CHEMISTRY LETTERS, pp. 677-680, 1991 © 1991 The Chemical Society of Japan

Palladium-Catalyzed Germylation of Organic Halides with a Digermane. Unexpected Formation of Germylene-Insertion Type Products

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Organic halides (RX) underwent dehalogenative germylation and germylene insertion type reactions with $ClMe_2GeGeMe_2Cl$ in the presence of $Pd(PPh_3)_4$ as catalyst to give $RGeMe_2Cl$ and $RGeMe_2X$ respectively.

Germanium[1)] compounds and polymers containing germanium[2)] gained considerable importance in recent years. But the synthetic methods are limited in comparison with silicon analogues. We have described the double germylation of alkenes, alkadienes, and alkynes with sym-dichlorotetramethyldigermane (**1**) leading to α,ω-bis(chlorodimethylgermyl) compounds in good yields.[3)] Another possible way to synthesize organogermyl compounds might be dehalogenative germylation of organic halides with digermanes. Although such reactions with disilanes have been long known,[4,5)] little attention has been focused on the reactions with digermanes and only a few low-yield examples with fully organic digermanes have been briefly commented.[5)] Herein reported is the successful germylation which partly involves the unexpected germylene insertion type reaction.

When a benzene (0.6 cm^3) solution of benzyl chloride (0.4 mmol) was treated with **1** (0.4 mmol) in the presence of $Pd(PPh_3)_4$ (0.02 mmol) at 120 °C for 10 h, dehalogenative germylation cleanly proceeded. GC analysis revealed the formation of benzylchlorodimethylgermane (**3**, 93%) and dimethyldichlorogermane (**4**, ≈100%) (Eq. 1, Table 1). Only a trace of bibenzyl was detected in the reaction mixture. On the other hand,

$$\underset{\mathbf{2}}{PhCH_2Cl} + \underset{\mathbf{1}}{ClMe_2GeGeMe_2Cl} \longrightarrow \underset{\mathbf{3}}{PhCH_2GeMe_2Cl} + \underset{\mathbf{4}}{GeMe_2Cl_2} \qquad (1)$$

when the starting organic halide was a bromide or iodide, the outcome was somewhat complicated by the formation of both the normal product (**6**) and the abnormal product (**7**) (Eq. 1, Table 1).[6)] $GeMe_2ClX$ (**8**), the expected coproduct corresponding to **6**, was not found in germylation of iodobenzene while it was formed in

$$\underset{\mathbf{5}}{RX} + \mathbf{1} \longrightarrow \underset{\mathbf{6}}{RGeMe_2Cl} + \underset{\mathbf{7}}{RGeMe_2X} + \underset{\mathbf{8}}{GeMe_2ClX} + \underset{\mathbf{4}}{GeMe_2Cl_2} \qquad (2)$$

(R = benzyl, phenyl, β-styryl; X = Br, I)

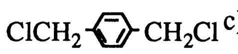
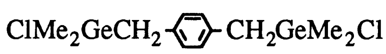
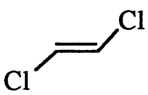
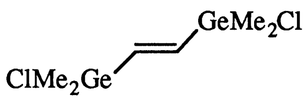
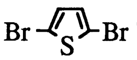
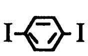
very little amounts (4 - 6%) in the reactions of organic bromides (vide infra). The combined yield of **6** and **7** was generally good to excellent except in the reaction of benzyl bromide which was largely transformed into bibenzyl (30%). Thus the procedure has proved to provide a convenient route to organogermyl compounds.

Table 1. Germylation of Organic Halides (RX) with $ClMe_2GeGeMe_2Cl$[a)]

RX	Time/h	Yield/% [b)]		
		$RGeMe_2Cl$	$RGeMe_2X$	$GeMe_2Cl_2$
$PhCH_2Cl$	10	93(80)	—	100
$PhCH_2Br$	5	19	21	51
PhCH=CHBr [c)]	10	32(30) [d)]	56(40) [d)]	69
PhBr	10	39	31	54
PhI	5	31(30)	68(46)	87

a) Benzene (2 cm^3 per 1 mmol of RX) was used as solvent. Reaction temperature was 120 °C. Ratio of RX, **1**, and $Pd(PPh_3)_4$ was 1 : 1 : 0.05. b) GC yields based on the amount of the halide. Isolated yields are shown in parentheses. c) Cis/trans was 13 : 87. d) Trans products. Yields of the combined cis products were < 2%.

Table 2. Germylation of Organic Dihalides (X-R-X) with $ClMe_2GeGeMe_2Cl$[a)]

X-R-X	Time/h	Temp/°C	Product	Yield/% [b)]
 [c)]	10	120		60(47)
 [c)]	15	180		34
 [d)]	12	150		(56)
 [d)]	10	120		(51)

a) X-R-X/benzene was 1 mmol/4 cm^3. b) GC - yield based on the amount of halide. Isolated yields are shown in parentheses. c) X-R-X : **1** : $Pd(PPh_3)_4$ was 1 : 2.5 : 0.1. d) After completion of the reaction, the mixture was treated with MeLi. X-R-X : **1** : $Pd(PPh_3)_4$ was 1 : 4 : 0.05.

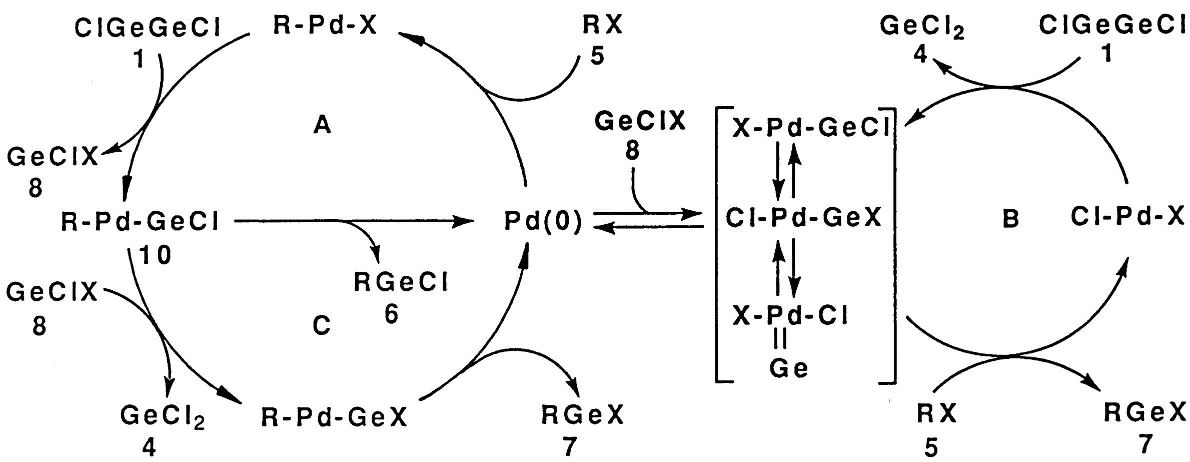
As summarized in Table 2, organic dihalides also react similarly,[7)] and bis(halodimethylgermyl) compounds, potential monomers for polycarbogermanes, [8)] were obtained in reasonable yields.

The formation of **7** from **5** is seemingly an insertion of dimethylgermylene into the R-X bond whatever the detailed pathways may be. It is interesting to note that silicon analogues of **7** have never been reported to be formed in the reactions of organic halides with sym-dichlorotetramethyldisilane.[9)] One of the mechanistic possibilities might be the halogen exchange between **6** and **8** to result in the formation of **7** and **4** (Eq. 3). However, this can be safely excluded for the following reason. In the catalytic reactions of benzyl bromide and

$$\underset{\mathbf{6}}{RGeMe_2Cl} + \underset{\mathbf{8}}{GeMe_2ClX} \not\longrightarrow \underset{\mathbf{7}}{RGeMe_2X} + \underset{\mathbf{4}}{GeMe_2Cl_2} \qquad (3)$$

β-bromostyrene, $GeMe_2ClBr$ is supposed to be formed as the coproduct **8** corresponding to the normal product **6**. But, in a separate experiment, the addition of benzylchlorodimethylgermane (**3**) to the β-bromostyrene reaction did not give benzylbromodimethylgermane at all. If the halogen exchange was occuring, **3** should have been converted into benzylbromodimethylgermane by reacting with $GeMe_2ClBr$, which was being generated while the germylation of β-bromostyrene was in progress.

We propose the normal and abnormal products being formed via the catalytic cycle outlined in Scheme 1, which accommodates the following mechanistic features. An equimolar benzene-d_6 solution of $Pd(PPh_3)_4$ and **1**, when monitored by ^1H NMR, did not show any reaction even at 120 °C. On the other hand, $Pd(PPh_3)_4$ readily underwent the well-established oxidative addition with iodobenzene at room temperature to give $PhPdI(PPh_3)_2$ (**9**). The reaction of **9** (0.1 mmol) with **1** (0.1 mmol) in benzene at 120 °C for 1 h exclusively gave **6** (92%). The NMR spectrum and GC-MS did not show the formation of **7** at all. Accordingly, the formation of the normal product via the catalytic cycle **A** looks quite probable. On the other hand, under the same conditions, the 1 : 1 : 0.3 mixture of iodobenzene, **1**, and $Pd(PPh_3)_4$, when heated at 120 °C in benzene-d_6 initially (at 23 min reaction time) gave only **6** (16%), and later (at 33 min reaction time) produced **7** as major product (**6**: 23%, **7**: 23%). These findings seem to indicate that as the reaction was in progress, other palladium species which was a capable germylene source was emerging. $GeMe_2ClX$ (**8**, X = Br, I), the incidental coproduct to the normal product **6** was not detected in iodobenzene reaction and formed in little amounts in the reactions of organic bromides (vide supra). Instead, **4** was formed in large excess of the corresponding abnormal product. Accordingly, **8**, which is envisaged to have been generated upon the formation of **6**, must have reacted further. One of the possibilities is the formation of palladium germylene intermediate complex[10,11] as shown in Scheme 1 (cycle **B**). Insertion of germylenes into carbon-halogen bonds is well established and transition metal complexes ligated by silylenes, germylenes, and stannylenes as well as



(Pd = $Pd(PPh_3)_2$, Ge = $GeMe_2$)

Scheme 1.

insertion and deinsertion processes of these ligands into transition metal-halogen bonds have been described in quite a few publications.[13] Another possibility is the reaction of the intermediate **10** with $GeMe_2ClX$ (cycle C, Scheme 1) which is supported by the following experiment. Thus, when a benzene solution of $PhCH_2PdCl(PPh_3)_2$ was treated with $GeMe_2Br_2$ in the presence of $ClMe_2SiSiMe_2Cl$ at 120 °C for 1 h gave $PhCH_2GeMe_2Br$ (45%) and $PhCH_2SiMe_2Cl$ (15%) (Eq. 4).

$$PhCH_2PdCl(PPh_3)_2 + GeMe_2Br_2 + ClMe_2SiSiMe_2Cl \longrightarrow \underset{45\%}{PhCH_2GeMe_2Br} + \underset{15\%}{PhCH_2SiMe_2Cl} \quad (4)$$

Further studies on mechanistic aspects and synthesis of germanium containing polymers are in progress.

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6) All new compounds gave satisfactory spectral and/or analytical data.
7) As expected, a mixture of three halogermylated products were observed by GC and GC-MS in the reactions of 2,5-dibromothiophene and 1,4-diiodobenzene. Methylation of the reaction mixture with methyllithium gave only one product in respective reactions.
8) Treatment of 1,2-bis(chlorodimethylgermyl)ethylene with sodium dispertion resulted in the formation of poly[(tetramethyldigermanylene)(ethenylene)], Mw = 33000. A thin solid film obtained by spin coating, when doped with SbF_5, showed a conductivity of 1.3×10^{-3} S/cm. Detailed results of conductive germanium containing polymers will be published separately.
9) Calas et al. have reported $PhSiBrCl_2$ being formed in $NiCp_2$-catalyzed reaction of PhBr with $SiCl_4$ in the presence of $Cl_2MeSiSiMeCl_2$ used as chlorine trapping agent . See M. Lefort, C. Simmonet, M. Birot, G. Deleris, J. Dunogues, and R. Calas, *Tetrahedron Lett.*, **21**, 1857 (1980).
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(Received January 7, 1991)