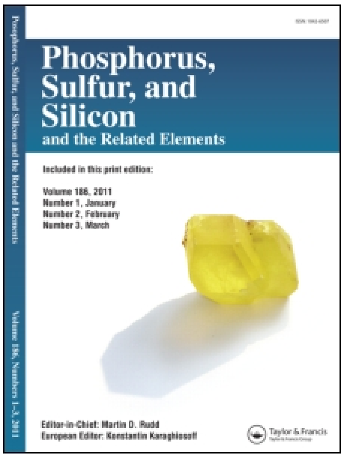

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Narula, Suraj P. , Soni, Sajeev , Puri, Meenu , Anand, Rishi D. and Puri, Jugal K.(2006) 'Polyfluorophenylaminosilane-Titanium (IV) Chloride Adducts', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 7, 1647 — 1654

To link to this Article: DOI: 10.1080/10426500500366681

URL: http://dx.doi.org/10.1080/10426500500366681

Phosphorus, Sulfur, and Silicon, 181:1647–1654, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500366681

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$Si(NHC_6H_{5\text{-}n}F_n)_4.xTiCl_4$ [n = 2–5; x = 3,4] are obtained from the disproportionation reactions between $(CF_3CH_2O)_3SiNHC_6H_{5\text{-}n}F_n$ (n = 2–5) and $TiCl_4$ in petroleum ether (40–60°C) at 0°–10°C. These complexes are characterized by elemental analyses and IR, ^1H, and ^{19}F NMR spectroscopy. Unlike the reported[5] complex $Si(NHC_6H_4F\text{-}o)_4.3TiCl_4$, these are non-ionic in nature. All complexes give double adducts with CH_3NO_2 and CH_3CN within 24 h.

Keywords Disproportionation; double adducts; non-ionic

INTRODUCTION

A Lewis acid promoted disproportion of a large number of chloro/organoxy/organo-organoxy/organo aminosilanes have been studied.[1–4] We have reported[5] the formation of 1,1,1,1-tetrakis(o-fluorophenylamino)silane tris(titanium(IV) chloride) adduct from the reaction

$$4(CF_3CH_2O)_3SiNHC_6H_4F\text{-o} + 3TiCl_4 \xrightarrow[-10^\circ C]{\text{Pet. Ether}(40-60^\circ C)} Si(NHC_6H_4F\text{-o})_4. \times 3TiCl_4 + 3(CF_3CH_2O)_4Si \quad (1)$$

Received June 20, 2005; accepted August 29, 2005.

Sajeev Soni is thankful to CSIR New Delhi, India, for the award of Junior Research Fellowship during this work.

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This complex is extremely unstable, and deteriorates on standing as well as in solution, except in CH_3NO_2, where it is stable for a short duration (<1 h). During this time, the complex was characterized in a solution and is believed to consist of $[Si(NHC_6H_4F\text{-}o)_4.\,Ti_2Cl_7]^+[TiCl_5]^-$ ions. The proposed titanium cation is the first of its kind reported so far. This cation is very reactive, even toward weak donors to afford the formation of double adducts. Encouraged by the formation of this new titanium (IV) cation, we planned to probe the generality of such reactions. Therefore, a range of fluorophenyl amine ligands are employed, and results obtained are recorded herein.

RESULTS AND DISCUSSION

The disproportionation reactions between N-(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) silanamines, and titanium(IV) chloride give complexes as shown.

$$4(CF_3CH_2O)_3SiNHC_6H_{5\text{-}n}F_n + xTiCl_4 \xrightarrow[0\text{—}10^\circ C]{\text{Pet. ether}(40\text{—}60^\circ C)}$$

$$Si(NHC_6H_{5\text{-}n}F_n)_4.xTiCl_4 + \underset{\substack{n=2,3;\ x=3\\ n=4,5;\ x=4}}{3(CF_3CH_2O)_4Si} \qquad (2)$$

These complexes are orange red to yellow, extremely hygroscopic solids, and insoluble in most of the common organic solvents, except in CH_3NO_2 and CH_3CN, where these are stable for 24 h. Elemental analyses correspond to the compositions given, while their molar conductances in CH_3NO_2 and CH_3CN show them as non-electrolytes. These compounds are characterized by IR, ^1H, and ^{19}F NMR spectroscopy.

Spectral Data

Major infrared absorptions of the compounds along with possible assignments are given in Table I. $Si(NHC_6H_3F_2)_4.3TiCl_4$ and $Si(NHC_6H_2F_3)_4.3TiCl_4$ reveal νNH absorption at 3380–3390 and 3210–3220 cm^{-1} assignable to uncoordinated and coordinated NH groups, respectively. Claire et al.[6] have shown similar observations for cyclosilazane adducts of $TiCl_4$. νCF_3 modes[7] at 660–665 and 530–540 cm^{-1} in the spectra of parent silanamines (see Experimental section) have disappeared in the adducts. Peaks at 440–445, 390–392, and 355–360 cm^{-1} are attributed to Ti-Cl modes[8] in complexes.

The infrared spectral data of other complexes such as $Si(NHC_6HF_4)_4.4TiCl_4$ and $Si(NHC_6F_5)_4.4TiCl_4$ differ with those of the previously discussed complexes in having only one type of νNH

TABLE I Major Infrared Absorptions (cm^{-1}) of Various Fluorophenyl Aminosilane Titanium (IV) Chloride Adducts and Their Double Adducts with Acetonitrile and Nitromethane

Compounds	υNH	υCH (Aromatic)	υC=N	C=C (Skeletal)	υCF (Aromatic)	υTi-Cl
$Si(HNC_6H_3F_2)_4.3TiCl_4$	3380, 3210	3060	—	1620, 1500	1250	440, 390, 360
$Si(HNC_6H_2F_3)_4.3TiCl_4$	3390, 3220	3080	—	1610, 1510	1245	445, 392, 355
$Si(HNC_6HF_4)_4.4TiCl_4$	3300	3070	—	1620, 1510	1245	445, 392, 355
$Si(HNC_6F_5)_4.4TiCl_4$	3290	3070	—	1620, 1500	1245	440, 390, 360
$Si(HNC_6H_3F_2)_4.3TiCl_4.3CH_3NO_2$	3170	3080	—	1600, 1490	—	440, 377, 320
$Si(HNC_6H_2F_3)_4.3TiCl_4.3CH_3CN$	3165	3085	2010	1610, 1490	—	488, 324
$Si(HNC_6HF_4)_4.4TiCl_4.4CH_3NO_2$	3170	3080	—	1610, 1510	—	445, 348, 324, 315
$Si(HNC_6F_5)_4.4TiCl_4.4CH_3CN$	3160	3080	2005	1610, 1510	—	490, 320

TABLE II ^{1}H and ^{19}F NMR Spectral Data of Various Fluorophenylamino Silanes Titanium (IV) Chloride Adducts

	Chemical Shift (δ) [ppm from $Me_4Si(^1H)/CF_3Cl$ (^{19}F)] ^{1}H				^{19}F
Compounds	NH	OCH_2	Ring	CF_3	Ring Fluorine
$Si(HNC_6H_3F_2)_4.3TiCl_4$ (1)	3.7 (b,1H)	—	7.2 (m, 12H)	—	124.0, 121.0 (2F)
$Si(HNC_6H_2F_3)_4.3TiCl_4$ (2)	3.7 (b,1H)	—	7.2 (m, 8H)	—	131.0, 124.5 (3F)
$Si(HNC_6HF_4)_4.4TiCl_4$ (3)	3.7 (b,1H)	—	7.1 (m, 4H)	—	160.4, 141.5 (4F)
$Si(HNC_6F_5)_4.4TiCl_4$ (4)	3.7 (b,1H)	—	—	—	1732, 165.2, 163.1 (5F)

absorptions at 3290–3300 cm^{-1}. This suggests that only coordinated NH groups are present in these complexes. It may indicate the complexation of each NH group of the 1,1,1,1-tetrakis(fluorophenylamino)silane by a $TiCl_4$ molecule. The peaks at a lower region at 355, 390, and 445 cm^{-1} assignable to νTi-Cl modes[8] clearly point to the presence of $TiCl_4$ in complexes.

The ^{1}H NMR of all complexes show multiplets between 7.1 to 7.2 ppm for phenyl groups, showing thereby minor downfield shifts as compared to the parent silanamines[9] (6.8–7.0 ppm). NH groups give weak signals at 3.7 ppm, while those due to OCH_2 groups of pure silanamines are completely absent. ^{19}F NMR spectra of complexes show resonances between 121.0 and 173.2 ppm. Details are given in Table II.

^{13}C and ^{29}Si NMR spectral data do not significantly contribute to the structural information about these complexes and, hence, are not recorded. None of the complexes gave suitable crystal for X- ray structural studies.

The solution of these complexes in solvents like CH_3NO_2/CH_3CN are stable for nearly 24 h. Thereafter, a brown/pink solid precipitates out in each case. Elemental analyses (see Experimental section) and IR spectra [νNH 3160–3170; νCH(aromatic) 3080–3085 and νCN 2005–2010 cm^{-1} (Table I)] of these adducts correspond to the composition $Si(NHC_6H_{5\text{-}n}F_n)_4.xTiCl_4.xS$ (where n = 2–3; x = 3, and n = 4,5; x = 4. S = solvent CH_3NO_2/CH_3CN). The extreme insolubility of these double complexes in organic solvents preclude a recording of interpretable multinuclear (^{1}H, ^{13}C, and ^{19}F) NMR spectra. However, the formation of these double adducts clearly indicates the coordinative unsaturation of $TiCl_4$ in complexes.

It may therefore be concluded that

1. unlike the ionic nature of the 1,1,1,1 tetrakis(fluorophenylamino) silane tris(titanium(IV) chloride) adduct already reported,[5] the

complexes obtained here are more stable in solution and are nonionic; and

2. the number of $TiCl_4$ molecules bonded to the 1,1,1,1 tetrakis (fluorophenyl amino) silanes are related to the number of fluorine substituents in the phenyl ring.

EXPERIMENTAL

Chemicals

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. $(CF_3CH_2O)_3SiCl$ was prepared by known methods. $TiCl_4$ (Fluka) was used without further purification. The solvents petroleum ether (40–60°C), n-hexane, nitromethane, and acetonitrile were dried by standard procedures, and purity was checked before use.

All manipulations were carried out under an inert atmosphere using an all-glass vacuum line.

Analytical

IR spectra were recorded as neat liquids, nujol mulls, or HCB mulls on KBr and CsI optics on a Perkin Elmer (model 1430) ratio recording spectrophotometer. ^1H and ^{19}F NMR spectra were obtained using a 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 a digital conductance meter NDC 732 Naina Electronics at 25 ± 0.5°C. Silicon and titanium were determined gravimetrically by standard procedures.

TABLE III Physical and Analytical Data of tris N-(2) Fluoro/(2,4) Difluoro/(2,4,6) Trifluoro (2,3,5,6) Tetrafluoro/(2,3,4,5,6) Penta Fluorophenyl-1, 1, 1-Tris (2,2,2-Trifluorethoxy) Silanamines

Compounds	Yields%	B.P.* °C/10 mm Hg	Analytical Data% Found (Required) N	Si
$(CF_3CH_2O)_3SiNHC_6H_3F_2$	75	120–123	3.1 (3.0)	6.3 (6.1)
$(CF_3CH_2O)_3SiNHC_6H_2F_3$	65	125–128	2.7 (2.9)	5.7 (5.9)
$(CF_3CH_2O)_3SiNHC_6HF_4$	60	130–134	2.7 (2.8)	5.6 (5.7)
$(CF_3CH_2O)_3SiNHC_6F_5$	55	135–138	2.8 (2.7)	5.7 (5.5)

*Boiling points are uncorrected.

TABLE IV Major Infrared Absorptions (cm^{-1}) of Various Fluorophenyl Aminosilanes

Compounds	υNH	υCH (aromatic)	υSiOC	δCF_3
$(CF_3CH_2O)_3SiNHC_6H_3F_2$	3465	3020	1070	660, 630, 540
$(CF_3CH_2O)_3SiNHC_6H_2F_3$	3465	3030	1065	665, 630, 535
$(CF_3CH_2O)_3SiNHC_6HF_4$	3470	3040	1060	665, 630, 530
$(CF_3CH_2O)_3SiNHC_6F_5$	3475	3040	1070	665, 635, 535

C, H, and N analyses were carried out on a Perkin Elmer model 2400 elemental analyzer.

Preparations

$(CF_3CH_2O)_3SiNHC_6H_3F_2$

To a solution of 2,4-difluoroaniline (1.02 mL, 10 mmol) and triethylamine (1.4 mL, 10 mmol) in pet. ether (40–60°C) (30 mL) maintained at 0–10°C, $(CF_3CH_2O)_3SiCl$ (3.62 g, 10 mmol) was added dropwise. A white precipitate of triethylammonium chloride was formed. After the complete addition of the chlorosilane, the reaction mixture was refluxed for 4–5 h. Thereafter, the precipitate was filtered off, and the solvent was removed from the filtrate. The liquid left behind was purified by distillation. The analytical and physical data are given in Table III. The compounds have been characterized by IR (Table IV) and multinuclear (^1H and ^{19}F) NMR (Table V) spectral data.

$(CF_3CH_2O)_3SiNHC_6H_{5\text{-}n}F_n (n = 3\text{–}5)$

2,4,6-trifluoro/2,3,5,6-tetrafluoro/2,3,4,5,6- pentafluoro aniline (5 mmol) was taken in n-hexane (30 mL) separately and cooled to 0–10°C. n-BuLi (5 mmol) in n-hexane was added slowly to this solution.

TABLE V ^1H and ^{19}F NMR Spectral Data of Various Fluorophenylamino Silanes

	Chemical Shift (δ) [ppm from Me_4Si (^1H)/CF_3Cl(^{19}F) in $CDCl_3$] ^1H				^{19}F
Compounds	NH	OCH_2	Ring	CF_3	Ring Fluorine
$(CF_3CH_2O)_3SiNHC_6H_3F_2$	3.7 (b,1H)	4.3 (q, 6H)	7.0 (m, 3H)	77.0 (t, 9F)	124.0, 120.0 (2F)
$(CF_3CH_2O)_3SiNHC_6H_2F_3$	3.6 (b,1H)	4.2 (q, 6H)	6.9 (m, 2H)	78.0 (t, 9F)	130.5, 124.8 (3F)
$(CF_3CH_2O)_3SiNHC_6HF_4$	3.7 (b,1H)	4.2 (q, 6H)	6.8 (m, 1H)	78.0 (t, 9F)	162.2, 141.0 (4F)
$(CF_3CH_2O)_3SiNHC_6F_5$	3.6 (b,1H)	4.3 (q, 6H)	—	79.0 (t, 9F)	173.8, 165.6, 163.2 (5F)

TABLE VI Analytical Data of Various Fluorophenyl Aminosilane Titanium (IV) Chloride Complexes and Their Double Adducts With Nitromethane and Acetonitrile

	% Found (calculated)					
Compounds	C	H	N	Cl	Ti	Si
$Si(NHC_6H_3F_2)_4.3TiCl_4$	—	—	5.1 (5.0)	38.1 (38.3)	12.4 (12.9)	2.3 (2.5)
$Si(NHC_6H_2F_3)_4.3TiCl_4$	—	—	4.5 (4.7)	35.8 (36.0)	11.9 (12.1)	2.1 (2.3)
$Si(NHC_6HF_4)_4.4TiCl_4$	—	—	3.6 (3.8)	39.1 (39.3)	13.4 (13.2)	1.8 (1.9)
$Si(NHC_6F_5)_4.\ 4TiCl_4$	—	—	3.5 (3.6)	37.2 (37.4)	12.2 (12.6)	2.0 (1.8)
$Si(NHC_6H_3F_2)_4.\ 3TiCl_4.\ 3CH_3NO_2$	24.8 (25.0)	1.8 (1.9)	7.3 (7.5)	32.7 (32.9)	10.9 (11.1)	2.0 (2.1)
$Si(NHC_6HF_4)_4.4TiCl_4.\ 4CH_3NO_2$	19.6 (19.9)	1.0 (1.1)	6.4 (6.6)	33.4 (33.6)	11.0 (11.3)	1.5 (1.6)
$Si(NHC_6H_3F_5)_4.3TiCl_4.\ 3CH_3CN$	29.3 (29.1)	1.9 (2.0)	7.5 (7.9)	34.3 (34.5)	11.4 (11.6)	2.1 (2.2)
$Si(NHC_6HF_4)_4.3TiCl_4.\ 4CH_3CN$	23.5 (23.8)	1.1 (1.2)	6.7 (6.9)	35.2 (35.3)	11.7 (11.9)	1.6 (1.7)

After stirring for 1/2 h, $(CF_3CH_2O)_3SiCl$ (1.8 g, 5 mmol) was added dropwise when white precipitates separated out. The reaction mixture was allowed to attain r.t. and then was refluxed for 2–3 h. Thereafter, LiCl precipitates were filtered off, and a filtrate on the evaporation of a solvent gave a liquid in each case, which was distilled. The analytical and physical data are given in Table III. Compounds have been characterized by IR (Table IV) and multinuclear (^1H and ^{19}F) NMR (Table V) spectral data.

$Si(NHC_6H_{5-n}F_n)_4.x\ TiCl_4$

A solution of $TiCl_4$(570 mg, 3.0 mmol) in dry pet. ether (40–60°C) (10 mL) was added dropwise into a solution of $(CF_3CH_2O)_3$ $SiNHC_6H_nF_{5-n}$ (3.0 mmol). The mixture was maintained at 0–10°C for 1/2 h. An orange red to yellow solid was precipitated out in each case. The mixture was stirred for 2 h, the solid was filtered off, washed with pet. ether (40–60°C), and dried in vacuum. The analytical data are given in Table VI.

Adducts of $Si(NHC_6H_{5-n}F_n)_4.\ x\ TiCl_4$ with CH_3NO_2/CH_3CN

Each of the $Si(NHC_6H_{5-n}F_n)_4.xTiCl_4$ (2.0 mmol) (where n = 2,3; x = 3 , n = 4,5; x = 4) was dissolved in CH_3CN (20 mL) or CH_3NO_2 (20 mL). The solution was kept under an inert atmosphere for 24 h. A pale yellow to brown solid precipitated in each case. The solid was filtered off, washed with pet. ether, and dried under vacuum. Analytical data are given in Table VI.

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