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INTERACTION OF PENTAFLUOROPHENYL HYDRIDES OF GERMANIUM WITH TRIETHYLTHALLIUM

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Summary

$(C_6F_5)_3GeTlEt_2$ and $[(C_6F_5)_3Ge]_2TlEt$ have been prepared by reaction of tris(pentafluorophenyl)germane with triethylthallium. The reaction of the dihydride $(C_6F_5)_2GeH_2$ with triethylthallium gives an unusual product of composition $[(C_6F_5)_2GeTlEt]_n$. The possible isomeric forms of this compound are discussed. Reactions of the compound obtained with $(C_6F_5)_2GeH_2$, bromine, hydrogen chloride and benzoyl peroxide have been studied. In the reaction with benzoyl peroxide the migration of an ethyl group from thallium to germanium has been noted.

Introduction

The first organometallic compound containing a germanium–thallium bond, $(Et_3Ge)_3Tl$, was prepared as an undistillable coloured liquid in the reaction of triethylgermane with triethylthallium [1]. Germyl- and stannyl-thallium derivatives with bulky trimethylsilyl-methyl substituents are more stable [2]. Pentafluorophenyl substituents also exert as a rule a significant influence on the properties (in particular on the stability) of heteroelement groupings [3]. However, C_6F_5 derivatives with a covalent Ge–Tl bond are not yet known. The oxidation-reduction transmetallation between metallic thallium and bis[tris(pentafluorophenyl)germyl]mercury, as already reported [4], leads to an ionic complex containing a Tl^+ cation. In the present paper we report on the use of the hydride method for the preparation of pentafluorophenylgermylthallium compounds.

Results and discussion

We have found that tris(pentafluorophenyl)germane reacts with triethylthallium under mild conditions to form covalent germyl-thallium compounds. However, in this case only two ethyl groups are substituted in Et_3Tl unlike reactions with Et_3GeH, $(Me_3SiCH_2)_3GeH$ and $(Me_3SiCH_2)_3SnH$. It should be noted that the first Et group is abstracted much more readily than the second one. This allowed us to

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prepare both mono- and di-substituted products by selecting suitable reaction conditions.

$$n(C_6F_5)_3GeH + Et_3Tl \xrightarrow[20-40^\circ C]{toluene} [(C_6F_5)_3Ge]_nTlEt_{3-n} + nEtH \qquad (1)$$

$n = 1, 2$

The reaction gives only the disubstituted product at a ratio of hydride and triethylthallium of 3 : 1 under these reaction conditions. Under more drastic conditions (90–95°C) the decomposition of intermediates with precipitation of metallic thallium was observed.

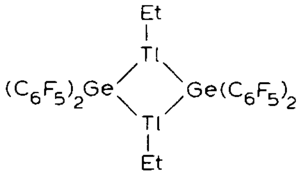
The germylthallium products were isolated from hexane or toluene solutions as yellow, light-sensitive crystals, which are slowly oxidized in air. Their stability is comparable with the stability of analogous non-fluorinated compounds (the temperature of decomposition is 100–120°C). Earlier, we assumed that intramolecular coordination between *ortho*-fluorine atoms and the β-heteroatom in pentafluorophenyl polynuclear compounds can decrease their stability in those cases where the β-heteroatom has (like thallium) appropriate vacant orbitals and a low redox potential [3].

As was recently shown, the dihydride $(C_6F_5)_2GeH_2$ reacts with triethylbismuth to give an unusual pentanuclear product containing three germylbismuth cycles [5]. The reaction of triethylthallium with the same dihydride also gives an unusual compound, but are having quite another structure. According to data from elemental analysis, infrared spectra and some chemical reactions given below the product has the composition $[(C_6F_5)_2GeTlEt]_n$.

$$(C_6F_5)_2GeH_2 + Et_3Tl \xrightarrow[20-40^\circ C]{hexane} 1/_n\underset{(I)}{[(C_6F_5)_2GeTlEt]_n} + 2EtH \qquad (2)$$

Compound I was isolated from the reaction mixture as a darkgreen precipitate which is practically insoluble in hexane and sparingly soluble in toluene. It should be noted that solutions of I have a yellow colour. I is better soluble in THF and 1,2-dimethoxyethane but it is quickly decomposed in these solvents with precipitation of thallium. The product is unstable in air and decomposed at 115–120°C in an evacuated sealed capillary. The IR spectrum of ethyl[bis(pentafluorophenyl)germyl]thallium (I) exhibits absorption bands at 1650, 1525, 1480, 1390, 1290, 1090, 1025, 810 and 625 cm^{-1}, characteristic of the C_6F_5–Ge fragment [6] and low intensity bands at 1230, 1180, 670 and 480 cm^{-1} due to the Et–Tl group. The above mentioned diethyl[tris(pentafluorophenyl)germyl]thallium and ethyl{bis[tris-(pentafluorophenyl)germyl]}thallium have analogous spectra exception that the band intensities of Et–Tl fragments are significantly greater in their spectra.

As in the IR spectum of I absorptions of ethyl groups bonded to germanium are



(A)

$(C_6F_5)_2Ge{=}TlEt$

(B)

$(C_6F_5)_2Ge{:}\rightarrow TlEt$

(C)

absent [7], three structural isomeric forms may be suggested for compound I.

In our opinion, form A is the most likely for the compound in solid state. When dissolved, I is probably dissociated to the monomeric form B, which is accompanied by the change of colour from dark green to yellow. The similar association–dissociation of a polynuclear compound under the influence of the solvent was observed earlier for the examples of $[MFe(CO)_4]_4$ (M = Cd, Hg) [8,9] and $[R_2SnFe(CO)_4]_n$ [10]. It should be also noted that quite recently [11] stable compounds containing Mn–Ge double bonds, $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2Ge$ and $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_3Ge$, were obtained. Therefore, form B seems to be perfectly probable. Structure C is a complex of germylene and monovalent thallium. It is more difficult to explain the change of colour of I and the formation of products of the reactions given below, in particular with HCl and benzoyl peroxide by this form. However it should be noted that similar complexes of germylenes with transition metals are well known [12].

The thermal decomposition of I in toluene proceeds at 150°C to afford a complex mixture of viscous products from which we failed to isolate and identify any individual components. However, the thermal decomposition of I in dihydride $(C_6F_5)_2GeH_2$ medium proceeds smoothly according to eq. 3.

$$(C_6F_5)_2GeTlEt \xrightarrow[100^\circ C]{(C_6F_5)_2GeH_2} Tl + EtH + (C_6F_5)_2Ge(H)Ge(H)(C_6F_5)_2 + [(C_6F_5)_2Ge]_n \tag{3}$$

Yields of thallium, ethane, digermane dihydride and polygermane are 98, 77, 52 and 42%, respectively. It may be assumed that in the first step of this reaction the hydride substitutes the ethyl group at thallium and that the unstable intermediate formed is decomposed to afford metallic thallium and germylene, $(C_6F_5)_2Ge$:. The latter are known [13] to polymerize to give $[(C_6F_5)_2Ge]_n$ or to insert into the Ge–H bond of the starting dihydride with the formation of digermanedihydride. This reaction may be considered as the third step of the interaction of triethylthallium with bis(pentafluorophenyl)germane.

The reaction of I with bromine in hexane proceeds readily at room temperature during 3–5 min according to eq. 4. Yields of products are rather high.

$$(C_6F_5)_2GeTlEt + 2Br_2 \xrightarrow[20^\circ C]{\text{hexane}} TlBr + EtBr + (C_6F_5)_2GeBr_2 \tag{4}$$

The interaction of I with excess hydrogen chloride occurs under the same conditions but more slowly (30 min). The reaction affords the expected TlCl (100%) and EtH together with $(C_6F_5)_2GeHCl$, $(C_6F_5)_2GeHEt$, digermanedihydride, $(C_6F_5)_2Ge(H)Ge(H)(C_6F_5)_2$, and unidentified products. Such composition of the products testifies to the complicated nature of the process. The mechanism is not entirely clear.

Diacyl peroxide cleave M–M bonds in polynuclear organometallic compounds under mild conditions [14]. Reactions proceed intramolecularly and are not complicated by elimination of free radicals into the solution or migration of radicals from metal to metal. The interaction of I with benzoyl peroxide also occurs under these conditions except for the spontaneous homolytic cleavage of the peroxide group. However, in this reaction the migration of an ethyl group from thallium to germanium takes place (eq. 5).

$$(C_6F_5)_2GeTlEt + (PhCOO)_2 \xrightarrow[25^\circ C,\ 10\ min]{benzene} TlOCOPh + (C_6F_5)_2Ge(Et)OCOPh \qquad (5)$$

It should be noted that if our supposition concerning the structure of I is correct, and it is one of the above forms A, B or C, then the two latter reactions are the first examples of the migration of an organic radical from metal to metal in a polynuclear organometallic compound. Such migration is apparently realized in the intermediate reaction complex and testifies to the bridged character of the ethyl group at thallium.

Experimental

All reactions were carried out in evacuated sealed systems or under dry argon. GLC analyses were carried out on a Tsvet-129 chromatograph with a heat conductivity detector using columns (50 × 0.4 cm and 100 × 0.4 cm) packed with OV-17 (7%) on Chromatone N-AW-DMCS, with helium as the carrier gas. IR spectra were recorded on a UR-20 and 'Perkin-Elmer' spectrophotometers. Samples of the solid compounds were prepared in the form of a suspension in Vaseline oil. The melting points of the compounds are given without correction.

Diethyl[tris(pentafluorophenyl)germyl]thallium

2.05 g (3.6 mmol) of $(C_6F_5)_3GeH$ and 6 ml of hexane were placed in the ampoule linked to a gas burette. To a solution was added 1.05 g (3.6 mmol) of triethylthallium at room temperature. The mixture was kept for 20 min at room temperature and for 20 min at 40°C. During this time 69 ml (85%) of ethane was evolved and the colour of the solution turned yellow. The solution was decanted from traces of precipitated thallium. On cooling the solution to room temperature yellow crystals were precipitated which were recrystallized from hexane and dried in vacuo to give 2.1 g (70%) of diethyl[tris(pentafluorophenyl)germyl]thallium, m.p. 115–116°C (dec.). (Found: C, 31.74; H, 1.36. $C_{22}H_{10}F_{15}GeTl$ calcd.: C, 31.60; H, 1.20%.)

Ethyl{bis[tris(pentafluorophenyl)germyl]}thallium

A mixture of 0.49 g (1.7 mmol) of triethylthallium and 2 g (3.5 mmol) of tris(pentafluorophenyl)germane in 10 ml of hexane was heated as above. After 30 min at 40°C, 40 ml of ethane was evolved and a yellow residue was formed in solution. The reaction was complete in 2 h and the yield of ethane was 68 ml (90%). The residue precipitated was twice recrystallized from toluene to afford 1.44 g (62%) of $[(C_6F_5)_3Ge]_2TlEt$, m.p. 97–100°C (dec.). (Found: C, 33.08; H, 0.45. $C_{38}H_5F_{30}Ge_2Tl$ calcd.: C, 33.05; H, 0.37%.)

Ethyl[bis(pentafluorophenyl)germyl]thallium (I)

To a solution of 4.48 g (11.0 mmol) of $(C_6F_5)_2GeH_2$ in 15 ml of hexane was added a solution of 3.2 g (11.0 mmol) of triethylthallium in 5 ml of hexane. The mixture was kept for 20 min at 20°C and for 15 min at 40°C. 245 ml (100%) of ethane was evolved and 0.21 g (9%) of metallic thallium was precipitated as a mirror. After centrifugation of the reaction mixture, the dark-green amorphous residue formed was separated by decanting off the hexane solution. The residue was washed three times with hexane and dried in vacuo to give 4.65 g (66%) of I, m.p. > 115°C (dec.). (Found: C, 26.45; H, 0.69; Tl, 31.33. $C_{14}H_5F_{10}GeTl$ calcd.: C, 26.27; H, 0.79; Tl, 31.93%.)

Thermal decomposition of I in the medium of bis(pentafluorophenyl)germane

A mixture of 0.79 g (1.2 mmol) of I and 8.13 g (19.9 mmol) of $(C_6F_5)_2GeH_2$ was heated for 1 h at 100°C. During this time the mixture was completely discoloured. Metallic thallium (0.25 g, 98%) was precipitated and 21 ml (76%) of ethane was evolved. The solution was decanted from thallium, the unreacted bis(pentafluorophenyl)germane was distilled in vacuo and the solid residue was sublimed at 140°C/0.1 mmHg to give 0.51 g (52%) of $(C_6F_5)_2Ge(H)Ge(H)(C_6F_5)_2$, m.p. (mixed) 149–150°C. The product was also identified by GLC and IR spectroscopy. The unsublimed residue of polygermane (0.21 g, 42%) was converted to the volatile hydride $(C_6F_5)_2GeHCl$ by reaction with hydrogen chloride as described [15] and identified by GLC and IR spectroscopy.

Reaction of I with bromine

To a suspension of 0.75 g (1.2 mmol) of I in 10 ml of hexane was added in small portions of 5% solution of bromine in hexane until the yellow colour of mixture appeared. A residue of TlBr (0.33 g, 100%) was precipitated and the organic layer was decanted from TlBr. Ethyl bromide (0.11 g, 86%) and bis(pentafluorophenyl)germanium dibromide $(C_6F_5)_2GeBr_2$ (0.62 g, 94%) were found in the organic layer by GLC.

The interaction of I with hydrogen chloride

Onto a solution of 1.0 g (1.6 mmol) of I in 12 ml of benzene gaseous HCl (110 ml, 4.9 mmol) was condensed by cooling with liquid nitrogen. The mixture was kept at room temperature for 30 min. After this time the dark-green colour of the mixture had disappeared and 15 ml (49%) of ethane was evolved. The colourless crystalline residue formed was washed three times with hot benzene. The insoluble residue was identified as TlCl (0.37 g, 100%). The solvent was removed from the benzene extracts and the residue was recrystallized from hexane to give 0.15 g (24%) of 1,2-dihydro-1,1,2,2-tetrakis(pentafluorophenyl)digermane, m.p. 148–150°C. No depression of the m.p. was caused by mixing the sample with the pure substance. After separating of gaseous and solid products, GLC analysis of the mixture showed that $(C_6F_5)_2GeHCl$ (0.12 g, 17%), $(C_6F_5)_2GeHEt$ (0.12 g, 17%) and two unidentified compounds were present.

Reaction of I with benzoyl peroxide

A solution of 1.05 g (1.6 mmol) of I in 10 ml of benzene was added to a solution of 0.41 g (1.7 mmol) of benzoyl peroxide in 5 ml of benzene. After 10 min at 20°C the mixture was completely discoloured. The organic layer was decanted from the residue of TlOCOPh (0.52 g, 97%). Benzene was removed in vacuo and the residue was recrystallized from hexane to afford 0.78 g (86%) of $(C_6F_5)_2Ge(Et)OCOPh$, m.p. 155–158°C. (Found: C, 45.61; H, 1.85; F, 33.47. $C_{21}H_{10}F_{10}GeO_2$ calcd.: C, 45.29; H, 1.81; F, 34.11%.)

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