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$$\mathrm{GeCl_4} + n\text{-}\mathrm{Bu_3SnAr} \longrightarrow \mathrm{ArGeCl_3} + n\text{-}\mathrm{Bu_3SnCl}$$

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Convenient Syntheses of Aryl and Perfluoroaryl Trichlorogermanes and Germatranes via an Organotin Route

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Aryl- and (perfluoroaryl)trichlorogermanes $ArGeCl_3$ (Ar = C_6H_5, 2-FC_6H_4, 3,5-$(CF_3)_2C_6H_3$, C_6F_5, 2,3,5,6-F_4C_5N) are easily obtained in 60−80% yields from the corresponding tributylstannanes and $GeCl_4$ (1:1) at 150 °C in the absence of a solvent. Although the tin-to-germanium transmetalation of C_6F_5 group is sluggish, it is facilitated by addition of 1−2 mol % AIBN (2,2′-azobis(isobutyronitrile)).

Recently there has been an interest in developing germanium-based reagents for organic synthesis.[1] In particular, in palladium-catalyzed cross-coupling reactions aryltri-2-furylgermanes have been shown to be viable reagents for biaryl synthesis,[1b] while carba-[1a] and oxagermatranes[1c,d] have been applied with various degrees of success to the arylation, allylation, alkenylation, and ethynylation of aryl halides and triflates. Due to our interest in the cross-coupling reactions of arylgermatranes, we were looking for a convenient method of synthesis of $C_6H_5GeCl_3$ (**2a**). Although it is commercially available,[2] it is quite expensive. Many of the reported methods of its synthesis can hardly be employed in a typical chemistry laboratory, due to the necessity of using high temperature and pressure[3a,b] and/or reagents that are not readily available.[3c] The method involving transmetalation between diaryl mercurials and germanium tetrachloride works but suffers from the necessity of dealing with presumably higly toxic compounds, as well as the fact that only one aryl group is utilized.[3d,e] The apparently straightforward route via reaction of germanium tetrachloride with aryl iodides in the presence of copper was reported[3f] to fail when substituent(s) were introduced in the aromatic ring.

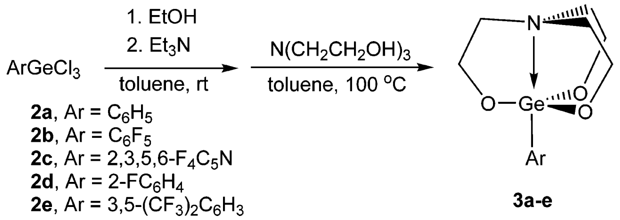
Since transmetalation from tin to germanium had been previously used for the syntheses of alkenyl,[4a,b] alkynyl,[4c,d] propargyl,[4e] and various allylic[4f] trichlorogermanes, it was only logical to extend these studies to the transfer of aryl groups. Preliminary experiments with n-$Bu_3SnC_6H_5$ (**1a**) and $GeCl_4$ demonstrated that the phenyl group transfer has to be carried out at a higher temperature than those of the unsaturated groups above. Heating the mixture of **1a** and $GeCl_4$ (1:1) at 150 °C for 18 h resulted in complete conversion to **2a**, which was isolated in 72% yield after vacuum distillation. Neither the reduction of reaction time to 12 h nor addition of AIBN had significant impact on the isolated yield of **2a** (Table 1, entries 1 and 2). According to the standard procedure[5] **2a** was converted to phen-

Table 1. Reaction of Aryl Tributylstannanes 1a−e with $GeCl_4$ (1:1) at 150 °C

entry	n-Bu_3SnAr	AIBN, mol %	reacn time, h	isolated yield of $ArGeCl_3$, %
1	C_6H_5, **1a**		12	76
2	C_6H_5, **1a**	2.1	22	76
3	C_6F_5, **1b**	1.3	33	73
4	2,3,5,6-F_4C_5N, **1c**	2.1	5	72
5	2,3,5,6-F_4C_5N, **1c**		13	69
6	2-FC_6H_4, **1d**		12	60
7	3,5-$(CF_3)_2C_6H_3$, **1e**	2.0	15	59[a]
8	3,5-$(CF_3)_2C_6H_3$, **1e**		15	57[a]
9	3,5-$(CF_3)_2C_6H_3$, **1e**		12	70

[a] Stannane not distilled prior to reaction.

Scheme 1



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(2) For example, the Sigma-Aldrich price is $37.50 per gram.

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10.1021/om0400189 CCC: $27.50

ylgermatrane **3a**, which was isolated in 93% yield (Scheme 1).

It was of interest to explore the possibility of the analogous pentafluorophenyl group transfer paving the way to the preparation of $C_6F_5Ge(OCH_2CH_2)_3N$ (**3b**) and its evaluation as a possible C_6F_5 transfer reagent. The synthesis of $C_6F_5GeCl_3$ (**2b**) from $GeCl_4$ is known to be nontrivial. With C_6F_5Li, $(C_6F_5)_3GeCl$ is the major product,[6a] while using C_6F_5MgBr results in a mixture of $C_6F_5GeCl_{3-n}Br_n$ (n = 0−3).[6b] Although both **2b** and $C_6F_5GeBr_3$ have been previously prepared by Bardin et al.[6c] via transmetalation between C_6F_5HgEt and GeX_4, the yields were moderate, not to mention the drawback of working with organomercury compounds. An alternative reaction between iodopentafluorobenzene and $GeCl_4$ in the presence of copper at 250 °C resulted in only a 30% yield of **2b** contaminated with decafluorobiphenyl.[6c] The same authors have also studied the reaction between $Me_3SnC_6F_5$ and GeX_4 (X = Cl, Br) at 240 °C and reported very low conversions for X = Cl. Not surprisingly, the reaction between n-$Bu_3SnC_6F_5$ (**1b**) and $GeCl_4$ at 150 °C was found to be sluggish as well. However, addition of AIBN (2 mol %) to the reaction mixture led to significant improvement with respect to the rate of the transmetalation. Thus, the ^{119}Sn and ^{19}F NMR spectra taken after 32 h at 150 °C were free of the signals of stannane **1b**. Instead, a new signal ascribable to n-Bu_3SnCl in the ^{119}Sn NMR and three new signals in the ^{19}F NMR spectra due to **2b** indicated the completeness of the pentafluorophenyl group transfer according to eq 1. The same reaction without AIBN

$$GeCl_4 + n\text{-}Bu_3SnC_6F_5 \rightarrow C_6F_5GeCl_3 + n\text{-}Bu_3SnCl \qquad (1)$$

is much slower. Thus, when two reactions were run in parallel and checked after 23 h, almost all of the **1b** reacted in the presence of AIBN, while only about 25% of **1b** was consumed without AIBN. Trichlorogermane **2b** isolated after vacuum distillation was converted to germatrane **3b** (Scheme 1). The latter was apparently contaminated with another germatrane, as indicated by characteristic methylene signals in its ^1H NMR spectrum. GC-MS analysis of the distillate obtained from the reaction mixture revealed the presence of a byproduct, n-$BuGeCl_3$ (m/z 200 ($BuGeCl_2^+$), 178 ($GeCl_3^+$), 165 ($BuGeCl^+$), 143 ($GeCl_2^+$), 108 ($GeCl^+$), 57 ($C_4H_9^+$)). In addition, n-$BuGeCl_3$ was identified by its ^1H[3c] and ^{13}C NMR spectra. The **2b** to n-$BuGeCl_3$ molar ratio in the distillate, estimated from the integration of the methylene signals in the ^1H NMR spectrum of the **3b**/n-$BuGe(OCH_2CH_2)_3N$ mixture, was 9:1. In contrast, only a trace amount of n-$BuGeCl_3$ was observed in the ^1H NMR spectrum after the phenyl transfer reaction. This suggests the correlation between the ease of transmetalation of an aryl group and the amount of n-$BuGeCl_3$ formed as a byproduct. The rate of the n-Bu transfer must be very slow compared to that of the phenyl group, but as the aryl group becomes less prone to transmetalation, the reaction time increases and more of n-$BuGeCl_3$ would be seen in the product mixture. Discarding the lowest boiling fraction after the vacuum distillation of the reaction mixture resulted in **3b** containing only traces of n-$BuGe(OCH_2CH_2)_3N$. Germatrane **3b** was easily purified by recrystallization from CH_2Cl_2−hexanes. The molecular structures of both **3b** and **3a** were determined by single-crystal X-ray diffraction analysis at low temperature (Figure 1).[7] Relevant metrical data and crystallographic parameters are reported in Tables 2 and 3 and in the Supporting Information. Most notably, the N−Ge distance in **3b**, although shorter than that in **3a**, falls somewhere in the middle of the range reported[8] for various germatranes (2.01−2.29 Å), despite the strong electron-withdrawing character of the C_6F_5 group. Within experimental error the perfluorophenyl ring is eclipsed with a Ge−O bond in the solid state, whereas there is an 18° twisting in the phenyl case. In **3a** there is a displacement of Ge and N out of the C1−C6 plane (pointed out by Lukevics[8]). This is less pronounced in the perfluorinated analogue **3b** (Table 2).

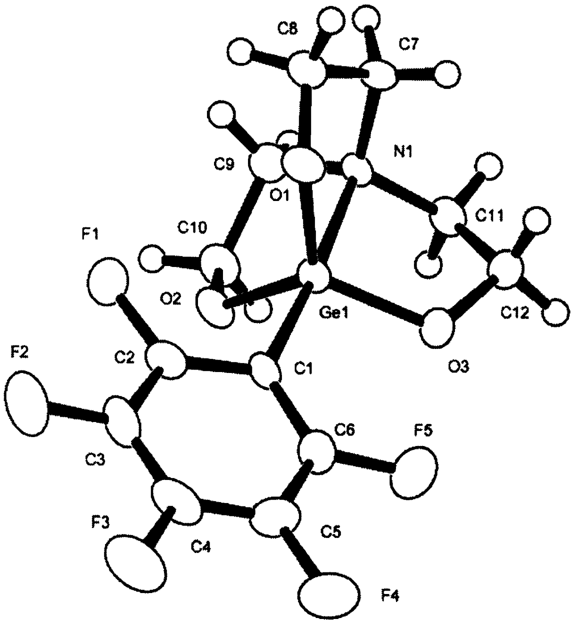

Figure 1. ORTEP drawing of **3b**.

Table 2. Metrical Data for 3b and 3a

	3b	3a
Ge−N, Å	2.156(2)	2.212(3)
Ge−C1, Å	1.990(3)	1.950(4)
Ge−O (mean), Å	1.789(2)	1.802(3)
N−Ge−C, deg	176.3(1)	177.3(2)
O3−Ge−C1−C6, deg	0.2(3)	−18.3(3)
C1−C6 plane to Ge, Å	0.061	0.252
C1−C6 plane to N, Å	0.188	0.622

Another perfluoroaryl moiety readily available for the tin-to-germanium transmetalation study is the 2,3,5,6-tetrafluoropyridyl group. Two methods have been evaluated for the synthesis of the corresponding tin precursor, both using an exchange reaction with n-BuLi (Scheme 2). The reaction with 2,3,5,6-tetrafluoropyridine is preferred, because it yields stannane n-$Bu_3SnC_5NF_4$

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(7) The room-temperature X-ray molecular structure of **3a** has been reported.[8]

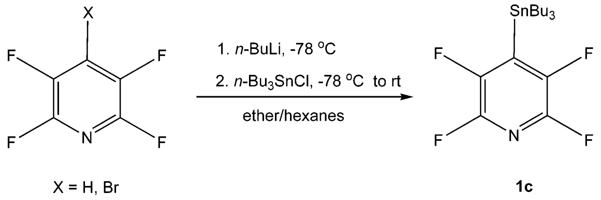
(8) Lukevics, E.; Ignatovich, L.; Belyakov, S. *J. Organomet. Chem.* **1999**, *588*, 222.

Table 3. Crystallographic Data for 3b

color, shape	colorless, needle
empirical formula	$C_{12}H_{12}F_5GeNO_3$
formula wt	385.81
radiation, λ/Å	Mo Kα (monochr), 0.71073
T/K	183
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell dimens	
a/Å	6.7491(2)
b/Å	9.6839(3)
c/Å	20.7819(7)
β/deg	94.713(1)
V/Å^3	1353.66(7)
Z	4
D_{calcd}/g cm^{-3}	1.893
μ/cm^{-1} (Mo Kα)	23.33
R_{int}	0.037
no. of params, restraints	199, 0
R1,[a] wR2,[b] GOF	0.033, 0.033, 1.06
min, max resid density/e Å^{-3}	−0.44, 0.39

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Scheme 2



(**1c**) in higher purity using a substantially cheaper starting material.[9] Transmetalation between **1c** and $GeCl_4$ in the presence of AIBN was over in less than 5 h, leading to the isolation of 2,3,5,6-$F_4C_5NGeCl_3$ (**2c**) (Table 1, entry 4) containing only traces of n-$BuGeCl_3$. The ease of transmetalation prompted us to carry out the same reaction without AIBN. According to the ^{19}F and ^{119}Sn NMR spectra of the reaction mixture, there was still some unreacted **1c** left after 6 h. Additional heating at 150 °C for 4 h resulted in complete disappearance of the corresponding signals. Thus, although in the presence of AIBN the transmetalation occurs faster, the reaction without AIBN is still complete in less than 10 h, a behavior very different from that of the pentafluorophenyl group.

Transmetalation of the partially fluorinated aryl groups 2-FC_6H_4 and 3,5-$(CF_3)_2C_6H_3$ from tin to germanium did not seem to benefit from the use of AIBN. For example, the yields of **2e** were almost identical, regardless of the AIBN presence (Table 1, entries 7 and 8). Judging by ^1H NMR spectra of the crude products, the amounts of n-$BuGeCl_3$ formed in these reactions were obviously higher than in the phenyl case, indicating that partial fluorination results in reduced reactivity toward transmetalation. The lower isolated yield of **2d** relative to **2e** is probably due to the higher boiling point of the former, resulting in its less efficient separation from n-Bu_3SnCl. Both 2-$FC_6H_4Ge(OCH_2CH_2)_3N$ (**3d**) and 3,5-$(CF_3)_2C_6H_3Ge(OCH_2CH_2)_3N$ (**3e**) obtained from the corresponding trichlorogermanes **2d** and **2e** were easily purified by recrystallization.

In conclusion, transmetalation from tin to germanium provides a convenient approach to the preparation of the compounds $ArGeCl_3$ and $ArGe(OCH_2CH_2)_3N$ in good yields. The amount of n-$BuGeCl_3$ formed as a byproduct seems to indicate that the facility of transmetalation decreases in the following order: $C_6H_5 \approx$ 2,3,5,6-$F_4C_5N >$ 3,5-$(CF_3)_2C_6H_3 \approx$ 2-$FC_6H_4 \gg C_6F_5$. In the C_6F_5 case addition of AIBN (1−2 mol %) accelerates the reaction considerably, making this route synthetically viable. The scope of the reaction is obviously limited by the availability of the precursor stannanes, as well as the proximity of the boiling points of $ArGeCl_3$ and n-Bu_3SnCl, unless the separation from the latter can be achieved by a method other than distillation.

Experimental Section

General Information. Ether and toluene were dried over sodium/benzophenone and distilled prior to use. n-$Bu_3SnC_6F_5$ was prepared according to the method of Deacon et al.[10] Germanium tetrachloride, bromopentafluorobenzene (Strem), 2,3,5,6-tetrafluoropyridine (Lancaster), and all other reagents (Aldrich) were used as received. NMR spectra were obtained on Varian Unity 300 (^1H, 299.9 MHz; ^{13}C, 75.4 MHz; ^{19}F, 282.2 MHz; ^{119}Sn, 111.9 MHz) and Mercury 400 (^1H, 400.1 MHz) spectrometers. ^1H NMR spectra were referenced versus residual $CHCl_3$ in $CDCl_3$ (7.27 ppm). ^{13}C NMR spectra were referenced versus $CDCl_3$ (77.0 ppm). ^{19}F spectra were referenced externally to $CFCl_3$ in $CDCl_3$, and ^{119}Sn spectra were referenced externally to 50% $(CH_3)_4Sn$ in $CDCl_3$ (in both cases δ 0.0 ppm). Coupling constants are reported in Hz. Hydrogen atoms of the aryl substituent in **1d**, **2d**, and **3d** are numbered consecutively, starting with the atom nearest to tin or germanium and ending with the atom next to the fluorine. Elemental analyses were performed by Atlantic Microlab, Inc. Trichlorogermanes **2b**−**e** were not analyzed, due to their tendency toward hydrolysis. Instead, the high-resolution mass spectra were obtained at the UCLA mass spectrometry facilities. The ^1H NMR spectrum of **3a** agreed with that reported in the literature.[8]

General Procedure for the Synthesis of Aryltrichlorogermanes. A 17−20 cm heavy-walled pressure tube (Ace Glass) equipped with a magnetic stirring bar was charged in air with 5−10 mmol of an aryltributylstannane. Under a dry argon atmosphere in a glovebox an equimolar amount of germanium tetrachloride was added via a syringe. When needed, AIBN (1−2 mol %) was added to the stannane prior to the addition of $GeCl_4$. The tube was sealed with a PTFE cap and immersed in an oil bath that was preheated to 150 °C. After 5−33 h the tube was cooled to room temperature. With CH_2Cl_2 its content was quickly transferred in air in a distillation apparatus consisting of a 25 mL round-bottom flask, 10 cm Vigreaux column, micro distillation head, thermometer, and receiving flask. Without heating the flask, a dynamic vacuum was applied slowly to remove the solvent. After its removal and replacement of the receiving flask, three to four fractions of aryltrichlorogermane were collected by heating the 25 mL flask in an oil bath. The lowest boiling fraction usually contained some n-$BuGeCl_3$. The distillation was stopped after an appreciable amount of n-Bu_3SnCl could be detected in the fraction being collected (usually more than 6−7 mol %).

(Pentafluorophenyl)trichlorogermane (2b). $GeCl_4$ (13.94 mmol), **1b** (13.96 mmol), and AIBN (0.19 mmol) gave 10.14 mmol of **2b** (73%) as a colorless liquid after vacuum distillation; bp 59−62 °C/ 4 mm (lit.[6c] bp 85−88 °C/20 mm). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −126.7 (m, F_o), −143.4 (tt, $^3J = 19.9$, $^4J = 6.1$, F_p), −157.7 (m, F_m).

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(9) 2,3,5,6-Tetrafluoropyridine can be obtained from Lancaster for \$23.50 per gram.

(10) Deacon, G. B.; Gatehouse, B. M.; Nelson-Reed, K. T. *J. Organomet. Chem.* **1989**, *359*, 267.

(Pentafluorophenyl)germatrane (3b). Triethanolamine (9.57 mmol) and **2b** (9.59 mmol) gave 8.62 mmol of **3b** (90%) as a white solid after recrystallization from CH_2Cl_2−hexanes; mp 169−171 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.93 (t, 6H, ^3J = 5.7, CH_2O), 2.98 (t, 6H, ^3J = 5.7, CH_2N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 57.1, 52.1. ^{19}F{^{1}H} NMR ($CDCl_3$): δ −125.1 (m, F_o), −153.7 (t, ^3J = 19.9, F_p), −161.9 (m, F_m). Anal. Calcd for $C_{12}H_{12}O_3F_5NGe$: C, 37.36; H, 3.14; N, 3.63; F, 24.62. Found: C, 37.50; H, 3.12; N, 3.64; F, 24.35.

1-(Tri-*n*-butylstannyl)-2,3,5,6-tetrafluoropyridine (1c). A 100 mL Schlenk flask equipped with a magnetic stirbar and a rubber septum was charged under nitrogen with 40 mL of dry ether, followed by 1.64 mL of 97% 2,3,5,6-tetrafluoropyridine (15.8 mmol). The resulting solution was cooled to −78 °C, followed by addition of 6.40 mL of 2.47 M *n*-BuLi in hexanes (15.8 mmol) within a 10 min period. The reaction mixture was stirred for 25 min before 4.40 mL of 96% *n*-Bu_3SnCl (15.6 mmol) was added within 5 min. After 1.5 h of stirring at −78 °C, the flask was removed from the cold bath, and the stirring was continued overnight (12 h) at room temperature. The reaction mixture was transferred into a 250 mL round-bottom flask using ether, and the volatiles were removed on a rotary evaporator. The residue was partitioned between dichloromethane and water in a separatory funnel. Ammonium chloride was added to assist in phase separation. The aqueous phase was washed with a fresh portion of dichloromethane, followed by combining two organic phases, drying over $MgSO_4$, and filtering. The solvent was removed on the rotary evaporator, leaving behind the crude product as an oil. Upon distillation of this oil under vacuum using a 10 cm Vigreaux column, three fractions were collected. The first fraction contained significant amounts of impurities, while the other two yielded 4.781 g of clean **1c** as a colorless oil (70%); bp 145−149 °C/4 mm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.62−1.48 (m, 6H, CH_2), 1.40−1.26 (m, 12H, CH_2CH_2), 0.90 (t, 9H, ^3J = 7.2, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.7 ($^2J_{CSn}$ = 21.6), 27.1 ($^3J_{CSn}$ = 65), 13.5, 11.4 ($^1J_{C^{119}Sn}$ = 343, $^1J_{C^{117}Sn}$ = 358). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −94.0 (m, F_{m-Sn}), −125.3 (m, F_{o-Sn}). ^{119}Sn{^{1}H} NMR: δ −18.1 (tt, $^3J_{SnF}$ = 12.6, $^4J_{SnF}$ = 6.3). Anal. Calcd for $C_{17}H_{27}F_4NSn$: C, 46.39; H, 6.18; N, 3.18; F, 17.27. Found: C, 46.65; H, 6.26; N, 3.21; F, 17.57.

1-(Trichlorogermyl)-2,3,5,6-tetrafluoropyridine (2c). $GeCl_4$ (6.14 mmol) and **1c** (6.14 mmol) gave 4.25 mmol of **2c** (69%) as a colorless liquid after vacuum distillation; bp 58−59 °C/4 mm. ^{19}F{^{1}H} NMR ($CDCl_3$): δ −87.2 (m, F_{m-Ge}), −129.5 (m, F_{o-Ge}). HRMS (EI): calcd for $C_5NF_4{}^{35}Cl_3{}^{74}Ge$, *m/z* 328.8234; obsd, *m/z* 328.8246.

(2,3,5,6-Tetrafluoropyridyl)germatrane (3c). Triethanolamine (3.50 mmol) and **2c** (3.42 mmol) gave 3.02 mmol of **3c** (88%) as a white solid after recrystallization from CH_2Cl_2−hexanes; mp 182−194 °C dec. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.96 (t, 6H, ^3J = 5.7, CH_2O), 3.02 (t, 6H, ^3J = 5.7, CH_2N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 57.1, 52.1. ^{19}F{^{1}H} NMR ($CDCl_3$): δ −93.6 (m, F_{m-Ge}), −128.1 (m, F_{o-Ge}). Anal. Calcd for $C_{11}H_{12}O_3F_4N_2Ge$: C, 35.82; H, 3.28; N, 7.60; F, 20.60. Found: C, 35.91; H, 3.30; N, 7.52; F, 20.75.

1-(Tri-*n*-butylstannyl)-2-fluorobenzene (1d). A 100 mL Schlenk flask equipped with a magnetic stirbar and a rubber septum was charged under nitrogen with 25 mL of dry ether followed by 7.00 mL of 2.40 M *n*-BuLi in hexanes (16.8 mmol). The resulting solution was cooled to −78 °C. After 15 min addition of 1.83 mL of 99% 2-fluoro-1-bromobenzene (16.6 mmol) started, which was finished in 10 min. The reaction mixture was stirred for 15 min before 4.70 mL of 96% *n*-Bu_3SnCl (16.6 mmol) was added within 8 min. After 2 h of stirring at −78 °C the flask was removed from the cold bath and the stirring was continued at room temperature for 16 h. The reaction mixture was transferred into a 250 mL round-bottom flask using ether, and the volatiles were removed on a rotary evaporator. The residue was partitioned between dichloromethane and water in a separatory funnel. The aqueous phase was washed with a fresh portion of dichloromethane followed by combining two organic phases, drying over $MgSO_4$, and filtering. The solvent was removed on the rotary evaporator, leaving behind the crude product as an oil. Upon distillation of this oil under vacuum using a 10 cm Vigreaux column, three fractions were collected. The first fraction contained significant amounts of impurities, while the other two yielded 3.955 g of clean **1d** as a colorless oil (62%); bp 143−146 °C/6 mm (lit.[11] 127−130 °C/12 mm). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (ddd, 1H, $^3J_{HH}$ = 6.9, $^4J_{HF}$ = 3.9, $^4J_{HH}$ = 2.0, H_1), 7.38−7.29 (m, 1H, H_3), 7.16 (dddd, 1H, $^3J_{HH}$ = 7.2; 7.2, $^4J_{HH}$ = $^5J_{HF}$ = 1.2, H_2), 7.09−6.98 (m, 1H, H_4), 1.72−1.46 (m, 6H, CH_2CH_2-Sn), 1.38 (qt, 6H, $^3J_{HH}$ = 7.3, 7.3, $CH_2CH_2CH_3$), 1.28−1.04 (m, 6H, CH_2Sn), 0.94 (t, 9H, $^3J_{HH}$ = 7.3, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.3 ($^1J_{CF}$ = 234), 137.3 ($^3J_{CF}$ = 15.6, $^2J_{CSn}$ = 16.1), 130.2 ($^3J_{CF}$ = 7.5, $^4J_{CSn}$ = 7.1), 126.9 ($^2J_{CF}$ = 46.3), 124.1 ($^4J_{CF}$ = 3.0, $^3J_{C^{119}Sn}$ = 30.8, $^3J_{C^{117}Sn}$ = 35.8), 114.2 ($^2J_{CF}$ = 28.2, $^3J_{CSn}$ = 16.3), 29.0 ($^2J_{CSn}$ = 20.1), 27.3 ($^3J_{CSn}$ = 61), 13.7, 9.9 ($^4J_{CF}$ = 1.0, $^1J_{C^{119}Sn}$ = 336, $^1J_{C^{117}Sn}$ = 353). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −94.0. ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ −37.9 (d, $^3J_{SnF}$ = 35.7). Anal. Calcd for $C_{18}H_{31}FSn$: C, 56.13; H, 8.11. Found: C, 56.06; H, 8.30.

1-(Trichlorogermyl)-2-fluorobenzene (2d). $GeCl_4$ (8.42 mmol) and **1d** (8.39 mmol) gave 5.04 mmol of **2d** (60%) as a colorless liquid after vacuum distillation; bp 78 °C/4 mm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (ddd, 1H, $^3J_{HH}$ = 7.2, $^4J_{HF}$ = 5.6, $^4J_{HH}$ = 1.8, H_1), 7.69−7.62 (m, 1H, H_3), 7.36 (br dd, 1H, $^3J_{HH}$ = 7.6, 7.6, H_2), 7.24 (ddd, 1H, $^3J_{HF}$ = 8.2, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.0, H_4). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.1 (d, $^1J_{CF}$ = 249), 135.8 (d, $^3J_{CF}$ = 8.1), 133.1 (d, $^3J_{CF}$ = 5.5), 125.1 (d, $^4J_{CF}$ = 3.0), 121.3 (d, $^2J_{CF}$ = 25.2), 116.5 (d, $^2J_{CF}$ = 22.2). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −99.7. HRMS (EI): calcd for $C_6H_4F{}^{35}Cl_3{}^{74}Ge$, *m/z* 273.8565; obsd, *m/z* 273.8574.

(2-Fluorophenyl)germatrane (3d). Triethanolamine (4.83 mmol) and **2d** (4.84 mmol) gave 3.67 mmol of **3d** (76%) as a white solid after recrystallization from CH_2Cl_2−hexanes; mp 219−221 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (ddd, 1H, $^3J_{HH}$ = 7.3, $^4J_{HF}$ = 5.2, $^4J_{HH}$ = 2.0, H_1), 7.31−7.25 (m, 1H, H_3), 7.07 (dddd, 1H, $^3J_{HH}$ = 7.2, 7.2, $^4J_{HH}$ = $^5J_{HF}$ = 1.0, H_2), 6.99 (ddd, 1H, $^3J_{HH}$ = $^3J_{HF}$ = 8.4, $^4J_{HH}$ = 1.0, H_4), 3.92 (t, 6H, ^3J = 5.7, CH_2O), 2.95 (t, 6H, ^3J = 5.7, CH_2N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.4 (d, $^1J_{CF}$ = 242), 135.7 (d, $^3J_{CF}$ = 10.6), 131.1 (d, $^3J_{CF}$ = 8.5), 125.2 (d, $^2J_{CF}$ = 31), 123.6 (d, $^4J_{CF}$ = 3.0), 115.1 (d, $^2J_{CF}$ = 25), 56.9, 51.9. ^{19}F{^{1}H} NMR ($CDCl_3$): δ −99.2 (ddd, $^3J_{FH}$ = 9.3, $^4J_{FH}$ = 5.9, 5.9). Anal. Calcd for $C_{12}H_{16}O_3NFGe$: C, 45.92; H, 5.14; N, 4.46; F, 6.05. Found: C, 46.08; H, 5.22; N, 4.54; F, 6.10.

1-(Tri-*n*-butylstannyl)-3,5-bis(trifluoromethyl)benzene (1e). A 100 mL Schlenk flask equipped with a magnetic stirbar and a rubber septum was charged under nitrogen with 20 mL of dry ether followed by 4.20 mL of 99% 3,5-bis(trifluoromethyl)-1-bromobenzene (24.1 mmol). The resulting solution was cooled to −78 °C, followed by addition of 10.05 mL of 2.40 M *n*-BuLi in hexanes (24.1 mmol) within a 15 min period. The reaction mixture was stirred for 10 min before 6.80 mL of 96% *n*-Bu_3SnCl (24.1 mmol) was added within 6 min. After the mixture was stirred for 2 h at −78 °C, the flask was removed from the cold bath and stirring was continued at room temperature for 16 h. The reaction mixture was transferred into a 250 mL round-bottom flask using ether, and the volatiles were removed on a rotary evaporator. The residue was partitioned between dichloromethane and water in a separatory funnel. The aqueous phase was washed with a fresh portion of dichloromethane followed by combining two organic phases, drying over $MgSO_4$, and filtering. The solvent was removed on the rotary evaporator, leaving behind the crude product as an oil. Upon distillation of this oil under vacuum using a 10 cm Vigreaux column, three fractions were collected.

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[11] Jaura, K. L.; Churamani, L. K.; Sharma, K. K. *Indian J. Chem.* **1966**, *4*, 329.

The first fraction contained significant amounts of impurities, while the other two yielded 9.662 g of clean **1e** as a colorless oil (80%); bp 138−142 °C/8 mm. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.89 (br s with Sn satellites, 2H, $^3J_{\mathrm{HSn}} = 34$, H_2, H_6), 7.80 (br s, 1H, H_4), 1.60−1.51 (m, 6H, CH_2CH$_2$Sn), 1.36 (qt, 6H, $^3J_{\mathrm{HH}} = 7.3, 7.3$, CH$_2CH_2CH_3$), 1.28−1.04 (m, 6H, C$H_2$Sn), 0.91 (t, 9H, $^3J_{\mathrm{HH}} = 7.3$, CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 145.8, 135.9 ($^2J_{\mathrm{CSn}} = 28$, $^3J_{\mathrm{CF}} = 2.0$), 130.3 (q, $^2J_{\mathrm{CF}} = 34$), 123.8 (q, $^1J_{\mathrm{CF}} = 273$), 121.8 (septet, $^3J_{\mathrm{CF}} = 4.0$), 28.9 ($^2J_{\mathrm{CSn}} = 20.7$), 27.2 ($^3J_{\mathrm{CSn}} = 57.9$), 13.6, 9.8 ($^1J_{\mathrm{C^{119}Sn}} = 332$, $^1J_{\mathrm{C^{117}Sn}} = 347$). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −63.3. ^{119}Sn{^{1}H} NMR (CDCl$_3$): δ −33.8. Anal. Calcd for $C_{20}H_{30}F_6Sn$: C, 47.74; H, 6.01. Found: C, 47.61; H, 6.11.

1-(Trichlorogermyl)-3,5-bis(trifluoromethyl)benzene (2e). GeCl$_4$ (7.89 mmol) and **1e** (7.89 mmol) gave 5.52 mmol of **2e** (70%) as a colorless liquid after vacuum distillation, bp 63 °C/3 mm. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.20 (br s, 2H, H_2, H$_6$), 8.14 (br s, 1H, H_4). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 137.4, 132.9 (q, $^2J_{\mathrm{CF}} = 34$), 131.7 (br s), 126.8 (septet, $^3J_{\mathrm{CF}} = 4$), 122.6 (q, $^1J_{\mathrm{CF}} = 274$). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −63.1. HRMS (EI): calcd for $C_8H_3F_6{}^{35}Cl_3{}^{74}Ge$, *m*/*z* 391.8416; obsd, *m*/*z* 391.8402.

(3,5-Bis(trifluoromethyl)phenyl)germatrane (3e). Triethanolamine (3.97 mmol) and **2e** (3.90 mmol) gave 3.48 mmol of **3e** (89%) as a white solid after recrystallization from CH$_2$Cl$_2$−hexanes; mp 192−204 °C dec. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.20 (br s, 2H, H_2, H_6), 7.80 (br s, 1H, H_4), 3.91 (t, 6H, $^3J = 5.7$, CH_2O), 2.96 (t, $^3J = 5.7$, CH_2N). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 143.0, 133.9 (br s), 130.3 (q, $^2J_{\mathrm{CF}} = 33$), 123.7 (q, $^1J_{\mathrm{CF}} = 273$), 122.7 (septet, $^3J_{\mathrm{CF}} = 3.9$), 56.7, 51.6. ^{19}F{^{1}H} NMR (CDCl$_3$): δ −62.7. Anal. Calcd for $C_{14}H_{15}O_3F_6NGe$: C, 38.94; H, 3.50; N, 3.24; F, 26.39. Found: C, 39.03; H, 3.51; N, 3.31; F, 26.53.

Structure Determination and Refinement of 3b. Crystals of **3b** were obtained by crystallization from methylene chloride/ethylcyclohexane. Data were collected on a Nonius Kappa CCD (Mo Kα radiation) and corrected for absorption. The structure was solved by direct methods and refined on *F* for all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Crystallographic data collection and refinement parameters are summarized in Table 3.

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Supporting Information Available: Text giving NMR spectroscopic data for *n*-BuGeCl$_3$ and synthetic procedures for germatranes **3a**−**e**, tables giving crystallographic data for **3a** and **3b**, and an ORTEP drawing of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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