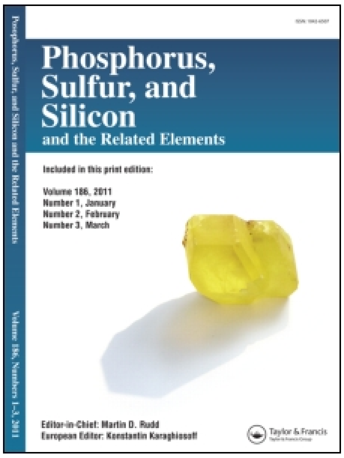

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Polyfluorophenylamino Germanes and Their Titanium (IV) Chloride Adducts

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Polyfluorophenylamino Germanes and Their Titanium (IV) Chloride Adducts

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Disproportionation reactions between $(CF_3CH_2O)_3GeNHC_6H_{5-n}F_n$ *and* $TiCl_4$ *in petroleum ether (40–60°C) at 0° to −10°C give* $(CF_3CH_2O)_2Ge(NHC_6H_{5-n}F_n)_2 \cdot 2TiCl_4$ *and* $(CF_3CH_2O)Ge(NHC_6H_{5-n}F_n)_3 \cdot 2TiCl_4$ *adducts. However, complete disproportionation of* $(CF_3CH_2O)_3Ge(NHC_6H_{5-n}F_n)$ *(n = 1,2) occurs at −55 to −60°C to give* $Ge(NHC_6H_{5-n}F_n)_4 \cdot 3TiCl_4$*. These complexes give double adducts on reactions with* CH_3NO_2 *and* CH_3CN*. All the products are characterized by elemental analyses and IR,* ^1H*, and* ^{19}F *NMR spectroscopy. A comparative disproportionation of the germanamines and analogous silanamines is discussed.*

Keywords Disproportionation; double adduct; germanamines

INTRODUCTION

Lewis acid promoted disproportionation of a large number of chloro/organoxy/organo-organoxy/organo aminosilanes and germanes have been studied.[1–4] We have reported[5] the formation of $Si(NHC_6H_4F)_4 \cdot 3TiCl_4$, which is believed to constitute a new titanium cation $[Si(NHC_6H_4F\text{-}o)_4Ti_2Cl_7]^+$ before precipitating as a double adduct with the solvent.[5] However disproportination of polyfluoropheny-laminosilanes $(CF_3CH_2O)_3SiNHC_6H_{5-n}F_n$ (n = 2–5) in the presence of $TiCl_4$ leads to formation of different polyfluorophenylaminosilanes-titanium (IV) chloride adducts which are non ionic.[6] Now, the reactions

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with analogous germanium compounds have been attempted, and the details of formation and characterization these germane complexes are reported herein.

RESULTS AND DISCUSSION

$(CF_3CH_2O)_mGe(NHC_6H_{5-n}F_n)_{4-m}2TiCl_4$ (m = 1,2)

The reactions between N-(2)-Fluoro/2,4-difluoro/2,4,6-trifluoro/2,3,5,6-tetrafluoro/2,3,4,5,6-pentafluoro phenyl 1,1,1-tris(2,2,2-trifluoroethoxy)germanamines and titanium (IV) chloride give the complexes as shown by the following reaction:

$$\begin{gathered}\text{pet. ether } (40-60^\circ C)\\ (CF_3CH_2O)_3GeNHC_6H_{5-n}F_n + 2TiCl_4 \longrightarrow\\ (CF_3CH_2O)_2Ge(NHC_6H_{5-n}F_n)_2.2TiCl_4 +\\ 3(CF_3CH_2O)_4Ge - 10 \text{ to } 0^\circ C,\\ \text{where } (n = 1-5). \end{gathered} \tag{1}$$

Elemental analyses of adducts give the composition as assigned (Table I). These are hygroscopic orange yellow solids insoluble in most of the organic solvents except CH_3NO_2 and CH_3CN. Conductance of their millimolar solutions show them as non-electrolytes. However, in

TABLE I Analytical Data of Titanium (IV) Adducts of Various Germanamines

	Analytical data %found (required)			
Compounds	Cl	Ge	Ti	N
$(CF_3CH_2O)_2Ge(NHC_6H_4F)_2.2TiCl_4$	32.4 (32.6)	8.0 (8.3)	10.7 (11.0)	3.1 (3.2)
$(CF_3CH_2O)_2Ge(NHC_6H_3F_2)_2.2TiCl_4$	31.2 (31.3)	7.4 (7.9)	10.7 (10.5)	2.9 (3.0)
$(CF_3CH_2O)_2Ge(NHC_6H_2F_3)_2.2TiCl_4$	30.0 (30.1)	7.2 (7.6)	9.6 (10.1)	2.9 (2.9)
$(CF_3CH_2O)_2Ge(NHC_6HF_4)_2.2TiCl_4$	29.1 (29.0)	7.0 (7.4)	9.4 (9.8)	2.7 (2.8)
$(CF_3CH_2O)_2Ge(NHC_6F_5)_2.2TiCl_4$	27.7 (27.9)	6.8 (7.1)	9.5 (9.3)	2.8 (2.7)
$CF_3CH_2OGe(NHC_6H_4F)_3.2TiCl_4$	32.1 (32.2)	7.6 (8.2)	10.5 (10.8)	4.5 (4.7)
$CF_3CH_2OGe(NHC_6H_3F_2)_3.2TiCl_4$	30.0 (30.3)	7.4 (7.7)	10.4 (10.2)	4.5 (4.4)
$CF_3CH_2OGe(NHC_6H_2F_3)_3.2TiCl_4$	28.5 (28.7)	7.0 (7.3)	10.0 (9.7)	4.3 (4.2)
$CF_3CH_2OGe(NHC_6HF_4)_3.2TiCl_4$	27.1 (27.2)	6.3 (6.9)	9.4 (9.1)	4.1 (4.0)
$CF_3CH_2OGe(NHC_6F_5)_3.2TiCl_4$	25.5 (25.8)	5.9 (6.6)	8.5 (8.7)	3.6 (3.8)
$Ge(NHC_6H_4F)_4.3TiCl_4$	39.1 (39.3)	6.4 (6.6)	13.1 (13.3)	4.9 (5.1)
$Ge(NHC_6H_3F_2)_4.3TiCl_4$	36.6 (36.8)	5.9 (6.2)	12.3 (12.4)	4.6 (4.8)

contrast to the reactivity of analogous silanamines 6, the germanamines do not reveal complete disproportionation of the fluoroethoxy groups.

Spectral Data

Major infrared absorptions of the complexes with their possible assignments are given in Table II. νNH absorption appear at 3280–3290 cm^{-1} indicating negative spectral shift of about 200 cm^{-1} from that of the parent germanamine thus suggesting coordination of the nitrogen atoms to $TiCl_4$ molecules. The νNH absorption values are similar to those reported[6] for coordinated NH groups in analogous $Si(NHC_6H_{5-n}F_n)_2^{\cdot}xTiCl_4$. The presence of absorptions due to CF_3 show up at 1280–1290 cm^{-1} and 650–660, 635–640, and 520–530 cm^{-1}, while νGeOC is spotted at 1040–1060 cm^{-1}. Phenyl ring stretchings appear at their routine positions. νTiCl modes come up at 330, 395, and 440 cm^{-1}. These absorption values are comparable to those observed for analogous silane derivatives.[6]

^1H NMR spectral data reveal the resonance signals at δ 3.6–3.7 (br, NH), 4.2–4.3 (q, OCH_2), and 7.2–7.9 (phenyl ring). The integrated intensity of various proton signals agrees with the composition. ^{19}F NMR spectra of the compounds reveal the signals at 77.0 to 78.0 ppm (t, CF_3). The resonance peaks of variously substituted fluorines of the ring are located between 120.6 to 173.8 ppm thus indicating the presence of fluorophenylamine groups on germanium in the complexes. Further, the chemical shift values observed are similar to those observed for the fluorophenylaminosilanes and their adducts. The relevant data are given in Table III.

^{13}C NMR spectral data do not significantly contribute to the structural information of these compounds and hence not recorded.

Keeping the complexes for 24 h in the solvents results in the precipitation of brown pink solids which analyze as double adducts of composition $(CF_3CH_2O)_2Ge(NHC_6H_{5-n}F_n)_2^{\cdot}2TiCl_4.2S$ (S = CH_3NO_2, CH_3CN). Analytical and IR data for a representative adduct $(CF_3CH_2O)_2Ge(NHC_6H_4F)_2^{\cdot}2TiCl_4^{\cdot}2S$ (S = CH_3NO_2, CH_3CN) is given (Tables IV and V).

$(CF_3CH_2O)Ge(HNC_6H_{5-n}F_n)_3^{\cdot}2TiCl_4$ (n = 1–5)

To continue the search for the completely disproportionate germanamines, the filtrates of the above reactions (which are still colored unlike those from silanamine reactions[6]) were examined. Each filtrate was concentrated under vacuum to half the volume and kept

TABLE II Major Infrared Absorptions (cm^{-1}) of Titanium (IV) Adducts of Various Germanamines

Compounds	νNH	νCH (aromatic)	νCH (aliphatic)	C=C skeletal	ν_{as} CF_3	νGe-O(C)	Ring	δCF_3	νTi-Cl
$(CF_3CH_2O)_2Ge(NHC_6H_4F)_2.2TiCl_4$	3280	3060	2920	1610,1490	1290	1050	740,690	665,530	430,331
$(CF_3CH_2O)_2Ge(NHC_6H_3F_2)_2.2TiCl_4$	3285	3050	2940	1620,1500	1280	1040	740,690	660,530	442,335
$(CF_3CH_2O)_2Ge(NHC_6H_2F_3)_2.2TiCl_4$	3290	3060	2920	1610,1490	1285	1055	740,685	665,535	441,331
$(CF_3CH_2O)_2Ge(NHC_6HF_4)_2.2TiCl_4$	3280	3050	2940	1610,1490	1290	1050	740,685	665,535	440,335
$(CF_3CH_2O)_2Ge(NHC_6F_5)_2.2TiCl_4$	3285	3060	2920	1610,1490	1285	1055	740,690	660,530	445,330
$CF_3CH_2OGe(NHC_6H_4F)_3.2TiCl_4$	3285	3060	2920	1620,1500	1290	1060	740,690	660,530	440,330
$CF_3CH_2OGe(NHC_6H_3F_2)_3.2TiCl_4$	3290	3060	2920	1620,1510	1290	1055	740,690	660,530	445,325
$CF_3CH_2OGe(NHC_6H_2F_3)_3.2TiCl_4$	3280	3060	2920	1610,1490	1290	1040	740,690	660,530	450,310
$CF_3CH_2OGe(NHC_6HF_4)_3.2TiCl_4$	3285	3050	2920	1610,1490	1280	1055	740,690	660,535	442,335
$CF_3CH_2OGe(NHC_6F_5)_3.2TiCl_4$	3290	3060	2920	1610,1490	1290	1040	740,690	660,540	440,335
$Ge(NHC_6H_4F)_4.3TiCl_4$	3300,3210	3020	—	1620,1510	—	—	760,720,690	—	435,395
$Ge(NHC_6H_3F_2)_4.3TiCl_4$	3290,3210	3020	—	1610,1520	—	—	760,720,685	—	435,395

TABLE III ^{1}H and ^{19}F NMR Spectral Data of Titanium (IV) Adducts of Various Germanamines

	Chemical shift (δ) in ppm				
	^{1}H			^{19}F	
Compounds	NH	OCH_2	Ring protons	CF_3	Ring fluorine
$(CF_3CH_2O)_2Ge(NHC_6H_4F)_2.2TiCl_4$	3.7 (b, 2H)	4.2 (q, 4H)	7.0 (m, 8H)	77.0 (t, 6F)	136.0 (2F)
$(CF_3CH_2O)_2Ge(NHC_6H_3F_2)_2.2TiCl_4$	3.6 (b, 2H)	4.2 (q, 4H)	7.0 (m, 6H)	78.0 (t, 6F)	124.0, 120.5 (4F)
$(CF_3CH_2O)_2Ge(NHC_6H_2F_3)_2.2TiCl_4$	3.7 (b, 2H)	4.3 (q, 4H)	6.9 (m, 4H)	78.0 (t, 6F)	130.4, 124.5 (6F)
$(CF_3CH_2O)_2Ge(NHC_6HF_4)_2.2TiCl_4$	3.6 (b, 2H)	4.2 (q, 4H)	6.9 (m, 2H)	78.0 (t, 6F)	162.2, 141.4 (8F)
$(CF_3CH_2O)_2Ge(NHC_6F_5)_2.2TiCl_4$	3.7 (b, 2H)	4.2 (q, 4H)	–	78.0 (t, 6F)	173.8, 165.6, 163.2 (10F)
$CF_3CH_2OGe(NHC_6H_4F)_3.2TiCl_4$	3.6 (b, 3H)	4.2 (q, 2H)	6.9 (m, 12H)	77.0 (t, 3F)	137.0 (3F)
$CF_3CH_2OGe(NHC_6H_3F_2)_3.2TiCl_4$	3.7 (b, 3H)	4.2 (q, 2H)	6.9 (m, 9H)	78.0 (t, 3F)	124.4, 120.6 (6F)
$CF_3CH_2OGe(NHC_6H_2F_3)_3.2TiCl_4$	3.6 (b, 3H)	4.3 (q, 2H)	7.0 (m, 6H)	77.0 (t, 3F)	130.4, 124.6 (9F)
$CF_3CH_2OGe(NHC_6HF_4)_3.2TiCl_4$	3.7 (b, 3H)	4.2 (q, 2H)	6.9 (m, 3H)	78.0 (t, 3F)	162.2, 141.6 (12F)
$CF_3CH_2OGe(NHC_6F_5)_3.2TiCl_4$	3.6 (b, 3H)	4.3 (q, 2H)	–	78.0 (t, 3F)	173.8, 165.4, 163.2 (15F)
$Ge(NHC_6H_4F)_4.3TiCl_4$	3.8 (b, 1H)	–	7.2 (m, 4H)	–	136.0
$Ge(NHC_6H_3F_2)_4.3TiCl_4$	3.8 (b, 1H)	–	7.2 (m, 3H)	–	131.0,123.0

TABLE IV Analytical Data of CH_3CN and CH_3NO_2 Adducts of $(CF_3CH_2O)_2Ge(NHC_6H_4F)_2{\cdot}2TiCl_4$ and $CF_3CH_2OGe(NHC_6H_4F)_3{\cdot}2TiCl_4$

	Analytical data %found (required)					
Compounds	C	H	N	Cl	Ti	Ge
$(CF_3CH_2O)_2Ge(NHC_6H_4F)_2.2TiCl_4.\ 2CH_3CN$	24.9 (25.1)	2.1 (2.0)	5.5 (5.8)	29.7 (29.8)	9.4 (10.0)	7.2 (7.6)
$(CF_3CH_2O)_2Ge(NHC_6H_4F)_2.2TiCl_4.2CH_3NO_2$	21.4 (21.7)	1.9 (2.2)	5.5 (5.6)	28.5 (28.6)	9.8 (9.6)	7.4 (7.3)
$CF_3CH_2OGe(NHC_6H_4F)_3.2TiCl_4.\ 2CH_3CN$	29.6 (29.8)	2.1 (2.0)	7.1 (7.2)	29.2 (29.4)	9.7 (9.9)	7.3 (7.5)
$CF_3CH_2OGe(NHC_6H_4F)_3.2TiCl_4.\ 2CH_3NO_2$	26.1 (26.3)	2.1 (2.2)	6.7 (6.9)	28.1 (28.3)	9.3 (9.5)	6.9 (7.2)

TABLE V Major Infrared Absorptions (cm^{-1}) of CH_3CN and CH_3NO_2Adducts of $(CF_3CH_2O)_2Ge(NHC_6H_4F)_2.2TiCl_4$ and $CF_3CH_2OGe(NHC_6H_4F)_3.2TiCl_4$

Compounds	νCH aliphatic	νC=N	C=C skeletal	Ti-Cl
$(CF_3CH_2O)_2Ge(NHC_6H_4F)_2.2TiCl_4.\ 2CH_3CN$	2610,2590	2010	1600,1480	440,370
$(CF_3CH_2O)_2Ge(NHC_6H_4F)_2.2TiCl_4.2CH_3NO_2$	2600,2585	–	1600,1490	440,375
$CF_3CH_2OGe(NHC_6H_4F)_3.2TiCl_4.\ 2CH_3CN$	2600,2580	2000	1610,1510	448,372
$CF_3CH_2OGe(NHC_6H_4F)_3.2TiCl_4.\ 2CH_3NO_2$	2610,2580	–	1600,1510	445,375

at room temperature under anhydrous conditions. After 48−72 h, very hygroscopic orange yellow solids were separated out. The elemental analyses (Table I) of these solids suggested the composition $(CF_3CH_2O)Ge(HNC_6H_{5-n}F_n)_3^{\cdot}2TiCl_4$ (n = 1–5). The molar conductances show these compounds to be non-electrolytes.

From these observations it may be imagined that a competing reaction occurs in solution. The order of separation of the product from the solution may depend upon the relative solubility of the products formed. The reaction may be written as:

$$\begin{aligned}&\text{pet. ether}(40-60^{\circ}\text{C})\\&3(CF_3CH_2O)_3GeNHC_6H_{5-n}F_n + 2TiCl_4 \longrightarrow\\&CF_3CH_2OGe(NHC_6H_{5-n}F_n)_3.2TiCl_4 +\\&2(CF_3CH_2O)_4Ge - 10\text{ to }0^{\circ}\text{C}\\&\text{where } (n = 1-5).\end{aligned} \tag{2}$$

Spectral Data

Major IR absorption bands along with possible assignments are given in Table II. νNH mode appears at 3280−3290 and 3190−3200 cm^{-1}. The former values may be due to uncoordinated NH groups and the later due to the coordinated ones as described earlier. νCH (aliphatic), νCH (aromatic), C=C skeletal, δCF_3, νGe-OC, and νTiCl modes appear nearly at the same position as discussed above. ^1H and ^{19}F NMR spectra exhibit similar chemical shift values as obtained in $(CF_3CH_2O)_2Ge(NHC_6H_{5-n}F_n)_2^{\cdot}2TiCl_4$ (Table III). Proton integration ratios of the complexes agree with the composition suggested. These complexes also undergo double adduct formation as is evident from the data of a representative compound

$(CF_3CH_2O)Ge(NHC_6H_4F)_3.2TiCl_4^{\cdot}2S$ (S = CH_3NO_2, CH_3CN) as evidenced by elemental analyses (Table IV) and IR spectral data (Table V).

Here again ^{13}C NMR spectra was not obtained as it did not yield additional information.

$Ge(NHC_6H_{5-n}F_n)_4^{\cdot}3TiCl_4$ (n = 1,2)

With a view to achieve complete disproportionation of 2,2,2-trifluoroethoxy groups on germanium, the reaction mixture was heated up to 100°C. This reaction resulted in the cleavage of Ge-N bonds resulting in decomposition of the germanamines. Interestingly, when the reactions between N-(2)-Fluoro/2,4-difluoro phenyl 1,1,1-tris(2,2,2-trifluoroethoxy)germanamines and titanium (IV) chloride are carried out at low temperature (−55 to −60°C), immediate precipitation of orange red solids takes place. The compounds isolated are very hygroscopic solids, soluble in CH_3NO_2 and CH_3CN. Elemental analyses (Table I) correspond to the composition $Ge(NHC_6H_{5-n}F_4)_4^{\cdot}3TiCl_4$ (n = 1,2). Unlike analogous $Si(NHC_6H_4F)_4^{\cdot}3TiCl_4^5$, These complexes are not ionic in nature.

These complexes are also characterized by IR, ^1H, and ^{19}F NMR spectroscopy. Major IR spectral bands along with possible assignments are given in Table II. νNH modes appear at 3290−3300 and 3200−3210 cm^{-1}, which corresponds to uncoordinated and coordinated NH groups in the complexes, respectively. νCH (aromatic) absorptions appear at 3080−3090 cm^{-1}. The absence of GeOC and CF_3 absorptions and the presence of absorptions at 395 and 495 cm^{-1} due to νTiCl may indicate the formation of the complex. ^1H NMR signals appear as multiplet at 7.2 ppm, which can be assigned to phenyl ring protons. ^{19}F NMR peaks are observed at 136.0 (s,1F) and 131.0, 123.0 (2F) characterizing the fluorophenylamine groups(Table III).

CONCLUSION

On comparison of the $TiCl_4$ adducts of silanamines and germanamines, it has been observed that the formation of $Si(NHC_6H_{5-n}F_n)_4{\cdot}3TiCl_4$ complexes is more facile than formation of $Ge(NHC_6H_{5-n}F_n)_4{\cdot}3TiCl_4$. The later could be achieved only at very low temperature (−55°C to −60°C). The difference in reactivity of the two classes of alkoxyamine compounds may be due to the nature of central metal atom. The Ge-N bonds are more labile than the Si—N bonds.

EXPERIMENTAL

Chemicals

2-fluoro, 2,4-difluoro, 2,4,6-trifluoro, 2,3,5,6- tetrafluoro and 2,3,4,5,6-pentafluoro anilines (Aldrich) were used as received. Germanium tetrachloride (Aldrich) was used as received. $TiCl_4$(Fluka) was used without further purification. Solvents (petroleum ether, n- hexane, nitromethane, and acetonitrile) were dried by standard procedures and purity checked before use. All manipulations were carried out under inert atmosphere using an all glass vacuum line.

Analytical

IR spectra were recorded as neat liquids, as nujol mulls or HCB mulls on KBr and CsI optics on Perkin Elmer (model 1430) ratio recording spectrophotometer. ^1H and ^{19}F NMR spectra were obtained using Varian EM 390-90 MHz spectrometer operating at 90 MHz for ^1H nuclei and 84.6 MHz for ^{19}F nuclei. Me_4Si (^1H) and $CFCl_3$ (^{19}F) were used as internal standards. Conductances were recorded on digital conductance meter NDC 732 Naina Electronics at 25 ± 0.5°C. Ge and Ti were determined gravimetrically. C, H, N analyses were carried out on a Perkin Elmer model 2400 elemental analyzer.

Preparations

$(CF_3CH_2O)_3GeCl$

$(CF_3CH_2O)_3GeCl$ was prepared by the reaction of $GeCl_4$ (0.11 mmol) with sodium 2,2,2-trifluoroethoxide (0.30 mmol) using diethyl ether as solvent in a similar manner as reported[7] for $(CH_3CH_2O)_3GeCl$. After removal of sodium chloride and then solvent, liquid obtained was purified by fractional distillation. Relevant data are given in Table VI.

$(CF_3CH_2O)_3\ GeNHC_6H_nF_{5-n}$ ($n = 1$–5)

A solution of fluoroaniline (1.0 mmol) in pet. ether (40°C−60°C) (20 ml) was added to n-BuLi (1 mmol) in n-hexane(10ml) at 0°C–10°C. $(CF_3CH_2O)_3GeCl$ (406 mg, 1 mmol) was added dropwise to this solution of lithium amide. After the addition of the chlorogermane was complete, the reaction mixture was allowed to attain room temperature slowly. Thereafter, the reaction mixture was refluxed for 2 h. LiCl formed during the reaction was filtered off. On evaporation of the solvent from the filtrate, germanamines were isolated. These were purified by distillation. Analytical and physical data are given in Table 5. The purity of

TABLE VI Physical and Analytical Data of Tris(2,2,2-trifluoroethoxy) Chlorogermane and Various N-fluorophenyl Tris(2,2,2-trifluoroethoxy) Germanamines

		Analytical data % Found (required)	
Compounds	B. p. (°C/mmHg)	Cl/N	Ge
$(CF_3CH_2O)_3GeCl$	120–123/740	8.5 (8.7)	17.5 (17.9)
$(CF_3CH_2O)_3GeNHC_6H_4F$	125–127/10	2.8(2.9)	15.3 (15.1)
$(CF_3CH_2O)_3GeNHC_6H_3F_2$	130–132/10	2.7 (2.8)	14.2 (14.5)
$(CF_3CH_2O)_3GeNHC_6H_2F_3$	134–136/10	2.8 (2.7)	13.7 (14.0)
$(CF_3CH_2O)_3GeNHC_6HF_4$	137–139/10	2.5 (2.6)	13.1 (13.5)
$(CF_3CH_2O)_3GeNHC_6F_5$	140–142/10	2.6 (2.5)	12.6 (13.1)

compounds was checked by IR, ^1H and ^{19}F NMR spectral data (Tables VI, VII, and VIII).

Reactions of $(CF_3CH_2O)_3GeNHC_6H_nF_{5-n}$ with $TiCl_4$

A solution of $TiCl_4$ (0.570 g, 3.0 mmol) in pet ether (40°C–60°C) (10ml) was added dropwise into a solution of $(CF_3CH_2O)_3GeNHC_6H_nF_{5-n}$ (3.0 mmol) in the same solvent (30 ml) maintained at 0°C to –10°C. An orange red solid was obtained immediately in each case. After stirring the mixture for another 2 h, the solid was filtered off under reduced pressure, washed with pet. ether and dried in vacuum. The analytical data are given in Table I.

TABLE VII Major Infrared Absorptions (cm^{-1}) of Various N-fluorophenyl Tris(2,2,2-trifluoroethoxy) Germanamines

Assignments	$(CF_3CH_2O)_3$ $GeNHC_6H_4F$	$(CF_3CH_2O)_3$ $GeNHC_6H_3F_2$	$(CF_3CH_2O)_3$ $GeNHC_6H_2F_3$	$(CF_3CH_2O)_3$ $GeNHC_6HF_4$	$(CF_3CH_2O)_3$ $GeNHC_6F_5$
ν_{NH}	3475	3480	3470	3475	3480
ν_{CH}(aromatic)	3040	3020	3040	3030	3020
C=C skeletal	1620,1490	1610,1500	1610,1490	1620,1500	1620,1490
δCH_2	1440,1370	1440,1360	1450,1320	1440,1320	1440,1320
νCF_3	1270	1275	1280	1270	1275
νC—O	1150	1160	1140	1150	1155
νGe—O(C)	1060	1050	1065	1060	1050
Benzene ring	740,720,690	740,720,690	740,720,680	740,715,690	740,720,690
δCF_3	655,635,530	660,640,530	660,640,530	660,640,535	660,640,540
νGe—O	460	465	470	460	465

TABLE VIII ^{1}H and ^{19}F NMR Spectral Data of Various N-fluorophenyl Tris(2,2,2-trifluoroethoxy) Germanamines

Compounds	Chemical shift (δ) in ppm				
	^{1}H			^{19}F	
	NH	OCH_2	Ring protons	CF_3	Ring fluorine
$(CF_3CH_2O)_3GeCl$	—	4.2 (q)	—	78.0 (t)	—
$(CF_3CH_2O)_3GeNHC_6H_4F$	3.7 (b, 1H)	4.2 (q, 6H)	6.9 (m, 4H)	7.9 (t, 9F)	136.0 (1F)
$(CF_3CH_2O)_3GeNHC_6H_3F_2$	3.6 (b, 1H)	4.2 (q, 6H)	6.9 (m, 3H)	7.9 (t, 9F)	124.0, 120.0 (2F)
$(CF_3CH_2O)_3GeNHC_6H_2F_3$	3.7 (b, 1H)	4.3 (q, 6H)	6.9 (m, 2H)	7.9 (t, 9F)	130.4, 124.5 (3F)
$(CF_3CH_2O)_3GeNHC_6HF_4$	3.6 (b, 1H)	4.2 (q, 6H)	6.9 (m, 1H)	7.9 (t, 9F)	160.9, 140.8 (4F)
$(CF_3CH_2O)_3GeNHC_6F_5$	3.7 (b, 1H)	4.2 (q, 6H)	—	7.9 (t, 9F)	173.8,165.4,163.2 (5F)

The filtrates obtained above were concentrated under reduced pressure and kept under dry nitrogen atmosphere for 48–72 h. Orange yellow solid obtained in each case was filtered, dried under vacuum and analyzed (Table I).

Adducts of $(CF_3CH_2O)_mGe(NHC_6H_4F)_{4-m}^{\cdot}2TiCl_4$ (m = 1,2) with CH_3NO_2/CH_3CN

Each of the $(CF_3CH_2O)_mGe(NHC_6H_4F)_{4-m}^{\cdot}2TiCl_4$ (2.0 mmol) was dissolved in CH_3CN (20 ml) or CH_3NO_2 (20 ml). The solution was kept under nitrogen for 24 h. The solid precipitated in each case was filtered off, washed with pet. ether and dried under vacuum. Analytical data are given in Table IV.

$Ge(NHC_6H_nF_{5-n})_4^{\cdot}3TiCl_4$

Each of the $(CF_3CH_2O)_3Ge(NHC_6H_{5-n}F_n)$ (n = 1,2) (3.0 mmol) was taken into pet. ether (30 ml) separately and cooled to $-55°C$ to $-60°C$ for 1h using acetone-liquid nitrogen slurry. A solution of $TiCl_4$ (570 mg, 3.0 mmol) in pet. ether (10 ml) was added dropwise to the reaction mixture. An orange red solid was immediately precipitated in each case. The reaction mixture was maintained at this temperature for 4 h and was then brought to room temperature and filtered. The solid was washed with pet. ether, dried under vacuum and analyzed (Table I).

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