

Preliminary communication

TRIFLUOROMETHYLGERMYLMERCURY DERIVATIVES

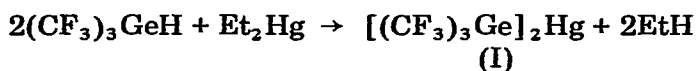
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Summary

Bis[tris(trifluoromethyl)germyl]mercury (I) was synthesized by the hydride method. A trifluoromethyl derivative containing a GeHgPtGe chain was prepared by insertion of Pt(PPh₃)₂ into the Ge—Hg bond of I. The stability and reactivity of the compounds obtained resemble those of C₆F₅ derivatives more closely than those of their unfluorinated alkyl analogues.

Pentafluorophenyl polynuclear derivatives are known to be more stable and less reactive than their unfluorinated aryl and alkyl analogues [1,2]. To gain a better understanding of organic ligand effects on the properties of compounds containing metal—metal bonds we have synthesized perfluoroalkyl tri- and tetra-nuclear derivatives. To our knowledge perfluoroalkyl compounds of this type are reported for the first time.

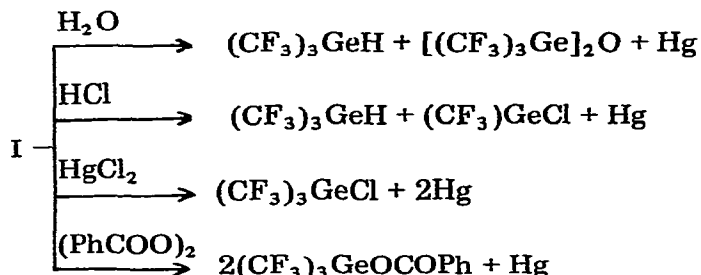
Bis[tris(trifluoromethyl)germyl]mercury (I) was isolated in 78% yield from the reaction of diethylmercury and (CF₃)₃GeH in benzene at room temperature.



It is worth noting that the reaction in other solvents such as hexane, THF, or in the absence of a solvent, is complicated by side processes leading to the precipitation of mercury metal which decreases the yield to 3—10%.

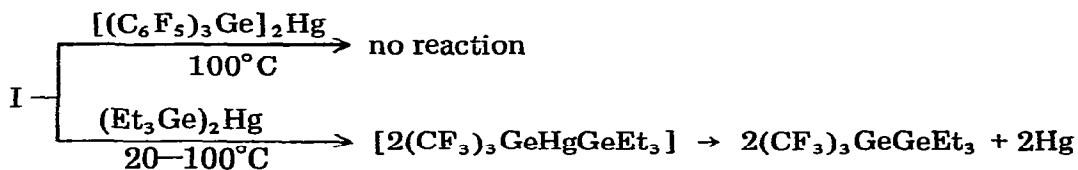
Compound I was isolated from the dry residue formed after removal of benzene from the reaction mixture as colourless crystals by sublimation (70°C/0.1 mmHg) (Table 1). Thermal decomposition of I with release of mercury metal occurs at 160°C. Unlike unfluorinated alkyl- and arylgermylmercury derivatives [3] crystalline I decomposes only very slowly in the air and resembles stable [(C₆F₅)₃Ge]₂Hg [4]. However it readily undergoes

hydrolysis under the action of water. Note that all the $(R_3Ge)_2Hg$ compounds known earlier are stable towards hydrolysis. Compound I reacts with HCl (benzene, $100^\circ C$, 5 h), $HgCl_2$ (THF, $100^\circ C$, 5 h) and benzoyl peroxide under conditions similar to those reported for $[(C_6F_5)_3Ge]_2Hg$, whereas $(Et_3Ge)_2Hg$ reacts exothermally with the same reagents.



Photolysis of I in toluene under UV irradiation proceeds at a low rate. After 50 h, only 20% of mercury metal was recovered. The reaction was not studied in more detail.

Disproportionation reactions leading to unsymmetrical compounds are highly characteristic for germylmercury derivatives. However, with the trifluoromethyl derivative (I), these reactions did not give the expected products. The reaction with bis(triethylgermyl)mercury in benzene resulted in complete demercuration of an unsymmetrical product probably formed as intermediate. No reaction occurred with the C_6F_5 analogue even after prolonged heating at $100^\circ C$ in the same solvent.



It should be noted that fairly stable $(C_6F_5)_3GeHgGeEt_3$ is readily formed in the reaction of $(Et_3Ge)_2Hg$ with $[(C_6F_5)_3Ge]_2Hg$ [5].

Oxidative insertion of triphenylphosphine -platinum, -palladium and -nickel complexes into the Ge—Hg bond of $(R_3Ge)_2Hg$ results in the formation of tetranuclear complexes containing $GeHgMGe$ ($M = Pt, Pd, Ni$) chains [1]. With $R = C_6F_5$, the products are stable to heating and are not attacked by air oxygen, with $R = Ph$, the complexes are stable but readily undergo oxidation, and with $R = Et$, the complexes have exceedingly low stabilities and cannot be isolated. The trifluoromethyl derivative (I) reacts with platinum complexes to give a fairly stable product, which is stable in the air and precipitates from



ether as yellow crystals. Its solubility in aromatic hydrocarbons is far lower than that of its C_6F_5 and Ph analogues. It is noteworthy that, unlike reactions of $(Ph_3Ge)_2Hg$ and $[(C_6F_5)_3Ge]_2Hg$ with $Pt(PPh_3)_4$, the one here reported involves formation of a deep-red intermediate. Its conversion to the final weakly coloured product takes 2 days. Complex $Pt(PPh_3)_3$ reacts similarly.

The IR spectra of the compounds isolated contain bands at 1165 and 735 cm^{-1} characteristic of CF_3Ge groups [6]. The spectrum of the platinum complex also contains five poorly resolved bands at 450 to 650 cm^{-1} , characteristic of triphenylphosphine ligands bound to metal complexes. The spectrum of $(\text{CF}_3)_3\text{GeGeEt}_3$ is produced by an interaction between the spectra of $(\text{CF}_3)_3\text{Ge}$ and Et_3Ge groups; the $\nu(\text{C}-\text{Ge})$ band (568 cm^{-1}) of the Et_3Ge fragment is shifted by 18 cm^{-1} to the higher frequencies of Et_6Ge_2 [7] because of a powerful electron-withdrawing action by the $(\text{CF}_3)_3\text{Ge}$ group. A similar shift is observed in the spectra of $(\text{C}_6\text{F}_5)_3\text{GeGeEt}_3$ [8] and ClGeEt_3 [7].

Comparison of the ^{199}Hg chemical shifts in series I ($\delta(\text{Hg})^* -671.7$ ppm, $J(\text{Hg}-\text{F})$ 82.0 Hz, toluene), $(\text{Me}_3\text{Ge})_2\text{Hg}$ ($\delta(\text{Hg})$ 114 ppm [9]), $(\text{Et}_3\text{Ge})_2\text{Hg}$ ($\delta(\text{Hg})$ 51.3 ppm, toluene [10]) and $[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Hg}$ ($\delta(\text{Hg}) -704.1$ ppm, $J(\text{Hg}-\text{F})$ 73.0 Hz, toluene) points to a strong electron-withdrawing action of fluorinated substituents. The upfield shift in the ^{199}Hg NMR spectrum of the C_6F_5 derivative from the trifluoromethyl analogue indicates that the $(\text{C}_6\text{F}_5)_3\text{Ge}$ group has a stronger $-I$ -effect than $(\text{CF}_3)_3\text{Ge}$ has. The same conclusion follows from comparison of the $\nu(\text{Ge}-\text{H})$ frequencies observed in the IR spectra of $(\text{CF}_3)_3\text{GeH}$ (2155 cm^{-1} [6]) and $(\text{C}_6\text{F}_5)_3\text{GeH}$ (2224 cm^{-1} [11]).

The ^{19}F NMR spectrum of I in toluene has the parameters $\delta(\text{F}) -43.2$ ppm (from CCl_3F), $^1J(\text{Hg}-\text{F})$ 82.0 \pm 1 Hz, $^2J(\text{C}-\text{F})$ 116.6 Hz.

All reactions were carried out in evacuated sealed tubes. The initial compound, $(\text{CF}_3)_3\text{GeH}$, was isolated from the exchange reaction between Et_3GeH and iodogermane, $(\text{CF}_3)_3\text{GeI}$. The latter was synthesized as described in ref. 6.

TABLE 1

ANALYTICAL DATA FOR THE TRIFLUOROMETHYLGGERMYL DERIVATIVES OBTAINED

Compound	Yield (%)	M.p. ($^{\circ}\text{C}$)	Analysis (Found (calcd.) (%))		
			C	H	F
$(\text{CF}_3)_3\text{GeOCOPh}$	98	—	30.65 (30.00)	1.72 (1.30)	—
$(\text{CF}_3)_3\text{GeGeEt}$	95	—	23.81 (24.60)	3.49 (3.44)	—
$[(\text{CF}_3)_3\text{Ge}]_2\text{Hg}$	78	135	9.60 (9.48)		45.15 (45.01)
$(\text{CF}_3)_3\text{GeHgPt}(\text{PPh}_3)_2\text{Ge}(\text{CF}_3)_3$	75	193	34.42 (34.10)	2.31 (2.04)	23.32 (23.11)

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