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INSERTION REACTIONS OF ELECTRON-DEFICIENT SPECIES: INSERTION OF GERMYLENES AND PHENYLPHOSPHINIDENE INTO GERMANIUM—GERMANIUM BONDS

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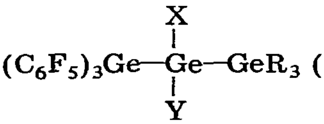
Summary

The reactions of germylenes with pentafluorophenyl- and alkylpentafluorophenyl-digermanes give the trigermanes  $(C_6F_5)_3Ge{-}\overset{X}{\underset{Y}{Ge}}{-}GeR_3$ ($X = F, Cl$; $Y = F, Ph$; $R = C_6F_5, Et$). Their thermal decomposition involves α-elimination to give halogermanes and germylgermylenes. These last bivalent species were trapped with dimethylbutadiene to give germylgermacyclopentenes. Insertion of phenylphosphinidene into the very reactive germanium—germanium bond of $(C_6F_5)_3GeGe(C_6F_5)_3$ was also observed.

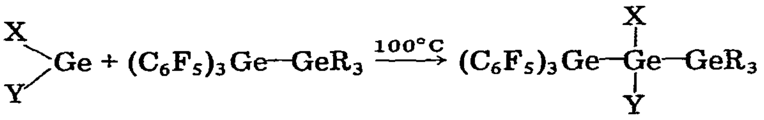
Introduction

Insertions of germylenes into various M_{IVb}—Y σ bonds ($Y = H$, halogen, OR, NR_2, PR_2 etc) have been widely studied [1]. We have previously observed insertion of germylenes into the tin—tin bond of dissymetric distannanes [2,3], but no insertion reactions into germanium—germanium bonds have been reported up to now, presumably because of the very low reactivity of this bond in alkyl or aryl digermanes.

Perfluorophenyl- and perfluorophenylalkyl-digermanes show enhanced reactivity of the germanium—germanium bond [4—6], which is explained in terms of the high polarisability of the $\geqq$Ge—Ge$\leqq$ bond under the influence of polar solvents and active reagents. We therefore decided to study the possibility of insertion of a series of divalent species (Ph_2Ge, PhGeCl, F_2Ge) and phenylphosphinidene into the germanium—germanium bond of the pentafluorophenyldigermanes $(C_6F_5)_3GeGe(C_6F_5)_3$ and $(C_6F_5)_3GeGeEt_3$.

Results and discussion

Difluorogermylene and phenylchlorogermylene are fairly reactive towards both digermanes studied:

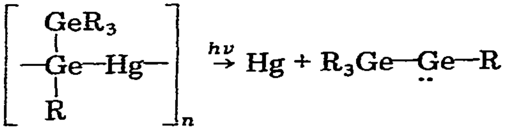


$$\begin{smallmatrix}X\\ Y\end{smallmatrix}\!\!>Ge + (C_6F_5)_3Ge{-}GeR_3 \xrightarrow{100^\circ C} (C_6F_5)_3Ge{-}\overset{\overset{X}{|}}{\underset{\underset{Y}{|}}{Ge}}{-}GeR_3$$

(X = F, Cl; Y = F, Ph) (R = Et, C_6F_5)

Diphenylgermylene, which generally shows a lower reactivity, does not react under these conditions.

The symetrical trigermanes $(C_6F_5)_3Ge{-}\overset{\overset{X}{|}}{\underset{\underset{Y}{|}}{Ge}}{-}Ge(C_6F_5)_3$ (I) were found to be more stable than the unsymetrical trigermanes $(C_6F_5)_3Ge{-}\overset{\overset{X}{|}}{\underset{\underset{Y}{|}}{Ge}}{-}GeEt_3$ (II) and could be isolated in the crystalline state. The trigermanes I with X and Y = F are stable at room temperature but decompose through a thermally induced α-elimination process to give the corresponding halogermanes and germylgermylenes (Scheme 1). Other germylgermylenes were previously prepared using this type of organohalotrigermane decomposition reaction, and also by thermal or photolytic decomposition of digermylmercury compounds [8]:

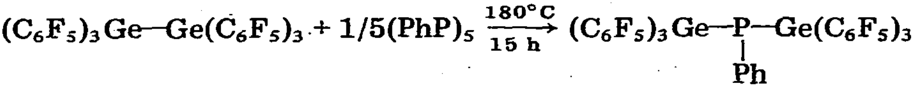


$$\left[\begin{array}{c}GeR_3\\ |\\ {-}Ge{-}Hg{-}\\ |\\ R\end{array}\right]_n \xrightarrow{h\nu} Hg + R_3Ge{-}\underset{\cdot\cdot}{Ge}{-}R$$

Germylgermylenes are easily trapped by dimethylbutadiene to give germylgermacyclopentenes (III) ([8] and Scheme 1).

The trigermanes I and germylgermacyclopentenes III can be stabilized by arylation of the germanium—halogen bonds which take part in the α-elimination process. Thus phenylpentafluorophenyltrigermane (IV) and the germylgermacyclopentene (V) are relatively stable up to 200—250° C, but they decompose at higher temperatures.

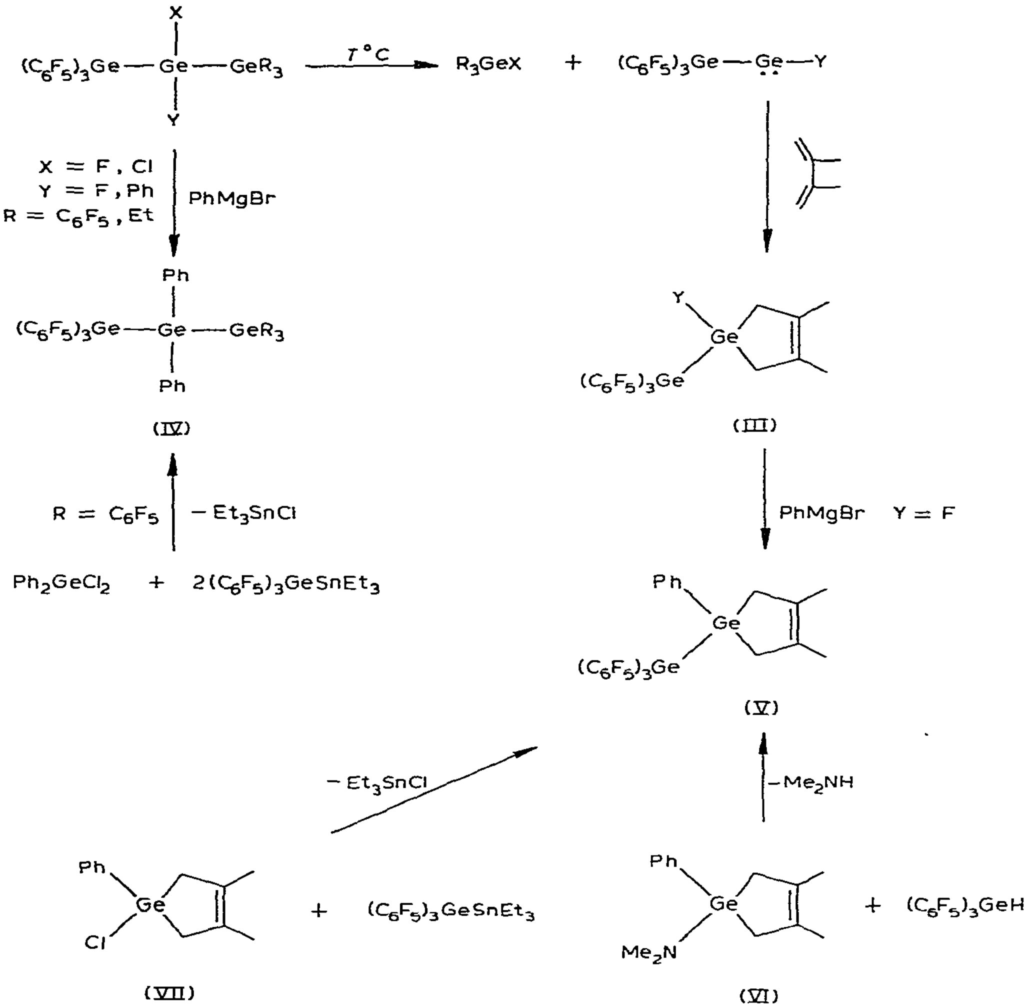
Reaction of phenylphosphinidene with hexa(pentafluorophenyl)digermane gives a germylphosphine:



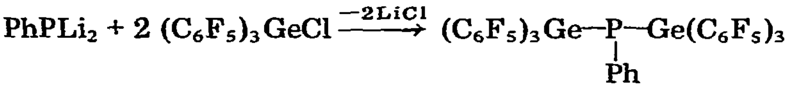
$$(C_6F_5)_3Ge{-}Ge(C_6F_5)_3 + 1/5(PhP)_5 \xrightarrow[15\ h]{180^\circ C} (C_6F_5)_3Ge{-}\underset{\underset{Ph}{|}}{P}{-}Ge(C_6F_5)_3$$

($\delta(^{31}P) = 22.4$ ppm)

SCHEME 1



The same product was also synthesized by treating dilithium phenylphosphine with tris(pentafluorophenyl)chlorogermane:



$$PhPLi_2 + 2\ (C_6F_5)_3GeCl \xrightarrow{-2LiCl} (C_6F_5)_3Ge{-}\underset{\displaystyle Ph}{\underset{|}{P}}{-}Ge(C_6F_5)_3$$

However, these insertions were not observed in the case of the less reactive germanium—germanium bond of hexamethyl- and hexaethyl-digermanes.

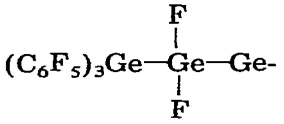
Experimental

The compounds described in this paper were characterized using standard techniques: GC (Aerograph 1400, SE 30, DEGS; internal reference Et_4Ge or Bu_4Ge); NMR (EM 360 A, Varian T 60 and Bruker WP 90 (36.4 MHz); IR

(Perkin-Elmer 457), liquid film. Elemental analyses were carried out by the Service Central de microanalyse du CNRS. Melting points were determined with a Reichert Microscope.

Reaction of F_2Ge with $(C_6F_5)_3GeGe(C_6F_5)_3$

F_2Ge (0.13 g; 0.0012 mol) was added to a solution of $[(C_6F_5)_3Ge]_2$ (1.38 g; 0.0012 mol) in 10 ml of THF. The mixture was heated for 5 h at 100°C in a Carius tube and then left for 10 h at room temperature under argon in a Schlenk tube. The unreacted digermane and F_2Ge were then filtered off (~10—15%). Evaporation of the solvent under vacuum gave a solid residue, which gave cubic crystals by recrystallisation from toluene/hexane:



$(C_6F_5)_3Ge{-}\underset{F}{\overset{F}{\overset{|}{\underset{|}{Ge}}}}{-}Ge(C_6F_5)_3$

(I) (0.56 g, 37% yield), m.p. = 174—176°C; Found: C, 34.12; F, 48.66. $C_{36}F_{32}Ge_3$ calcd.: C, 34.37; F, 48.32%. The remaining amorphous solid consisted of a mixture of I, $(C_6F_5)_3GeF$ and $((C_6F_5)_3GeGeF)_n$ (0.71 g, 43%).

When the same product mixture was arylated using a 100% excess of PhMgBr in ether, $(C_6F_5)_3Ge{-}GePh_2{-}Ge(C_6F_5)_3$ was obtained, and was characterized by GC comparison with an authentic sample (see below).

When the same product mixture was allowed to react with dimethylbutadiene (2 ml) in 10 ml of ether in a Carius tube at 130°C for 2 h, then arylated with excess PhMgBr as above, hydrolysis, extraction and solvent evaporation under vacuum gave V, which was identified by comparison with an authentic sample (GC, NMR) (see below) (27% yield by NMR).

Preparation of V

$(C_6F_5)_3GeH$ (1.50 g; 0.003 mol) was added dropwise to a solution of VI (0.72 g; 0.003 mol) in 10 ml THF. After quantitative formation of Me_2NH, evaporation of the solvent under vacuum gave crude V, which was characterized by NMR and IR (see below). Attempted distillation of the product mixture resulted in explosive decomposition. The same digermane was therefore synthesized by a second route, as follows: 1.56 g (0.002 mol) of $(C_6F_5)_3Ge$-$SnEt_3$ was mixed with 0.53 g (0.002 mol) of VII in 5 ml of THF, and the mixture was heated (70°C) for 4 h. Quantitative formation of Et_3SnCl was observed by GC analysis. The Et_3SnCl was removed with the solvent under vacuum. The residue showed the same NMR and IR spectra and GC retention time as the sample obtained by the previous method. IR: $\nu(C{=}C) = 1640\ cm^{-1}$; NMR: $\delta(CH_3) = 160$ (s), $\delta(CH_2) = 1.80$ ppm (s) (C_6D_6).

Preparation of $(C_6F_5)_3GeGePh_2Ge(C_6F_5)_3$ (IV)

$(C_6F_5)_3GeSnEt_3$ (2.1 g; 0.0026 mol) was added to a solution of Ph_2GeCl_2 (0.4 g; 0.0013 mol) in 10 ml THF. The mixture was heated at 50°C for 4 h and at 100°C for 1 h. The course of the reaction was monitored by the formation of Et_3SnCl. The amount of Et_3SnCl formed and its purity were determined by GC analysis (0.54 g; 83%). The solvent and Et_3SnCl were removed by evaporation under vacuum. Hexane was added to the residue to precipitate $(C_6F_5)_3Ge$-$GePh_2Ge(C_6F_5)_3$ as a white powder. (0.46 g; 25% yield); m.p. 296—310°C.

Found: C, 41.15; H, 0.73; F, 42.28. $C_{48}H_{10}F_{30}Ge_3$ calcd.: C, 41.95; H, 0.73; F, 41.47%.

Reaction of PhGeCl with $(C_6F_5)_3GeGe(C_6F_5)_3$

A mixture of PhGeCl (0.0002 mol) with 0.21 g (0.0002 mol) of $(C_6F_5)_3Ge$-$Ge(C_6F_5)_3$ was heated for 2 h at 100°C in a Carius tube to give mixture of the trigermane $(C_6F_5)_3Ge$—GePh(Cl)—$Ge(C_6F_5)_3$ and its decomposition products. Arylation of the mixture with an excess of PhMgBr in ether led to $(C_6F_5)_3Ge$-$GePh_2Ge(C_6F_5)_3$ (detected only by GC), while treatment with dimethylbutadiene (2 ml) (2 h at 130°C) followed by arylation with an excess of PhMgBr in ether gave V (24% by NMR).

Reactions of germylenes with $(C_6F_5)_3GeGeEt_3$

Using the conditions described in the previous paragraph, either F_2Ge or PhGeCl were treated in THF with equimolar amounts of $(C_6F_5)_3GeGeEt_3$. In these cases, however the trigermanes formed were not themselves characterized but their decomposition products were isolated or characterized. GC analysis of the mixture showed quantitative formation of Et_3GeF in the case of F_2Ge, and of Et_3GeCl in the case of PhGeCl. Et_3GeX (X = F, Cl) was distilled at 80°C under vacuum (2×10^{-3} mm Hg), trapped at —196°C and identified by GC.

The crude germylgermylenes obtained were allowed to react at 100°C (Carius tube) with an excess of dimethylbutadiene. The crude germylgermacyclopentenes formed were arylated with an excess of PhMgBr in ether to give V, which was shown by NMR spectroscopy to be identical with the sample synthesized above (27% from GeF_2; 13% from PhGeCl). (There was no reaction in the case of Ph_2Ge.)

In all these reactions significant quantities of amorphous polygermanes remained even after arylation; they are formed by polycondensation reactions of intermediate germylenes, which are less stable than halogenogermylenes [1]. For example, in the reaction of F_2Ge with $(C_6F_5)_3GeGeEt_3$ an amorphous solid (decomposing on fusion) was isolated and shown to have the composition $[(C_6F_5)_3GeGeF]_n$. Found: C, 32.17; F, 45.86. $C_{18}F_{16}Ge_2$ calcd.: C, 32.49; F, 45.69%.

Reaction of phenylphosphinidene with hexa(pentafluorophenyl)digermane

A suspension of $(C_6F_5)_3GeGe(C_6F_5)_3$ (1.43 g; 0.0012 mol) and of pentaphenylcyclopentaphosphine, $(PhP)_5$, (0.13 g; 0.0002 mol) in benzene (2 ml) was heated for 15 h at 180°C in a Carius tube to give a colourless solution. The solvent was removed under vacuum and the residual crystals, which were soluble in most organic solvents, were washed with pentane and dried to give $(C_6F_5)_3GeP(Ph)Ge(C_6F_5)_3$ (0.61 g; 39% yield); m.p.: 90—92°C. Found: C, 40.15; H, 0.49; F, 44.86; P, 2.70. $C_{42}H_5F_{30}Ge_2P$ calcd.: C, 40.18; H, 0.40; F, 45.38; P, 2.46%.

Reaction of dilithiumphenylphosphine with tris(pentafluorophenyl)chlorogermane

$PhPLi_2$ was prepared from phenylphosphine (0.106 g; 0.0010 mol) and BuLi, 1.20 *M* (1.56 ml) in ether. THF (5 ml) was added, and solution of $(C_6F_5)_3GeCl$

(1.22 g; 0.0020 mol) in 3 ml of ether was introduced dropwise. The LiCl was centrifuged out and the solution concentrated under vacuum to give $(C_6F_5)_3Ge\cdot P(Ph)Ge(C_6F_5)_3$ (0.54 g; 45% yield); m.p.: 90—93°C.

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