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SYNTHESIS AND COORDINATION CHEMISTRY OF ORGANOXY/ORGANO ORGANOXY SILICON COMPOUNDS CONTAINING Si-N BOND(S)*

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Benzylamino *tris*(2–chloroethoxy)/*tris*(2,2,2–trifluoroethoxy)/*bis* (2 chloroethoxy) alkoxy/*bis*(2–chloroethoxy) methyl/*bis*(2,2,2–trifluoroethoxy) alkoxy/methyl chloro, dialkoxy silanes, anilino *tris*(2–chloroethoxy)/*tris*(2,2,2–trifluoroethoxy)/chloro, dialkoxy silanes, *o*–chloroanilion, chloro, dialkoxy silanes 2–fluoro–/2,4–difluoro–anilino *tris*(2,2,2–trifluoroethoxy)/tri–*n*–propoxy silanes as well as N–triorganoxy silyl N′–phenyl hydrazines have been isolated under strictly anhydrous conditions and characterised by elemental analyses and IR, PMR and ^{19}F NMR spectroscopy. Reactions of these ligands with $SnCl_4/TiCl_4$ in petroleum ether at –5 to –15 °C give solid compounds of composition $R_{3-n-m}R'_n$ Si $(NHR'')_m$. $xMCl_4$ (where $R = ClC_2H_4O$, OEt, OPr–*n*, OBu–*n*, CF_3CH_2O; $R = R'$ or CH_3; $R'' = CH_2C_6H_5$, C_6H_5, NHC_6H_5, C_6H_4F, $C_6H_4F_2$, *o*–ClC_4H_4; $n = 0$ or 1; $m = 2$, 3 or 4 and $x = 1$, 2 or 3). Elemental analyses, infrared and NMR spectra, ligand exchange reactions as well as adduct formation by a different route point towards ligand disproportionation in these reactions. Reactions of N–triorganoxy silyl N′ phenylhydrazines with $SnCl_4$ or $TiCl_4$ at –40 to –60 °C under the same conditions afford simple 1 : 1 adducts. A tentative mechanism has been proposed.

Key Words : Organoxy/Organo Si–N Compounds

INTRODUCTION

DONOR properties of organo/organoxy silicon compounds with silicon-nitrogen bond(s) have been the subject of interest recently.[1-4] A large number of complexes have been isolated and characterised. Whereas, organamino organosilanes by and large afford normal adducts,[5] the organoamino organoxy/organo-organoxy silanes give adducts of the rearranged ligands.[6-8] The relative strength of amino triorganoxy silanes has also been measured thermochemically and is found to be dependent upon the inductive (+ I) effect of the substituents on silicon atom.[9] It has also been demonstrated that the presence of at least one organoxy group is necessary to bring about the disproportionation.[6,7] However, such types of ligands with more than one nitrogen atom in the molecule as well as silicon carrying well-known electro negative groups/atoms, have not been studied for their donor properties. Presently, some such systems have been taken up and in some cases

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these studies are affected at two temperatures with a view to throw light on the possible mechanism.

EXPERIMENTAL

All operations were carried out under dry nitrogen atmosphere. The solvents used were dried by conventional methods. Silicon tetrachloride (BDH, pure), methyl trichlorosilane (Fluka AG) and tin(IV) and titanium(IV) chlorides (Reidel, pure) were distilled before use. 2,2,2–Trifluoroethanol (Fluka AG), *n*-propanol, *n*-butanol (BDH, pure), 2–fluoro and 2,4–difluoroaniline (Fluka A. G.), 2–chloroethanol (BDH, pure) were used as obtained. Benzylamine, aniline, *o*–chloroaniline, phenyl hydrazine (all BDH, pure) were distilled before use.

Infrared spectra were recorded as neat liquids or as nujol mulls using KBr and CsI optics on a Perkin Elmer (model 621) double beam grating spectrophotometer.

PMR and ^{19}F NMR spectra were recorded on a Varian (EM 390) 90MHz spectrometer in $CDCl_3$ or $CDCl_3$ + DMSO (d_6) mixtures (for the adducts) using TMS as internal and Freon–11 as external references respectively.

Ligands

All the ligands were prepared by the reactions of the chloro/dichloro dialkoxy/alkoxy alkyl silanes with the corresponding amines/hydrazine in molar ratio 1 : 2 or 1 : 1 in presence of an equivalent amount of Et_3N. The purity of these compounds were checked by infrared and ^1H NMR spectral data.

Reactions of the Ligands with $SnCl_4$ and $TiCl_4$ at –5 to –15 °C

Addition of equimolar quantities of tin(IV) or titanium(IV) chlorides in petroleum ether or *n*-hexane to any of the above bases in the same solvent result in the precipitation of a solid product in each case. These adducts were washed, dried under reduced pressure and analysed.

Similar reactions of N–triethoxy/tri-*n*-propoxy/tri-*n*-butoxy silyl N′-phenyl hydrazines at –40 to –60 °C under the same conditions also resulted in the formation of solid products which were isolated as above.

Ligand Exchange Reaction

An adduct (10mmol) was added to ethylene diamine (25 mmol) or molten 2, 2′–bipyridyl (25mmol) or pyridine (d_5) (25mmol) in a round bottom flask fitted with a reflux condenser having silica gel moisture guard tube and a dry nitrogen inlet tube. The contents were kept at 35–40 °C for 3–4hr, thereafter, dry carbon tetrachloride (5–10ml) was added to the reaction mixture and contents filtered and concentrated. The liberated bases were characterised by NMR spectral data.

RESULTS AND DISCUSSION

Ligands

N–Triethoxy/tri-*n*-propoxy/tri-*n*-butoxy silyl N′-phenyl hydrazines; benzylamino *tris*(2-chlorothoxy)/*bis* (2-chloroethoxy ethoxy/*n*-propoxy/*n*-butoxy/methyl silanes,

anilino *tris*(2-chloro-ethoxy) silane and benzylamino, chloro, diethoxy/di-*n*-propoxy silanes as well as anilino/*o*-chloroanilino, chloro, di-*n*-propoxy silane have been obtained by the reactions of the amine/aniline/hydrazine with the corresponding chloro/dichloro silanes in molar ratio 2 : 1. The *tris*(2,2,2-tri-fluoroethoxy)/*bis*(2,2,2-trifluoroethoxy) methyl/tri-*n*-propoxy-2-flouoro/2,4-difluoro-anilino/anilino/benzylamino silanes are formed by the reactions of chlorosilanes and amine/aniline in the molar ratio 1 : 1 in the presence of equivalent quantity of triethylamine. The reactions may be given as :

$$R_{3-n}\,R'_n\,\mathrm{Si\,Cl} + 2R''\mathrm{NH_2} \longrightarrow R_{3-n}R'_n\,\mathrm{SiNH}R'' + R''\mathrm{NH_3Cl}$$

(R = OEt, OPr-*n*, OBu-*n*, Cl EtO; R' = Cl,CH_3; R'' = $CH_2C_6H_5$, C_6H_5, ClC_6H_4, NHPH and n = 0 or 1)

$$(CF_3CH_2O)_{3-n}R'_n\,\mathrm{SiCl} + R''\mathrm{NH_2} \xrightarrow{Et_3N} (CF_3CH_2O)_{3-n}R'_n\,\mathrm{SiNH}R'' + Et_3NHCl$$

(R' = CH_3, OPr-*n*; R'' = $C_6H_5CH_2$, C_6H_5, C_6H_4F or $C_6H_3F_2$; and n = 0, 1 or 3)

IR Spectra—The infrared spectra of the hydrazino/amino silanes as thin films exhibit νNH mode between 3410–3360cm^{-1}. The bands due to νCF_3, δCF_3, ν_{as} SiO(C) and δSiO(C) are observed in the regions 1280–1260, 660 and 540, 1090–1020 and 490–470cm^{-1} respectively. In addition, benzene ring absorptions (whereever applicable) are observed at 750–700 ± 10cm^{-1}.

NMR Spectra—The PMR spectra of the ligands exhibit signals at 0.3, 1.0, 1.3–1.8, 3.8–4.3 and 6.9–7.35ppm for Si–CH_3, CH_3, CH_2,CH_2O/CH_2Cl and aromatic ring protons respectively. The signals due to NH protons vary between 1.4 to 4.6ppm depending upon their chemical environments. In case of hydrazino derivatives there are two NH proton signals (for PhNH and $(RO)_3$ SiNH group) observed at 3.0 to 3.4 and 4.8 to 5.2ppm respectively. ^{19}F NMR spectra show CF_3 at 77ppm and C_6H_4F and $C_6H_3F_2$ at 135–137 and 120–124ppm respectively.

These spectral data are useful to ascertain their purity.

Coordination Complexes—The analytical data of the complexes obtained are recorded in Tables I and II. The comounds isolated from the reactions of the above ligands with $SnCl_4$ and $TiCl_4$ at –5 to –15 °C are white and pale yellow to brick red coloured hygroscopic solids, insoluble in common organic solvents. The composition of the products can be given as : $R_{3-n-m}R'_n\,\mathrm{Si(NH}R'')_m.\ x\mathrm{MCl_4}$ (where R = ClC_2H_4O, OEt, OPr-*n*, OBu-*n*, CF_3CH_2O; R' = R or CH_3; R'' = $CH_2C_6H_5$, C_6H_5, NHC_6H_5, C_6H_4F, $C_6H_3F_2$, *o*-ClC_6H_4; n = 0 or 1; m = 2, 3 or 4 and x = 1, 2 or 3). All these compounds deteriorate on long standing. Because of their insolubility all attempts to obtain single crystals failed.

IR Spectra—The IR spectra of the adducts reveal that νNH modes suffer a negative spectral shift and are observed at 3230–3180cm^{-1}. ν_{as}SiO(C), δSiO(C), C=C skeletal, νCF_3 (whereever present), etc absorptions remain almost unaltered

TABLE I

Analytical data of complex compounds of organoamino/hydrazino trialkoxy/dialkoxy alkylchloro silanes with titanium(IV) chloride at -5 to- 15 °C

	Ligand	Complex	Analytical data % Found/(Regd.)			
			Cl	Ti	Si	N
1.	$(C_2H_5O)_3$ SiNHNHPh	$(C_2H_5O)_2$ Si$(NHNHPh)_2.2TiCl_4$	39.8 (39.8)	13.4 (13.4)	3.4 (3.9)	7.6 (7.8)
2.	$(C_3H_7O)_3$ SiNHNHPh	$(C_3H_7O)_2$ Si$(NHNHPh)_2.2TiCl_4$	38.1 (38.3)	13.5 (12.9)	4.1 (3.8)	7.4 (7.5)
3.	$(C_4H_9O)_3$ SiNHNHPh	$(C_4H_7O)_2$ Si$(NHNHPh)_2.2TiCl_4$	36.2 (36.9)	13.0 (12.5)	3.9 (3.6)	7.6 (7.3)
4.	$(ClC_2H_4O)_3$ $SiNHCH_2Ph$	$(ClO_2H_4O)_2$ Si$(NHCH_2C_6H_5)_2.TiCl_4$	36.1 (36.1)	8.0 (8.1)	4.6 (5.7)	4.3 (4.7)
5.	$(ClC_2H_4O)_2$ (C_2H_5O) $SiNHCH_2Ph$	(ClC_2H_4O) Si$(NHCH_2C_6H_5)_3.2TiCl_4$	39.2 (39.6)	11.8 (11.9)	3.4 (3.4)	5.3 (5.2)
6.	$(ClC_2H_4O)_2$ (C_3H_7O) $SiNHCH_2Ph$	(ClC_2H_4O) (C_3H_7O) Si$(NHCH_2C_6H_5)_2.2TiCl_4$	42.1 (42.1)	12.4 (12.6)	3.6 (3.7)	3.3 (3.7)
7.	$(ClC_2H_4O)_2$ (C_4H_9O) $SiNHCH_2Ph$	(ClC_2H_4O) (C_4H_9O) Si$(NHCH_2C_6H_5)_2.2TiCl_4$	42.2 (41.3)	9.0 (12.4)	3.5 (3.6)	3.5 (3.6)
8.	$(ClC_2H_4O)_2$ $CH_3SiNHCH_2Ph$	$(ClC_2H_4O)_2$ Si$(NHC_6H_5)_2$ $TiCl_4$	38.4 (38.3)	12.8 (12.9)	3.2 (3.7)	5.4 (5.6)
9.	$(ClC_2H_4O)_3$ SiNHPh	$(ClC_2H_4O)_2$ Si$(NHC_6H_5)_2$ $TiCl_4$	37.4 (37.8)	8.4 (8.5)	4.8 (5.0)	4.9 (4.9)
10.	$(C_2H_5O)_2$ $ClSiNHCH_2Ph$	(C_2H_5O) ClSi$(NHCH_2C_6H_4)_2.TiCl_4$	34.6 (34.7)	9.2 (9.4)	5.3 (5.5)	5.3 (5.5)
11.	$(C_3H_7O)_2$ $ClSiNHCH_2Ph$	(C_3H_7O) ClSi$(NHCH_2C_6H_5)_2.TiCl_4$	33.6 (33.8)	9.0 (9.1)	5.2 (5.3)	5.1 (5.3)
12.	$(C_3H_7O)_2$ ClSiNHPh	(C_3H_7O) Si$(NHCH_2C_6H_5)_3.2TiCl_4$	38.0 (38.2)	12.7 (12.9)	3.6 (3.7)	5.5 (5.6)
13.	$(C_3H_7O)_2$ $ClSiNHC_6H_4Cl$	(C_3H_7O) Si$(NHC_6H_4Cl)_3.2TiCl_4$	33.4 (33.5)	11.2 (11.3)	3.2 (3.3)	4.8 (4.9)
14.	$(CF_3CH_2O)_3$ $SiNHCH_2Ph$	(CF_3CH_2O) Si$(NHCH_2Ph)_3.2TiCl_4$	34.2 (34.4)	11.2 (11.6)	3.2 (3.4)	4.9 (5.1)
15.	$(CF_3CH_2O)_2$ $CH_3SiNHCH_2Ph$	$CH_3Si(NHCH_2PH)_3.2TiCl_4$	38.0 (38.3)	12.4 (12.9)	3.5 (3.7)	5.3 (5.6)
16.	$(CF_3CH_2O)_3$ SiNHPh	(CF_3CH_2O) Si$(NHPh)_3.2TiCl_4$				
17.	$(CF_3CH_2O)_3$ $SiNHC_6H_4F$	$(NHC_6H_4F)_4.3TiCl_4$	40.1 (41.0)	13.2 (13.8)	2.5 (2.6)	5.1 (5.4)
18.	$(C_3H_7O)_3$ $SiNHC_6H_4F$	$(C_3H_7O)_2$ Si$(NHC_6H_4F)_2.TiCl_4$	25.2 (25.5)	8.4 (8.6)	4.7 (5.0)	5.0 (5.0)
19.	$(C_3H_7O)_3$ $SiNHC_6H_3F_2$	$(C_3H_7O)_2$ Si$(NHC_6H_3F_2)_2.TiCl_4$	23.7 (23.9)	7.6 (8.1)	4.4 (4.7)	4.4 (4.7)

TABLE II

Analytical data of complex compounds of organoamino/hydrazino trialkoxy/dialkoxy alkyl/chloro silanes with tin(IV) chloride at –5 to –15 °C

	Ligand	Complex	Analytical data % Found (Regd.)			
			Cl	SN	Si	N
1.	$(C_2H_5O)_3$ SiNHNHPh	(C_2H_5O) Si$(NHNHPh)_2.2SnCl_4$	33.4 (33.2)	27.6 (27.8)	3.2 (3.2)	6.2 (6.5)
2.	$(C_3H_7O)_3$ SiNHNHPh	$(C_3H_7O)_2$ Si$(NHNHPh)_2.2SnCl_4$	32.0 (33.2)	26.8 (26.9)	3.0 (3.1)	5.9 (6.3)
3.	$(C_4H_9O)_3$ SiNHNHPh	$(C_4H_9O)_2$ Si$(NHNHPh)_2.2SnCl_4$	31.4 (31.2)	25.6 (26.1)	2.7 (3.0)	5.9 (6.1)
4.	$(ClC_2H_4O)_3$ SiNHCH$_2$Ph	$(ClC_2H_4O)_2$ Si$(NHCH_2Ph)_2.SnCl_4$	33.0 (32.3)	17.6 (17.9)	4.0 (4.2)	4.7 (4.2)
5.	$(ClC_2H_4O)_2$ (C_2H_5O) SiNHCH$_2$Ph	(ClC_2H_4O) Si$(NHCH_2Ph)_3.2SnCl_4$	33.6 (33.7)	24.8 (25.0)	2.7 (2.9)	4.8 (4.4)
6.	$(ClC_2H_4O)_2$ (C_3H_7O) SiNHCH$_2$Ph	$(ClC_2H_4O)_2$ (C_3H_7O) Si$(NHCH_2Ph)_2.2SnCl_4$	34.9 (35.5)	26.1 (26.4)	2.9 (3.1)	2.9 (3.1)
7.	$(ClC_2H_4O)_2$ (C_4H_9O) SiNHCH$_2$Ph	(ClC_2H_4O) (C_4H_9O) Si$(NHCH_2Ph).2SnCl_4$	34.7 (34.9)	2.9 (3.0)	25.6 (25.8)	2.8 (3.0)
8.	$(ClC_2H_4O)_2$ CH$_3$SiNHCH$_2$Ph	$CH_3Si(NHCH_2Ph)_3.2SnCl_4$	32.0 (32.1)	26.6 (26.7)	2.8 (3.1)	4.5 (4.7)
9.	(ClC_2H_4O) SiNHPh	$(ClC_2H_4O)_2$ Si$(NHPh)_2.SnCl_4$	33.7 (33.6)	18.2 (18.6)	3.8 (4.4)	4.1 (4.4)
10.	$(C_2H_5O)_2$ ClSiNHCH$_2$Ph	(C_2H_5O) ClSi$(NHCH_2Ph)_2.SnCl_4$	30.4 (30.5)	20.0 (20.3)	4.6 (4.8)	4.6 (4.8)
11.	$(C_3H_7O)_2$ ClSiNHCH$_2$Ph	(C_3H_7O) ClSi$(NHCH_2Ph)_2.SnCl_4$	29.6 (29.8)	19.8 (19.8)	4.7 (4.7)	4.5 (4.7)
12.	$(C_3H_7O)_2$ ClSiNHPh	(C_3H_7O) Si$(NHPh)_3.2SnCl_4$	32.0 (32.1)	26.5 (26.7)	3.1 (3.0)	4.6 (4.7)
13.	$(C_3H_7O)_2$ ClSiNHC$_6$H$_4$Cl	(C_3H_7O) Si$(NHC_6H_4Cl)_3.2SnCl_4$	28.6 (28.7)	23.8 (23.9)	2.7 (2.8)	4.1 (4.2)
14.	$(CF_3CH_2O)_3$ SiNHCH$_2$Ph	(CF_3CH_2O) Si$(NHCH_2C_6H_5)_3.2SnCl_4$	29.2 (29.4)	24.0 (24.4)	2.7 (2.9)	4.1 (4.3)
15.	$(CF_3CH_2O)_2$ CH$_3$SiNHCH$_2$Ph	$CH_3Si(NHCH_2C_6H_5)_3.2SnCl_4$	31.8 (32.2)	26.5 (26.7)	2.9 (3.1)	4.5 (4.7)
16.	$(CF_3CH_2O)_3$ SiNHPh	(CF_3CH_2O) Si$(NHPh)_3.2SnCl_4$	30.5 (30.7)	25.8 (25.7)	2.8 (3.0)	4.4 (4.5)
17.	$(CF_3CH_2O)_3$ SiNHC$_6$H$_4$F	$(C_6H_4FNH)_4$ Si.$3SnCl_4$	33.9 (34.1)	27.9 (28.3)	2.0 (2.2)	4.1 (4.4)
18.	$(C_3H_7O)_3$ SiNHC$_6$H$_4$F	$(C_3H_7O)_2$ Si$(NHC_6H_4F)_2.SnCl_4$	22.2 (22.6)	17.2 (17.3)	4.5 (4.6)	4.4 (4.6)
19.	$(C_3H_7O)_3$ SiNHC$_6$H$_3$F$_2$	$(C_3H_7O)_2$ Si$(NHC_6H_3F_2)_2.SnCl_4$	21.5 (21.4)	18.0 (17.9)	4.4 (4.2)	4.3 (4.2)

in position. On close scrutiny it is observed that the intensity of νSiO(C) band is reduced while that of the phenyl group attached to nitrogen atom (whereever present) is enhanced. In addition, νMCl frequencies appear between 380–320cm^{-1}. On the basis of these observations the nitrogen atom may be considered to be the donor site in all these silyl bases used here.

PMR Spectra—PMR spectra (Table III) show signals due Si-CH_3, CH_3, CH_2, CH_2O, CH_2Cl and benzene ring protons at ~ 0.3, 0.9, 1.2, 3.7 and 7.1–7.3ppm respectively, as in the pure ligands. NH proton signals are observed between 1.4 to 4.6ppm. In case of hydrazino derivatives NH protons are located at 3.7 and 4.8 to 5.0ppm corresponding to $(RO)_3SiNH$ and PhNH groups. Thus there is a definite downfield shift of silicon bonded NH group. This may indicate that metalloidal nitrogen is the site of reaction in silyl hydrazines. The relative ratios of the protons through proton counts indicate that the ligand in the complexes is $R_{4-n-m}R'_n Si(NHR''_m)$.

The nature of the bases in the adducts can be further supported by the actual isolation of these adducts from *tris*(benzylamino/anilino) alkoxy silanes and N-diorganoxy silyl *bis*(N'-phenyl hydrazine) with $TiCl_4$ and $SnCl_4$ in the molar ratio 1:2 under the same experimental conditions. The complexes so formed are identical in all respects with those obtained above.

The data cleary indicate that disproportionation of the base molecule is occurring on reaction with the Lewis acids.

Whereas, the reactions with $Ph(BhO)_2SiNHCH_2Ph$ and $Ph(PrO)_2SiNHPh$ formed the adducts of composition $PhSi(NHCH_2Ph)_3.2MCl_4$ and $Ph(PrO)Si(NHNHPH)_2.2MCl_4$ respectively, (PrO) $Et_2SiNHCH_2Ph$ gives only the *bis*(benzylamino) diethyl silane complexes $Et_2Si(NHCH_2Ph_2.2MCl_4$ while $Me_3SiNHCH_2Ph$ and $Me_3SiNHNHPh$ result in the formation of simple 1:1 adducts and no disportionation product is isolated.

It may thus be concluded that at least one organoxy group is required to bring about the disproportionation of the organoamino/hydrazino triorganoxy/organo organoxy silanes.

A persual of the results also reveals that benzylamino/anilino, *bis*(2-chloroethoxy), *n*-propoxy/*n*-butoxy silanes as well as N-triorganoxy-N'-phenyl hydrazines disproportionate to the *bis*-amino/hydrazino organoxy stage only. 2-Fluoro/2,4-difluoro-anilino tri-*n*-propoxy silanes also afford the corresponding *bis*(fluoroanilino) di-*n*-propoxy silane adducts. These observations are different from those reported for organoamino triorganoxy/organo organoxy silanes. However, fluoroanilino *tris*(2,2,2-trifluoroethoxy) silanes on reaction form tetrakis (2 fluoroanilino) sialne adducts. These observations can be rationalised that inductive effect of the substituents on silicon and the electron donating strength of the organoamino/anilino coups coupled with the disproportionating tendencies of the alkoxy groups play a major role in these type of reactions, in some cases steric factors may be of importance as well.

TABLE III

NMR spectral data of compounds of organoamino/hydrazino alkoxy/alkyl alkoxy silanes with $SnCl_4$ and $TiCl_4$ at –5 to –15 °C

Compound	CH_3	CH_2	CH_3O/Cl	SiNH	NH	Ring protons	CH_3N	$SiCH_3$
$(CH_3CH_2O)\,Si(NHNHC_6H_5)_2.2MCl_4$	1.1 (*t*, 6H)		3.6 (*q*, 4H)	3.75 (*s*, 2H)	5.05 (*s*, 2H)	7.3 (*m*, 10H)	(*s*, 4H)	(*s*, 3H)
$(CH_3CH_2CH_2O)_2\,Si(NHNHC_6H_5)_2.2MCl_4$	0.7 (*t*, 6H)	1.4 (*q*, 4H)	3.4 (*t*, 4H)	3.8 (*s*, 2H)	5.0 (*s*, 2H)	7.3 (*m*, 10H)		
$(CH_3CH_2CH_2CH_2O)_2\,Si(NHNHC_6H_5)_2.2MCl_4$	0.7 (*t*, 6H)	1.1 (*m*, 8H)	3.0 (*t*, 4H)	3.8 (*s*, 2H)	5.0 (*s*, 2H)	7.3 (*m*, 10H)		
$(ClCH_2CH_2O)\,Si(NHCH_2C_6H_5)_2.MCl_4$			3.5 (*m*, 8H)	1.4 (*s*, 2H)		7.1 (*s*, 10H)	4.1 (*s*, 4H)	
$(ClCH_2CH_2O)\,Si(NHCH_2C_6H_5)_3.2MCl_4$			3.5 (*m*, 8H)	1.4 (*s*, 2H)		7.2 (*s*, 10H)	4.2 (*s*, 4H)	
$(ClCH_2CH_2O)\,(CH_3CH_2CH_2O)\,Si(NHCH_2C_6H_5)_2.2MCl_4$	0.8 (*t*, 3H)	1.1 (*q*, 2H)	3.6 (*m*, 6H)	1.3 (*s*, 2H)		7.3 (*s*, 10H)	4.1 (*s*, 4H)	
$(ClCH_2CH_2O)\,(CH_3CH_2CH_2CH_2O)\,Si(NHCH_2C_6H_5)_2.2MCl_4$	0.8 (*t*, 3H)	1.2 (*m*, 4H)	3.8 (*m*, 6H)	1.5 (*s*, 2H)		7.1 (*s*, 10H)	4.2 (*s*, 4H)	
$CH_3Si(NHCH_2C_6H_5)_3.2MCl_4$				1.4 (*s*, 3H)		7.2 (*s*, 15H)	4.1 (*s*, 6H)	0.3 (*s*, 3H)
$(ClCH_2CH_2O)_2\,Si(NHC_6H_5)_2.MCl_4$			3.7 (*m*, 4H)	4.6 (*s*, 2H)		7.1 (*m*, 10H)		
$(CH_3CH_2O)\,ClSi(NHCH_2C_6H_5)_2.MCl_4$	1.0 (*t*, 3H)		3.6 (*q*, 2H)	1.4 (*s*, 2H)		7.2 (*s*, 10H)	4.1 (*s*, 4H)	
$(CH_3CH_2CH_2O)\,ClSi(NHCH_2C_6H_5)_2.MCl_4$	0.9 (*t*, 3H)	1.2 (*q*, 2H)	3.6 (*t*, 2H)	1.3 (*s*, 2H)		7.1 (*s*, 10H)	4.8 (*s*, 4H)	
$(CH_3CH_2CH_2O)\,Si(NHCH_2C_6H_5)_3.2MCl_4$	0.9 (*t*, 3H)	1.2 (*q*, 2H)	3.8 (*t*, 2H)	1.4 (*s*, 3H)		7.2 (*s*, 15H)	4.1 (*s*, 6H)	
$(CH_3CH_2CH_2O)\,Si(NHC_6H_4Cl)_3.2MCl_4$	0.9 (*t*, 3H)	1.1 (*q*, 2H)	3.7 (*t*, 2H)	4.6 (*s*, 3H)		7.3 (*m*, 12H)		
$(CF_3CH_2O)\,Si(NHCH_2C_6H_5)_3.2MCl_4$			3.8 (*q*, 2H)			7.2 (*s*, 15H)	4.2 (*s*, 6H)	
$CH_3Si(NHCH_2C_6H_5)_3.2MCl_4$				1.1 (*s*, 6H)		7.2 (*s*, 15H)		0.3 (*s*, 3H)
$(CF_3CH_2O)\,Si(NHC_6H_5)_3.2MCl_4$			3.8 (*q*, 2H)	4.6 (*s*, 6H)		7.2 (*s*, 15H)		
$Si(NHC_6H_4F)_4.3MCl_4$						7.1 (*m*)		
$(CH_3CH_2CH_2O)_2\,Si(NHC_6H_4F)_2.MCl_4$	0.9 (*t*, 3H)	1.1 (*q*, 4H)	3.6 (*t*, 4H)	4.6 (*s*, 2H)		7.1 (*m*, 8H)		
$(CH_3CH_2CH_2O)_2\,Si(NHC_6H_3F_2)_2.MCl_4$	0.8 (*t*, 6H)	1.2 (*q*, 4H)	3.7 (*t*, 4H)	4.6 (*s*, 2H)		7.3 (*m*, 6H)		

A comparison between the alkoxy and chloro groups situated on the same silicon atom reveals that in most of the cases studied here, the chloro group is preferably redistributed as compared to the alkoxy groups. However, when benzylamino, chloro, alkoxy silanes are used, alkoxy groups are easy to be cleaved. With a view to determining the effect of temperatures, the reactions of N-triorganoxy silyl N'-phenyl hydrazines with $SnCl_4$ and $TiCl_4$ have been carried out at temperatures ranging from −40 to −50 °C. The products obtained are white and brick red hygroscopic solids in the case of $SnCl_4$, and $TiCl_4$, respectively. These have been found to be simple 1:1 (acid : base) adducts of composition $(RO)_3$ SiNHNHPh.MCl_4 (Table IV).

TABLE IV

Analytical data of compounds of N-trialkoxy silyl N'-phenyl hydrazine with tin(IV) and titanium(IV) chlorides at −40 to −60 °C

Compound	Analytical data % Found (Regd.)			
	Cl	Ti/Sn	Si	N
1. $(C_2H_5O)_3$ SiNHNHPh.$SnCl_4$	26.5 (26.7)	22.1 (22.4)	5.3 (5.2)	5.1 (5.2)
2. $(C_2H_5O)_3$ SiNHNHPh.$TiCl_4$	30.6 (30.8)	10.3 (10.4)	5.8 (6.1)	6.1 (6.1)
3. $(C_3H_7O)_3$ SiNHNHPh.$SnCl_4$	24.7 (24.8)	20.6 (20.8)	4.7 (4.8)	4.3 (4.8)
4. $(C_3H_7O)_3$ SiNHNHPh.$TiCl_4$	28.1 (28.3)	9.3 (9.5)	5.3 (5.5)	5.2 (5.5)
5. $(C_4H_9O)_3$ SiNHNHPh.$SnCl_4$	23.1 (23.1)	18.8 (19.3)	4.2 (4.5)	4.7 (4.5)
6. $(C_4H_9O)_3$ SiNHMHPh.$TiCl_4$	25.9 (26.1)	8.6 (8.8)	5.2 (5.1)	5.0 (5.1)

Infrared Spectra—The infrared spectral data are similar to those obtained above, showing a negative spectral shift in the νNH frequency while νSi–O–(C), δSiO(C), C=C (skeletal) and νMCl frequencies are at their usual positions (1080–1060, 470, 1590, 750 and 380–320cm^{-1} respectively). In this case there is not much change in the absorption intensities of νSiO(C) and ring modes as compared to the parent ligand.

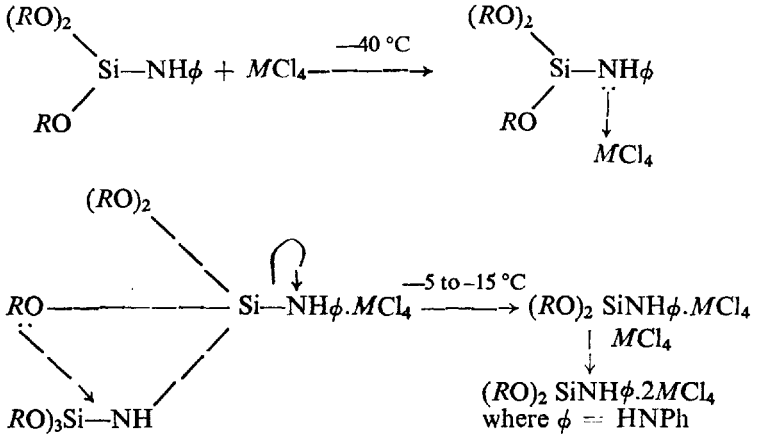
PMR Spectra—PMR spectra show the presence of CH_3, CH_2, CH_2O, SiNH, NHPh and C_6H_5 groups at ~ 0.8, 1.2, 3.6, 3.8, 5.0 and 7.3ppm respectively. Proton count ratios show the base to be $(RO)_3$ SiNHNHPh in the adducts. All these data show that normal 1:1 adducts are formed at these temperatures. The nature of the ligands in these complexes are further confirmed by ligand exchange reaction as reported above.

TABLE V

NMR spectral data of compounds of N-trialkoxy silyl N'-phenyl hydrazines with tin(IV) and titanium(IV) chlorides at –40 to –60 °C

	Compounds	Chemical shifts (δ) ppm					
		CH_3	CH_2	CH_2O	SiNH	NHPh	C_6H_5
1.	(CH_3CH_2O) $SiNHNHC_6H_5.MCl_4$	1.1 (*t*, 9H)		3.6 (*q*, 6H)	3.8 (*s*, 1H)	5.0 (*s*, 1H)	7.4 (*m*, 5H)
2.	$(CH_3CH_2CH_2O)$ $SiNHNHC_6H_5.MCl_4$	0.7 (*t*, 9H)	1.4 (*q*, 6H)	3.5 (*t*, 6H)	3.8 (*s*, 1H)	4.9 (*s*, 1H)	7.4 (*m*, 5H)
3.	$(CH_3CH_2CH_2CH_2O)_3$ $SiNHNHC_6H_5.MCl_4$	0.8 (*t*, 9H)	1.2 (*m*, 12H)	3.4 (*t*, 6H)	3.8 (*s*, 1H)	4.8 (*s*, 1H)	7.2 (*m*, 5H)

Accordingly, the mechanism of the reaction may be proposed as :



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