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Fluoride-Promoted Cross-Coupling of Chloro(mono-, di-, or triphenyl)germanes with Aryl Halides in “Moist” Toluene. Multiple Transfer of the Phenyl Group from Organogermane Substrates and Comparison of the Coupling Efficiencies of Chloro(phenyl)germanes with their Corresponding Stannane and Silane Counterparts

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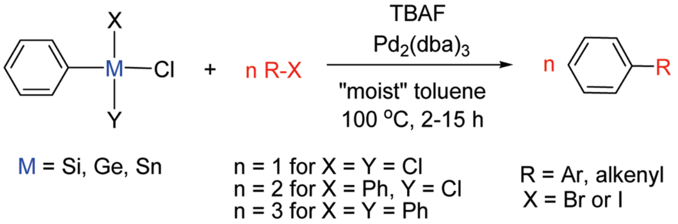

The trichlorophenyl-, dichlorodiphenyl-, and chlorotriphenylgermanes undergo Pd-catalyzed cross-couplings with aryl bromides and iodides in the presence of tetrabutylammonium fluoride in toluene with addition of the *measured* amount of water. One chloride ligand on the Ge center allows efficient activation by fluoride to promote transfer of one, two, or three phenyl groups from the organogermanes. The corresponding chlorophenylstannanes were found to be more reactive than chlorophenylsilanes, which in turn were more effective than chlorophenylgermanes. One chloride ligand on the Ge or Si center allows efficient activation by fluoride to promote transfer of up to three aryl groups from germane or silicon. However, no haloligand was necessary to be present on the Sn center, since tetraphenyltin efficiently transferred up to four phenyl groups during fluoride-promoted couplings with aryl halides. ^{19}F NMR studies suggested formation of the fluorophenylgermanes and the hypervalent germanate species as possible intermediates.

Introduction

Pd-catalyzed cross-coupling reactions are a powerful method for the formation of carbon−carbon bonds under conditions that are compatible with a broad range of functional groups.[1] Among these methods, couplings between organometallics derived from group 14 metals and various electrophiles are well developed. Despite widespread application of organostannanes[2,3] and organosilanes[4,5] to coupling reactions, the Pd-catalyzed coupling of organogermanes has not been utilized,[6] even though germanium lies between silicon and tin in the periodic table. The development of organogermanes as transmetalation reagents in Pd-catalyzed coupling reactions has been limited by the lower reactivity of tetracoordinated organogermanium species, the less developed syntheses of vinyl/aryl germanyl derivatives, and the higher cost of germanium relative to that of silicon.[7]

The 1-aza-5-germa-5-organobicyclo-[3,3,3]undecanes (carbagermatranes) **1** were the first examples of reactive tetracoordinated germanes utilized in Pd-catalyzed cross-coupling reactions

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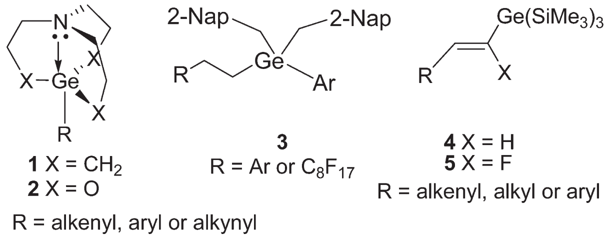

FIGURE 1. Examples of organogermanes employed in Pd-catalyzed cross-couplings.

with aryl bromides due to the activation of germanium by internal coordination to nitrogen[8] (Figure 1). The allyl, aryl, alkenyl, and alkynyl oxagermatranes **2** were found to be more efficient than carbagermatranes **1** and triethoxygermanes.[9] The couplings were promoted by fluoride, and in fact, arylalkynyl oxagermatranes **2** underwent couplings even with less reactive aryl chlorides and triflates under milder conditions than are usually required for Sonogashira couplings with triorganosilicon reagents.[10] The fluoride-promoted couplings with aryltri(2-furyl)germanes[11] and the NaOH-activated couplings with arylgermanium trichlorides[12] or their hydrolyzed and stable sesquioxide alternatives[13] were also reported. Bis(2-naphthylmethyl)arylgermanes **3** were developed as the photochemically activated "safety-catch" arylgermanes for the synthesis of biaryls.[14,15] The vinyl tris(trimethylsilyl)germanes **4** were employed as transmetalation reagents in "ligand-free" and "fluoride-free" cross-coupling reactions with aryl and alkenyl halides under oxidative conditions (H_2O_2) in either aqueous or anhydrous basic conditions.[16,17] Interestingly, the (α-fluoro)vinyl germanes **5** provided a synthetic route to fluoroalkenes and fluorodienes.[18] In contrast, the use of (α-fluoro)vinyl stannanes and silanes as transmetalation reagents in Pd-catalyzed couplings proved to be of very limited value.[19,20] Maleczka et al. reported that the Pd-mediated coupling of vinyltributylgermanes with aryl halides occurred more efficiently under Heck than Stille conditions to give preferentially *Z*-alkenes, especially when oxygen was present at the allylic position.[21]

Couplings with organogermanes appear to be promoted either by intramolecular chelation of a pendant Lewis basic heteroatom which renders the Ge center "permanently" pentavalent[8,9,21] or by the presence of at least one heteroatom bound to the Ge center that renders the Ge center more susceptible to coordination by an external Lewis basic ligand (e.g., fluoride, hydroxide, etc.), thereby also rendering the Ge center pentavalent.[11–13,17,22] Although the effects of the fluoride or base activation and Pd-catalyst/ligand combination on the coupling of organogermanes are still ambiguous, all but one[8] of the successful examples of organogermane couplings with aryl/alkenyl halides involved activation with either base or fluoride. Proposed reactive species were $Na_n[ArGe(OH)_{3+n}]$ (n = 1, 2),[12] $[ArGe(OH)_3F]^-$,[11] or $RGe(OH)_n(SiMe_3)_{3-n}/NaOH$ (n = 1, 2, 3).[17]

We have recently communicated that $(\text{phenyl})_n(\text{chloro})_{4-n}$-germanes ($n$ = 1, 2, or 3) undergo Pd-catalyzed cross-couplings with aryl halides in the presence of TBAF in "moist" toluene, with transfer of up to three phenyl groups from germane.[22] Interestingly, organotin halides were initially considered to be inactive in Pd-catalyzed couplings due to the deactivating nature of the halogen.[3,23] However, coupling between halostannanes (e.g., $ArBu_2SnCl$) and organic halides were later found to be facilitated by TBAF.[3,24] Hypervalent organotin species[3] were suggested as the active species in the Pd-catalyzed coupling reactions of organotin trichlorides with aryl halides in aqueous base.[25,26] Moreover, alkenylsilyl chlorides and fluorides were among the first alkenyl silanes to act as effective and general substrates in the coupling reactions.[4] Hatanaka and Hiyama found that introduction of fluorine atom(s) into the silicon substituent accelerates the cross-coupling reactions.[27] Thus, reaction of the alkenyl/aryl-substituted fluoro(alkyl)-silanes and difluoro(alkyl)silanes with organic halides or triflates in the presence of fluoride promoters (TASF) provided cross-coupling products in a stereo- and regioselective manner and in good yields.[27,28] Interestingly, trifluorosilanes were ineffective in the cross-coupling with 1-iodonapthalene[27] but coupled with alkenyl triflates.[28] The (aryl)halosilanes were also employed successfully in the coupling with aryl halides promoted by KF in DMF.[29] Yet again, aryl(trifluoro)- and aryl(trichloro)silanes failed to generate cross-coupling products.[29] Couplings of organochlorosilanes with aryl chlorides promoted by KF[30] or NaOH[31] and aryl iodides in aqueous KOH media[32] have been also reported.

Although systems which will allow direct comparison of the cross-coupling reactions between the organometallic reagents derived from group 14 metals and electrophiles are lacking,[33–35] organochlorogermanes can render a coupling efficiency *comparable* to the usually more reactive stannane and silane counterparts.[12,22] Therefore, herein,

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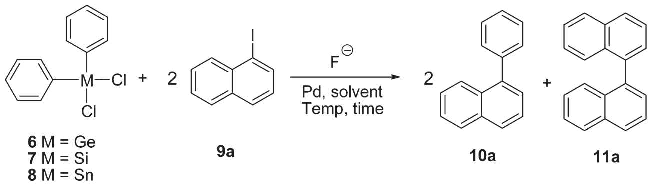
(33) For example, $PhSnBu_3$ efficiently transfers a phenyl group,[3] and so does $PhSi(OMe)_3$ when activated with fluoride.[5] On the other hand $PhGe(OEt)_3$ was basically ineffective under various conditions.[9]

TABLE 1. **Effect of Various Reaction Parameters on the Efficiency of Cross-Coupling of Dichlorodiphenylgermane 6, Silane 7, and Stannane 8 with 1-Iodonaphthalene**[a]



entry	Pd	TBAF[b] or base (equiv)	solvent	from germane **6** (15 h)		from silane **7** (5 h)		from stannane **8** (2 h)	
				yield (%)[c,d] **10a**	ratio[d,e] **10a**:**11a**	yield (%)[c,d] **10a**	ratio[d,e] **10a**:**11a**	yield (%)[c,d] **10a**	ratio[d,e] **10a**:**11a**
1	$Pd_2(dba)_3$	1.0	toluene	–	–	–	–	14	99:1
2	$Pd_2(dba)_3$	3.0	toluene	7	18:1	6	25:1	63	99:1
3	$Pd_2(dba)_3$	5.0	toluene	34	9:1	52	15:1	93	99:1
4	$Pd_2(dba)_3$	7.0	toluene	58[f]	2.2:1	83[g]	10:1	97[h]	99:1
5	$Pd(OAc)_2$	7.0	toluene	49	3.7:1	70	8:1	81	25:3
6	$Pd(PPh_3)_4$	7.0	toluene	14	2.3:1	18	15:1	89	199:1
7	$Pd_2(dba)_3$	7.0[i]	toluene	72	3.5:1	92	33:1	96	125:1
8	$Pd_2(dba)_3$	7.0	DMF[j]	64	4:1	33	3:1	97	35:1
9	$Pd_2(dba)_3$	7.0	THF[k]	38	6:1	56	2:1	95	199:1
10	$Pd_2(dba)_3$	7.0	dioxane[l]	64	12:1	71	17:1	97	199:1
11	$Pd_2(dba)_3$	NaOH[m]	dioxane/H_2O[n]	48[o]	2:1	54	26:1	75	125:1
12	$Pd_2(dba)_3$	$KOSiMe_3$[m]	toluene	8	3:1	52	30:1	58	53:1

[a] Couplings were performed on 0.14 mmol scale of organometallics (0.04 M) with 2.2 equiv of 1-iodonaphthalene and 0.05 equiv of Pd catalyst. [b] Commercial 1 M THF solution containing 5% H_2O, unless otherwise noted. [c] Based upon transferring two phenyl groups from **6-8**. [d] Determined by GC−MS of the crude reaction mixture. [e] Molar ratio. [f] At 60 °C (19%, 10:1) and at 80 °C (43%, 4:1). [g] At 60 °C (43%, 30:1) and at 80 °C (80%, 15:1). [h] At 60 °C (87%, 199:1) and at 80 °C (94%, 199:1). [i] TBAF·$3H_2O$. [j] 100 °C. [k] 60 °C. [l] 80 °C. [m] 7 equiv. [n] 2:1; v/v. [o] With $Pd(OAc)_2$ (21%, 8:1).

we report a comparative study on the reactivity of chlorophenylgermanes and their corresponding silanes and stannanes counterparts toward TBAF-promoted Pd-catalyzed cross-couplings with aryl halides in wet toluene, as well as some mechanistic considerations.

Results and Discussion

We first explored the effect of the Pd-catalysts, solvent, time, temperature, and the amount and type of fluoride promoter on the coupling between dichlorodiphenylgermane **6** and the corresponding silane **7** and stannane **8** counterparts and 1-iodonaphthalene (**9a**; 2.2 equiv) as electrophile. The results are summarized in Table 1. Thus, the amount of TBAF was found to be crucial for the successful coupling of **6**−**8** with **9a** in the presence of $Pd_2(dba)_3$ in toluene (entries 1−4). At least 7 equiv of TBAF were required to produce the maximum yield of the cross-coupling product **10a** from germane **6** and silane **7**, whereas 5 equiv were sufficient for stannane **8**. Reactions required 15 h for germane **6**, 5 h for silane **7**, and only 2 h for stannane **8** for the best results at 100 °C. Dichlorodiphenyl organometallic reagents **6**−**8** allowed us to test for multiple phenyl group transfer from Ge, Si, and Sn atoms, a concept which has been sparsely developed (*vide infra*). Thus, two phenyl groups can be efficiently transferred from all three reagents **6**−**8** but coupling with germane **6** and silane **7** produced also varying amounts of binaphthyl homocoupling byproduct **11a** (5−10%) while stannane **8** produced **10a** almost quantitatively.

Other Pd catalysts afforded **10a** in lower yields and similar ratios of **10a** to **11a** (entries 5−6). Replacement of 1 M TBAF/THF solution with neat TBAF·$3H_2O$ also gave the product **10a** (entry 7); however, coupling in the presence of Me_4NF (as well as CsF and NH_4F) failed to produce **10a** most probably because of the low solubility of the salts in toluene. Coupling of stannane **8** also proceeded in high yield at 80 °C and even at 60 °C, while reactions with silane **7** and germane **6** required at least 80 and 100 °C, respectively, to produce **10a** in high yields with the transfer of two phenyl groups (Table 1, footnotes *f*−*h*). Toluene was the solvent of choice, although attempts in DMF (100 °C), THF (60 °C), and dioxane (80 °C) afforded cross-coupling product **10a** in good (from germane **6** and silane **7**) to excellent (from stannane **8**, entries 8−10) yields. The higher yields for the coupling in dioxane than in THF may be attributable to the increased temperature of the reaction as well as the difference in dielectric constant [7.58 for THF as compared to those for dioxane (2.21) and toluene (2.15)].[36] Bases such as NaOH (dioxane/H_2O, 2:1) or $KOSiMe_3$ (toluene) in place of TBAF promoted couplings less efficiently (entries 11−12).

Following our initial finding[22] that couplings of organogermanes with aryl halides in toluene with addition of the *measured* amount of water gave optimal yields of the cross-coupling products, we investigated couplings of $(phenyl)_n$-$(chloro)_{4-n}$germanes, -silanes, and -stannanes (n = 1, 2, 3 or

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(34) In fact, the lower reactivity of vinyl trialkyl- and triarylgermanes, as compared to the corresponding silanes,[34a] stannanes,[34b,c] and halides,[34d] has been employed to advantage in organic synthesis. For example, doubly substituted α-germanyl-β-stannyl(or silyl or halo)alkenes undergo Pd-catalyzed couplings chemoselectively at the β carbon to afford α-germanyl-β-substituted alkenes: (a) Spivey, A. C.; Turner, D. J.; Turner, M. L.; Yeates, S. *Org. Lett.* **2002**, *4*, 1899–1902. (b) David-Quillot, F.; Marsacq, D.; Balland, A.; Thibonnet, J.; Abarbri, M.; Duchene, A. *Synthesis* **2003**, 448–454. (c) Kataishi, T.; Kato, K.; Makihara, Y.; Kitashima, Y.; Ohara, S.; Anzai, F.; Inokuma, S.; Oku, H.; Ubukata, M.-a.; Takahashi, Y.; Nakano, T. *Appl. Organometal. Chem.* **2008**, *22*, 665–670. (d) Efimova, I. V.; Golyavin, A. A.; Kazankova, M. A.; Beletskaya, I. P. *Zh. Organ. Khim.* **1995**, *31*, 330–333.

(35) Vinyl tris(trimethylsilyl)germanes[17] and silanes[35a] undergo Pd-catalyzed cross-couplings with aryl and alkenyl halides with comparable efficiency upon oxidative treatment with hydrogen peroxide in basic aqueous solution: (a) Wang, Z.; Pitteloud, J.-P.; Montes, L.; Rapp, M.; Derane, D.; Wnuk, S. F. *Tetrahedron* **2008**, *64*, 5322–5327.

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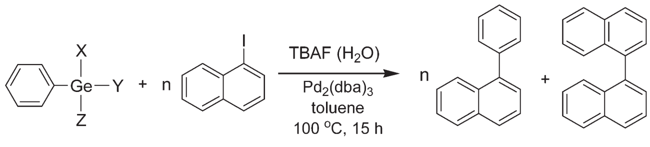
TABLE 2. Cross-Coupling of Germanes 6, 12, 13, and 14 with 1-Iodonaphthalene Promoted by TBAF and TBAF/H_2O



12 Z = Y = X = Cl
6 Z = Ph, Y = X = Cl
13 Z = Y = Ph, X=Cl
14 Z = Y = X = Ph

9a **10a** **11a**

entry	germane	**9a** (equiv)	method[a]	yield (%)[b,c] **10a**	ratio[d] **10a**:**11a**
1	**12**	1.1	A	88 (81)	19:1
2	**12**	1.1	B	99 (96)	35:1
3	**6**	1.1	A	32[e] (30)	2.7:1
4	**6**	2.2	A	58 (55)	2.2:1
5	**6**	1.1	B	45 (42)	23:1
6	**6**	2.2	B	91 (89)	10:1
7	**13**	1.1	A	13[f] (12)	1:1.4
8	**13**	2.2	A	37 (35)	2:1
9	**13**	3.3	A	40 (39)	1.2:1
10	**13**	1.1	B	18 (17)	2.5:1
11	**13**	2.2	B	60 (59)	9:1
12	**13**	3.3	B	95[g] (88)	13:1
13	**14**	4.4	A	0	–
14	**14**	4.4	B	0	–

[a] Method A: Couplings were performed on 0.14 mmol scale of germane (0.04 mM) with 0.05 equiv of Pd catalyst, 7 equiv of TBAF (1 M/THF solution containing 5% of water). Method B: as in Method A with addition of H_2O (~40 equiv). [b] Based on total transferring of one, two, or three phenyl groups from **12**, **6**, or **13**, respectively. [c] Determined by GC–MS of crude reaction mixture (isolated yields in parentheses). [d] Molar ratio. [e] 26% and 31% with 6 and 8 equiv of TBAF. [f] 11% and 14% with 6 and 8 equiv of TBAF. [g] 57% (3.8:1) with 50 μL H_2O; 82% (7:1) with 150 μL H_2O.

4) in "moist" toluene and their capability of transferring multiple phenyl groups. Results for couplings of $PhGeCl_3$ **12**, Ph_2GeCl_2 **6**, Ph_3GeCl **13**, or Ph_4Ge **14** with 1.1, 2.2, 3.3, or 4.4 equiv of 1-iodonaphthalene **9a** (100 °C, 15 h) promoted by 7 equiv of TBAF in toluene (Method A) and in toluene with an additional amount of water added (40 equiv; 1 M TBAF/THF//H_2O, ~1:5 M/M; Method B) are presented in Table 2.[37] The biphasic reaction mixture (toluene//THF/H_2O or toluene//H_2O when neat TBAF was used) in the presence of high concentration of tetrabutylammonium ions might promote conversion of Pd catalyst to the active Pd-colloids which are known[38] to be reactive species in Pd-catalyzed coupling reactions. Thus, coupling of **12** with 1.1 equiv of **9a** afforded **10a** (entries 1–2), although it was previously noted that fluoride ion did not promote the couplings of $PhGeCl_3$ with aryl halides.[12] Coupling of **6** with 1.1 or 2.2 equiv of **9a** resulted in total consumption of iodide to afford **10a** and **11a** (entries 3–6). Two phenyl groups were efficiently transferred in the presence of excess iodide (entry 6). Couplings of **13** with 1.1, 2.2, or 3.3 equiv of **9a** proceeded with efficient transfer of up to three phenyl groups to give **10a** (entries 7–12).[37b] The yields of **10a** and **10a**:**11a** ratios increased when wet toluene and excess of halide were used. Unlike the present work, halides are often used in couplings as limiting reagents to reduce formation of homocoupling byproducts, and the yields are based on the halide components. As expected,[11] coupling attempts with Ph_4Ge **14** failed (entries 13–14), confirming the need for at least one labile heteroatom ligand at the Ge center. The necessity of two halogen ligands was proposed for nucleophilic activation by F^- or OH^- ions.[15]

We found that outcome of the coupling reactions sometimes varied with different batches of TBAF. It became apparent that the older bottles of TBAF reagents often provided the best results. Correspondingly, the poorest performance was obtained with newly purchased bottles that were carefully stored and when no additional amount of water was added to the reactions mixtures. Therefore, to find the optimal water content for the reaction and to establish a reproducible protocol for the cross-coupling, we carried out a study in which we varied the amount of water added to the reaction mixture. Thus, coupling of Ph_3GeCl (**13**, 0.14 mmol) with 1-iodonaphthalene (**9a**, 3.3 equiv) promoted by TBAF (7 equiv) was performed in dry toluene (0.04 M solution) with the addition of 40, 70, 100, 130, 160, and 200 μL of water (16–80 equiv). The best results both in terms of yields and ratios of coupled product **10a** to homocoupled byproduct **11a** were obtained by the addition of 100 μL of water (40 equiv) to the reaction mixture (Figure 2). The commercially available 1 M TBAF solution in THF containing 5% of water was used for this study. Replacement of the 1 M TBAF/THF solution with neat TBAF·$3H_2O$ also produced a similar yield and ratio dependence on the addition of a *measured* amount of water. It is noteworthy that each of these fluoride reagents introduced approximately the same amount of water to the reaction mixture. Water might play multiple roles[39] in enhancing the efficiency of the couplings including the formation of the reactive hydroxypalladium intermediates.[6,40,41] For example, the hydration levels of Cs_2CO_3 and CsOH were found to be decisive factors during the coupling of the aryl(dimethyl)-silanols with aryl halides.[42] Also, Denmark and Sweis showed that water was a critical additive in the fluoride-promoted reaction of alkenylsilanols with phenyl nonaflate.[6,43]

Results for the couplings of $PhSiCl_3$ **15**, Ph_2SiCl_2 **7**, Ph_3SiCl **16**, or Ph_4Si **17** with 1.1, 2.2, 3.3, or 4.4 equiv of iodonaphthalene **9a** (100 °C, 5 h) promoted by TBAF in toluene (Method A) and in "moist" toluene (Method B) are presented in Table 3. Thus, coupling of **15** with 1.1 equiv of **9a** afforded **10a** (entries 1–2). Attempts to couple either **15** or trifluoro(phenyl)silane with aryl bromides and halides (KF/DMF) failed to yield the products in detectable amount.[29] Coupling of **7** with 1.1 or 2.2 equiv of **9a** in toluene (Method A) afforded **10a** in moderate yield in addition to **11a** (10%). However, analogous coupling in wet toluene (Method B) gave **10a** in quantitative yield with no detectable amount of homocoupling byproduct **11a** (entries 5 vs 3 and 6 vs 4). Couplings of **16** with 1.1, 2.2, or 3.3 equiv of **9a** allowed the efficient transfer of up to three phenyl groups to give

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(37) (a) Yields for the cross-coupling products **10**, throughout the manuscript, are based upon the theoretical possibilities of transferring one, two, three or four phenyl groups from the organometallic precursors (**6**–**8** and **12**–**21**) independent of the equivalency of halides used. (b) It is noteworthy that yields of cross-coupling products **10**, based on 1-iodonaphthalene as limiting reagents, would be, for instance, 49% (entry 10) and 81% (entry 11) in Table 2.

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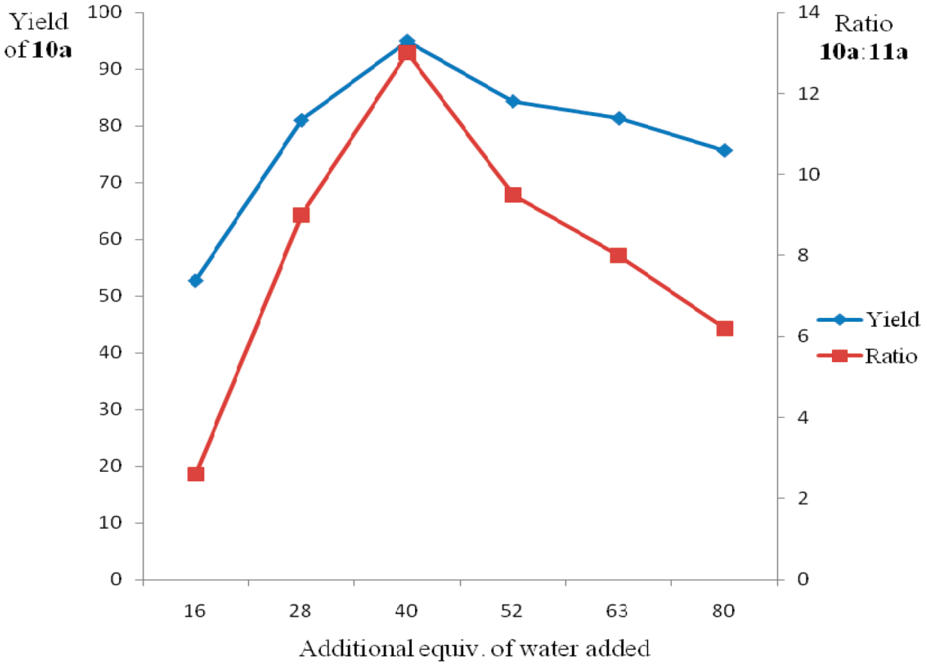
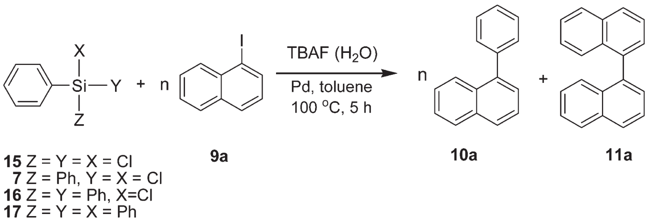


FIGURE 2. Water-dependent efficiency of TBAF-promoted coupling of Ph_3GeCl **13** with 1-iodonaphthalene **9a** in toluene.

TABLE 3. Cross-Coupling of Silanes 7, 15, 16 and 17 with 1-Iodonaphthalene Promoted by TBAF and TBAF/H_2O



entry	silane	**9a** (equiv)	method[a]	yield (%)[b,c] **10a**	ratio[d] **10a**:**11a**
1	**15**	1.1	A	91	59:1
2	**15**	1.1	B	96	67:1
3	**7**	1.1	A	34	9:1
4	**7**	2.2	A	83 (80)	10:1
5	**7**	1.1	B	53	99:1
6	**7**	2.2	B	99 (96)	99:1
7	**16**	1.1	A	31	8:1
8	**16**	2.2	A	49	4:1
9	**16**	3.3	A	55	3:1
10	**16**	1.1	B	35	20:1
11	**16**	2.2	B	68	20:1
12	**16**	3.3	B	91 (84)	8:1
13	**17**	1.1	A	5[e]	2:3
14	**17**	4.4	A	4[e]	1:3
15	**17**	1.1	B	4[e]	1:3
16	**17**	4.4	B	8[e]	1:2

[a] Method A: Couplings were performed on 0.14 mmol scale of silane (0.04 M) with 0.05 equiv of Pd catalyst, 7 equiv of TBAF (1 M/THF solution containing 5% of water). Method B: as in Method A with addition of H_2O (~40 equiv). [b] Based on total transferring of one, two, three, or four phenyl groups from **15**, **7**, **16** or **17**, respectively. [c] Determined by GC-MS of crude reaction mixture (isolated yields in parentheses). [d] Molar ratio. [e] After 16 h.

10a (entries 7−12). The yields of **10a** and **10a**:**11a** ratios increased when wet toluene and excess of electrophiles were used. Our atom-efficient methodology offers advantages to the previously reported couplings utilizing **7** where excess of silanes were used to avoid formation of the reductive homocoupling byproducts.[29,44] It is worth noting that attempts to induce multiple transfer of the phenyl group during fluoride-promoted couplings of diallyl(diphenyl)- and allyl(triphenyl)silanes with aryl halides were unsuccessful.[45] However, vinylpolysiloxanes were shown to transfer each of their vinyl groups during Pd-catalyzed couplings with aryl and alkenyl iodides in the presence of TBAF.[46] Coupling attempts of Ph_4Si **17** with **9a** were not successful; however extended heating (18 h) did produce the cross-coupling product **10a** albeit in low yields (entries 13−16).

Results for the couplings of $PhSnCl_3$ **18**, Ph_2SnCl_2 **8**, Ph_3SnCl **19**, or Ph_4Sn **20** with 1.1, 2.2, 3.3, or 4.4 equiv of iodonaphthalene **9a** (100 °C, 2 h) promoted by 7 equiv of TBAF in toluene (Method A) and in "moist" toluene (Method B) are presented in Table 4. All stannanes were coupled with **9a** to produce almost exclusively **10a** with efficient transfer of up to four phenyl groups (entries 1−20). Addition of water has little effect on the reaction outcomes, but the **10a**:**11a** ratio improved slightly for the couplings with **19** and **20** in wet toluene (entries 7−20). The couplings with tin substrates can be also accomplished in a shorter time and at lower temperature (entries 4 and 6). Atom-efficient Stille cross-couplings of Ar_4Sn with aryl halides, where all four substituents on tin participate in the carbon−carbon bond formation, are known.[24,47]

In general, it appears that chlorophenylstannanes are more reactive than chlorophenylsilanes, which in turn are more reactive than chlorophenylgermanes in these fluoride-assisted Pd-catalyzed cross-couplings with 1-iodonaphthalene in toluene. For the silanes and germanes, reactivity seems to increase with the number of halogen ligands on

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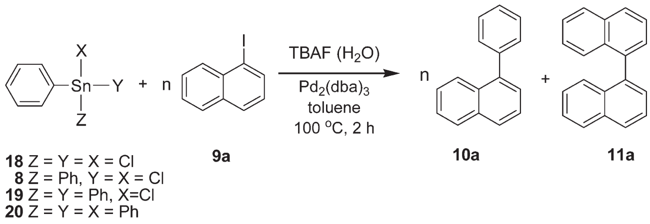
TABLE 4. Cross-Coupling of Stannanes 8, 18, 19, and 20 with 1-Iodonaphthalene Promoted by TBAF and TBAF/H_2O



entry	stannane	**9a** (equiv)	method[a]	yield (%)[b,c] **10a**	ratio[d] **10a**:**11a**
1	**18**	1.1	A	96	54:1
2	**18**	1.1	B	96 (93)	56:1
3	**8**	1.1	A	52	99:1
4	**8**	2.2	A	97 (93)[e]	99:1
5	**8**	1.1	B	54 (50)	99:1
6	**8**	2.2	B	96 (94)[f]	99:1
7	**19**	1.1	A	33	30:1
8	**19**	2.2	A	69	30:1
9	**19**	3.3	A	96	30:1
10	**19**	1.1	B	36	99:1
11	**19**	2.2	B	72	99:1
12	**19**	3.3	B	99 (95)	99:1
13	**20**	1.1	A	24	20:1
14	**20**	2.2	A	56	20:1
15	**20**	3.3	A	72	20:1
16	**20**	4.4	A	86	15:1
17	**20**	1.1	B	27	99:1
18	**20**	2.2	B	54	99:1
19	**20**	3.3	B	81	99:1
20	**20**	4.4	B	99 (91)	99:1

[a] Method A: Couplings were performed on 0.14 mmol scale of stannane (0.04 M) with 0.05 equiv of Pd catalyst, 7 equiv of TBAF (1M/THF solution containing 5% of water). Method B: as in Method A with addition of H_2O (~40 equiv). [b] Based on total transferring of one, two, three, or four phenyl groups from **18**, **8**, **19**, or **20**, respectively. [c] Determined by GC−MS of crude reaction mixture (isolated yields in parentheses). [d] Molar ratio. [e] At 60 °C (87%, 199:1) and at 80 °C (94%, 199:1). [f] After 1 h (85%, 99:1).

the Si or Ge center ($PhMCl_3 > Ph_2MCl_2 > Ph_3MCl > Ph_4M$, where M = Si or Ge).[48] It is reasonable to assume that the silicon or germanium species with extra halogen ligands, which are formed after each transmetalation cycle, are more reactive for the efficient transfer of a second or third phenyl group from the Si or Ge atom. Addition of water to the reaction mixture has a profound effect on the efficiency of coupling of halogermanes. It also increases the effectiveness of the coupling of halosilanes while having little or no effect on coupling with halostannanes.

The results of couplings of phenylchlorogermanes **12**, **6**, and **13** with aryl, alkenyl, and heterocyclic iodides and bromides with 1.1, 2.2, or 3.3 equiv of halides, respectively promoted by TBAF/H_2O are presented in Table 5 (entries 1−33). Thus, couplings with 1-bromonaphthalene **9a′** afforded biaryl **10a** (entries 1, 12 and 23), although with lower yield and worse **10a**:**11a** ratio than the coupling with 1-iodonaphthalene (e.g., entry 12 vs entry 6 in Table 2). Less reactive electrophiles such as 1-chloronaphthalene failed to produce **10a** (entry 12). The reactivity of the phenylchlorogermanes increases with the number of halogen ligands on the Ge center (**13** < **6** < **12**). Hence, $PhGeCl_3$ **12** efficiently afforded coupling products **10** (entries 1−11). This finding is in contrast to a previous report that fluoride ion did not promote the couplings of $PhGeCl_3$ with aryl halides (as opposed to NaOH in dioxane/H_2O medium[12,13]); however, there were no experimental details.[12] The germanes showed *comparable* reactivity with aryl iodides having either electron-donating (e.g., entries 2, 13, and 24) or electron-withdrawing substituents (entries 5, 16, and 27) on the phenyl ring. However, less reactive germanes appear to be more efficient with aryl iodides bearing EDG (e.g., entry 24 vs entries 28 and 29). On the other hand, couplings of the aryl bromides bearing EWG were found to be more efficient than those having EDG (entries 8, 19, and 30 vs 3, 14, and 25, respectively). Methoxy substituents at the *ortho* postion lower the coupling yields, especially for less reactive germanes (series **c** vs **b**; i.e., entries 4, 15, and 26 vs 2, 13, and 24, respectively). Reaction of Ph_2GeCl_2 **6** or Ph_3GeCl **13** with 4-iodoacetophenone **9f** produced **10f** in low yield in addition to large quantities of the reductive homocoupling byproduct **11f**. However, coupling of the less reactive 4-bromoacetophenone **9f′** at elevated temperature and prolonged time resulted in higher yields and improved **10f**:**11f** ratios (entries 19 vs 18 and 30 vs 29). In general, cross-coupling turned out to be more efficient with aryl halides than with other halides (series a−f vs g−i). Interestingly, formation of the biphenyl byproduct (5−50%), via the oxidative self-coupling of the organogermane component **6**, has been only observed in limited cases, mainly when coupling products **10** were formed in lower yields (e.g., entries 9, 10, 20, and 21).

In order to investigate the effects of electro-donating alkyl substituents at Ge atom on the fluoride-promoted couplings of chlorogermanes in toluene, we have examined cross-couplings of chlorodimethyl(phenyl)germane **21** with a variety of halides (1.1 equiv, Table 6). Once again reactions were more efficient with aryl halides than with other vinyl halides (entries 1−12). Reactivity of monochlorogermane **21** was found to be slightly higher than that of Ph_3GeCl **13** but lower than with $PhGeCl_3$ **12**. Thus, Pd-catalyzed cross-coupling reactions of the chlorogermanes in “moist” toluene promoted by fluoride is general in character and is suitable for phenyl as well as phenyl/alkyl substituted germanes.

Couplings of chlorophenylsilanes **15**, **7**, and **16** with the same halides under similar conditions, which are presented in Table 7 (entries 1−33), showed that: (a) reactivity of silanes increases with the number of halogen ligands on the Si center (**16** < **7** < **15**), just as was observed for germanes, (b) couplings were more efficient with aryl halides than with other halides, and (c) reactions with iodides were again more efficient than with bromides. Likewise with chlorogermanes, the nature and position of the substituents on the aryl halides had a similar effect on the coupling efficiency. These results to the best of our knowledge represent the first example of the multiple transfers of phenyl groups from organosilane precursors in Pd-catalyzed couplings.[29,44,45] Our methodology which utilizes wet toluene also resulted in excellent coupling efficiency with $PhSiCl_3$ **15**, which failed to generate the cross-coupling products under other conditions.[29] Comparison of the coupling efficiency of chlorosilanes with the analogous chlorogermanes indicates that: (a) chlorophenylsilanes are, in general, more reactive than the analogous chlorophenylgermanes, and (b) the largest difference of reactivity was found to be between Ph_3SiCl **16** and Ph_3GeCl **13**, whereas $PhSiCl_3$ **15** and $PhGeCl_3$ **12** both showed high reactivity, although shorter reaction time (5 h vs 15 h) was

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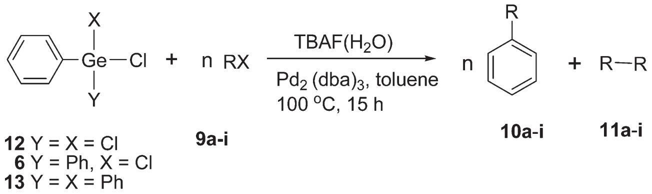
[48] Hiyama et al. reported that the reactivity of the silicates critically depends on the number of fluorine atoms on the silicon.[29]

TABLE 5. Cross-Coupling of Chlorogermanes 6, 12, and 13 with Halides[a]



entry	germane	halide		equiv	product	yield (%)[b,c]	ratio (**10**:**11**)[d]
1	**12**	1-bromonaphthalene	**9a′**	1.1	**10a**	90[e] (82)	99:1
2	**12**	4-$CH_3OC_6H_4I$	**9b**	1.1	**10b**	88[e] (80)	10:1
3	**12**	4-$CH_3OC_6H_4Br$	**9b′**	1.1	**10b**	5[f]	2:3
4	**12**	2-$CH_3OC_6H_4I$	**9c**	1.1	**10c**	71	15:1
5	**12**	3-$CF_3C_6H_4I$	**9d**	1.1	**10d**	93 (87)	9:1
6	**12**	4-$CF_3C_6H_4I$	**9e**	1.1	**10e**	98 (87)	20: 1
7	**12**	4-$CH_3COC_6H_4I$	**9f**	1.1	**10f**	99 (88)	99:1
8	**12**	4-$CH_3COC_6H_4Br$	**9f′**	1.1	**10f**	91	99:1
9	**12**	PhCH=CHBr[g]	**9g**	1.1	**10g**	30[e,h] (28)	3:1
10	**12**	2-iodo-5-methylthiophene	**9h**	1.1	**10h**	48[e,h] (35)	3:2
11	**12**	bromomethylenecyclohexane	**9i**	1.1	**10i**	5	3:1
12	**6**	1-bromonaphthalene[i]	**9a′**	2.2	**10a**	54 (44)	7.2:1
13	**6**	4-$CH_3OC_6H_4I$	**9b**	2.2	**10b**	86[f] (85)	9.8:1
14	**6**	4-$CH_3OC_6H_4Br$	**9b′**	2.2	**10b**	4[f]	1:2
15	**6**	2-$CH_3OC_6H_4I$	**9c**	2.2	**10c**	49	199:1
16	**6**	3-$CF_3C_6H_4I$	**9d**	2.2	**10d**	70 (68)	3.4:1
17	**6**	4-$CF_3C_6H_4I$	**9e**	2.2	**10e**	72 (70)	7:2
18	**6**	4-$CH_3COC_6H_4I$	**9f**	2.2	**10f**	12 (10)	3:2
19	**6**	4-$CH_3COC_6H_4Br$	**9f′**	2.2	**10f**	26[f] (21)	99:1
20	**6**	PhCH=CHBr[g]	**9g**	2.2	**10g**	8[h] (5)	1:3
21	**6**	2-iodo-5-methylthiophene	**9h**	2.2	**10h**	13[h] (6)	2:3
22	**6**	bromomethylenecyclohexane	**9i**	2.2	**10i**	24	2:1
23	**13**	1-bromonaphthalene	**9a′**	3.3	**10a**	24	1.4:1
24	**13**	4-$CH_3OC_6H_4I$	**9b**	3.3	**10b**	48[j] (40)	4:1
25	**13**	4-$CH_3OC_6H_4Br$	**9b′**	3.3	**10b**	14[f]	4:1
26	**13**	2-$CH_3OC_6H_4I$	**9c**	3.3	**10c**	1	1:2
27	**13**	3-$CF_3C_6H_4I$	**9d**	3.3	**10d**	48	3:2
28	**13**	4-$CF_3C_6H_4I$	**9e**	3.3	**10e**	12	3:4
29	**13**	4-$CH_3COC_6H_4I$	**9f**	3.3	**10f**	3	1:20
30	**13**	4-$CH_3COC_6H_4Br$	**9f′**	3.3	**10f**	24[f]	1:1
31	**13**	PhCH=CHBr [g]	**9g**	3.3	**10g**	3	1:8
32	**13**	2-iodo-5-methylthiophene	**9h**	3.3	**10h**	3	2:3
33	**13**	bromomethylenecyclohexane	**9i**	3.3	**10i**	2	1:6

[a] Couplings were performed on 0.14 mmol scale of germane (0.04 M) with 1.1, 2.2, or 3.3 equiv of halides, 0.05 equiv of Pd catalyst, and TBAF (1 M/THF containing 5% of water, 7 equiv) with additional water (~40 equiv), unless otherwise noted. [b] Based on total transferring of one, two, or three phenyl groups from **12**, **6**, or **13**, respectively. [c] Determined by GC−MS of the crude reaction mixture (isolated yield in parentheses). [d] Molar ratio. [e] Without water. [f] 115 °C. [g] *E*/*Z*, 85:15. [h] Various amounts of biphenyl homocoupling byproducts (5−50%) were also observed. [i] Coupling with 1-chloronaphthalene failed. [j] 28 h.

necessary for silanes. Coupling with Ph_4Si **17** either failed or produced the products **10** in low yields (entry 34). These results were only a slight improvement on the unsuccessful coupling attempts with Ph_4Ge **14** (see Table 2, entries 13−14). Also, they provided further evidence that a labile heteroatom at the Si center is required for effective coupling.

Couplings of chlorophenylstannanes **18**, **8**, or **19** and tetraphenyltin **20** with the same halides under similar conditions are presented in Table 8 (entries 1−44). Stannanes were more reactive than either silanes or germanes in fluoride-promoted couplings in wet toluene. One, two, three, or four[24,47] phenyl groups were efficiently transferred from **18**, **8**, **19**, or **20**, respectively, to produce biaryls **10a**−**f** in only 2 h in excellent yields with a high **10**:**11** ratio. As was shown already for 1-iodonaphthalene (See Table 4), the couplings with stannanes can be accomplished in an even shorter time and at lower temperature (entry 16) as well as with less excess of TBAF (entries 13, 19, and 20). Aryl and alkenyl bromides (e.g., series a′, b′, and i) again showed lower reactivity; however, the yields of their couplings with stannanes can be increased by using elevated temperatures and/or longer reaction times (entries 11 and 12).

During the optimization of the cross-coupling reactions between chlorogermanes and 1-iodonaphthalene (see Table 2) it became obvious that the outcome of the couplings strongly depended on TBAF/organogermanes ratios.[22] TBAF most likely facilitates coupling by generating the more reactive hypervalent fluorogermanium species, and the reactivity of these species could be superior in toluene solvent due to weak solvation. Hypervalent fluorotin[49−51] and silicon[52−55] species have been established as active intermediates in Pd-catalyzed coupling

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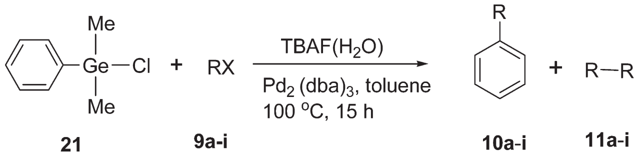
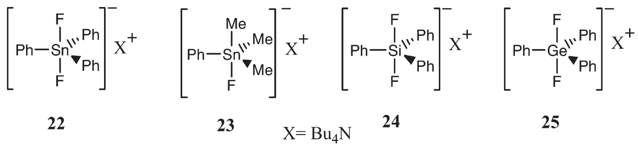
TABLE 6. Cross-Coupling of Chlorodimethyl(phenyl)germane 21 with Halides[a]



entry	halide		product	yield (%)[b]	ratio (**10:11**)[c]
1	1-iodonaphthalene	**9a**	**10a**	93[d] (81)	20:1
2	1-bromonaphthalene[e]	**9a′**	**10a**	44[d]	6:1
3	4-$CH_3OC_6H_4I$	**9b**	**10b**	88[d] (78)	10:1
4	4-$CH_3OC_6H_4Br$	**9b′**	**10b**	6	1:9
5	2-$CH_3OC_6H_4I$	**9c**	**10c**	8	1:8
6	3-$CF_3C_6H_4I$	**9d**	**10d**	61[d] (54)	2.4:1
7	4-$CF_3C_6H_4I$	**9e**	**10e**	31[d] (27)	1.2:1
8	4-$CH_3COC_6H_4I$	**9f**	**10f**	10[d]	1.2:1
9	4-$CH_3COC_6H_4Br$	**9f′**	**10f**	8	1:1.5
10	PhCH=CHBr[f]	**9g**	**10g**	8[d,g]	1:5
11	2-iodo-5-methylthiophene	**9h**	**10h**	3[d]	1:16
12	bromomethylenecyclohexane	**9i**	**10i**	12	1:1.5

[a] Couplings were performed on 0.14 mmol scale of germane **21** (0.04 M) with 1.1 equiv of halides, 0.05 equiv of $Pd_2(dba)_3$ and TBAF (1 M/THF containing 5% of water, 7 equiv) with additional water (~40 equiv), unless otherwise noted. [b] Determined by GC−MS of the crude reaction mixture (isolated yield in parentheses). [c] Molar ratio. [d] Without water. [e] Coupling with 1-chloronaphthalene failed. [f] *E*/*Z*, 85:15. [g] Biphenyl homocoupling byproducts (~25%) were also observed.



22:[49-50] ^{19}F NMR ($CDCl_3$) δ -159.0 ($^1J_{^{19}F-^{119}Sn}$=1971 Hz, $^1J_{^{19}F-^{117}Sn}$= 1887 Hz).

23:[51] ^{19}F NMR (C_6D_6) δ -144.8

24:[54] ^{19}F NMR (DMSO-d_6) δ -96.0 ($^1J_{^{19}F-^{29}Si}$= 252.0 Hz)

25:[57] ^{19}F NMR ($CDCl_3$) δ -118.9

FIGURE 3. Examples of hypervalent fluorostannates, -silicates, and -germanates.

reactions. Thus, a stable tetrabutylammonium difluorotriphenylstannate **22**[49] (Figure 3) efficiently undergoes Pd-catalyzed cross-coupling with alkenyl and aryl triflates.[50] It was also assumed that coupling of trimethylphenyltin with arylchlorides occurred via a hypervalent fluorotin intermediate such as **23**.[51] Similarly, a stable difluorotriphenylsilicate (TBAT) **24**[52,54] has been shown to be a versatile nucleophilic reagent for the transfer of a phenyl group in coupling reactions with aryl halides and allylic alcohols.[53,55] On the other hand, treatment of triphenylgermanium fluoride[56] with KF and tetrabutylammonium hydrogensulphate in DMF afforded pentavalent difluorotriphenylgermanate **25**.[57] However, the application of **25** to Pd-catalyzed cross-coupling reactions and the role that these hypervalent germanium species might play in couplings have not been explored.

In order to get insight about the role that hypervalent germanium species play in the coupling of chlorogermanes **6**, **12**, **13**, and **21**, we have studied their interaction with TBAF. Initial experiments were conducted using $PhMe_2GeCl$ **21**. Thus, mixing **21** and TBAF (1.5 equiv of 1 M/THF) in benzene-d_6 at room temperature resulted in the substitution of the chlorine ligand by the fluoride anion and formation of $PhMe_2GeF$. The observed septet centered at −194.3 ppm [^{19}F NMR (CCl_3F)] formed by coupling with the six equivalent protons of the two methyl groups ($^3J_{F-H} \approx 6.0$ Hz, spectrum *a*, Figure 4) had a chemical shift in agreement with the literature value (−196.0 ppm) for analogous fluorodimethylgermanes.[15] Heating the sample at 50 °C for 3 h resulted in broadening of the signal at −194.6 ppm and appearance of a new broad singlet at −150.8 ppm, suggesting equilibrium between $PhMe_2GeF$ and its hypervalent species (spectrum *b*), which are most likely fluorine-bridged species analogous to **27** (*vide infra,* Scheme 1). The pentavalent difluorogermanate $Ph(Me)_2GeF_2^-$ appears as a minor peak at −126.4 ppm (septet, $^3J_{F-H} \approx 5.8$ Hz) in agreement with the reported chemical shift for the analogous hypervalent difluorotriphenylgermanate **25**.[57] Overnight heating resulted in the additional broadening of the peaks at −150.8 ppm and −194.3 ppm as well as in the increased intensity of the signal(s) at −126.4 ppm (spectrum *c*). Interestingly, extracting the sample with D_2O resulted in the reappearance of the septet at −194.3 ppm for $Ph(Me)_2GeF$ (spectrum *d*).

Treatment of Ph_3GeCl **13** with TBAF (1.5 equiv) in toluene-d_8 led to a parallel pattern of peaks to those observed for the reaction of **21** with TBAF. Hence, the signal for Ph_3GeF (**26**, 201.9 ppm) and a broad singlet at −151.6 ppm (spectrum *c*, Figure 5) were observed. Heating at 50 °C for 3 h resulted in the increased intensity for the peak at −151.6 ppm (spectrum *d*), which was tentatively assigned as hypervalent fluorine-bridged species of type **27** (*vide infra,* Scheme 1). Such species **27** could be formed during a fluorine exchange between the five-coordinate germanate **25** (not identified on ^{19}F NMR spectra recorded in toluene or benzene solution) and four-coordinate germane **26**. Similar bridged structures containing tin and silicon centers have been documented by Janzen[58] and Tamao[59] and their co-workers as possible intermediates in a comparable ligand exchange processes. The formation of **27** is temperature dependent, since ^{19}F NMR experiments at −20 °C and −50 °C revealed the presence of only four-coordinate Ph_3GeF **26** (spectra *b* and *a*).

Furthermore, treatment of the independently synthesized Ph_3GeF[56] (**26**) with a substoichiometric amount of TBAF (0.7 equiv) in benzene-d_6 at ambient temperature resulted in the formation of the fluorine-bridged species **27** as the sole product (^{19}F NMR). Washing the sample with D_2O resulted in the reappearance of the signal for the four-coordinate fluoride **26** (as observed with **21**, see Figure 4), but with lower intensity. Most likely the bridged species **27** and/or the corresponding hypervalent germanates (e.g., **25**) are hydrolyzed[60] into **26** and the more stable hexaphenyldigermoxane **28**, which was isolated from the reaction mixture.

As expected, reactions of di- and trichlorogermanes **6** and **12** with TBAF led to more complex mixtures. Nevertheless, treatment of dichlorogermane **6** produced the difluorinated tetravalent germane Ph_2GeF_2, which shows a signal at −163.9

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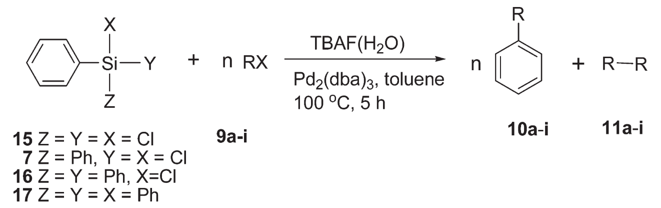
(57) Bujok, R.; Makosza, M. *Synlett* **2004**, 371–373.

(58) Jang, M.; Janzen, A. F. *J. Fluorine Chem.* **1994**, *66*, 129–135.

(59) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099–2114.

(60) Conversion of the analogous fluorosilanes with tetraethylammonium fluoride and water or hypervalent fluorosilicates with water to produce corresponding disilioxane has been reported: Johnson, S. E.; Deiters, J. A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 3250–3258.

TABLE 7. Cross-coupling of silanes 7, 15, 16 and 17 with halides[a]



entry	silane	halide		equiv	product	yield (%)[b,c]	ratio (**10:11**)[d]
1	**15**	1-Bromonaphthalene	**9a′**	1.1	**10a**	42[e]	30:1
2	**15**	4-$CH_3OC_6H_4I$	**9b**	1.1	**10b**	99	99:1
3	**15**	4-$CH_3OC_6H_4Br$	**9b′**	1.1	**10b**	3[f]	1:13
4	**15**	2-$CH_3OC_6H_4I$	**9c**	1.1	**10c**	77[g]	30:1
5	**15**	3-$CF_3C_6H_4I$	**9d**	1.1	**10d**	94 (83)	29:1
6	**15**	4-$CF_3C_6H_4I$	**9e**	1.1	**10e**	88	15:1
7	**15**	4-$CH_3COC_6H_4I$	**9f**	1.1	**10f**	91	99:1
8	**15**	4-$CH_3COC_6H_4Br$	**9f′**	1.1	**10f**	59[h] (56)	99:1
9	**15**	PhCH═CHBr[i]	**9g**	1.1	**10g**	66	4:1
10	**15**	2-iodo-5-methylthiophene	**9h**	1.1	**10h**	57	4.8:1
11	**15**	bromomethylenecyclohexane	**9i**	1.1	**10i**	6	10:1
12	**7**	1-bromonaphthalene[j]	**9a′**	2.2	**10a**	94	7.2:1
13	**7**	4-$CH_3OC_6H_4I$	**9b**	2.2	**10b**	78	10:1
14	**7**	4-$CH_3OC_6H_4Br$	**9b′**	2.2	**10b**	9[f,k]	3:1
15	**7**	2-$CH_3OC_6H_4I$	**9c**	2.2	**10c**	29[k]	30:1
16	**7**	3-$CF_3C_6H_4I$	**9d**	2.2	**10d**	57 (54)	3:1
17	**7**	4-$CF_3C_6H_4I$	**9e**	2.2	**10e**	66[l] (64)	5:1
18	**7**	4-$CH_3COC_6H_4I$	**9f**	2.2	**10f**	54	3:2
19	**7**	4-$CH_3COC_6H_4Br$	**9f′**	2.2	**10f**	79	99:1
20	**7**	PhCH═CHBr[i]	**9g**	2.2	**10g**	22[h]	1:3
21	**7**	2-iodo-5-methylthiophene	**9h**	2.2	**10h**	30[h] (28)	2:3
22	**7**	bromomethylenecyclohexane	**9i**	2.2	**10i**	18[k]	2:1
23	**16**	1-bromonaphthalene	**9a′**	3.3	**10a**	26	12:1
24	**16**	4-$CH_3OC_6H_4I$	**9b**	3.3	**10b**	62	5:1
25	**16**	4-$CH_3OC_6H_4Br$	**9b′**	3.3	**10b**	11[f]	2:3
26	**16**	2-$CH_3OC_6H_4I$	**9c**	3.3	**10c**	11[f]	6:1
27	**16**	3-$CF_3C_6H_4I$	**9d**	3.3	**10d**	45 (42)	1.4:1
28	**16**	4-$CF_3C_6H_4I$	**9e**	3.3	**10e**	44	3:2
29	**16**	4-$CH_3COC_6H_4I$	**9f**	3.3	**10f**	78	4.8:1
30	**16**	4-$CH_3COC_6H_4Br$	**9f′**	3.3	**10f**	73	20:1
31	**16**	PhCH═CHBr[i]	**9g**	3.3	**10g**	31	1:1.3
32	**16**	2-iodo-5-methylthiophene	**9h**	3.3	**10h**	14	1:1.3
33	**16**	bromomethylenecyclohexane	**9i**	3.3	**10i**	12	3:1
34	**17**[m]	3-$CF_3C_6H_4I$	**9d**	4.4	**10d**	13	1:3.7

[a] Couplings were performed on 0.14 mmol scale of silanes (0.04 M) with 1.1, 2.2, 3.3, or 4.4 equiv of halides, 0.05 equiv of Pd catalyst and TBAF (1 M/THF containing 5% of water, 7 equiv) with additional water (~40 equiv), unless otherwise noted. [b] Based on total transferring of one, two, three or four phenyl groups from **15**, **7**, **16**, or **17** respectively. [c] Determined by GC−MS of the crude reaction mixture (isolated yields in parentheses). [d] Molar ratio. [e] 16 h (51%, 99:1). [f] 115 °C. [g] 16 h (86%, 99:1). [h] Biphenyl homocoupling byproducts (10−20%) were also observed. [i] *E*/*Z*, 85:15. [j] Coupling with 1-chloronaphthalene failed. [k] Longer reaction time (11 h) did not affect yield and **10:11** ratio. [l] Without additional water (54%, 4:1). [m] Coupling of **17** with other halides **9** gave **10a−i** with the overall yields less than 5%.

ppm in ^{19}F NMR that is in agreement with the value reported by Spivey et al. for the analogous difluoride (−165 ppm).[15]

To correlate the formation, spectroscopic characteristic, and reactivity of the hypervalent germanium species with those of the corresponding silicon and tin counterparts in the fluoride-promoted couplings, reactions of chloro(triphenyl)silane **16** and chloro(triphenyl)stannane **19** with TBAF in benzene-d_6 were also explored. Thus, heating of **19** with TBAF (1.5 equiv) resulted in the appearance of two singlets at −158.6 ppm and −159.5 ppm which were accompanied by F−Sn satellite signals (spectrum *a*, Figure 6). Further addition of 1.5 equiv of TBAF resulted in the formation of difluorotriphenylstannate **22** which appeared as a sharp singlet at −160.5 ppm with satellite peaks ($^1J_{F-Sn}$ = 2034.2 Hz, $^1J_{F-Sn}$ = 1940.2 Hz) in agreement with the values reported for the isolated **22**[49] (spectrum *b*). Treatment of **16** with TBAF (1.5 equiv) produced a broad peak of Ph_3SiF[61] at −168.4 ppm which exists in equilibrium with $Ph_3SiF_2^-$ **24** (−94.5 ppm) (spectrum *c*). The characteristic signal[54] for the pentavalent complex **24** was, however, clearly observed with 3 equiv of TBAF [δ −94.6 ppm ($^1J_{F-Si}$ = 255.1 Hz) and −95.3 ppm ($^1J_{F-Si}$ = 255.1 Hz)] (spectrum *d*). In contrast, chlorogermane **13**, under similar conditions, produced only small amount of the fluorine-bridged species **27** (−154.68 ppm) in addition to **26** (−201.6 ppm, spectrum *e*). Addition of another portion of TBAF and extra heating resulted in the broadening of the peak(s) and disappearance of the signal for **26** [spectrum *f*; note that the singlet at −125.9 ppm is most probably not related to germanium species since it was also observed in experiments of chlorosilane **16** with higher excess of TBAF (see also spectrum *c*)].

It appears that Ph_3SnCl **19** is more susceptible than its silicon and germanium counterparts to form the reactive

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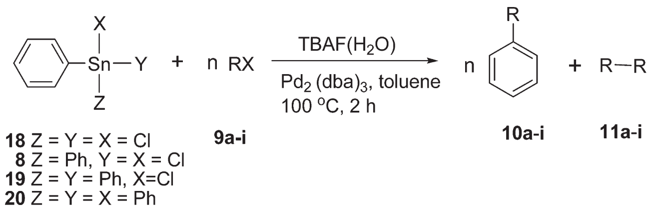
(61) Lickiss, P. D.; Lucas, R. *J. Organomet. Chem.* **1996**, *510*, 167–172.

TABLE 8. Cross-Coupling of Stannanes 8, 18, 19, and 20 with Halides[a]



entry	stannane	halide		equiv	product	yield (%)[b,c]	ratio (**10:11**)[d]
1	**18**	1-bromonaphthalene	**9a′**	1.1	**10a**	41	30:1
2	**18**	4-$CH_3OC_6H_4I$	**9b**	1.1	**10b**	98	30:1
3	**18**	4-$CH_3OC_6H_4Br$	**9b′**	1.1	**10b**	18[e]	10:1
4	**18**	2-$CH_3OC_6H_4I$	**9c**	1.1	**10c**	88	30:1
5	**18**	3-$CF_3C_6H_4I$	**9d**	1.1	**10d**	97	35:1
6	**18**	4-$CF_3C_6H_4I$	**9e**	1.1	**10e**	97 (89)	29:1
7	**18**	4-$CH_3COC_6H_4I$	**9f**	1.1	**10f**	99 (88)	199:1
8	**18**	4-$CH_3COC_6H_4Br$	**9f′**	1.1	**10f**	84[f]	199:1
9	**18**	PhCH=CHBr[g]	**9g**	1.1	**10g**	75[h]	8:1
10	**18**	2-iodo-5-methylthiophene	**9h**	1.1	**10h**	69	7:1
11	**18**	bromomethylenecyclohexane	**9i**	1.1	**10i**	8[i]	15:1
12	**8**	1-bromonaphthalene[j]	**9a′**	2.2	**10a**	47[k]	20:1
13	**8**	4-$CH_3OC_6H_4I$	**9b**	2.2	**10b**	84[l]	16:1
14	**8**	4-$CH_3OC_6H_4Br$	**9b′**	2.2	**10b**	31[e]	1:1
15	**8**	2-$CH_3OC_6H_4I$	**9c**	2.2	**10c**	70	7.7:1
16	**8**	3-$CF_3C_6H_4I$	**9d**	2.2	**10d**	94[m,n]	11:1
17	**8**	4-$CF_3C_6H_4I$	**9e**	2.2	**10e**	83	11:1
18	**8**	4-$CH_3COC_6H_4I$	**9f**	2.2	**10f**	99[o] (88)	199:1
19	**8**	4-$CH_3COC_6H_4Br$	**9f′**	2.2	**10f**	92[l]	199:1
20	**8**	PhCH=CHBr[g]	**9g**	2.2	**10g**	76[l]	40:1
21	**8**	2-iodo-5-methylthiophene	**9h**	2.2	**10h**	94 (80)	20:1
22	**8**	bromomethylenecyclohexane	**9i**	2.2	**10i**	7	1:1
23	**19**	1-bromonaphthalene	**9a′**	3.3	**10a**	37	199:1
24	**19**	4-$CH_3OC_6H_4I$	**9b**	3.3	**10b**	93 (92)	11:1
25	**19**	4-$CH_3OC_6H_4Br$	**9b′**	3.3	**10b**	13[e]	6:1
26	**19**	2-$CH_3OC_6H_4I$	**9c**	3.3	**10c**	79 (76)	13:1
27	**19**	3-$CF_3C_6H_4I$	**9d**	3.3	**10d**	90	9:1
28	**19**	4-$CF_3C_6H_4I$	**9e**	3.3	**10e**	94	11:1
29	**19**	4-$CH_3COC_6H_4I$	**9f**	3.3	**10f**	100	199:1
30	**19**	4-$CH_3COC_6H_4Br$	**9f′**	3.3	**10f**	96 (92)	199:1
31	**19**	PhCH=CHBr[g]	**9g**	3.3	**10g**	35	20:1
32	**19**	2-iodo-5-methylthiophene	**9h**	3.3	**10h**	70	3.2:1
33	**19**	bromomethylenecyclohexane	**9i**	3.3	**10i**	9	20:1
34	**20**	1-bromonaphthalene	**9a′**	4.4	**10a**	11[p]	20:1
35	**20**	4-$CH_3OC_6H_4I$	**9b**	4.4	**10b**	80[p]	7:1
36	**20**	4-$CH_3OC_6H_4Br$	**9b′**	4.4	**10b**	2	1:1
37	**20**	2-$CH_3OC_6H_4I$	**9c**	4.4	**10c**	20	30:1
38	**20**	3-$CF_3C_6H_4I$	**9d**	4.4	**10d**	75	4.5:1
39	**20**	4-$CF_3C_6H_4I$	**9e**	4.4	**10e**	75[p]	8:1
40	**20**	4-$CH_3COC_6H_4I$	**9f**	4.4	**10f**	68	27:1
41	**20**	4-$CH_3COC_6H_4Br$	**9f′**	4.4	**10f**	97	99:1
42	**20**	PhCH=CHBr[g]	**9g**	4.4	**10g**	55	2:1
43	**20**	2-iodo-5-methylthiophene	**9h**	4.4	**10h**	50	2:1
44	**20**	bromomethylenecyclohexane	**9i**	4.4	**10i**	5	3:1

[a] Couplings were performed on 0.14 mmol scale of stannanes (0.04 M) with 1.1, 2.2, 3.3, or 4.4 equiv of halides, 0.05 equiv of Pd catalyst and TBAF (1 M/THF containing 5% of water, 7 equiv) with additional water (~40 equiv), unless otherwise noted. [b] Based on total transferring of one, two, three, or four phenyl groups from **18**, **8**, **19**, or **20**, respectively. [c] Determined by GC−MS of the crude reaction mixture (isolated yields in paretheses). [d] Molar ratio. [e] 115 °C. [f] 6 h (87%, 99:1). [g] *E*/*Z*, 85:15. [h] 6 h (78%, 7:1). [i] 20 h at 115 °C (52%, 13:1). [j] Couplings with 1-chloronaphthalene failed. [k] 5 h (64%, 18:1). [l] 5 equiv of TBAF gave similar yield and ratio. [m] At 80 °C (89%, 13:1). [n] After 1 h (85%, 11:1). [o] Without additional water (93%, 99:1). [p] Longer reaction time (28 h) did not affect yield and **10**:**11** ratio.

pentavalent complex **22** in benzene solution, even at low concentrations of fluoride ions. On the other hand, the silicon analogue **16**, although it requires higher concentration of TBAF to afford the corresponding pentavalent complex **24** than the tin counterpart, is more prone to form hypervalent species than the analogous organogermane precursor. Since germane **13**, silane **16**, and stannane **19** substrates undergo fluoride-promoted coupling in toluene but require different reaction conditions (time/temperature), these results indicate that the differences in the coupling efficiencies of these substrates might reflects their ability to generate reactive hypervalent intermediates upon fluoride activation. The lower susceptibility of the organogermanes toward fluoride activation (coupling) is probably the result of Ge anomalously high electronegativity, as compared to other group 14 elements (C, 2.50; Si, 1.74; Ge, 2.02; Sn, 1.72),[7,15] which makes C−Ge bonds less polarized than C−Si and C−Sn bonds and therefore less prone to nucleophilic attacks.

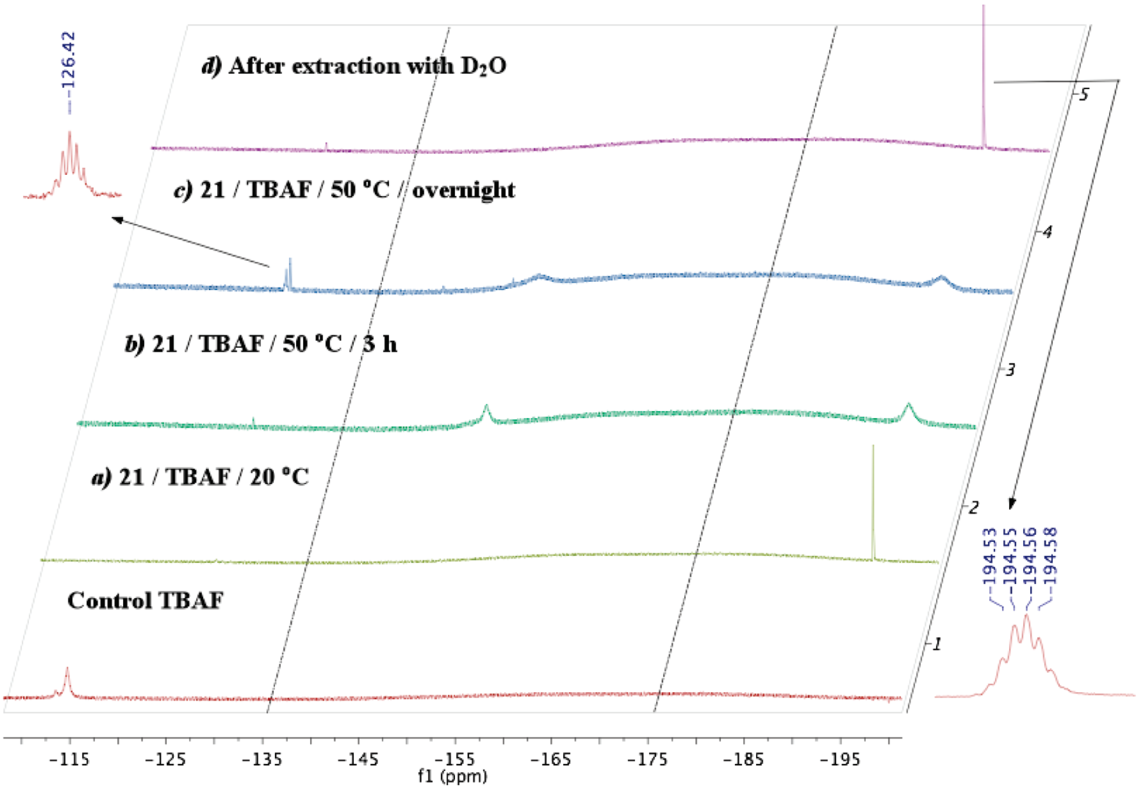
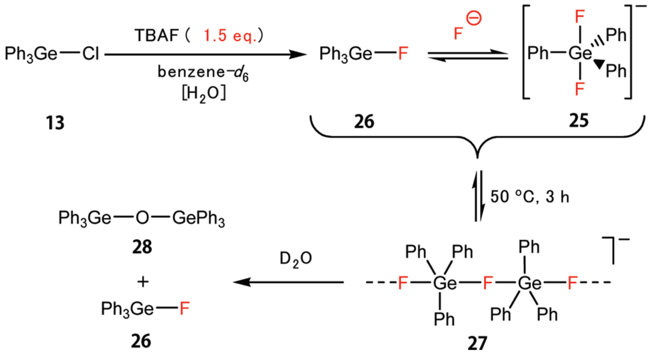


FIGURE 4. ^{19}F NMR spectra of the reaction of $PhMe_2GeCl$ **21** with 1.5 equiv of TBAF in benzene-d_6.

SCHEME 1. Plausible Interaction of Chloro(triphenyl)germane 13 with TBAF/H_2O



To investigate the effect of water on the coupling of chlorogermanes with aryl halides, reactions of **13** (0.2 mmol) with TBAF (1.5 equiv) in benzene-d_6 (2.0 mL) in the presence of various amounts of water (25, 50, and 100 μL) were also analyzed by ^{19}F NMR (Figure 7, see SI). The conversion to Ph_3GeF **26** (δ −202.3 ppm) increased at higher water loading (spectrum *a* vs *c* vs *e*). It is known that fluorination of bulky chlorosilanes are also accelerated by the addition of water[61] and hydrated TBAF showed enhanced nucleophilicity for converting alkyl halides into alkyl fluorides.[62] Heating at 50 °C produced the same species **27** (−152.9 ppm) that was observed in the experiments without the additional water added (spectrum *e*, Figure 6). Washing the sample with D_2O resulted in the detection of **26** (the sole signal on ^{19}F NMR) and digermoxane **28** (Scheme 1). When using a higher concentration of TBAF (4.5 equiv; 50 °C/overnight), washing with D_2O resulted in disappearance of signal(s) on the ^{19}F NMR spectrum.

To establish a role of the digermoxane **28** in the coupling of chlorogermanes, the reactions of **28** with aryl iodides were carried out. Thus, treatment of the commercially available **28** with 1 equiv of 1-iodonapthalene **9a** or 4-iodoanisole **9b** in the presence of TBAF (7 equiv) and $Pd_2(dba)_3$ in toluene afforded biaryls **10a** (32%) or **10b** (60%; based on the transfer of one phenyl group from **28**) in addition to the homocoupling byproducts **11a** (34%) and **11b** (18%, Scheme 2). Analogous coupling of **28** with 3 and 6 equiv of **9a** also afforded **10a** in 68% and 96% yield, respectively in addition to larger quantities of unreacted **9a** and homocoupling byproduct **11a**. Treatment of **28** with excess of 4-iodoanisole **9b** gave similar results (e.g., coupling with 3 equiv of **9b** produced **10b** in 92% yield). The fact that total yields of **10a** or **10b** do not exceed theoretical yields of 100% indicates that multiple transfers of phenyl groups from **28** did not occur. All attempts at changing coupling conditions (e.g., using wet toluene, THF or 1,4-dioxane at reflux as solvent as well as addition of Ag_2O/TBAF or NaOH as base) failed to increase the yield of **10a**. It appears that although **28** can couple with aryl iodides, the pathway for cross-coupling between Ph_3GeCl **13** and aryl halides most likely involves other intermediates which could be responsible for the multiple transfer of the phenyl group.

Our data suggest that the fluoride-promoted cross-coupling of chlorogermanes (e.g., **13**) in "wet" toluene involves displacement of Cl ligands from the Ge center by the nucleophilic fluoride ions to generate four-coordinate fluorogermanes

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[62] Albanese, D.; Landini, D.; Penso, M. *J. Org. Chem.* **1998**, *63*, 9587–9589.

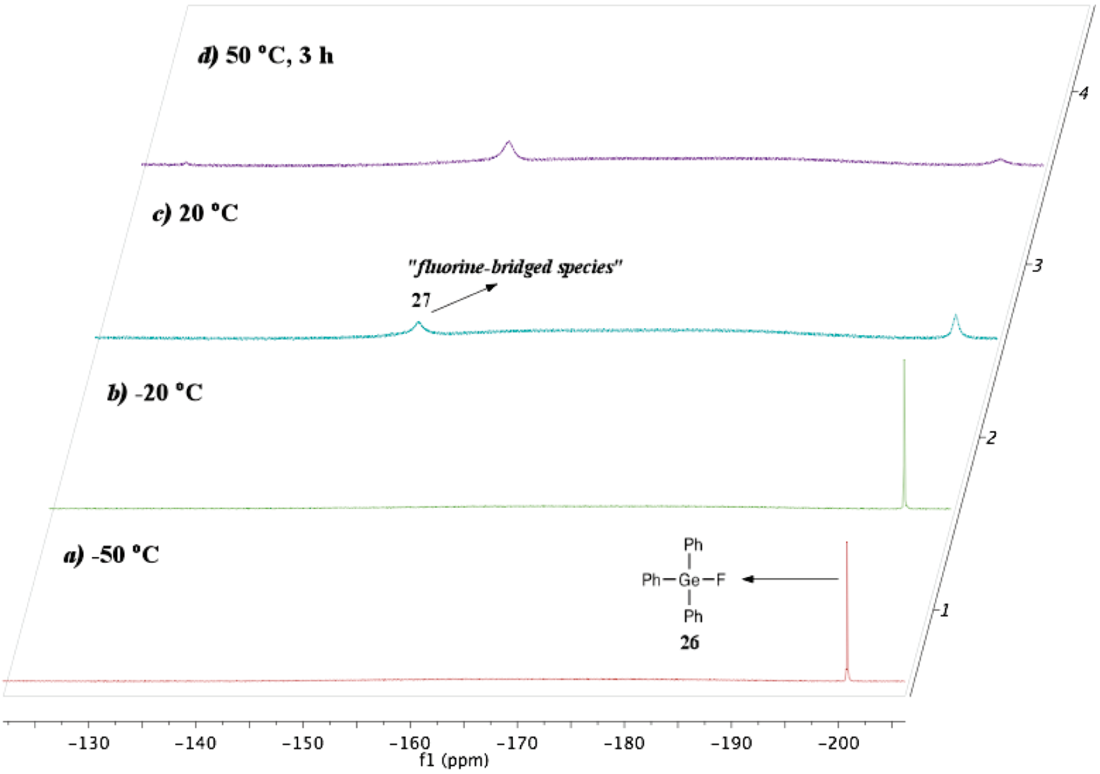


FIGURE 5. ^{19}F NMR spectra of the reaction of Ph_3GeCl **13** with 1.5 equiv of TBAF in toluene-d_8 at various temperature.

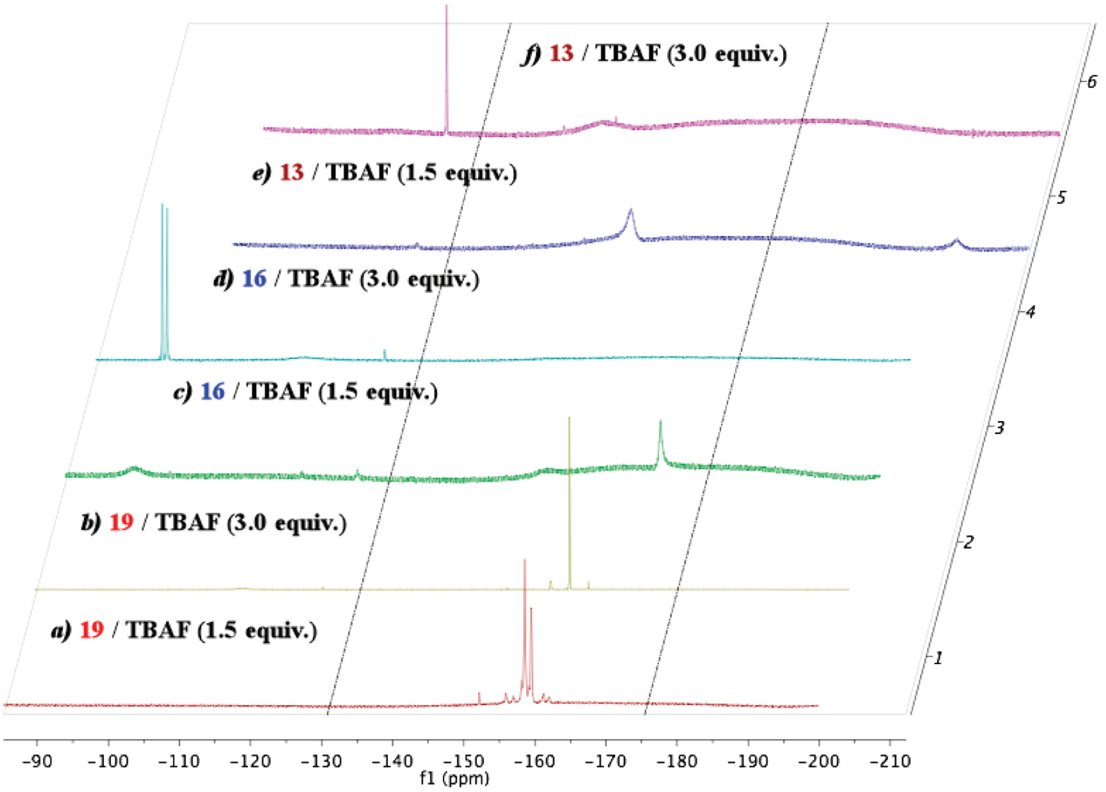
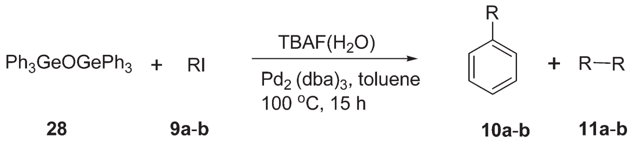


FIGURE 6. ^{19}F NMR spectra of the reaction of Ph_3GeCl **13**, Ph_3SiCl **16**, and Ph_3SnCl **19** with TBAF in benzene-d_6 (50 °C/3 h).

(e.g., **26**). This in turn leads to the hypervalent fluorogermanates (e.g., **25**) and fluorine-bridged species of type **27**. The germanates and/or fluorine-bridged species could be directly engaged in transmetalation with reactive aryl-Pd-X (X = halogen, OH) complex(es) to give cross-coupling products. Alternatively, hypervalent species of type **25** and/or **27** might

SCHEME 2. Cross-Coupling of Hexaphenyldigermoxane 28 with Aryl Halides



Series **a**: R = 1-naphthyl; **b** R = 4-methoxyphenyl

react with water to generate the reactive fluoro(hydroxo)-triphenylgermanate species or the triphenylgermanol hydrogen-bonded complexes to TBAF. The analogous hypervalent silicate species were proposed for the fluoride-promoted coupling of vinyl silanols.[6,40] Although a mechanism that will support the multiple transfer of the phenyl groups from the same metallic center requires additional investigation, it is likely that the tin, silicon, or germanium species with extra halogen ligands formed after each transmetalation cycle are rendered more reactive to efficiently transfer a second or third phenyl group from the Sn, Si, or Ge atom.

In summary, we have demonstrated that $(\text{chloro})_{4-n}(\text{phenyl})_n$germanes and -silanes ($n = 1, 2$, or 3) as well as -stannanes ($n = 1, 2, 3$, or 4) undergo Pd-catalyzed cross-couplings with aryl iodides and bromides in the presence of TBAF in “moist” toluene. The chlorophenylstannanes are more reactive than chlorophenylsilanes, which in turn are more effective than chlorophenylgermanes. One chloride ligand on either Ge or Si center allows efficient activation by fluoride to promote transfer of up to three aryl groups from germanium or silicon. For the silanes and germanes reactivity increases with the number of halogen ligands on the Si or Ge center ($PhMCl_3 > Ph_2MCl_2 > Ph_3MCl > Ph_4M$, where M = Si or Ge). For the germanes and to some extent for the silanes, the reactions with addition of a *measured* amount of water showed increased overall yields and higher cross-coupling to homocoupling product ratios. Stannanes were found to be most reactive, and even tetraphenyltin, which lacks a halogen ligand, can transfer efficiently up to four phenyl groups during fluoride-promoted couplings with aryl halides. The methodology shows that organogermanes can render a coupling efficiency *comparable* to that of the more established stannane and silane counterparts. ^{19}F NMR studies suggested formation of the fluorophenylgermanes and the hypervalent fluorogermanate species as possible intermediates.

Experimental Section

General Procedure for Coupling of Chlorophenylgermanes. Method A. Commercial TBAF (1 M THF solution containing ~5 wt % of water, 7 equiv) was added to a stirred solution of 0.14 mmol of $PhGeCl_3$ **12** or Ph_2GeCl_2 **6** or Ph_3GeCl **13** or $PhMe_2GeCl$ **21** or Ph_4Ge **14** containing the appropriate halide **9a**−**i** (1.1−4.4 equiv; see Table 2, 5, and 6) and $Pd_2(dba)_3$ (0.05 equiv) in toluene (3.0 mL) at ambient temperature under nitrogen atmosphere. The resulting brownish mixture was heated at 100 °C (oil bath) for 15 h. The volatiles were evaporated, and the residue was partitioned (H_2O/CH_2Cl_2). The organic layer was dried ($MgSO_4$), evaporated, and purified by column chromatography (hexane) to give cross-coupling products **10** followed by homocoupling byproducts **11**. Yields of **10a**−**i** and ratios of coupling products **10a**−**i** to homocoupling byproducts **11a**−**i** are given in Tables 2, 5, and 6. Representative typical procedures are included in Supporting Information (SI).

Method B. Couplings were carried out as in Method A with the additional amount of water (~40 equiv) added. Representative typical procedures are included in SI.

General Procedure for Coupling of Chlorophenylsilanes. Method A. Commercial TBAF (1 M THF solution containing ~5 wt % of water, 7 equiv) was added to a stirred solution of 0.14 mmol of $PhSiCl_3$ **15** or Ph_2SiCl_2 **7** or Ph_3SiCl **16** or Ph_4Si **14** containing the appropriate halide **9a**−**i** (1.1−4.4 equiv; see Table 3 and 7) and $Pd_2(dba)_3$ (0.05 equiv) in toluene (3.0 mL) at ambient temperature under nitrogen atmosphere. The resulting brownish mixture was heated at 100 °C (oil bath) for 5 h. The volatiles were evaporated, and the residue was partitioned (H_2O/CH_2Cl_2). The organic layer was dried ($MgSO_4$), evaporated, and purified by column chromatography (hexane) to give cross-coupling products **10** followed by homocoupling byproducts **11**. Yields of **10a**−**i** and ratios of coupling products **10a**−**i** to homocoupling byproducts **11a**−**i** are given in Tables 3 and 7. Representative typical procedures are included in SI.

Method B. Couplings were carried out as in Method A with the additional amount of water (~40 equiv) added. Representative typical procedures are included in SI.

General Procedure for Coupling of Chlorophenylstannanes and Tetraphenyltin. Method A. Commercial TBAF (1 M THF solution containing ca. 5 wt % of water, 7 equiv) was added to a stirred solution of 0.14 mmol of $PhSnCl_3$ **18** or Ph_2SnCl_2 **8** or Ph_3SiCl **19** or Ph_4Si **20** containing the appropriate halide **9a**−**i** (1.1−4.4 equiv; see Tables 4 and 8) and $Pd_2(dba)_3$ (0.05 equiv) in toluene (3.0 mL) at ambient temperature under nitrogen atmosphere. The resulting brownish mixture was heated at 100 °C (oil bath) for 2 h. The volatiles were evaporated, and the residue was partitioned (H_2O/CH_2Cl_2). The organic layer was dried ($MgSO_4$), evaporated, and purified by column chromatography (hexane) to give cross-coupling products **10** followed by homocoupling byproducts **11**. Yields of **10a**−**i** and ratios of coupling products **10a**−**i** to homocoupling byproducts **11a**−**i** are given in Tables 4 and 8. Representative typical procedures are included in SI.

Method B. Couplings were carried out as in Method A with the additional amount of water (~40 equiv) added. Representative typical procedures are included in SI.

Procedure for Coupling of Hexaphenyldigermoxane. TBAF (1 M/THF, 1.12 mL, 1.12 mmol) was added to a stirred solution of $(Ph_3Ge)_2O$ (**28**; 100 mg, 0.16 mmol) containing 1-iodonaphthalene (**9a**; 23.4 μL, 40.1 mg, 0.16 mmol) and $Pd_2(dba)_3$ (7.3 mg, 0.008 mmol) in toluene (3.5 mL) at ambient temperature under nitrogen atmosphere. The resulting brownish mixture was heated at 100 °C (oil bath) for 15 h. The volatiles were evaporated and the residue was partitioned (H_2O/CH_2Cl_2). The organic layer was dried ($MgSO_4$), evaporated, and purified by column chromatography (hexane) to give **10a** (10.4 mg, 32%) followed by **11a** (14.0 mg, 34%; 68% consumption of **9a**).

Analogous treatment **28** (100 mg, 0.16 mmol) with **9a** (70.2 μL, 122 mg, 0.48 mmol) gave **10a** (22.2 mg, 68%) and **11a** (39.5 mg, 32%).

Analogous treatment **28** (100 mg, 0.16 mmol) with **9a** (140.4 μL, 244 mg, 0.96 mmol) gave **10a** (31.3 mg, 96%) and **11a** (98 mg, 40%).

Analogous treatment **28** (100 mg, 0.16 mmol) with 4-iodoanisole (**9b**; 37.4 mg, 0.16 mmol) gave **10b** (17.6 mg, 60%) and **11b** (6.1 mg, 18%).

Analogous treatment **28** (100 mg, 0.16 mmol) with **9b** (112.3 mg, 0.48 mmol) gave **10b** (27.1 mg, 92%) and **11b** (27 mg, 26%).

Typical Procedure for the Reaction of Chlorotriphenylgermane with TBAF. TBAF (0.30 mL, 0.30 mmol; 1 M in THF) and H_2O (0.10 mL, 5.55 mmol) were added to a solution of Ph_3GeCl **13** (68.5 mg, 0.20 mmol) in benzene or benzene-d_6 (2 mL), and the resulting mixture was stirred at 50 °C for 3 h. After cooling, the solution was extracted with H_2O, the separated organic layer was dried (Na_2SO_4), and volatiles were evaporated to give a crude mixture of **26** and **28** (~1:3; ^{19}F and ^{13}C NMR) in addition to the small amount of other byproducts (~10%). Column chromatography (EtOAc/hexane, 1:9) afforded hexaphenyldigermoxane **28**[63] (31 mg, 51%) as white crystals with data identical to those of the commercial sample: mp 178−180 °C (Lit.[63] 180−182 °C). ^{1}H NMR δ 7.24−7.31 (m, 6H), 7.37 (tt, J = 7.5 Hz, 1.9 Hz, 3H), 7.43−7.48 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 128.2, 129.5, 134.6, 137.7; ^{13}C NMR (benzene-d_6) 128.5, 129.8, 134.9, 138.1.

Analogous treatment (50 °C, overnight) of **13** (68.5 mg, 0.20 mmol) in benzene (2 mL) with TBAF (0.90 mL, 0.90 mmol; 1 M in THF) and H_2O (0.10 mL, 5.55 mmol) gave **28** (51 mg, 82%) which crystallized directly from benzene solution (after washing) with H_2O upon slow evaporation.

Fluorotriphenylgermane (26). A suspension of commercially available hexaphenyldigermoxane **28** (120 mg, 0.19 mmol) in MeOH (2 mL) in a polyethylene (Nalgene) screw-capped vial was chilled for 15 min at 0 °C. Aqueous HF (48 wt %; 55 μL, 1.5 mmol,) was added and the mixture was slowly warmed to ambient temperature. After stirring for 3 h, water was added, and the resulting white precipitate was filtered off and washed with additional portions of water to give **26**[56] (108.0 mg, 87%): mp 72−74 °C (Lit.[56] 77−78 °C); ^{1}H NMR (benzene-d_6) δ 7.00−7.10 (m, 9H), 7.53−7.58 (m, 6H); ^{13}C NMR (benzene-d_6) δ 128.9, 130.8, 134.5 ($^3J_{F-C}$ = 1.5 Hz), 134.6 ($^2J_{F-C}$ = 13.9 Hz); ^{19}F NMR (benzene-d_6) δ −202.24 (s);

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Supporting Information Available: General experimental details and NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[63] Cerveau, G.; Colomer, E.; Corriu, R. J. P.; Young, J. C. *J. Organomet. Chem.* **1981**, *205*, 31–45.