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$PdCl_2$ and $NiCl_2$-catalyzed hydrogen–halogen exchange for the convenient preparation of bromo- and iodosilanes and germanes

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Abstract

Bromination and iodination of hydrosilanes and germanes were studied. Treatment of hydrosilanes with an excess of ethyl, propyl, or allyl bromide in the presence of a catalytic amount of $PdCl_2$ or $NiCl_2$ gave bromosilanes in good to high yield by hydrogen–halogen exchange. By using methyl, propyl, or allyl iodide as the iodine source, similar iodination of hydrosilanes was readily performed. Halogenation of hydrogermanes also proceeded by similar treatment.

Keywords: Bromosilane; Iodosilane; Bromogermane; Iodogermane

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1. Introduction

Halosilanes and germanes are of important reagents as the building units for a variety of organosilicon and germanium compounds. In addition, bromo- and iodosilanes exhibit high Lewis-acidity to permit the interaction with C–O and C=O bonds, unlike fluoro- and chlorosilanes [1]. Examples include the reactions of ethers and esters with iodo- and bromosilanes, which afford silyl ethers and esters, respectively, together with halides arising from C–O bond cleavage, in good yield [2,3]. It is also known that aldehydes react with iodosilanes to give silyl α-iodoalkyl ether, by iodosilylation of the carbonyl bond [4,5].

Conventional methods to prepare bromo- and iodosilanes [1] and germanes [6] involve the cleavage of M–M, M–H, M–allyl, and M–aryl bonds (M = Si, Ge) with X_2 (X = Br, I), reactions of M–H with HX (X = Br, I) and NBS, and halogen exchange of M–Cl with inorganic halides. Reactions of an M–O–M bond with HX in the presence (M = Si) or absence (M = Ge) of a Lewis-acid also produce an M–X bond. Cleavage of an alkyl-Ge bond with X_2 and Lewis-acid-catalyzed redistribution reactions of R_4Ge and $GeBr_4$ are also often used for the formation of a Ge–X bond. However, most of these methods involve the use or by-production of unpleasant HX or X_2. Furthermore, traces of HX and X_2 may contaminate the resulting halosilanes and germanes.

Previously, we have found that the reactions of mono- and dihydrosilanes with alkyl iodides in the presence of a catalytic amount of $PdCl_2$ afford mono- and diiodosilanes in high yield [7]. We have also reported the CuI-catalyzed bromination of hydrosilanes with $CuBr_2$ [8], in which an Si–H bond is replaced with an Si–Br group with the use of two equivalents of $CuBr_2$. However, there may be a limitation that this method can not be applied to the preparation of tribromosilanes, and treatment of trihydrosilanes with six equivalents of the reagent gives dibromohydrosilanes as the sole isolable products. In this paper, we report a versatile method to prepare bromo- and iodosilanes, including tribromo- and triiodosilanes from $PdCl_2$- or $NiCl_2$-catalyzed hydrogen–halogen exchange reactions of hydrosilanes with alkyl bromides and iodides, respectively. Similar halogenation of hydrogermanes is also described.

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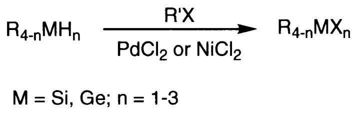
2. Results and discussion

2.1. Bromination of hydrosilanes

The reactions of hydrosilanes with alkyl or allyl bromides in the presence of a catalytic amount of $PdCl_2$ or $NiCl_2$ proceeded with the liberation of alkanes to give brominated products in good to high yields (Table 1 and Scheme 1). As can be seen in Table 1, the reactions proceeded more rapidly when allyl bromide, rather than ethyl and propyl bromide, was used as the halide. Typically, $PdCl_2$-catalyzed bromination of $PhMe_2SiH$ with EtBr or PrBr completed by refluxing the mixture without solvent for 12 h (runs 2 and 3), while with allyl bromide $PhMe_2SiH$ was wholly consumed within 1 h (run 4). Similar $NiCl_2$-catalyzed bromination of $PhMe_2SiH$ with allyl bromide proceeded less rapidly and required the use of a larger amount of the catalyst and a longer reaction period to complete the conversion (run 5), as compared with the $PdCl_2$-catalyzed one (run 4). Lower activity of $NiCl_2$-catalyst relative to $PdCl_2$ is evident for tribromination of $PhSiH_3$, in which the Nickel-catalyst was deactivated during the reaction progress and continuous addition of the catalyst into the reaction mixture was necessary to promote further the reaction (run 16). In contrast to this, $PhSiBr_3$ was obtained in 88% yield from $PhSiH_3$ with only 1 mol.% of the $PdCl_2$-catalyst (run 15).

Although partially brominated products were found to be formed by GC–MS analyses of the reaction mixtures in low yields in the bromination of di- and trihydrosilanes, they were readily separated from the perbrominated products by fractional distillation. In the reactions, from which rather low yields of bromosilanes were obtained (runs 9, 10, and 13), a few unidentified products in low yields in addition to the partially brominated products, were found to be formed by the GLC analysis of the reaction mixtures.



Scheme 1.

2.2. Iodination of hydrosilanes

Previously, we have reported that mono- and dihydrosilanes readily undergo periodination of Si–H bonds when they are treated with alkyl iodides in the presence of a catalytic amount of $PdCl_2$ [7]. As shown in Table 2, $NiCl_2$-catalyzed reactions also could be used for the synthesis of iodosilanes. Interestingly, the $NiCl_2$-catalyzed reaction of Et_2SiH_2 with MeI proceeded more selectively (run 3), as compared with the reaction with the $PdCl_2$ catalyst reported previously (run 1). Thus, the $PdCl_2$-catalyzed reaction gave Et_2SiI_2 and Et_2MeSiI in 37% and 20% yields (run 1, previous result), respectively, while with $NiCl_2$ as the catalyst, the reaction gave Et_2SiI_2 almost selectively (60% yield), with an only 4% yield of Et_2MeSiI. The use of i-PrI as the halide led to even more selective formation of the simply halogenated products (runs 4, 6, and 7), as reported previously (run 2) [7]. Triiodosilanes $HexSiI_3$ and $PhSiI_3$ also could be obtained from the corresponding trihydrosilanes by this method (runs 8 and 9).

Table 1
Bromination of hydrosilanes

Run	Hydrosilane (amt/mmol)	Halide (eq)	Catalyst (mol.%)	Temp/°C [a] (time/h)	Product (yield/%) [b]
1	Et_3SiH (64.2)	allylBr (1.8)	$PdCl_2$ (1)	80 (12)	Et_3SiBr (90)
2	$PhMe_2SiH$ (15.5)	EtBr (2.1)	$PdCl_2$ (1)	50 (12)	$PhMe_2SiBr$ (88)
3	(31.3)	*n*-PrBr (1.4)	$PdCl_2$ (1)	80 (12)	$PhMe_2SiBr$ (94)
4	(10.9)	allylBr (1.6)	$PdCl_2$ (1)	80 (1)	$PhMe_2SiBr$ (88)
5	(13.2)	allylBr (1.8)	$NiCl_2$ (6)	80 (16)	$PhMe_2SiBr$ (91)
6	Ph_2MeSiH (13.6)	EtBr (2.6)	$PdCl_2$ (1)	50 (36)	$Ph_2MeSiBr$ (76)
7	(7.8)	allylBr (1.5)	$PdCl_2$ (1)	80 (1)	$Ph_2MeSiBr$ (91)
8	(10.0)	allylBr (1.6)	$NiCl_2$ (5)	80 (24)	$Ph_2MeSiBr$ (78)
9	Et_2SiH_2 (36.1)	EtBr (3.0)	$PdCl_2$ (2)	50 (72)	Et_2SiBr_2 (61)
10	(40.0)	allylBr (2.3)	$PdCl_2$ (1)	80 (20)	Et_2SiBr_2 (37)
11	(24.0)	allylBr (2.9)	$NiCl_2$ (2)	80 (24)	Et_2SiBr_2 (85)
12	$PhMeSiH_2$ (18.0)	allylBr (3.5)	$PdCl_2$ (1)	80 (36)	$PhMeSiBr_2$ (79)
13	(39.2)	EtBr (3.0)	$NiCl_2$ (3)	50 (48)	$PhMeSiBr_2$ (59)
14	(18.0)	allylBr (3.5)	$NiCl_2$ (2)	80 (50)	$PhMeSiBr_2$ (80)
15	$PhSiH_3$ (17.0)	allylBr (4.0)	$PdCl_2$ (1)	80 (60)	$PhSiBr_3$ (88)
16	(24.1)	allylBr (2.8)	$NiCl_2$ (11) [c]	80 (90)	$PhSiBr_3$ (65)

[a] Bath temperature.

[b] Isolated yield.

[c] $NiCl_2$ was added in eight portions in every 10–12 h.

Table 2
Iodination of hydrosilanes

Run	Hydrosilane (amt/mmol)	Halide (eq)	Catalyst (mol.%)	Temp/°C [a] (time/h)	Product (yield/%) [b]
1 [c]	Et_2SiH_2 (33.8)	MeI (3.0)	$PdCl_2$ (4)	60 (24)	Et_2SiI_2 (37), Et_2MeSiI (20)
2 [c]	(56.1)	i-PrI (2.0)	$PdCl_2$ (1)	70 (24)	Et_2SiI_2 (74)
3	(36.5)	MeI (3.3)	$NiCl_2$ (6)	60 (40)	Et_2SiI_2 (60), Et_2MeSiI (4)
4	(10.0)	i-PrI (3.0)	$NiCl_2$ (3)	100 (18)	Et_2SiI_2 (52)
5	$PhMeSiH_2$ (46.3)	MeI (2.6)	$PdCl_2$ (1)	60 (72)	$PhMeSiI_2$ (48), $PhMe_2SiI$ (22)
6	(37.7)	i-PrI (2.6)	$PdCl_2$ (1)	100 (12)	$PhMeSiI_2$ (87)
7	(41.9)	i-PrI (2.4)	$NiCl_2$ (1)	100 (18)	$PhMeSiI_2$ (87)
8	$HexSiH_3$ (15.0)	i-PrI (4.5)	$PdCl_2$ (2)	90 (48)	$HexSiI_3$ (86)
9	$PhSiH_3$ (18.5)	i-PrI (4.5)	$PdCl_2$ (1)	90 (40)	$PhSiI_3$ (80)

[a] Bath temperature.

[b] Isolated yield.

[c] Ref. [7].

2.3. Halogenation of hydrogermanes

It has been reported that heating hydrogermanes with alkyl halides at 80–90 °C for several hours leads to the formation of halogermanes in high yield [12]. In contrast to this, $PdCl_2$-catalyzed halogenation of hydrogermanes with allyl halides proceeded even at room temperature (Table 3). In these reactions, allyl halide must be used as the halogen source. Indeed, no reactions occurred when Hex_3GeH was treated with EtBr at 50 °C in the presence of the $PdCl_2$ catalyst, while Hex_3GeBr was obtained in 80% yield by the reaction with allyl bromide at room temperature (run 1). Benzyl bromide could be also used for the preparation of Hex_3GeBr from Hex_3GeH (run 3). When Hex_3GeH was treated with an excess of MeI and a catalytic amount of $PdCl_2$ at 60 °C for 70 h and the resulting mixture was analyzed by GC–MS, Hex_3GeI was found to be formed only in 25% yield, together with the starting Hex_3GeH remaining in 70% yield. On the other hand, similar reaction with allyl iodide produced Hex_3GeI in 84% yield (run 9). Dihydrogermanes were readily converted to dibromogermanes (runs 5 and 6), while a longer reaction period was required to complete the tribromination of $HexGeH_3$ and the product $HexGeBr_3$ was isolated in rather low yield (58%, run 7). On the contrary, the reaction of $HexGeH_3$ with allyl iodide proceeded smoothly to afford $HexGeI_3$ in 87% yield (run 13). The use of $NiCl_2$ as the catalyst did not obviously accelerate the halogenation of hydrogermanes.

Table 3
$PdCl_2$-catalyzed halogenation of hydrogermanes at room temperature[a]

Run	Hydrosilane (amt/mmol)	Halide (eq)	time/h	Product (yield/%) [b]
1	Et_3GeH (1.5)	allylBr (1.7)	3	Et_3GeBr (84)
2	Hex_3GeH (1.0)	allylBr (2.3)	3	Hex_3GeBr (80)
3		$PhCH_2Br$ (1.5)	6	Hex_3GeBr (88)
4	Ph_3GeH (1.0)	allylBr (1.5)	3	Ph_3GeBr (72)
5	Hex_2GeH_2 (2.8)	allylBr (3.0)	6	Hex_2GeBr_2 (92)
6	Ph_2GeH_2 (1.9)	allylBr (3.0)	4	Ph_2GeBr_2 (81)
7	$HexGeH_3$ (3.1)	allylBr (3.6)	53	$HexGeBr_3$ (58)
8	Et_3GeH (5.0)	allylI (1.5)	6	Et_3GeI (83)
9	Hex_3GeH (5.0)	allylI (1.5)	12	Hex_3GeI (84)
10	Ph_3GeH (5.0)	allylI (1.5)	12	Ph_3GeI (98) [c]
11	Hex_2GeH_2 (3.0)	allylI (3.0)	3	Hex_2GeI2 (80)
12	Ph_2GeH_2 (3.0)	allylI (3.0)	5	Ph_2GeI_2 (75)
13	$HexGeH_3$ (3.1)	allylI (4.1)	12	$HexGeI_3$ (87)

[a] 1–3 mol.% of $PdCl_2$ was used.

[b] Isolated yield.

[c] 2 ml of benzene was added to the mixture after 6 h reaction, in order to dissolve the product Ph_3GeI.

In the present halogenation of hydrosilanes and germanes, the formation of fine black precipitates was observed, immediately after the contact of the reactants with the catalysts. At the same time, the corresponding chlorosilanes or germanes were found to be formed by GC–MS analysis of the reaction mixtures. This seems to indicate that the actual active species in these reactions were Pd(0) and Ni(0) metals, respectively, formed from the reduction of the chlorides with hydrosilanes or germanes, although we have obtained no clear evidences concerning the reaction mechanism. Presumably, the homolytic M–H (M = Si or Ge) bond cleavage occurred on the metal surface and the resulting silyl or germyl radicals abstract the halogen atom from the halides. Metathesis type reactions on the metal surface also would be involved.

3. Conclusions

In conclusion, we studied the $PdCl_2$- and $NiCl_2$-catalyzed hydrogen–halogen exchange of hydrosilanes and germanes with alkyl halides. The reactions proceeded more readily with the $PdCl_2$ catalyst, but more economic $NiCl_2$ also can be used as the catalyst for the preparation of halosilanes. This provides a versatile synthetic method leading to a variety of bromo- and iodosilanes and germanes, which would be expected as useful synthetic tools for various organosilicon and germanium compounds. However, we have not yet succeeded in performing the selective halogenation leading to halohydrosilanes and germanes by the present method, the metal-catalyzed exchange reaction. All attempts to prepare partially halogenated products selectively from dihydro- and trihydrosilanes and germanes were unsuccessful. In fact, the GLC-trace of the reaction progress indicated that the perhalogenated products were formed, together with the partially halogenated ones, even at the early stage of the reactions. Studies to optimize the reaction conditions for the selective halogenation are in progress.

4. Experimental

4.1. General

All reactions were carried out under an inert atmosphere. NMR spectra were recorded on JEOL Model JNM-EX 270 and JEOL Model JNM-LA 400 spectrometers. Mass spectra were measured with a Hitachi M80B spectrometer.

4.2. Materials

Alkyl halides and allyl halides were distilled from P_2O_5 and stored over molecular sieves in dark until use. The starting hydrosilanes [7,11] and germanes [6a,10] were prepared by the reactions of the respective chlorides with lithium aluminum hydride.

4.3. Halogenation of hydrosilanes and germanes

An illustrative procedure is as follows. A mixture of $PhMe_2SiH$ (4.25 g, 31.3 mmol), n-PrBr (5.21 g, 42.4 mmol), and $PdCl_2$ (75 mg, 0.42 mmol) was stirred at 80 °C for 12 h. After evaporation of excess n-PrBr, the residue was fractionally distilled under reduced pressure to give 6.34 g (b.p. 95–96 °C/17 mmHg, 29.5 mmol, 94% yield) of $PhMe_2SiBr$.

All spectral data obtained for iodosilanes Et_2SiI_2 and Et_2MeSiI [7] are identical with those reported in the literature.

Data for Et_3SiBr: b.p. 58–59 °C/18 mmHg (Lit. b.p. 163.2–163.3 °C/737 mmHg [9]); MS m/z 194 [M$^+$], 165 [M$^+$−Et], 137 [M$^+$−Et−C_2H_4], 115 [M$^+$−Br]; ^{1}H-NMR (in $CDCl_3$) δ 0.89 (t, 9H, $J=7.7$ Hz), 1.01 (q, 6H, $J=7.7$ Hz); ^{13}C-NMR (in $CDCl_3$) δ 6.98, 7.77; ^{29}Si-NMR (in $CDCl_3$) δ 37.39. Anal. Found: C, 37.08; H, 7.48. Calc. for $C_6H_{15}BrSi$: C, 36.92; H, 7.75%.

Data for $PhMe_2SiBr$: b.p. 95–96 °C/17 mmHg; MS m/z 214 [M$^+$], 199 [M$^+$−Me], 137 [M$^+$−Ph], 135 [M$^+$−Br]; ^{1}H-NMR (in $CDCl_3$) δ 0.84 (s, 6H), 7.36–7.65 (m, 5H); ^{13}C-NMR (in $CDCl_3$) δ 2.86, 128.09, 128.32, 130.58, 133.19; ^{29}Si-NMR (in $CDCl_3$) δ 16.78. Anal. Found: C, 44.66; H, 5.41. Calc. for $C_8H_{11}BrSi$: C, 44.66; H, 5.15%.

Data for $Ph_2MeSiBr$: b.p. 97–99 °C/1 mmHg; MS m/z 276 [M$^+$], 261 [M$^+$−Me], 199 [M$^+$−Ph], 197 [M$^+$−Br]; ^{1}H-NMR (in $CDCl_3$) δ 1.10 (s, 3H), 7.31–7.65 (m, 10H); ^{13}C-NMR (in $CDCl_3$) δ 1.78, 128.10, 128.25, 130.58, 134.27; ^{29}Si-NMR (in $CDCl_3$) δ 8.05. Anal. Found: C, 56.79; H, 4.80. Calc. for $C_{13}H_{13}BrSi$: C, 56.32; H, 4.73%.

Data for Et_2SiBr_2: b.p. 42–47 °C/11 mmHg (Lit. 166.2–166.3 °C/744 mmHg [9]); MS m/z 244 [M$^+$], 215 [M$^+$−Et]; ^{1}H-NMR (in $CDCl_3$) δ 1.09 (t, 6H, $J=8.1$ Hz), 1.27 (q, 4H, $J=8.1$ Hz); ^{13}C-NMR (in $CDCl_3$) δ 1.78, 6.90, 14.30.

Data for $MePhSiBr_2$: b.p. 66–68 °C/1 mmHg (Lit. 105 °C/12 mmHg [13]); MS m/z 278 [M$^+$], 263 [M$^+$−Me], 201 [M$^+$−Ph], 199 [M$^+$−Br]; ^{1}H-NMR (in $CDCl_3$) δ 1.33 (s, 3H), 7.46–7.49 (m, 3H), 7.73–7.77 (m, 2H); ^{13}C-NMR (in $CDCl_3$) δ 8.43, 128.32, 131.68, 133.14, 133.75; ^{29}Si-NMR (in $CDCl_3$) δ 8.92. Anal. Found: C, 29.96; H, 2.98. Calc. for $C_7H_8Br_2Si$: C, 30.02; H, 2.88%.

Data for $PhSiBr_3$: b.p. 58–69 °C/1 mmHg (Lit. 178.3 °C/80 mmHg [9]); MS m/z 342 [M$^+$], 265 [M$^+$−Ph], 263 [M$^+$−Br], 184 [M$^+$−Br_2], 105 [M$^+$−Br_3]; ^{1}H-NMR ($CDCl_3$) δ 7.26–7.56 (m, 3H), 7.80–7.84 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 128.44, 132.68, 132.96 (one carbon signal is overlapping). Anal. Found: C, 21.20; H, 1.64. Calc. for $C_6H_5Br_3Si$: C, 20.90; H, 1.46%.

Data for $MePhSiI_2$: b.p. 145–150 °C/15 mmHg; MS m/z 374 [M$^+$], 359 [M$^+$−Me]; ^{1}H-NMR ($CDCl_3$) δ 1.80 (s, 3H), 7.43–7.76 (m, 3H), 7.72–7.75 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 11.56, 128.16, 131.59, 133.23, 133.92. Anal. Found: C, 22.49; H, 2.18. Calc. for $C_7H_8SiI_2$: C, 22.48; H, 2.16%.

Data for $HexSiI_3$: b.p. 85–95 °C/1 mmHg; MS m/z 494 [M$^+$], 417 [M$^+$−Ph], 367 [M$^+$−I], 240 [M$^+$−I_2], 113 [M$^+$−I_3]; ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, 3H, $J=7.2$ Hz, CH_3), 1.31–1.49 (m, 8H), 2.15 (2H, t, $J=8.0$ Hz, CH_2Si); ^{13}C-NMR ($CDCl_3$) δ 14.22, 22.46, 25.41, 30.12, 31.22, 32.40. Anal. Found: C, 14.75; H, 2.68. Calc. for $C_6H_{13}I_3Si$: C, 14.59; H, 2.65%.

Data for $PhSiI_3$: b.p. 140–143 °C/2 mmHg; MS m/z 486 [M$^+$], 409 [M$^+$−Ph], 359 [M$^+$−I], 232 [M$^+$−I_2], 105 [M$^+$−I_3]; ^{1}H-NMR ($CDCl_3$) δ 7.36–7.52 (m, 3H), 7.79–7.83 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 128.03, 128.32, 132.38, 132.76.

Data for Et_3GeBr: b.p. 130–140 °C/80 mmHg (Lit. 190 °C [14]); MS m/z 240 [M$^+$], 211 [M$^+$−Et], 182 [M$^+$−2Et], 153 [M$^+$−3Et]; ^{1}H-NMR ($CDCl_3$) δ 1.13–

1.21 (m); ^{13}C-NMR (CDCl$_3$) δ 8.52, 10.82. Anal. Found: C, 30.02; H, 6.35. Calc. for $C_6H_{15}BrGe$: C, 30.07; H, 6.32%.

Data for *n*-Hex$_3$GeBr: b.p. 175–185 °C/1 mmHg; MS *m/z* 408 [M$^+$], 329 [M$^+$–Br], 323 [M$^+$–Hex], 238 [M$^+$–2Hex], 153 [M$^+$–3Hex]; ^{1}H-NMR (CDCl$_3$) δ 0.88 (t, 9H, $J = 6.6$ Hz), 1.18–1.53 (m, 30H); ^{13}C-NMR (CDCl$_3$) δ 14.07, 19.45, 22.54, 24.53, 31.36, 32.35. Anal. Found: C, 52.76; H, 9.92. Calc. for $C_{18}H_{39}BrGe$: C, 52.99; H, 9.63%.

Data for Ph$_3$GeBr: b.p. 175–185 °C/1 mmHg; MS *m/z* 307 [M$^+$–Ph], 305 [M$^+$–Br], 153 [M$^+$–3Ph]; ^{1}H-NMR (CDCl$_3$) δ 7.42–7.45 (m, 9H), 7.60–7.64 (m, 6H); ^{13}C-NMR (CDCl$_3$) δ 128.61, 130.42, 134.21, 134.66. Anal. Found: C, 56.03; H, 3.82. Calc. for $C_{18}H_{15}BrGe$: C, 56.33; H, 3.94%.

Data for HeX$_2$GeBr$_2$: b.p. 155–165 °C/1 mmHg; MS *m/z* 402 [M$^+$], 323 [M$^+$–Br], 317 [M$^+$–Hex]; ^{1}H-NMR (CDCl$_3$) δ 0.89 (t, 6H, $J = 6.8$ Hz), 1.30–1.71 (m, 20H); ^{13}C-NMR (CDCl$_3$) δ 14.00, 22.45, 24.23, 28.09, 31.23, 31.27. Anal. Found: C, 35.64; H, 6.80. Calc. for $C_{12}H_{26}Br_2Ge$: C, 35.79; H, 6.51%.

Data for Ph$_2$GeBr$_2$: b.p. 160–170 °C/1 mmHg; MS *m/z* 386 [M$^+$], 309 [M$^+$–Ph], 307 [M$^+$–Br]; ^{1}H-NMR (CDCl$_3$) δ 7.48–7.51 (m, 6H), 7.70–7.74 (m, 4H); ^{13}C-NMR (CDCl$_3$) δ 128.91, 131.64, 132.67, 135.29. Anal. Found: C, 37.46; H, 2.66. Calc. for $C_{12}H_{10}Br_2Ge$: C, 37.28; H, 2.61%.

Data for HexGeBr$_3$: b.p. 95–105 °C/1 mmHg; MS *m/z* 396 [M$^+$], 317 [M$^+$–Br], 238 [M$^+$–2Br]; ^{1}H-NMR (CDCl$_3$) δ 0.89 (t, 3H, $J = 6.6$ Hz), 1.31–1.69 (m, 10H); ^{13}C-NMR (CDCl$_3$) δ 13.95, 22.34, 24.26, 30.03, 31.09, 37.54. Anal. Found: C, 18.23; H, 3.59. Calc. for $C_6H_{13}Br_3Ge$: C, 18.13; H, 3.30%.

Data for Et$_3$GeI: b.p. 130–140 °C/20 mmHg (Lit. 212 °C [14]); MS *m/z* 288 [M$^+$], 259 [M$^+$–Et], 230 [M$^+$–2Et], 201 [M$^+$–3Et], 161 [M$^+$–I]; ^{1}H-NMR (CDCl$_3$) δ 1.10 (t, 9H, $J = 7.5$ Hz), 1.29 (q, 6H, $J = 7.5$ Hz); ^{13}C-NMR (CDCl$_3$) δ 9.62, 11.13. Anal. Found: C, 25.12; H, 5.19. Calc. for $C_6H_{15}IGe$: C, 25.14; H, 5.27%.

Data for *n*-Hex$_3$GeI: b.p. 165–175 °C/1 mmHg; MS *m/z* 371 [M$^+$–Hex], 329 [M$^+$–I], 286 [M$^+$–2Hex], 201 [M$^+$–3Hex]; ^{1}H-NMR (CDCl$_3$) δ 0.88 (t, 9H, $J = 6.9$ Hz), 1.27–1.54 (m, 30H); ^{13}C-NMR (CDCl$_3$) δ 14.08, 19.60, 22.54, 25.58, 31.34, 32.18. Anal. Found: C, 47.24; H, 8.56. Calc. for $C_{18}H_{39}IGe$: C, 47.51; H, 8.64%.

Data for Ph$_3$GeI: b.p. 160–170 °C/1 mmHg; MS *m/z* 355 [M$^+$–Ph], 305 [M$^+$–I], 201 [M$^+$–3Ph]; ^{1}H-NMR (CDCl$_3$) δ 7.41–7.46 (m, 9H), 7.63 (dd, 6H, $J = 1.9$, 6.8 Hz); ^{13}C-NMR (CDCl$_3$) δ 128.63, 130.48, 134.05, 134.73. Anal. Found: C, 50.37; H, 3.36. Calc. for $C_{18}H_{15}IGe$: C, 50.18; H, 3.51%.

Data for *n*-HeX$_2$GeI$_2$: b.p. 120–130 °C/1 mmHg; MS *m/z* 413 [M$^+$–Hex], 371 [M$^+$–I], 328 [M$^+$–2Hex]; ^{1}H-NMR (CDCl$_3$) δ 0.89 (t, 6H, $J = 6.8$ Hz), 1.30–1.93 (m, 20H); ^{13}C-NMR (CDCl$_3$) δ 14.00, 22.46, 26.17, 28.95, 30.75, 31.22. Anal. Found: C, 29.02; H, 5.23. Calc. for $C_{12}H_{26}I_2Ge$: C, 29.01; H, 5.28%.

Data for Ph$_2$GeI$_2$: b.p. 140–150 °C/1 mmHg; MS *m/z* 482 [M$^+$], 405 [M$^+$–Ph], 355 [M$^+$–I], 228 [M$^+$–2I]; ^{1}H-NMR (CDCl$_3$) δ 7.43–7.49 (m, 6H), 7.66 (dd, 4H, $J = 1.7$, 6.3 Hz); ^{13}C-NMR (CDCl$_3$) δ 128.61, 131.30, 132.61, 134.95. Anal. Found: C, 29.96; H, 2.07. Calc. for $C_{12}H_{10}I_2Ge$: C, 29.99; H, 2.10%.

Data for HexGeI$_3$: b.p. 120–130 °C/1 mmHg; MS *m/z* 540 [M$^+$], 455 [M$^+$–Hex], 413 [M$^+$–I], 286 [M$^+$–2I]; ^{1}H-NMR (CDCl$_3$) δ 0.90 (t, 3H, $J = 6.9$ Hz), 1.30–1.94 (m, 10H); ^{13}C-NMR (CDCl$_3$) δ 13.98, 22.41, 26.79, 28.74, 31.18, 38.92. Anal. Found: C, 13.66; H, 2.61. Calc. for $C_6H_{13}I_3Ge$: C, 13.38; H, 2.43%.

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