 Å and align essentially orthogonal to the ring plane (5.15−5.74 °).

Reactivity of Group 14 Trifluorovinyls. Investigation of the reactivity of group 14 trifluorovinyls toward nucleophiles has previously been confined to derivatives of silicon, typically $Et_3SiCF{=}CF_2$[6,7] and the products identified on the basis of NMR spectroscopy. However, there is no structural confirmation of these conclusions. It thus seemed logical, in seeking to characterize these systems structurally, to exploit the crystalline nature of $Ph_3SiCF{=}CF_2$. However, in our hands, preparation of the triphenylsilane proved ineffectual, it being formed along with Ph_3SiF and other products, in yields of ca. 10% according to ^{19}F NMR studies. We note that this is consistent with reports of its preparation from tetrafluoroethylene and triphenylsilyllithium, which resulted in only 18% yield.[27] In contrast, we have prepared the solid germane **2** in high yield and purity. Given the common reactivity traits shared by vinylsilanes and -germanes,[28] the reactions of this compound were studied in detail, confirming an analogous reactivity to the trifluorovinylsilanes. Similarly, our study of stannane **3** concurred with previous reports,[6] revealing no reactivity toward $LiAlH_4$ and a propensity for metathesis with organolithium reagents. It is noteworthy that plumbane **4** also undergoes metathesis with organolithiums, as it does with $LiAlH_4$, a fact that is attributed to the decreasing E−C bond strength upon descending group 14.

Synthesis of $Ph_3Ge(CF{=}CFH)$ (5). The reaction of trifluorovinyltriphenylgermane, **2**, with an excess of $LiAlH_4$ resulted in the isolation of **5** as a pale yellow solid in high yield. In the ^{19}F NMR spectrum of **5**, the characteristic trifluorovinyl signals were replaced by two mutually coupling (J_{FF} = 131 Hz) doublet of doublet resonances at −169.7 and −172.4 ppm. The large magnitude of the mutual $^{19}F-^{19}F$ coupling would seem consistent with assignment of the *trans*, or *Z*, isomer. This is supported by the presence of a high frequency (7.9 ppm) doublet of doublets in the proton NMR spectrum, which exhibits one large (78 Hz), typically *geminal* $^{19}F-^{1}H$ coupling and one smaller (10 Hz) *cis* interaction, concurring with related work by Clark et al.[10] On this basis, the higher frequency ^{19}F resonance is assigned to the fluorine nucleus *geminal* to the proton.

It has recently been reported that for $^{19}F-^{19}F$ coupling in a range of fluorolithioolefins, the magnitude of J_{gem} often exceeds that of J_{trans},[15] contrasting with the conventional view that $J_{trans} > J_{gem} > J_{cis}$. Though generally considered an anomaly arising from the low temperatures necessitated by these studies, such alternative interpretation is not precluded by previous work in respect to 1,2-difluorovinyl systems. However, here we report additional information obtained from ^{13}C NMR spectroscopy, where both fluorovinyl carbons are clearly observed, each exhibiting one large (>200 Hz) and one small (<60 Hz) $^{13}C-^{19}F$ coupling constant. Thus, the fluorine atoms must each reside on a different carbon center. The combined spectroscopic data therefore allow unequivocal assignment of compound **5** as *trans*-$Ph_3GeCF{=}CFH$.

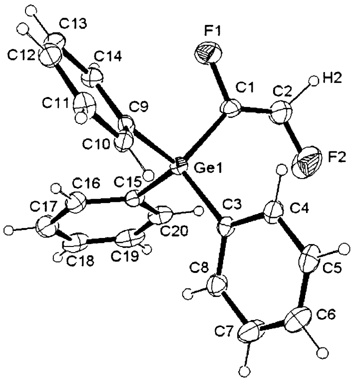

Figure 3. View of the molecular structure of $Ph_3GeCF{=}CFH$ (**5**); thermal ellipsoids are set at the 30% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Ph_3GeCF{=}CFH$ (**5**) with Estimated Standard Deviations in Parentheses

Ge−C1	1.958(9)	C2−F2	1.345(11)
C1−C2	1.275(13)	C2−H2	1.16(11)
C1−F1	1.388(9)		
F1−C1−Ge	114.5(6)	F2−C2−H2	103(5)
F1−C1−C2	114.3(8)	H2−C2−C1	135(5)
F2−C2−C1	120.8(9)		

Further, inseparable, species are evident, at trace levels, in the ^{19}F and ^{1}H NMR spectra. These are identified on the basis of data reported elsewhere[10] as the *cis* and *geminal* monosubstitution products and *cis*-$Ph_3GeCH{=}CFH$. It is noteworthy that, when extended reaction times are employed, the *cis*-1,2-dihydrofluorovinylgermane predominates, characterized in the ^{19}F NMR by a doublet of doublets at −91.4 ppm (J_{HF} 92.2, 64.9 Hz), with corresponding proton resonances at 7.3 (J_{HF} 92, 5.6 Hz) and 5.5 (J_{HF} 65, 5.6 Hz) ppm. After 12 h, this is the sole isolable product, albeit in an impure state.

Ultimately, confirmation of the geometry of **5** was obtained by X-ray diffraction studies. The asymmetric unit contains a single molecule that exhibits a pseudotetrahedral arrangement about the germanium center and a *trans* configuration across the double bond of the fluorovinyl moiety, as shown in Figure 3 (selected bond lengths and angles are summarized in Table 4). The molecule exhibits a short C=C distance [1.275(13) Å, vide supra], which is comparable to that in the parent germane **2** and, significantly, to that reported for *cis*-$[(CO)_5Mn(CF{=}CFH)]$ [1.28 Å], the only previous example of a structurally characterized 1,2-difluorovinyl compound.[29] In common with most recent reports,[23,24] the α-CF bond distance is the longer [1.388(9) Å cf. 1.345(11) Å β-CF], though this contrasts with the case of *cis*-$[(CO)_5Mn(CF{=}CFH)]$ where both distances are comparable [1.46 Å α-CF, 1.50 Å β-CF]. It is noteworthy that in **5** a lengthening of the β-CF distance [d(C2−F2) 1.345(11) Å] is observed, relative to trifluorovinylgermane **2** [1.298(8) Å]. This is presumably due to partial rehybridization at the β-carbon upon replacing fluorine with hydrogen, resulting in reduced

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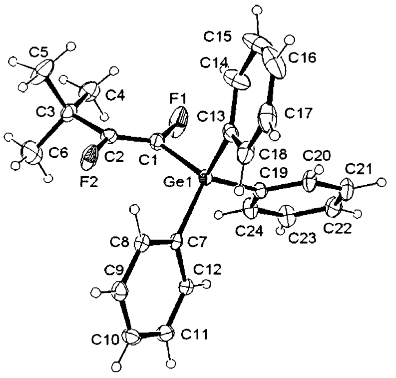

Figure 4. View of the molecular structure of $Ph_3GeCF{=}CFt\text{-}Bu$ (**8**) with thermal ellipsoids set at the 30% probability level. The atom numbering scheme is shown for one molecule; for the second molecule, 30 is added to each atom label.

Table 5. ^{19}F and ^{1}H NMR Data for the Vinyl Group of Compounds $Ph_3GeCF{=}CFR$ (R = Me **6**, Bu **7**, *t*-Bu **8**, and Ph **9**)

cmpd	δ (*J*/Hz)
$Ph_3GeCF{=}CFMe$ (**6**)	δ_F −134.5 (dq, 128, 17); −165.4 (dq, 128, 6) δ_H 2.2 (dd, 17.5, 6.5)
$Ph_3GeCF{=}CFn\text{-}Bu$ (**7**)	δ_F −141.8 (dt, 128, 23); −166.1 (dt, 127, 6) δ_H 2.6 (ddt, 23, 6.4, 6.4); 1.7−1.5 (m); 1.5−1.4 (m); 1.1−0.9 (m)
$Ph_3GeCF{=}CFt\text{-}Bu$ (**8**)	δ_F −143.9 (d, 126); −164.0 (dm, 127, 2) δ_H 1.3 (dd, 2.2, 1.7)
$Ph_3GeCF{=}CFPh$ (**9**)	δ_F −148.7 (d, 126); −156.3 (d, 126)

s character of the C−F bonding orbital. Carbon NMR data support this interpretation because the $^1J_{CF}$ coupling constant is reduced in **5** compared with that observed in **2**.

In the extended structure, molecules of **5** align in stacks along the *c* cell dimension, with a single molecular orientation. Adjacent stacks demonstrate aggregation of the fluorocarbon moieties and intermolecular hydrogen fluorine interactions to aromatic [*d*(F1···H12) 2.57 Å] and vinyllic [*d*(F1···H2) 2.60(8) Å] protons of adjacent molecules.

Reaction of $Ph_3GeCF{=}CF_2$ (2) with Organolithium Reagents. Treatment of germane **2** with an excess of organolithium reagents resulted, after workup, in compounds $Ph_3GeCF{=}CFR$ (R = Me, **6**; *n*-Bu, **7**; *t*-Bu, **8**; Ph **9**) in high yields. In each case, the ^{19}F NMR spectrum of the product consists of two multiplet resonances in the region −135 to −165 ppm, with one large ($J_{FF} > 120$ Hz) mutual doublet coupling. Additionally, for compounds **6**−**8**, $^1H-^{19}F$ coupling to the alkyl moiety is also observed, this being reflected in the ^1H NMR data (Table 5).

Structural Characterization of $Ph_3GeCF{=}CFt\text{-}Bu$ (8) and $Ph_3GeCF{=}CFPh$ (9). Crystals of **8** and **9** were obtained by the slow evaporation of mixed solvent (dichloromethane and hexane) solutions. The asymmetric unit of **8** contains two unique molecules, the molecular geometry of one is shown in Figure 4 with selected bond distances and angles summarized in Table 6. For the most part, there is little variation between the two molecules except that one exhibits no significant variation in C−F distances, in contrast to the parent germane **2** and difluorovinyl **5**. A similar trait is observed in **9**, which comprises a single molecule in the asymmetric unit (Figure 5 and Table 7). In both materials, there is evidence of extensive intramolecular hydrogen bonding between the alkyl/aryl moiety and vinyllic fluorine atoms. Thus, in **8**, C4 is coplanar with the fluorovinyl group with interactions between F1 and H4b and H4c (d_{av} 2.50 Å), augmented by F2···H5 and F2···H6 interactions [d_{av} 2.51 Å]. Analogous interactions are observed in the phenyl substituted fluorovinyl **9** [*d*(F1···H4) 2.29(3) Å; *d*(F2···H8) 2.37(4) Å]. Additionally, there is evidence for conjugation of the aromatic and vinyllic π-systems. The C=C distance [1.319(4) Å] is notably longer than that of the parent germane **2** [1.230(8) Å] although this may be anticipated because of the reduced motion of the fluorovinyl moiety. More significantly, this distance is also longer than that found in the other 1,2-difluorovinyls [**5** 1.275(13) Å; **8** 1.304(4) Å], and this is accompanied by a short C2−C3 bond [1.463(4) Å], as compared to the alkyl substituted system **8** [1.517(4) Å] and a typical C(sp^2)−C(ar) bond [1.488 Å].[18]

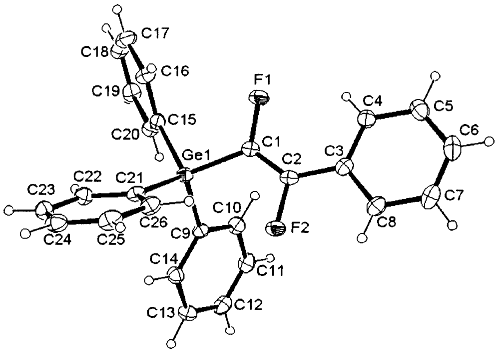

Figure 5. View of the molecular structure of $Ph_3GeCF{=}CFPh$ (**9**) with thermal ellipsoids drawn at the 30% probability level.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $Ph_3GeCF{=}CFt\text{-}Bu$ (**8**) with Estimated Standard Deviations in Parentheses

Ge1−C1	1.963(3)	Ge31−C31	1.959(3)
C1−C2	1.304(4)	C31−C32	1.306(5)
C1−F1	1.363(3)	C31−F31	1.379(4)
C2−F2	1.364(3)	C32−F32	1.371(4)
C2−C3	1.517(4)	C32−C33	1.515(5)
F1−C1−Ge1	113.46(19)	F31−C31−Ge31	114.4(2)
F1−C1−C2	117.8(3)	F31−C31−C32	118.6(3)
F2−C2−C1	112.9(3)	F32−C32−C31	113.4(3)
F2−C2−C3	111.5(2)	F32−C32−C33	111.1(3)
C1−C2−C3	135.5(3)	C31−C32−C33	135.4(4)

Table 7. Selected Bond Distances (Å) and Angles (deg) for $Ph_3GeCF{=}CFPh$ (**9**) with Estimated Standard Deviations in Parentheses

Ge1−C1	1.962(2)	C4−C5	1.384(4)
C1−C2	1.319(4)	C5−C6	1.380(5)
C1−F1	1.367(3)	C6−C7	1.385(5)
C2−F2	1.367(3)	C7−C8	1.386(4)
C2−C3	1.463(4)	C8−C3	1.397(4)
C3−C4	1.400(4)		
F1−C1−Ge1	116.22(19)	F2−C2−C3	113.5(2)
F1−C1−C2	117.8(2)	C1−C2−C3	133.6(2)
F2−C2−C1	112.9(2)	C4−C3−C8	119.0(3)

Synthesis of $Ph_3GeCF{=}CFOMe$ (10). In an analogous manner to its reaction with organolithium reagents, germane **2** was treated with an excess of methanolic sodium methoxide. After workup, a pale yellow solid was isolated, the ^{19}F NMR spectrum of which indicates predominantly a single species, again the *trans*-difluorovinylgermane, which exhibits two doublet resonances at −118 and −187.8 ppm, with a mutual coupling of 122 Hz. A single vinyllic carbon resonance could be resolved, having one $^1J_{CF}$ (264.6 Hz) and one $^2J_{CF}$ (31 Hz) C—F coupling constant.

Conclusion

The crystal structures of a series of trifluorovinyl group 14 compounds and their derivatives are reported. This is the first time such data have been obtained, and they show unequivocally that the interaction of a trifluorovinylgermane with nucleophiles leads to stereospecific replacement of the fluorine atom *trans* to germanium, in support of multinuclear NMR spectroscopic studies. Verification of the similarity in reactivity displayed by trifluorovinylsilicon and -germanium compounds mitigates the conclusion that these data are equally supportive of previous work on the stereospecific derivatization of trifluorovinylsilanes.

Acknowledgment. We thank the Engineering and Physical Sciences Research Council (EPSRC) and UMIST for financial support and Ineos Fluor and ICI Klea for donation of HFC-134a. We acknowledge the EPSRC for support of the UMIST NMR (GR/L52246) and FTIR Raman (GR/M30135) facilities, a Research Equipment Initiative grant for X-ray equipment, and also for access to the Chemical Database Service at Daresbury.

Supporting Information Available: For the single-crystal structure determinations, tables of crystal data and structure refinement, atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, packing diagrams, 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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