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Integrated Palladium-Catalyzed Arylation of Heavier Group 14 Hydrides

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Yoshinori Yamanoi,*[a] and Hiroshi Nishihara*[a]

Abstract: A convenient procedure has been developed for the preparation of Group 14 compounds by integrated palladium-catalyzed cross-coupling of aromatic iodides with the corresponding Group 14 hydrides in the presence of a base. The reaction conditions can be applied to the cross-coupling of tertiary, secondary, and primary Group 14 compounds. In most cases, the desired arylated products were obtained in synthetically useful yields. Even in the case of aryl iodides containing OH, NH_2, CN, or CO_2R groups, the reactions proceeded with good to high yields with tolerance of these reactive functional groups. A possible application of this method is the unique synthesis of a fungicidal diarylmethyl(1*H*-1,2,4-triazol-1-ylmethyl)silane derivative.

Keywords: cross-coupling · germanium · homogeneous catalysis · palladium · silicon

Introduction

Compounds containing heavier Group 14 elements have attracted considerable attention due to their widespread applications as intermediates for carbon–carbon bond formation,[1] as building blocks for the construction of novel materials,[2] and as biologically active pharmaceuticals or agrochemicals.[3] The conventional chemical routes to these compounds have predominantly involved nucleophilic substitution with Grignard or organolithium reagents.[4,5] These methods have limited applications because compounds that contain functional groups sensitive to organometallic reagents are only accessible in multiple steps. Consequently, more general synthetically useful methods for the preparation of functionalized Group 14 compounds remain in great demand.

The transition-metal-catalyzed cross-coupling of organometallics with organohalogen compounds is a powerful approach for connecting two molecules by carbon–carbon or carbon–heteroatom bonds.[6] Transition-metal-catalyzed reactions of Si- or Ge-centered hydrides form the basis of a number of important synthetic methodologies.[7] Recently, the development of efficient methods for transition-metal-catalyzed arylation of tertiary silanes has emerged as one of the most powerful synthetic methods for accessing aryl silanes. For example, pioneering coupling reactions of trialkoxysilanes with aryl halides have been recently reported independently by Murata, Masuda et al.,[8] DeShong et al.,[9] Denmark et al.,[10] Komuro et al.,[11] and Ito.[12] Although, satisfactory results were obtained for the preparation of aryltrialkoxysilanes, arylation of trialkylsilane[13] has met with limited success due to the tendency to give a reduced product (Scheme 1a).[14,15] Attention has also been paid to the Pd-catalyzed arylation of tris(2-furyl)germane[16] or hydrogermatrane[8e] with aryl halides. Despite these significant advances, other examples of arylation of hydrogermanes with aryl halides have not been described to date.

In the course of our research, we focused on the development of a new methodology based on transition-metal-catalyzed arylation using hydrosilanes.[17,18] We report herein a detailed study in which we obtained Si- or Ge-containing compounds by using the stepwise and integrated arylation of primary, secondary, or tertiary Group 14 compounds in the presence of a base, catalyzed by the commercially available complex $[Pd(PtBu_3)_2]$ (Scheme 1b).

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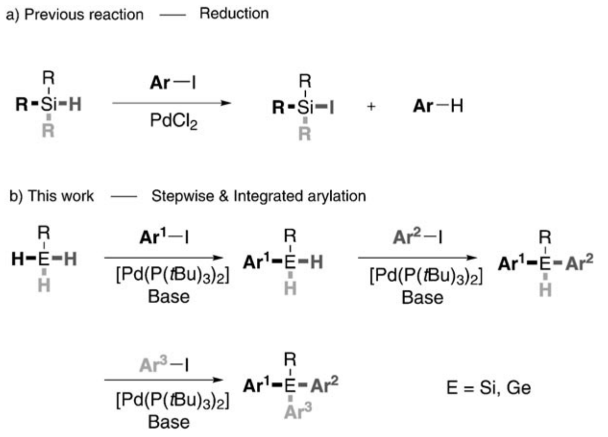


Scheme 1. a) Previous transition-metal-catalyzed reduction of aryl iodides with hydrosilanes. b) Pd-catalyzed stepwise arylation of Group 14 hydrides with aryl iodides.

Results and Discussion

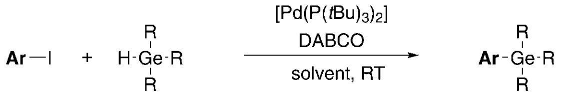
Arylation of tertiary germanes:[19,20] We recently developed a facile protocol to synthesize functionalized silane compounds by transition-metal-catalyzed arylation of tertiary silanes.[18a–c] Encouraged by the preliminary results, we investigated the arylation of a tertiary germane. Treatment of 4-iodoanisole with triphenylgermane in the presence of [Pd($PtBu_3$)$_2$] (5 mol %) and 1,4-diazabicyclo[2.2.2]octane (DABCO, 3.0 equiv) in DME at room temperature for 1 d led to (4-methoxyphenyl)triphenylgermane (**1**) in 95 % yield (Table 1, entry 1). Small amounts of anisole were detected under these conditions, as indicated by GC-MS analysis of the crude reaction mixture. Although we screened several reaction conditions, the [Pd($PtBu_3$)$_2$]/DABCO system in DME at room temperature proved to be optimal for this reaction.

Using the above-mentioned conditions, we investigated the scope of palladium-catalyzed arylation of tertiary germanes with various aryl iodides.[21] As summarized in Table 1, the reactions proceeded in moderate to good yields. The electronic properties of the aromatic ring had a large impact on the arylation yield. Electron-deficient aryl iodides gave lower yields than electron-rich aryl iodides. The reaction proceeded smoothly to give the arylated germanes in good yield even in the case of an *ortho*-substituted aryl iodide, which did not effectively couple with tertiary silanes in the presence of the palladium catalyst (Table 1, entries 3, 6, and 21).[18a] Heteroaryl iodides were also arylated with good efficiencies (Table 1, entries 18, 30, and 32). Functional groups, such as OH, NH_2, and CN, on the aromatic ring of the aryl iodides were tolerated under these conditions (Table 1, entries 13–15). In all case, byproducts were due to reduction (arenes), and no starting materials were observed by GC-MS.

Arylation of secondary silanes and germanes: To probe the generality of this catalytic arylation, we next examined the reactions of various Group 14 dihydrides. Tertiary silanes are commonly prepared by addition of organometallic reagents to secondary silanes. However, this method has limited application for compounds containing functional groups sensitive to organometallic reagents.[22] Previously, we reported that several aryl iodides and secondary silanes coupled in the presence of [Pd($PtBu_3$)$_2$] and Et_3N to give the corresponding tertiary silanes in good to high yields.[18d]

Having obtained satisfactory results in the above initial studies, we proceeded to screen cross-coupling between a broad range of aromatic iodides and secondary silanes or germanes. The scope and limitations of the [Pd($PtBu_3$)$_2$] cat-

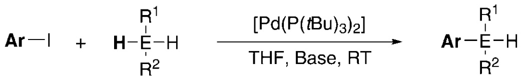
Table 1. Arylation of tertiary germanes.[a]



Entry	Ar	R	Time [d]	Product	Yield [%]	Entry	Ar	R	Time [d]	Product	Yield [%]
1	4-$MeOC_6H_4$	Ph	1	**1**	95	17	3-$F_3CC_6H_4$	Ph	2	**17**	23
2	3-$MeOC_6H_4$	Ph	3	**2**	23	18	2-C_4H_3S	Ph	2	**18**	67
3	2-$MeOC_6H_4$	Ph	3	**3**	37	19	4-$MeOC_6H_4$	Et	1	**19**	70
4	4-$Me_2NC_6H_4$	Ph	3	**4**	81	20	3-$MeOC_6H_4$	Et	1	**20**	42
5	3-$Me_2NC_6H_4$	Ph	3	**5**	35	21	2-$MeOC_6H_4$	Et	2	**21**	58
6	2-$Me_2NC_6H_4$	Ph	2	**6**	91	22	3-$Me_2NC_6H_4$	Et	1	**22**	75
7	4-MeC_6H_4	Ph	2	**7**	54	23	Ph	Et	2	**23**	36
8	4-EtC_6H_4	Ph	1	**8**	59	24	4-MeC_6H_4	Et	2	**24**	46
9	4-*i*PrC_6H_4	Ph	1	**9**	67	25	4-EtC_6H_4	Et	1	**25**	60
10	4-*t*BuC_6H_4	Ph	1	**10**	52	26	4-*i*PrC_6H_4	Et	1	**26**	62
11	3,5-$Me_2C_6H_3$	Ph	3	**11**	33	27	4-*t*BuC_6H_4	Et	1	**27**	53
12	Ph	Ph	2	**12**	49	28	3,5-$Me_2C_6H_3$	Et	2	**28**	65
13	4-HOC_6H_4	Ph	2	**13**	64	29	3-$F_3CC_6H_4$	Et	2	**29**	34
14	4-$H_2NC_6H_4$	Ph	2	**14**	65	30	2-C_4H_3S	Et	1	**30**	77
15	3-NCC_6H_4	Ph	1	**15**	30	31	4-$MeOC_6H_4$	*n*Bu	1	**31**	79
16	4-$F_3CC_6H_4$	Ph	1	**16**	27	32	2-C_4H_3S	*n*Bu	1	**32**	88

[a] Reaction conditions: aryl iodide (0.5 mmol), tertiary germane (0.6 mmol), DABCO (1.5 mmol), [Pd($PtBu_3$)$_2$] (0.025 mmol), DME (1.0 mL), RT.

Table 2. Single arylation of Group 14 dihydrides.



Entry	Ar	E	R^1	R^2	Time [d]	Product	Yield [%]	Entry	Ar	E	R^1	R^2	Time [d]	Product	Yield [%]
1[a]	3-MeOC$_6$H$_4$	Si	Ph	Ph	2	**33**	43	19[a]	3-MeC$_6$H$_4$	Si	Ph	Me	2	**49**	45
2[a]	2-MeC$_6$H$_4$	Si	Ph	Ph	2	**34**	80	20[a]	2-PhC$_6$H$_4$	Si	Ph	Me	2	**50**	95
3[a]	2,4-Me$_2$C$_6$H$_3$	Si	Ph	Ph	2	**35**	85	21[a]	4-F$_3$CC$_6$H$_4$	Si	Ph	Me	2	**51**	47
4[a]	2-EtC$_6$H$_4$	Si	Ph	Ph	2	**36**	80	22[a]	3-F$_3$CC$_6$H$_4$	Si	Ph	Me	2	**52**	30
5[a]	2-*i*PrC$_6$H$_4$	Si	Ph	Ph	2	**37**	67	23[a]	1-Np	Si	Ph	Me	2	**53**	37
6[a]	2-*t*BuC$_6$H$_4$	Si	Ph	Ph	2	–[e]	–[e]	24[a]	Ph	Si	Ph	Me	2	**54**	77
7[a]	2,6-Me$_2$C$_6$H$_3$	Si	Ph	Ph	2	–[e]	–[e]	25[a]	2-PhC$_6$H$_4$	Si	Et	Et	2	**55**	51
8[a]	4-*i*PrC$_6$H$_4$	Si	Ph	Ph	2	**38**	67	26[a]	2-*i*PrC$_6$H$_4$	Si	Et	Et	2	**56**	76
9[a]	4-*t*BuC$_6$H$_4$	Si	Ph	Ph	2	**39**	52	27[a]	4-MeOC$_6$H$_4$	Si	*t*Bu	*t*Bu	2	–[e]	–[e]
10[a]	3,5-Me$_2$C$_6$H$_3$	Si	Ph	Ph	2	**40**	61	28[d]	4-MeOC$_6$H$_3$	Ge	Ph	Ph	4	**57**	57
11[a]	4-Me$_2$NC$_6$H$_4$	Si	Ph	Ph	2	**41**	51	29[d]	3-MeOC$_6$H$_4$	Ge	Ph	Ph	4	**58**	60
12[a]	3-Me$_2$NC$_6$H$_4$	Si	Ph	Ph	2	**42**	64	30[d]	2-MeOC$_6$H$_4$	Ge	Ph	Ph	4	**59**	22
13[a]	4-H$_2$NC$_6$H$_4$	Si	Ph	Ph	2	**43**	89	31[d]	4-*t*BuC$_6$H$_4$	Ge	Ph	Ph	3	**60**	49
14[b]	3-NCC$_6$H$_4$	Si	Ph	Ph	2	**44**	52	32[d]	3-F$_3$CC$_6$H$_4$	Ge	Ph	Ph	4	**61**	37
15[c]	3-HOC$_6$H$_4$	Si	1-Np	Ph	5	**45**	49	33[d]	3-NCC$_6$H$_4$	Ge	Ph	Ph	6.5	**62**	62
16[a]	4-MeOC$_6$H$_4$	Si	Ph	Ph	2	**46**	38	34[d]	1-C$_{10}$H$_7$	Ge	Ph	Ph	3	**63**	52
17[a]	3-MeOC$_6$H$_4$	Si	Ph	Me	2	**47**	46	35[d]	2-*i*PrC$_6$H$_4$	Ge	Et	Et	1	**64**	63
18[a]	4-MeC$_6$H$_4$	Si	Ph	Me	2	**48**	65	36[d]	2-*t*BuC$_6$H$_4$	Ge	Et	Et	1	–[f]	–[f]

[a] Reaction conditions: aryl iodide (1.0 mmol), secondary silane (1.5 mmol), Et$_3$N (2.0 mmol), [Pd(P*t*Bu$_3$)$_2$] (0.05 mmol), THF (1.0 mL), RT. [b] Reaction conditions: aryl iodide (1.0 mmol), secondary silane (3.0 mmol), Et$_3$N (3.0 mmol), [Pd(P*t*Bu$_3$)$_2$] (0.05 mmol), THF (1.0 mL), RT. [c] Reaction conditions: aryl iodide (1.0 mmol), secondary silane (1.5 mmol), Et$_3$N (2.0 mmol), [Pd(P*t*Bu$_3$)$_2$] (0.05 mmol), THF (1.0 mL), 0 °C. [d] Reaction conditions: aryl iodide (1.0 mmol), secondary germane (2.5 mmol), *i*Pr$_2$EtN (1.5 mmol), [Pd(P*t*Bu$_3$)$_2$] (0.05 mmol), THF (1.0 mL), RT. [e] No arylsilane was obtained. [f] A trace amount of arylated product was observed by GC-MS analysis.

alyst system applied in these reactions are summarized in Table 2. In general, all reactions were very clean, and the corresponding tertiary silanes and germanes were obtained in moderate to good yields. In all cases, small amounts of the reduced products were detected by GC-MS, but these could be separated during purification by column chromatography. Doubly arylated side products were not obtained in any mono-arylation reaction. The electronic effects of the substituents on the aromatic ring did not significantly affect the reaction. We found that the catalyst system tolerated reactive functional groups, such as NH$_2$ (Table 2, entry 13), OH (Table 2, entry 15), and CN (Table 2, entries 14 and 33). However, attempts to perform the arylation using 2-*tert*-butyliodobenzene and 2,6-dimethyliodobenzene failed (Table 2, entries 6 and 7), which could be attributed to steric hindrance in the substrates. On studying the influence of hydrosilanes and hydrogermanes on the arylation reaction, we found that 1-NpPhSiH$_2$,[23] PhMeSiH$_2$, Et$_2$SiH$_2$, Ph$_2$GeH$_2$, and Et$_2$GeH$_2$ gave the corresponding tertiary Group 14 compounds in moderate to good yields. In contrast, the use of di-*tert*-butylsilane, which has a greater degree of steric hindrance, hampered the arylation reaction (Table 2, entry 27). Studies on material balance were performed for Table 2, entry 30 as a model reaction. In the course of the catalytic reaction, monoarylated product **59** (22 %) and reduced product (77 %) were produced with excellent material balance (99 %, Figure 1). No doubly arylated product was observed.

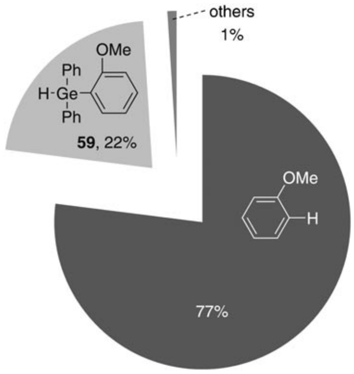
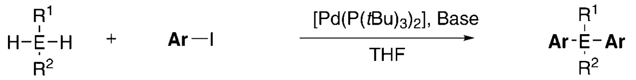


Figure 1. Material balance for Table 2, entry 30, based on 2-iodoanisole.

Encouraged by these promising results, double arylation of diphenylsilane was first attempted in the presence of an excess of 4-iodoanisole. Following the success of this reaction, the scope of double arylation was examined (Table 3). A diverse array of aryl iodides were good substrates for this transformation. The yields of the diarylated products were generally poor to moderate, and the reaction tolerated the presence of a variety of functional groups. Double arylation is sensitive to the steric and electronic effects of functional groups in the aryl iodide. Electron-withdrawing aryl substituents, such as the ethyl ester group (CO$_2$Et) in the substrate, led to an inferior yield (Table 3, entries 23 and 28). Electron-rich aryl iodides with *meta* and *para* substituents reacted well under optimized conditions, whereas ArI substrates with sterically demanding *ortho* substitution did not produce any diarylated product (Table 3, entry 6). Reaction of 1-naphthylphenylsilane with 4-iodoanisole also gave only the mono-arylated product; the diarylated product was pro-

Table 3. Double arylation of secondary silanes and germanes.



Entry	Ar	E	R^1	R^2	Time [d]	Product	Yield [%]	Entry	Ar	E	R^1	R^2	Time [d]	Product	Yield [%]
1[a]	4-$Me_2NC_6H_4$	Si	Ph	Ph	4	**65**	57	15[a]	3-$Me_2NC_6H_4$	Si	Et	Et	4	**78**	51
2[a]	4-MeC_6H_4	Si	Ph	Ph	4	**66**	30	16[a]	4-$H_2NC_6H_4$	Si	Et	Et	4	**79**	40
3[a]	4-EtC_6H_4	Si	Ph	Ph	4	**67**	32	17[a]	3-HOC_6H_4	Si	Et	Et	4	**80**	52
4[a]	4-*i*PrC_6H_4	Si	Ph	Ph	4	**68**	32	18[a]	Ph	Si	Et	Et	4	**81**	53
5[a]	4-*t*BuC_6H_4	Si	Ph	Ph	4	**69**	29	19[a]	2-C_4H_3S	Si	Et	Et	4	**82**	81
6[a]	2-MeC_6H_4	Si	Ph	Ph	4	–[c]	–[c]	20[a]	3-C_4H_3S	Si	Et	Et	4	**83**	77
7[a]	3,5-$Me_2C_6H_3$	Si	Ph	Ph	4	**70**	21	21[a]	3-$EtO_2CC_6H_4$	Si	Et	Et	4	**84**	23
8[a]	2-C_4H_3S	Si	Ph	Ph	4	**71**	70	22[a]	4-$MeOC_6H_4$	Si	Ph	Me	4	**85**	72
9[a]	4-$MeOC_6H_4$	Si	Et	Et	4	**72**	90	23[a]	3-$EtO_2CC_6H_4$	Si	Ph	Me	4	**86**	29
10[a]	4-$MeSC_6H_4$	Si	Et	Et	4	**73**	44	24[b]	4-$MeOC_6H_4$	Ge	Ph	Ph	2	**87**	41
11[a]	4-MeC_6H_4	Si	Et	Et	4	**74**	59	25[b]	2-C_4H_3S	Ge	Ph	Ph	2	**88**	49
12[a]	3-MeC_6H_4	Si	Et	Et	4	**75**	49	26[b]	4-$MeOC_6H_4$	Ge	Et	Et	1	**89**	50
13[a]	4-*i*PrC_6H_4	Si	Et	Et	4	**76**	70	27[b]	2-C_4H_3S	Ge	Et	Et	2.5	**90**	51
14[a]	4-$Me_2NC_6H_4$	Si	Et	Et	4	**77**	72	28[b]	3-$EtO_2CC_6H_4$	Ge	Et	Et	2.5	**91**	26

[a] Reaction conditions: aryl iodide (1.5 mmol), secondary silane (0.5 mmol), Et_3N (2.0 mmol), [Pd(P*t*$Bu_3)_2$] (0.05 mmol), THF (1.0 mL), RT. [b] Reaction conditions: aryl iodide (1.5 mmol), secondary germane (0.5 mmol), *i*Pr_2EtN (1.5 mmol), [Pd(P*t*$Bu_3)_2$] (0.05 mmol), THF (1.0 mL), RT. [c] No doubly arylated product.

duced only in trace amounts due to the steric hindrance of the 1-naphthyl moiety. Double arylation was also successful with heteroaromatic iodides (Table 3, entries 8, 19, and 20). These compounds were investigated as possible precursors for silanediols, which have been shown to be effective bioisosteres for hydrated carbonyl groups.[24] The mass balance of Pd-catalyzed double arylation was determined for the reaction of Table 3, entry 24. Careful workup and purification gave 17 % anisole (reduced product), 31 % 4-iodoanisole (starting material), and 41 % **87** (doubly arylated product) based on 4-iodoanisole (Figure 2).

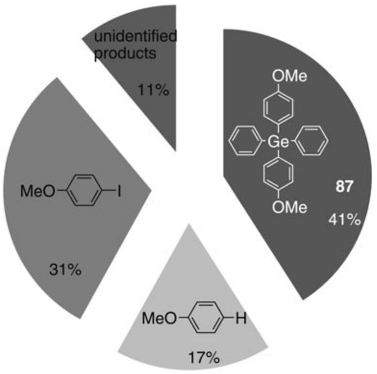
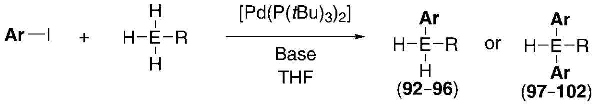


Figure 2. Material balance for Table 3, entry 24, based on 4-iodoanisole.

Arylation of primary silanes and germanes: Continuing interest in palladium-mediated arylation prompted us to explore the possibility of using primary Group 14 compounds as coupling partners. We initially investigated the single arylation of various primary silanes and germanes with aryl iodides. The reactions typically provided a complex mixture of inseparable products, including doubly arylated products, and only in the case of *tert*-butylgermane did the reaction proceed smoothly to give the corresponding secondary germanes in moderate to good yields (Table 4, entries 1–5). For example, when 2-ethyliodobenzene was treated with one equivalent of *tert*-butylgermane, mono-arylated product **95** was isolated (Table 4, entry 4). Careful workup and purification gave **95** in 62 % yield along with 21 % recovered starting material and 4 % reduced product (87 % overall mass balance, Figure 3). The remainder is likely lost to polymerization of starting material and/or product, which is not unexpected. No other products were observed. Unfortunately, the singly arylated product was not observed at all by GC-MS on the reaction mixture when other aryl iodides were used as substrates.

Table 4. Single and double arylation of primary silanes and germanes.



Entry	Ar	E	R	Product	Yield [%]
1[a]	1-$C_{10}H_7$	Ge	*t*Bu	**92**	87
2[a]	2-$Me_2NC_6H_4$	Ge	*t*Bu	**93**	29
3[a]	2-MeC_6H_4	Ge	*t*Bu	**94**	27
4[a]	2-EtC_6H_4	Ge	*t*Bu	**95**	62
5[a]	2-biphenyl	Ge	*t*Bu	**96**	78
6[b]	2-MeC_6H_4	Si	*n*Bu	**97**	16
7[b]	2-*i*PrC_6H_4	Si	*n*Bu	**98**	40
8[b]	2-*i*PrC_6H_4	Si	*c*C_5H_9	**99**	46
9[b]	2-$MeOC_6H_4$	Si	*c*C_5H_9	**100**	42
10[b]	1-$C_{10}H_7$	Si	*n*Bu	**101**	52
11[b]	2-$MeOC_6H_4$	Ge	*t*Bu	**102**	46

[a] Reaction conditions: primary germane (1.0 mmol), aryl iodide (1.0 mmol), DABCO (1.5 mmol), [Pd(P*t*$Bu_3)_2$] (0.05 mmol), THF (3.0 mL), RT, 3 d. [b] All reactions were carried out by using [Pd(P*t*$Bu_3)_2$] (0.05 mmol), DABCO (2.5 mmol), aryl iodide (2.0 mmol), primary silane or germane (1.0 mmol) in THF (3 mL) at RT for 3 d.

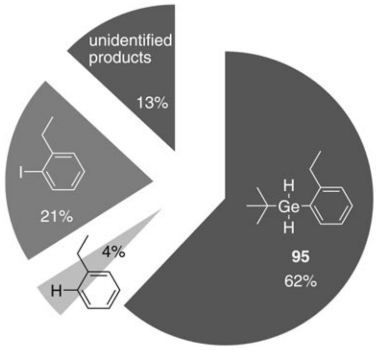
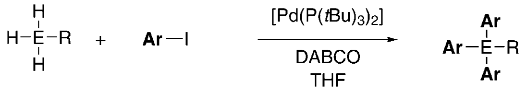


Figure 3. Material balance for Table 4, entry 4, based on 2-iodoethylbenzene.

Next, we focused on double arylation of primary silanes and germanes with aryl iodides (Table 4, entries 6–11). *ortho*-Substituted and electron-donating aryl iodides proved to be excellent double arylating reagents towards primary silanes and germanes. The effect of increased steric hindrance was studied by using four kinds of *ortho*-substituted aryl iodides (Table 4, entries 6–9). Steric hindrance at the *ortho* position appeared to have significant influence. Aryl iodides with substituents *meta* and *para* to the iodido group failed to generate the desired products. DABCO was found to be the most effective base for arylation. Due to the steric hindrance of the aryl iodides, no triply arylated product was observed, in good agreement with previous work. The reaction of *n*-butylsilane and 2-isopropyliodobenzene gave several products, identified after careful workup and purification (Figure 4). Polar impurities observed were likely produced by slow oxidation of **98** during workup.

We examined the possibility of triple arylation of primary Group 14 compounds (Table 5). Triarylated products were obtained in moderate to good yield when primary silanes or germanes were treated with 4 equiv of aryl iodide in the presence of the palladium catalyst and base. Employing even larger excesses of aryl iodide did not improve the yields. Since triply arylated products did not provide satisfactory yields, the reaction mixture was closely examined to identify other components by using Table 5, entry 1 as a model reaction. The biaryl compound and a considerable amount of unidentified byproducts most likely arise from decomposition of singly and doubly arylated silanes (Figure 5).

Table 5. Triple arylation of various primary silanes and germanes.[a]



Entry	Ar	E	R	Product	Yield [%]
1	4-$MeSC_6H_4$	Si	Ph	**103**	42
2	2-C_4H_3S	Si	4-MeC_6H_4	**104**	47
3	3-C_4H_3S	Si	4-MeC_6H_4	**105**	70
4	4-$MeSC_6H_4$	Si	4-MeC_6H_4	**106**	53
5	4-$MeOC_6H_4$	Si	cC_5H_9	**107**	46
6	5-Me-2-C_4H_3S	Si	cC_5H_9	**108**	55
7	4-$MeOC_6H_4$	Si	nC_4H_9	**109**	61
8	4-$MeOC_6H_4$	Si	nC_4H_9	**110**	60
9	2-C_4H_3S	Si	nC_8H_{17}	**111**	61
10	2-C_4H_3S	Si	$nC_{18}H_{37}$	**112**	45
11	3-C_4H_3S	Si	$nC_{18}H_{37}$	**113**	52
12	2-C_4H_3S	Ge	*t*Bu	**114**	52
13	3-C_4H_3S	Ge	*t*Bu	**115**	47
14	4-$MeSC_6H_4$	Ge	*t*Bu	**116**	46
15	4-$MeOC_6H_4$	Ge	*n*Bu	**117**	20

[a] All reactions were carried out with $[Pd(PtBu_3)_2]$ (0.05 mmol), DABCO (5.0 mmol), aryl iodide (4.0 mmol), primary silane or germane (1.0 mmol) in 3 mL of THF at RT for 7 d.

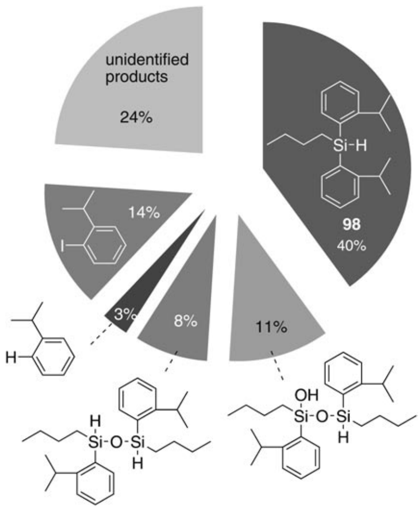


Figure 4. Material balance for Table 4, entry 7, based on 2-isopropyliodobenzene

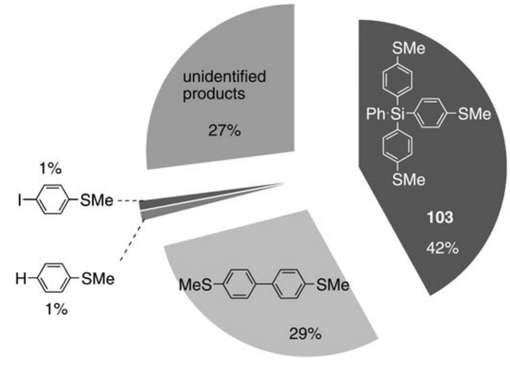
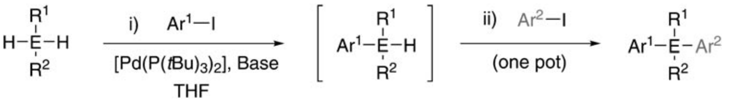


Figure 5. Material balance for Table 5, entry 1, based on 4-iodothioanisole.

Sequential arylation of Group 14 hydrides: Having established the feasibility of one-pot multi-arylation of Group 14 hydrides, we turned our attention to one-pot sequential double arylation with two different aryl iodides. Two aryl iodides, Ar^1I and Ar^2I, were cross-coupled with secondary silanes or germanes to produce the arylated product in good yields. Thus, a solution of Ar^1I, secondary silane or germane, organic base (Et_3N or iPr_2EtN), and a catalytic amount of $[Pd(PtBu_3)_2]$ in THF was stirred at room temperature for 2–

4 d to produce the mono-arylated product in situ. After consumption of Ar^1I was confirmed by thin-layer chromatographic monitoring, Ar^2I was added to the solution and the mixture was stirred for several additional days to produce the doubly arylated product.[25] The products and yields of this stepwise process are summarized in Table 6. Various electronically and structurally diverse aryl iodides were successfully used to produce the corresponding quaternary Group 14 compounds. In particular, a smoother transformation was observed when 4-iodoanisole was used as the first arylating agent, and doubly arylated compounds could be obtained in moderate to good yields by using a second arylating agent (Table 6, entries 1–12, 15–18). The reaction was sensitive to the electronic properties of the first arylating agent. Thus, use of 2-iodothiophene or 1-*tert*-butyl-4-iodobenzene instead of 4-iodoanisole resulted in slightly lower yields of the doubly arylated product (Table 6, entries 13, 14, and 19). Product distribution analysis of Table 6, entry 15 is shown in Figure 6 as an example. Although an excellent material balance was obtained, germanol was obtained in 15 % yield due to slow oxidation of tertiary germane during the purification.

Table 6. Stepwise arylation of primary and secondary Group 14 hydrides.



Entry	R^1	R^2	E	Ar^1	Ar^2	Product	Yield [%]
1[a]	Ph	Ph	Si	4-$MeOC_6H_4$	2-C_4H_3S	**118**	39
2[a]	Ph	Me	Si	4-$MeOC_6H_4$	2-C_4H_3S	**119**	74
3[a]	Ph	Me	Si	4-$MeOC_6H_4$	4-EtC_6H_4	**120**	60
4[a]	Ph	Me	Si	4-$MeOC_6H_4$	4-$i$$PrC_6H_4$	**121**	74
5[a]	Ph	Me	Si	4-$MeOC_6H_4$	4-$t$$BuC_6H_4$	**122**	76
6[a]	Ph	Me	Si	4-$MeOC_6H_4$	4-$MeSC_6H_4$	**123**	43
7[a]	Et	Et	Si	4-$MeOC_6H_4$	4-$i$$PrC_6H_4$	**124**	70
8[a]	Et	Et	Si	4-$MeOC_6H_4$	4-EtC_6H_4	**125**	50
9[a]	Et	Et	Si	4-$MeOC_6H_4$	4-$Me_2NC_6H_4$	**126**	62
10[a]	Et	Et	Si	4-$MeOC_6H_4$	4-$Bu_2NC_6H_4$	**127**	64
11[a]	Et	Et	Si	4-$MeOC_6H_4$	2-C_4H_3S	**128**	73
12[a]	Et	Et	Si	4-$MeOC_6H_4$	4-$t$$BuC_6H_4$	**129**	61
13[a]	Et	Et	Si	2-C_4H_3S	4-$MeOC_6H_4$	**128**	49
14[a]	Et	Et	Si	4-$t$$BuC_6H_4$	4-$MeOC_6H_4$	**129**	31
15[b]	Ph	Ph	Ge	4-$MeOC_6H_4$	4-$t$$BuC_6H_4$	**130**	39
16[b]	Ph	Ph	Ge	4-$MeOC_6H_4$	4-$Me_2NC_6H_4$	**131**	32
17[b]	Ph	Ph	Ge	4-$MeOC_6H_4$	2-$Me_2NC_6H_4$	**132**	43
18[b]	Ph	Ph	Ge	4-$MeOC_6H_4$	2-C_4H_3S	**133**	38
19[b]	Ph	Ph	Ge	2-C_4H_3S	4-$MeOC_6H_4$	**133**	9
20[c]	*t*Bu	H	Ge	1-$C_{10}H_7$	2-$Me_2NC_6H_4$	**134**	63
21[c]	*t*Bu	H	Ge	2-biphenyl	2-$Me_2NC_6H_4$	**135**	40
22[c]	*t*Bu	H	Ge	2-EtC_6H_4	2-$Me_2NC_6H_4$	**136**	48
23[c]	*t*Bu	H	Ge	2-MeC_6H_4	2-$Me_2NC_6H_4$	**137**	42

[a] Reaction conditions: i) Ar^1I (1.0 mmol), secondary silane (1.5 mmol), Et_3N (2.5 mmol), [$Pd(PtBu_3)_2$] (0.05 mmol), THF (4.0 mL), RT, 2 d; ii) Ar^2I (1.5 mmol), RT, additional 2–4 d. [b] Reaction conditions: i) Ar^1I (1.0 mmol), secondary germane (2.0 mmol), iPr_2EtN (3.0 mmol), [$Pd(PtBu_3)_2$] (0.05 mmol), THF (2.0 mL), RT, 2–4 d; ii) Ar^2I (2.0 mmol), RT, additional 3.5–6 d. [c] Reaction conditions: i) Ar^1I (1.0 mmol), *tert*-butylgermane (1.0 mmol), DABCO (2.5 mmol), [$Pd(PtBu_3)_2$] (0.05 mmol), THF (3.0 mL), RT, 1 d; ii) Ar^2I (1.0 mmol), RT, additional 3 d.

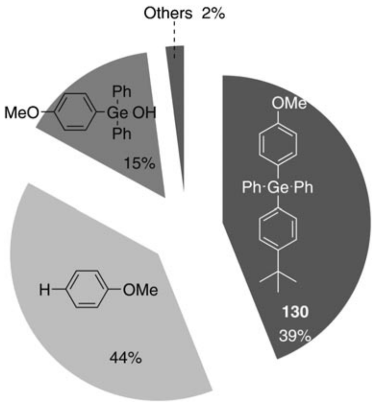


Figure 6. Material balance for Table 6, entry 15, based on 4-iodoanisole.

Next, this stepwise arylation reaction was applied to primary Group 14 compounds to produce unsymmetrically substituted Group 14 compounds. After careful screening of the substrates, we achieved sequential arylation only in the case of *tert*-butylgermane. 2-Iodo-*N*,*N*-dimethylaniline was a good second coupling partner. Although the yields were moderate (Table 6, entries 20–23), a variety of functional Groups were tolerated and afforded unsymmetrical tertiary germanes, which are difficult to synthesize by classical methods. Material balance studies on the reaction of Table 6, entry 23 showed that 42 % of 2-iodotoluene was converted to **137**, 28 % to germanol, and 9 % to toluene (Figure 7). Accordingly, the moderate yield may be due to formation of germanol by an oxidation process during workup.

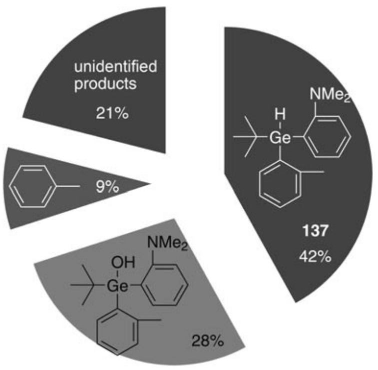
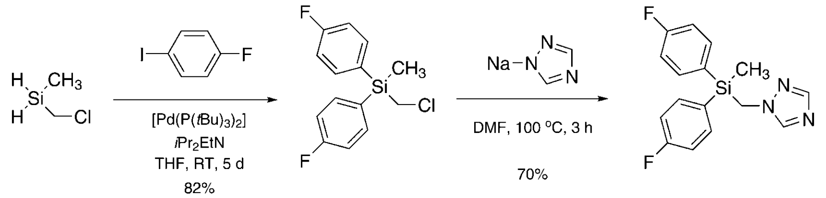


Figure 7. Material balance for Table 6, entry 23, based on 2-iodotoluene.

Agrochemical synthesis: Despite the recent introduction of novel antifungal agents with promising activity, invasive fungal infections have become a major cause in the reduction, by nearly 20 %, of food and crop yields.[26] Therefore, there has been increasing interest in developing structural variants of the newer fungicides. Derivatives of 1,2,4-triazole play an important role in agriculture and medicine, and silicon-containing groups have been used in biological research for some time.[3] Thus, the triazole-containing silane flusilazole (bis(4-fluorophenyl)methyl(1*H*-1,2,4-triazol-1-ylmethyl)silane) has been widely used as an antifungal agent against mildew and rusts of cereal grains, fruits, vegetables, and ornamentals.[27] Prompted by the diverse activities of 1,2,4-triazole derivatives, we prepared 1-(silylmethyl)-1,2,4-triazole derivatives as potential fungicidal agents by palladium-catalyzed double arylation of secondary silanes.

According to the literature, flusilazole can be prepared by two-step synthesis from dichloro(chloromethyl)methylsilane by using organometallic reagents. Our interest focused on the concise preparation of 1-(silylmethyl)triazole derivatives by using palladium-catalyzed arylation as the key step (Scheme 2). Methyl(chloromethyl)silane[28] was treated with 4-fluoroiodobenzene in the presence of $[Pd(PtBu_3)_2]$ and iPr_2EtN in THF to give the doubly arylated product **138** in 82 % yield. Notably, the C−Cl bond was unaffected by the palladium-catalyzed double arylation. Compound **138** was subjected to *N*-alkylation with the sodium salt of 1,2,4-triazole to give flusilazole (**139**) in 70 % yield. This procedure is a simple, reproducible method for the preparation of analytically pure flusilazole analogues on the laboratory scale.

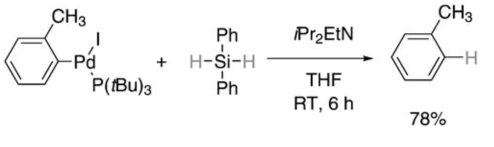


138

139
Flusilazole

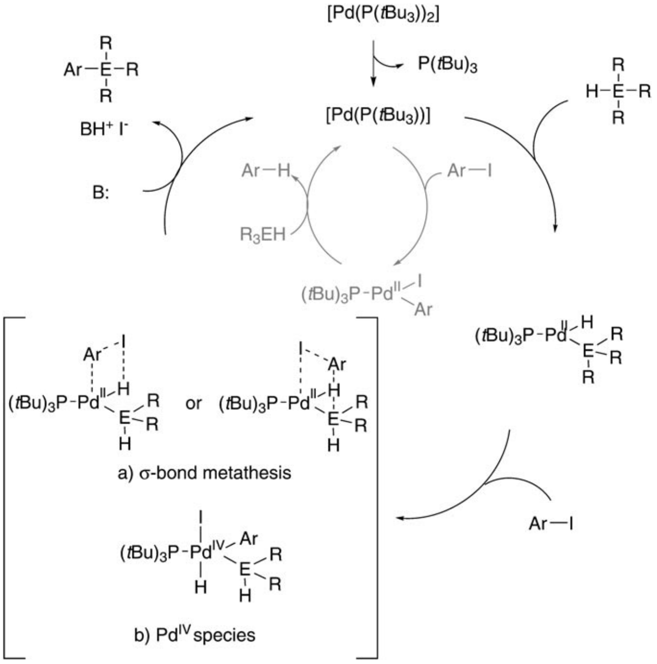
Scheme 2. Synthesis of flusilazole from secondary silane.

Mechanistic considerations: In a preliminary communication, we proposed a possible mechanism for the process described herein, with initiation by oxidative addition of hydrosilane to Pd^0 to generate a $H\text{-}Pd\text{-}SiR_3$ Pd^{II} intermediate. Oxidative addition of hydrosilane to a transition-metal complex has been reported previously.[29–31] To clarify the reaction mechanism of the palladium-catalyzed cross-coupling reaction, the palladium complex $[PdI(PtBu_3)(2\text{-}MeC_6H_4)]$, formed by oxidative addition of 2-iodotoluene to $[Pd(PtBu_3)_2]$, was prepared according to a modified literature method.[32] Treatment of the isolated aryl palladium iodide complex with Ph_2SiH_2 (1.0 equiv) and iPr_2EtN (1.0 equiv) in THF at RT for 6 h gave the reduced product (toluene) in 78 % yield, as determined by GC-MS (Scheme 3). Fu et al. reported that Suzuki coupling of aryl bromides can be accomplished by using the $[Pd_2(dba)_3]/PtBu_3$ (dba = *trans,trans*-dibenzylideneacetone) system at room temperature.[33] If oxidative addition of the haloarene to Pd^0 is the key step of this reaction, the arylated silane should also be obtained at room temperature in good yield if the aryl bromide is used as a starting material.



Scheme 3. Reactions in equivalent ratio.

On the basis of these observations, we propose a mechanism for the process described here, initiated by oxidative addition of Group 14 hydrides to Pd^0 to generate the Pd^{II} intermediate $H\text{-}Pd\text{-}ER_3$ (E = Si, Ge). A pathway through σ-bond metathesis[34] between the Pd^{II} species and the aryl iodide then leads to an arylated compound through reductive elimination (Scheme 4a). A pathway that proceeds through further oxidative addition, resulting in the formation of a Pd^{IV} species,[35] cannot be completely excluded (Scheme 4b). Finally, the palladium(0) catalyst can be regenerated by the removal of HI with the aid of a base.



Scheme 4. Plausible catalytic cycle for the arylation of Group 14 hydride (E = Si or Ge; B = Base).

Conclusion

We have demonstrated that arylated heavier Group 14 compounds are easily prepared in a one-step procedure in moderate to good yields, starting from commercially available aryl halides and the corresponding Group 14 hydride. This strategy differs from the classical preparation exemplified by the reaction of Grignard or organolithium reagents with a chlorosilane. Our methodology can be applied in the presence of a wide range of reactive functional groups on the aryl halide to produce a variety of aromatic Group 14 compounds. Pd-catalyzed decomposition or oxidation of intermediates seems to be the primary cause of low yields of triply arylated product. The secondary and tertiary Group 14 products were slightly reactive with oxygen and/or water at ambient temperature in the presence of catalyst.[36] Workup and purification with silica gel resulted in the partial formation of silanol, germanol, or other unidentified oligomeric products. The reaction gave complex mixtures without aryl iodides. In the presence of transition-metal complexes, secondary or primary silanes generally underwent a scrambling of the substituents together with dehydrogenative silane coupling via silylene complexes.[37] Accordingly, the formation of the oligomeric products described above can be also explained by the decomposition of hydrosilane with catalyst.

The simplicity of the reaction procedure coupled with the broad range of substrates renders this method particularly attractive for the efficient preparation of biologically, medicinally, and photochemically interesting Group 14 compounds.

Experimental Section

All experiments were carried out under an argon atmosphere in oven-dried glassware. Unless otherwise noted, the Group 14 hydrides and aryl halides were purchased from commercial sources and were used without purification. See the Supporting Information for details of the characterization of individual compounds.

Typical procedure for the palladium-catalyzed stepwise arylation of secondary silanes (Table 6, entry 5): Methylphenylsilane (206 µL, 1.5 mmol), 4-iodoanisole (234 mg, 1.0 mmol), and triethylamine (0.35 mL, 2.5 mmol) were added to a solution of [Pd(P*t*Bu$_3$)$_2$] (25 mg, 0.05 mmol) in THF (4.0 mL). After 2 d at RT, 1-*tert*-butyl-4-iodobenzene (266 µL, 1.5 mmol) was added. After a further 4 d, the reaction mixture was quenched with water, extracted three times with CH_2Cl_2, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and silica-gel column chromatography produced doubly arylated product **122** (274 mg, 76 %).

Typical procedure for the palladium-catalyzed stepwise arylation of primary germane (Table 6, entry 20): DABCO (280 mg, 2.5 mmol), 1-iodonaphthalene (146 µL, 1.0 mmol), and *tert*-butylgermane (137 µL, 1.0 mmol) were added to a solution of [Pd(P*t*Bu$_3$)$_2$] (25 mg, 0.05 mmol) in THF (3.0 mL). After 0.5 d at RT, 2-iodo-*N*,*N*-dimethylaniline (250 mg, 1.0 mmol) was added. After a further 3 d, the reaction mixture was quenched with water, extracted three times with CH_2Cl_2, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and silica-gel column chromatography produced doubly arylated product **134** (238 mg, 63 %).

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