

Organometallic Chemistry

Reactions of pentafluorophenylgermanium hydrides with Grignard reagents

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Dendritic and cross-linked polyphenylenepolygermanes have been obtained by reactions of EtMgBr with $(\text{C}_6\text{F}_5)_3\text{GeH}$ and $(\text{C}_6\text{F}_5)_2\text{GeH}_2$, respectively. The reaction of sodium naphthalenide with trihydride $\text{C}_6\text{F}_5\text{GeH}_3$ gives linear insoluble polymer $(\text{C}_6\text{F}_4\text{GeH}_2)_n$.

Key words: pentafluorophenylgermanium hydrides; dendrimer, polymer; polycondensation.

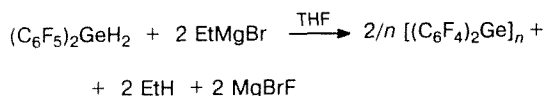
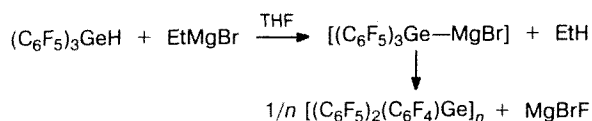
We have shown previously that pentafluorophenyl-substituted germanium hydrides $(\text{C}_6\text{F}_5)_x\text{GeH}_{4-x}$ ($x = 2$ or 3) react readily with Lewis bases to form products of polycondensation. Monohydride $(\text{C}_6\text{F}_5)_3\text{GeH}$ gives the soluble star-branched polymer (dendrimer)¹ $[(\text{C}_6\text{F}_5)_2(\text{C}_6\text{F}_4)\text{Ge}]_n$, while dihydride $(\text{C}_6\text{F}_5)_2\text{GeH}_2$ gives insoluble cross-linked poly[bis(tetrafluorophenyl)germane]² $[(\text{C}_6\text{F}_4)_2\text{Ge}]_n$. Attempts to perform polycondensation of trihydride $\text{C}_6\text{F}_5\text{GeH}_3$ in a similar way were unsuccessful, which is likely related to the reversal of polarity of the Ge—H bond on going from mono- and dihydrides to trihydride. At the same time, it seemed extremely interesting to synthesize polyorganogermane based on pentafluorophenylgermane, because the existence of three hydride functions and one pentafluorophenyl substituent in the initial compound allows one to expect the formation of a dendrimer of a new type, $(\text{C}_6\text{F}_4\text{Ge})_n(\text{C}_6\text{F}_4\text{GeH}_3)_m$, in which hydride atoms of Ge—H bonds play the role of peripheral functional groups. Of numerous dendrimers and superbranched

compounds synthesized recently (see, e.g., Ref. 3), only organosilane derivatives with terminal $\text{OSi}(\text{CH}_3)_2\text{H}$ (Ref. 4) and $\text{CH}_2\text{CH}_2\text{SiH}_3$ (Ref. 5) groups contain element—hydrogen bonds at the periphery of spherical macromolecules.

In this work, Grignard reagent was used for polycondensation of pentafluorophenylgermanes, and we attempted to synthesize dendrimeric polyhydrogermane by this method.

We have shown that germanium hydrides of the $(\text{C}_6\text{F}_5)_x\text{GeH}_{4-x}$ ($x = 1-3$) series readily react with Grignard reagents RMgX according to the scheme of the Razuvaev—Vyazankin reaction,⁶ i.e., hydrocarbon RH is evolved, and a germanium—metal bond is formed. The presence of strong electron-accepting C_6F_5 groups in a molecule of organogermanium hydride causes a strong polarity and heterolysis of the Ge—Mg bond, resulting in the formation of germanium-centered anions of the $(\text{C}_6\text{F}_5)_3\text{Ge}^-$ type. The latter, as established previously,⁷ readily react with C_6F_5 groups of adjacent

molecules *via* a nucleophilic substitution mechanism to form polymeric products: dendrimer¹ $[(C_6F_5)_2(C_6F_4)Ge]_n$ or cross-linked polygermane² $[(C_6F_4)_2Ge]_n$.

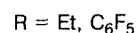
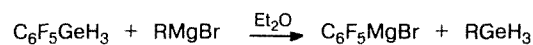


The reactions of $(C_6F_5)_3GeH$ and $(C_6F_5)_2GeH_2$ with $EtMgBr$ in THF are exothermic. After several minutes, the yield of ethane and polymeric products reaches 90–95 %. Trihydride $C_6F_5GeH_3$ reacts with two equivalents of $EtMgBr$ in THF accompanied by heating of the reaction mixture and vigorous evolution of ethane. The third mole of $EtMgBr$ does not enter the reaction even on heating to 70–90 °C. The germanium-containing product formed under these conditions is isolated after the hydrolysis of the reaction mixture as a light-yellow amorphous nearly insoluble substance. No absorption bands of vibrations of the Ge–H bond are observed in its IR spectrum, but there are intense bands at 1220, 970, and 430 cm^{-1} corresponding to the disubstituted pentafluorophenyl cycles, which are typical of poly(perfluorophenylgermanes),⁸ as well as absorption bands of OH groups in the range of 3000 cm^{-1} . The organic products of the hydrolysis of the substance obtained contain only $C_6F_4H_2$.

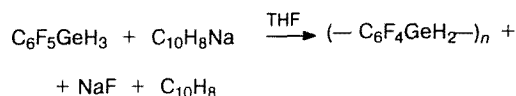
These data testify that $C_6F_5GeH_3$ does enter the polycondensation reaction under the action of $EtMgBr$ in THF to form Ge– C_6F_4 –Ge groups. The process is accompanied by side reactions resulting in the cleavage of all Ge–H bonds and formation of cross-linked polymeric forms. The similar products were obtained by the reaction with equimolar amounts of $C_6F_5GeH_3$ and $EtMgBr$, but, in this case, only some amount of unreacted trihydride remained in the mixture. Thus, pentafluorophenylgermane enters the polycondensation reaction in THF, but does not yield Ge–H-functional dendrimer expected.

The direction of the reaction changes, when it is carried out in ether. In this case, almost no ethane is evolved and no polymeric products are formed. After the hydrolysis of the reaction mixture, a considerable amount of C_6F_5H is observed, and the presence of $EtGeH_3$ is established quantitatively in volatiles. These data indicate the predominant direction of the attack of $EtMgBr$ to the Ge–C bond in the initial $C_6F_5GeH_3$. It is likely that C_6F_5MgBr reacts in a similar way. Weak heating of the mixture and the appearance of the yellowish-brown color testify that the reaction occurs. However, after its completion and hydrolysis of the reaction mixture, only

C_6F_5H and the initial trihydride, which is one of the products of ligand exchange in this case, were isolated.



The use of sodium naphthalenide instead of $RMgX$ makes it possible to prevent virtually side reaction upon polycondensation of $C_6F_5GeH_3$. However, linear polyphenylenegermane was obtained in this case instead of organogermanium dendrimer expected.



The product isolated is the insoluble infusible white powder that darkens on heating to the temperature higher than 280 °C. Its IR spectrum contains the bands at 1220, 970, and 430 cm^{-1} (Ge– C_6F_4 –Ge fragment) and 2060, 850, and 770 cm^{-1} (GeH_2 group), but no absorption bands of the GeH_3 groups (2140 and 870 cm^{-1}) are observed. These data along with a relatively low intensity of the bands corresponding to the GeH_2 groups (lower than that in the spectrum⁹ of $(C_6F_5)_2GeH_2$) testify, in our opinion, to the cyclic form of macromolecules and their partial cross-linking.

Experimental

IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer (suspensions in Vaseline oil).

GLC analysis of volatiles was performed on a Tsvet-104 gas chromatograph (katharometer as detector, helium as the carrier gas, columns: 300×0.4 cm filled with PEG 20M (15 %) on Chromaton N-AW and 50×0.4 cm filled with OV-17 (5–7 %) on Chromaton N-super).

Initial organogermanium hydrides $(C_6F_5)_3GeH$, $(C_6F_5)_2GeH_2$, and $C_6F_5GeH_3$ were obtained by the procedure described previously.⁹ Solvents were purified according to the standard procedures. Reactions were performed in an argon atmosphere.

Reaction of $(C_6F_5)_3GeH$ with $EtMgBr$. A solution of $(C_6F_5)_3GeH$ (1.3 g, 2.3 mmol) in 10 mL of THF was placed in a tube attached to a gas buret, and a solution of $EtMgBr$ (0.32 g, 2.4 mmol) in 4.5 mL of THF was added at room temperature. The reaction mixture was heated, and ethane (51 mL, 100 %) evolved. The reaction mass was stirred for 15 min and decomposed with water. The polymer isolated was washed with hexane several times and dried *in vacuo*. Polyphenylenegermane (1.2 g, 92 %) was obtained as a white amorphous powder. The IR spectrum of the polymer, its melting and decomposition points, the relative contents of C_6F_5 and C_6F_4 groups, and other characteristics correspond to the parameters of perfluorinated polyphenylenepolygermane obtained previously.¹

Reaction of $(C_6F_5)_2GeH_2$ with $EtMgBr$ was performed as described above for $(C_6F_5)_3GeH$. Ethane (56 mL, 87 %) evolved when a solution of $EtMgBr$ (0.039 g, 2.9 mmol) was added to a solution of $(C_6F_5)_2GeH_2$ (0.59 g, 1.4 mmol) in

10 mL of THF. After the decomposition of the reaction mixture with water and washing with hexane, 0.41 g (70 %) of the polymer as an infusible insoluble amorphous yellowish powder were obtained. The physicochemical characteristics of the product and its element composition correspond to those of cross-linked perfluorinated polyphenylenepolygermane synthesized by the reaction of $(C_6F_5)_2GeH_2$ with triethylamine.²

Reaction of $C_6F_5GeH_3$ with EtMgBr (C_6F_5MgBr). Ethane (200 mL, 67 %) evolved when a solution of EtMgBr (1.87 g, 14.0 mmol) in 5 mL of THF was added to a solution of $C_6F_5GeH_3$ (1.08 g, 4.4 mmol) in 10 mL of THF at room temperature. The reaction mass was heated for 10 min at 60 °C and was decomposed with water after cooling. The hydrolysis resulted in the evolution of 81 mL (27 %) of ethane. The organogermanium product was washed with hexane and dried *in vacuo*. A white infusible insoluble amorphous powder was obtained (0.7 g), which decomposed at the temperature >280 °C. IR, ν/cm^{-1} : 1240, 980, 430 (C_6F_4-Ge); 3000 ($Ge-OH$); 2150 ($Ge-H$). $C_6F_4H_2$ is the only organic product of the hydrolysis of the polymer (THF- H_2O , 40 % NaOH, 80 °C).

Reaction of $C_6F_5GeH_3$ with EtMgBr in ether. A solution of EtMgBr (0.62 g, 4.6 mmol) in 7 mL of ether was added to a solution of $C_6F_5GeH_3$ (1.1 g, 4.5 mmol) in 10 mL of ether. The mixture was kept for 15 min at room temperature and decomposed with water. An organic layer was separated and analyzed by GLC. The mixture contained more than 10 volatiles, and C_6F_5H (52 %) and $C_6F_5GeH_3$ (41 %) were identified as the main components.

The reaction with C_6F_5MgBr was performed in a similar way.

Reaction of $C_6F_5GeH_3$ with sodium naphthalenide. Small portions of a solution (7.5 mL) of sodium naphthalenide (obtained from 1.28 g (0.01 mmol) of naphthalene and 0.23 g (0.01 mmol) of sodium) in THF were added with stirring to a solution of $C_6F_5GeH_3$ (0.73 g, 3.0 mmol) in 15 mL of THF. The mixture was stirred for 30 min at room temperature. The solvent was removed *in vacuo*, and a residue was washed with

benzene and water and dried *in vacuo*. Polymer (0.61 g, 84 %) was obtained as a white infusible insoluble amorphous powder similar to that isolated in the reaction of $C_6F_5GeH_3$ with EtMgBr in THF. The powder continuously darkens on heating to the temperature >280 °C. Found (%): C, 33.47; H, 1.5. $C_6H_2F_4Ge$. Calculated (%): C, 32.36; H, 0.91. IR, ν/cm^{-1} : 2060, 1640, 1605, 1515, 1450, 1375, 1280, 1220, 1170, 1085, 1040, 970, 935, 907, 850, 820, 770, 720, 705, 585, 525, 430.

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