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PENTAFLUOROPHENYLGERMANIUM HYDRIDES

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Summary

A series of pentafluorophenylgermanium hydrides, $(C_6F_5)_{4-n}GeH_n$ ($n = 2, 3$), $(C_6F_5)_2Ge(Br)H$ and $(C_6F_5)_2Ge(H)—Ge(H)(C_6F_5)_2$ was prepared by reduction of the corresponding germanium bromides with lithium aluminium hydride and/or triethylgermane. The reactions of these compounds with diethylmercury and triethyl(diethylamino)stannane were investigated. In the latter case pentafluorophenyl derivatives containing an Sn—Ge group were obtained. The reaction of tris(pentafluorophenyl)germane with diethylzinc gave good yields of $[(C_6F_5)_3Ge]_2Zn$. When this product was treated with mercury a $(C_6F_5)_3Ge$ fragment migrated from one metal atom to the other.

Introduction

The common organo-silicon, -germanium and -tin hydrides are known to exhibit high reactivities and their syntheses have been investigated extensively [1]. On the other hand the pentafluorophenyl derivatives of Group IVB metal hydrides have been little studied possibly because of the absence of convenient synthetic procedures. Up to now only the tris(pentafluorophenyl)-silane [2] and -germane [3] were known of this class of compound. The present work is concerned with the synthesis of previously unknown pentafluorophenylgermanium hydrides and with some of their reactions including the formation of bimetallic organometallic compounds.

Results and discussion

We have shown that the compounds $(C_6F_5)_{4-n}GeH_n$ (where $n = 2$ or 3) are produced in high yields (analogously to tris(pentafluorophenyl)germane [3]) (see Table 1) by reduction of the respective bromides with lithium aluminium hydride in ether/toluene or ether/hexane mixtures (eqn. 1).

$$\underset{(a,\ n = 1;\ b,\ n = 2;\ c,\ n = 3)}{(C_6F_5)_{4-n}GeBr_n} \xrightarrow{LiAlH_4} \underset{(I)}{(C_6F_5)_{4-n}GeH_n} \qquad (1)$$

Dihydride (Ib) was also obtained together with $(C_6F_5)_2Ge(Br)H$ (II) by heating the dibromide, $(C_6F_5)_2GeBr_2$, with excess triethylgermane at 120° for 6 h. The formation of compound II in 67% yield demonstrated that this exchange reaction proceeds selectively by substitution of the bromine atom by hydrogen. In this case step 2b occurs probably at a slower rate than does step 2a. Under these conditions the yield of dihydride Ib does not exceed 20—25%. After longer periods of heating and under higher temperatures the yield of dihydride Ib increased significantly. It is unlikely that the dihydride Ib is produced by disproportionation of II since hardly any of the initial dibromide was in the reaction mixture. We found that disproportionation proceeds at an appreciable rate only above 140° and it is reversible. Thus at 150° a dynamic equilibrium is reached in about 3 h (eqn. 3).

$$\begin{tikzcd}
(C_6F_5)_2GeBr_2 + Et_3GeH \arrow[r, "a"'] & \underset{(II)}{(C_6F_5)_2Ge(Br)H} + Et_3GeBr \arrow[d, "b"', "+Et_3GeH"] & (2) \\
& \underset{(Ib)}{(C_6F_5)_2GeH_2} + Et_3GeBr &
\end{tikzcd}$$

$$\underset{(Ib)}{(C_6F_5)_2GeH_2} + (C_6F_5)_2GeBr_2 \overset{150^\circ}{\rightleftharpoons} 2\underset{(II)}{(C_6F_5)_2Ge(Br)H} \qquad (3)$$

The dihydride Ib reacts readily with elemental bromine in benzene to give high yields of $(C_6F_5)_2GeBr_2$. We failed to obtain the bromohydride II by selective bromination of the dihydride Ib.

Earlier we showed [3] that tris(pentafluorophenyl)germane (Ia) when treated with diethylmercury and diethylcadmium, produces bis[tris(pentafluorophenyl)germyl]-mercury and -cadmium, respectively. Treatment of Ia with diethylzinc leads to similar products and reaction is complete in 1 h at 60—100° (eqn. 4). It is interesting that the reaction of Et_3GeH with diethylzinc which is carried out under more drastic conditions (15 h, 125°) is complicated by side-reactions and produces a complex mixture of compounds, $Et_3GeZn(GeEt_2)_n$-$GeEt_3$ ($n = 0$, 1 or 2, etc.) [4].

$$2\underset{(Ia)}{(C_6F_5)_3GeH} + Et_2Zn \rightarrow \underset{(III)}{[(C_6F_5)_3Ge]_2Zn} + 2C_2H_6 \qquad (4)$$

Such reactions do not take place or are suppressed to a large extent in the case of reaction 4. Bis[tris(pentafluorophenyl)germyl]zinc (III) was isolated in the form of a crystalline solid, unstable in air, well soluble in benzene and toluene and poorly soluble in n-hexane. Its reaction with bromine is described by eqn. 5. Similarly to the cadmium analogue [3], when compound III is treated with mercury, migration of the $(C_6F_5)_3Ge$ fragments from metal to metal occurs.

$$\underset{(III)}{[(C_6F_5)_3Ge]_2Zn} + 2Br_2 \rightarrow 2(C_6F_5)_3GeBr + ZnBr_2 \qquad (5)$$

Compound III when recrystallized from diethyl ether gives the etherate $[(C_6F_5)_3Ge]_2Zn \cdot 2Et_2O$ (IV) which loses its coordinatively bonded ether on heating in vacuo. We note that the cadmium analogue, $[(C_6F_5)_3Ge]_2Cd$, afforded crystalline adducts with many monodentate ligands with the exception of diethyl ether [5].

It is known that Ph_2GeH_2 reacts with Et_2Hg to give ethane and a mixture of cyclic germylmercury compounds [6]. In the case of $(C_6F_5)_2GeH_2$ the exothermal reaction with Et_2Hg also involves evolution of ethane (more than 85%) but it is accompanied by partial demercuration of the products and the formation of a mixture of barely soluble compounds from which we failed to isolate any one compound. Unlike $(C_6F_5)_2GeH_2$, the trihydride Ic reacts slowly with diethylmercury only at 100°. The reaction products are ethane, mercury and a red, probably polymeric, solid.

The reaction of bromohydride II with Et_2Hg proceeds readily at room temperature in toluene, but for reaction to be complete the mixture must be heated at 100° for 20—30 min. The digermane $(C_6F_5)_2Ge(Br)\text{—}Ge(Br)(C_6F_5)_2$ (V) produced in this case is obviously the product of decomposition of a mercury transition compound $(C_6F_5)_2Ge(Br)\text{—}Hg\text{—}Ge(Br)(C_6H_5)_2$ (eqn. 6). Heating

$$\underset{\text{(II)}}{2(C_6F_5)_2Ge(Br)H} + Et_2Hg \rightarrow \underset{\text{(V)}}{(C_6F_5)_2Ge(Br)\text{—}Ge(Br)(C_6F_5)_2} + 2C_2H_6 + Hg \qquad (6)$$

compound V with excess triethylgermane (150°, 8 h) gives triethylgermanium bromide and VI, a symmetric dihydrodigermane which is a colourless crystalline solid and is stable in air (eqn. 7).

$$\underset{\text{(V)}}{(C_6F_5)_2Ge(Br)\text{—}Ge(Br)(C_6F_5)_2} + 2Et_3GeH \xrightarrow{150^\circ} \underset{\text{(VI)}}{(C_6F_5)_2Ge(H)\text{—}Ge(H)(C_6F_5)_2} + 2Et_3GeBr \qquad (7)$$

Alkylation of bromohydride II with ethylmagnesium bromide in benzene affords VII, $Et(C_6F_5)_2GeH$ (eqn. 8).

$$\underset{\text{(II)}}{(C_6F_5)_2Ge(Br)H} + EtMgBr \rightarrow \underset{\text{(VII)}}{Et(C_6F_5)_2GeH} + MgBr_2 \qquad (8)$$

It is known that Ph_3GeH and Ph_2GeH_2 react with (dialkylamino)tin derivatives to give compounds containing a Ge—Sn group [7, 8]. Pentafluorophenylgermanium hydrides undergo similar reactions (eqns. 9 and 10).

$$\underset{\text{(Ia)}}{(C_6F_5)_3GeH} + Et_3SnNEt_2 \xrightarrow{100^\circ} \underset{\text{(VIII)}}{(C_6F_5)_3GeSnEt_3} + Et_2NH \qquad (9)$$

$$\underset{\text{(Ib)}}{(C_6F_5)_2GeH_2} + 2Et_3SnNEt_2 \xrightarrow{100^\circ} \underset{\text{(IX)}}{Et_3SnGe(C_6F_5)_2SnEt_3} + 2Et_2NH \qquad (10)$$

It is also known that compounds of the series $R_{4-n}Ge(OR')_n$ (where R and R′ are hydrocarbon radicals) possess high reactivities and are widely used in synthesis reactions. Their perfluorophenyl analogues, $(C_6F_5)_{4-n}Ge(OR')_n$, have been undiscovered up to now but we have found that such compounds (where $n = 1, 2$) are obtained in good yields in the exchange reaction (eqn. 11).

TABLE 1

THE PROPERTIES OF THE PENTAFLUOROPHENYLGERMANIUM COMPOUNDS

Compound		Yield (%)	B.p. (°C/mmHg)	M.p. (°C)	n_D^{20}	d_{20}^{4}	Fluorine analysis found (calcd.) (%)	ν(Ge—H) (cm^{-1})
Ia	$(C_6F_5)_3GeH$	78.5		129-131			49.56 (49.58)	2224
Ib	$(C_6F_5)_2GeH_2$	86.2	103/5		1.4720	1.837	46.51 (46.48)	2142
Ic	$C_6F_5GeH_3$	58.3	130-133/740		1.4420	1.702	38.94 (39.14)	2120
II	$(C_6F_5)_2Ge(Br)H$	57.5	95-97/1		1.4998	2.041	38.59 (38.96)	2150
III	$[(C_6F_5)_3Ge]_2Zn$ [a]	69.3		178-180			46.94 (46.99)	
IV	$[(C_6F_5)_3Ge]_2Zn \cdot 2Et_2O$	50.6		150 (dec.)			41.87 (42.27)	
V	$(C_6F_5)_2Ge(Br)Ge(Br)(C_6F_5)_2$	49.5		232-235			39.19 (39.04)	
VI	$(C_6F_5)_2Ge(H)Ge(H)(C_6F_5)_2$	35.1		151-153			46.38 (46.59)	2170
VII	$(C_6F_5)_2Ge(Et)H$	24.4	120-124/5		1.4741	1.663	42.94 (43.49)	2120
VIII	$(C_6F_5)_3GeSnEt_3$ [b]	44.6		71-74			36.60 (36.57)	
IX	$Et_3SnGe(C_6F_5)_2SnEt_3$ [c]	53.7	160-163/1		1.5582		23.13 (23.21)	
Xa	$(C_6F_5)_3GeOMe$ [d]	74.6		80-82			47.39 (47.12)	
Xb	$(C_6F_5)_2Ge(OMe)_2$	66.8	122-125/5		1.4775		40.51 (40.53)	

[a] Found: Zn, 5.30. Calcd.: Zn, 5.38%. [b] Found: Sn, 15.90. Calcd.: Sn, 15.22%. [c] Found: C, 35.29; H, 3.68; Sn, 29.80. Calcd.: C, 35.22; H, 3.69; Sn, 29.00%. [d] Found: C, 38.00; mol. wt. 600. Calcd.: C, 37.74%; mol. wt. 605.

$$(C_6F_5)_{4-n}GeBr_n + n\ Et_3SnOMe \xrightarrow{100^\circ} \underset{(X)}{(C_6F_5)_{4-n}Ge(OMe)_n} + n\ Et_3SnBr \quad (11)$$

$(a, n = 1; b, n = 2)$

The IR spectra of the compounds obtained exhibit absorption bands at 1650, 1530, 1480, 1390, 1290, 1090, 980, 820 and 625 cm^{-1}, characteristic of C_6F_5 groups bonded to a germanium atom. In addition, the spectra of germanium hydrides contain supplementary bands at 780 cm^{-1} for Ia, II, VI and VII; 870 and 780 cm^{-1} for Ib and 880 and 840 cm^{-1} for Ic. The stretching modes of the Ge—H bond in germanium hydrides (see Table 1) are shifted noticeably to short wavelengths and are of lower intensities than those in unfluorinated analogues [9]. This may be explained by the presence of strong electronegative substituents (C_6F_5) at the germanium atom. The spectra of the methoxy derivatives Xa and b exhibit bands at 1050 cm^{-1} and 655 cm^{-1} which could be due to the Ge—O stretching mode. The IR spectra of VIII and IX contain absorption bands due to Et_3Sn fragments [10] besides the bands cited above for C_6F_5 rings.

Experimental

All reactions were carried out in evacuated apparatus or under argon. The hydrogermanes Ia-c were prepared in air. GLC analysis of the volatile compounds were carried out on a Tsvet-I chromatograph with a catarometer detector, using a 100 × 0.4 cm column packed with Apiezon L (20%) on Chromosorb W or a 50 × 0.4 cm column packed with Thermol 3 (15%) on Shimalite B, with helium as the carrier gas. IR spectra were recorded on a UR-20 spectrophotometer. Samples of crystalline compounds were prepared in the form of suspensions in Vaseline oil. Melting points were determined using sealed evacuated capillaries.

The synthesis of tris(pentafluorophenyl)germane (Ia) has been reported [3].

Bis(pentafluorophenyl)germane (Ib)

(a). 9.2 g (242.4 mmol) of lithium aluminium hydride was added to a solution of $(C_6F_5)_2GeBr_2$ (62.3 g, 110.0 mmol) in 140 ml of toluene. The mixture was cooled with ice-water and 110 ml of ether was added during 10 min. The mixture obtained was stirred for 10 min, and hydrolysed with water and hydrochloric acid. The organic layer was separated and the aqueous solution was extracted twice with ether. The toluene/ether solution was dried ($CaCl_2$) and the solvents evaporated at atmospheric pressure. Vacuum distillation of the residue (103°/5 mmHg) gave 38.88 g (86.2%) of dihydride Ib.

(b). A mixture of 19.1 g (33.6 mmol) of bis(pentafluorophenyl)germanium dibromide and 21.1 g (130.6 mmol) of triethylgermane was heated at 120° for 6 h. GLC analysis of the reaction mixture gave 11.1 g (67.9%) of bromohydride II and 3.87 g (23.7%) of Ib. Vacuum fractionation afforded 6.2 g (77.1%) of triethylgermanium bromide, identified by GLC, 1.1 g (8.0%) of bis(pentafluorophenyl)germane (Ib), b.p. 50—60°/1 mmHg and 9.4 g (57.5%) of bis(pentafluorophenyl)germanium bromide (II) (see Table 1).

Pentafluorophenylgermane (Ic)

40 ml of ether was added gradually during 15 min to a mixture of 28.1 (58.5 mmol) of $C_6F_5GeBr_3$ and 7.0 g (184.5 mmol) of $LiAlH_4$ in 60 ml of

hexane under vigorous cooling (—25 to —20°) and stirring. A vigorous reaction proceeded and the mixture darkened in colour when ether addition was complete the mixture was stirred for 10 min at room temperature and hydrolysed with water and dilute HCl. After separation and drying ($CaCl_2$), the organic layer was fractionated at atmospheric pressure. 8.26 g (58.3%) of Ic were obtained.

Bis[tris(pentafluorophenyl)germyl] zinc (III)

0.31 g (2.5 mmol) of diethylzinc was added at room temperature to a solution of 3.2 g (5.6 mmol) of $(C_6F_5)_3GeH$ in 25 ml of hexane and the temperature was gradually increased to 70° for 1 h. 110 ml (97.4%) of ethane was evolved. The crystalline product which formed was separated from the reaction mixture by filtration, washed with hot hexane and dissolved in 5 ml of benzene. Addition of the benzene solution to 35 ml of hexane precipitated crystals of pure $[(C_6F_5)_3Ge]_2Zn$ (III). Yield 2.2 g (69.3%).

$[(C_6F_5)_3Ge]_2Zn\cdot 2Et_2O$ (IV)

1.06 g (0.9 mmol) of III was dissolved on heating at 50° in 5 ml of ether. The solution was kept at —10° for 10 h. 0.6 g (50.6%) of IV was obtained as colourless crystals which decomposed above 150°.

Reaction of III with bromine

0.22 g (1.4 mmol) of bromine was added slowly to a solution of 0.81 g (0.7 mmol) of bis[tris(pentafluorophenyl)germyl] zinc in 10 ml of benzene at 20°. The reaction was completed by heating the mixture at 100° for one hour. 0.04 g (97.6%) of zinc bromide was obtained. After filtration and removal of benzene under reduced pressure, the residue was recrystallized from hexane to give 0.82 g (94.0%) of $(C_6F_5)_3GeBr$, identified by GLC.

Reaction of III with mercury

A mixture of 0.92 g (0.8 mmol) of III, 5.07 g (25.3 mmol) of mercury and 20 ml of benzene was heated for 25 h at 100° in an evacuated ampoule with periodic shaking. The organic layer was decanted from zinc amalgam and the benzene was removed by condensation in vacuo. Recrystallization of the residue from toluene gave 0.76 g (74.4%) of $[(C_6F_5)_3Ge]_2Hg$, m.p. 228—230°. A mixed melting point test with bis[tris(pentafluorophenyl)germyl] mercury prepared by method of ref. 3 gave no depression of the m.p. Titration of the amalgam gave 0.05 g (96.8%) of zinc.

Reaction of bis(pentafluorophenyl)germanium bromide (II) with diethylmercury

A solution of 0.74 g (2.9 mmol) of diethylmercury in 2.5 ml of toluene was added to 2.81 g (5.8 mmol) of $(C_6F_5)_2Ge(Br)H$ placed in an ampoule connected to a gas burette. After completion of an exothermic reaction accompanied by the evolution of ethane the mixture was heated at 100° for 20 min. A further 110 ml (82.0%) of ethane was evolved. The precipitate which formed was dissolved in toluene at 130°; the solution was decanted from mercury (0.41 g, 71.8%) and allowed to remain at room temperature overnight. 1.38 g (49.5%) of 1,2-bis(pentafluorophenyl)-1,2-dibromodigermane (V) was obtained, m.p. 224—227°. Repeated recrystallization led to a m.p. of 232—235°.

1,2-Bis(pentafluorophenyl)-1,2-dihydrodigermane (VI)

1.94 g (2.0 mmol) of V and 4.4 g (27.4 mmol) of triethylgermane were heated for 8 h at 150°. GLC analysis of the reaction mixture gave 0.32 g (66.0%) of triethylgermanium bromide. After removal of the solvent and volatile products the residue was recrystallized from hexane to afford 0.57 g (35.1%) of compound VI.

Bis(pentafluorophenyl)ethylgermane (VII)

Et MgBr (prepared from 9.45 g of ethyl bromide and 2 g of magnesium in 25 ml of ether) was added to 16.27 g (33.4 mmol) of compound II in 25 ml of benzene. The ether was evaporated and 25 ml of benzene was added to the mixture which was then refluxed for 10 h. Further operations were carried out as in the usual syntheses with Grignard reagents. Fractionation in vacuo provided 3.57 g (24.4%) of compound VII.

Reaction of tris(pentafluorophenyl)germane (Ia) with (diethylamino)triethyltin

3.08 g (5.4 mmol) of germane Ia, 2.03 g (7.4 mmol) of (diethylamino)-triethyltin in 5 ml of benzene were kept for 1 h at room temperature. The solid Ia dissolved completely. In order for the reaction to go to completion the mixture was heated at 100° for 4 h. Solvent and volatile products were removed by condensation in vacuo. Recrystallization of the residue from hexane (20 h, —78°) gave 1.86 g (44.6%) of compound VIII. Titration of the volatile products yielded 0.4 g (83.4%) of diethylamine. The latter was identified by means of GLC analysis.

Reaction of (diethylamino)triethyltin with dihydride Ib proceeds analogously. The product IX was isolated by fractionation in vacuo.

Tris(pentafluorophenyl)methoxygermane (Xa)

A solution of 6.01 g (9.2 mmol) of tris(pentafluorophenyl)germanium bromide and 3.75 g (15.8 mmol) of triethylmethoxytin in 10 ml of benzene was heated in a thermostatted bath for 15 h at 100°. Benzene and volatile products were removed by condensation in vacuo. 10 ml of hexane was added to the residue and the mixture filtered through a glass filter. The filtrate was kept at —80° for several hours. Precipitated Xa was washed twice with hexane and dried in vacuo. 4.11 g (74.6%) of $(C_6F_5)_3GeOMe$ was obtained. Fractionation of the volatile products gave 1.41 g (55.0%) of triethyltin bromide which was identified by means of GLC analysis.

Under similar conditions 2.3 g (4.1 mmol) of bis(pentafluorophenyl)germanium bromide and 2.31 g (9.8 mmol) of triethylmethoxytin afforded 1.27 g (66.8%) of compound Xb isolated by distillation in vacuo.

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