

Coordination Compounds of Organometallic Bases of Group(IV) Elements: Part XI—Reactions of N,N'-(Phenyl/*o*-chlorophenyl/*p*-methylphenyl/ benzyl/diethyl)-1,1-di-*n*-propoxy/*n*-butoxy-silanediamines† with Tin(IV) & Titanium(IV) Chlorides at –10°C

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The title reactions in 1:1 molar ratio in petroleum ether (40-60°) afford adducts having rearranged bases with composition $[(RO)_2Si(NHR')_{4-n} \cdot xMCl_4]$ where $R = C_3H_7$ or $n-C_4H_9$; $R' = C_6H_5CH_2$, *o*-ClC₆H₄ or *p*-CH₃C₆H₄; $n = 0$ or 1; and $x = 2$ or 3 as evidenced by elemental analyses, IR and PMR spectral data as well as base exchange reactions. Filtrates of these reactions after keeping at room temperature for 48-72 hr, give solid complexes of the type $[(RO)_2Si(NHR')_2 \cdot 2MCl_4]$ in each case. The reaction with the tertiary amines such as N,N'-diethyl-1,1-di-*n*-propoxy/di-*n*-butoxysilanediamine form normal 1:1 adducts $[(n-C_3H_7O/n-C_4H_9O)_2 Si[N(CH_2CH_3)_2]_2 \cdot MCl_4]$ and no base rearrangement is observed. A tentative mechanism of the disproportionation reactions is proposed.

The conversion of triorganoxy/organo-organoxy-silanamines into organoxy/organo-silanetriamines and even into silanetetramines in the presence of titanium(IV) and tin(IV) chlorides and antimony (III) halides, has been demonstrated by us¹⁻⁶. It has further been shown that the electronic and steric effects of substituents on silicon and nitrogen atoms significantly influence the conversion into silane polyamines⁴⁻⁷. For example N-(2-fluorophenyl)-1,1,1-trialkoxo silanamine is converted into N,N'-(2-fluorophenyl)-1,1-dialkoxo silanediamine while N-*n*-butyl/*p*-methylphenyl-1-chloro-1,1-dialkoxo silanamines are converted into N,N', N'',N'''-(*p*-methylphenyl/*n*-butyl)silanetetramines⁶. However, these studies have so far been confined to secondary silanamines $[(RO)_3SiNHR']$ containing single Si-N bond. With a view to checking the general validity of such reactions, it was thought appropriate to extend these investigations to other Si-N compounds. One such strategy is to attempt these reactions with secondary silanediamines $[(RO)_2Si(NHR')_2]$ and tertiary silanediamines $[(RO)_2Si(NR'_2)_2]$. The results of these studies are being reported here.

Materials and Methods

All experiments were carried out at –10°C under dry nitrogen atmosphere. The solvents used were dried by conventional methods. Tin(IV) and titanium(IV) chlorides (Reidel, pure) were distilled before use.

Infrared spectra were recorded in nujol on a

Perkin-Elmer model 621, double beam grating spectrophotometer having NaCl/KBr optics and PMR spectra in CDCl₃ + DMSO-*d*₆ on a Varian 390, 90 MHz instrument; chemical shifts are in δ -scale downfield from TMS internal reference.

The constant reaction temperature (–10°) of the bath was maintained using "cryo cool" model CC-100 II Neslab, Italy.

The ligands, N,N'-(phenyl/*o*-chlorophenyl/*p*-methylphenyl/benzyl/diethyl)-1,1-di-*n*-propoxy/di-*n*-butoxysilanediamines were prepared by the reaction of corresponding dichlorosilanes with amines in 1:4 molar ratio in dry diethyl ether at 0°C. The filtrates obtained after removal of the amine hydrochlorides were fractionally distilled under reduced pressure. All these silanediamines were characterised and their purity checked by IR and PMR spectral data.

Reactions of ligands with tin(IV) and titanium(IV) chlorides

Addition of a solution of tin(IV) or titanium(IV) chloride in petroleum ether to a solution of a silanediamine in the same solvent at –10°C in equimolar ratios resulted in the precipitation of a solid compound in each case. The compounds were filtered in the cold, washed and dried under reduced pressure. The filtrates on standing at room temperature for 48-72 hr afforded another solid in each case which was isolated as above and characterised.

Base exchange reactions

The above complexes (10 mmol) were added to

†Nomenclature in accordance with IUPAC rules

Table 1—Analytical Data of Complexes of N,N'-Organo-1,1-(diorganoxy)silanediamines

Sl No.	Compound	Found (Reqd) (%)			
		Cl	Ti/Sn	Si	N
1.	(PrO)Si(NHC ₆ H ₅) ₃ .2TiCl ₄	38.0 (38.22)	12.8 (12.92)	3.4 (3.77)	5.54 (5.65)
2.	(PrO)Si(NHC ₆ H ₅) ₃ .2SnCl ₄	32.21 (32.09)	26.70 (26.89)	2.91 (3.16)	4.65 (4.74)
3.	(BuO)Si(NHC ₆ H ₅) ₃ .2TiCl ₄	37.41 (37.52)	12.43 (12.68)	3.6 (3.7)	5.35 (5.55)
4.	(BuO)Si(NHC ₆ H ₅) ₃ .2SnCl ₄	31.41 (31.59)	26.35 (26.47)	2.99 (3.11)	4.53 (4.67)
5.	Si(NHC ₆ H ₄ CH ₃ - <i>p</i>) ₄ .3TiCl ₄	41.75 (41.68)	14.29 (14.09)	2.4 (2.74)	5.38 (5.48)
6.	Si(NHC ₆ H ₄ CH ₃ - <i>p</i>) ₄ .3SnCl ₄	34.2 (34.49)	28.4 (28.9)	2.15 (2.27)	4.40 (4.53)
7.	(PrO)Si(NHC ₆ H ₄ Cl- <i>o</i>) ₃ .2TiCl ₄	33.43 (33.55)	11.2 (11.34)	3.2 (3.31)	4.8 (4.96)
8.	(PrO)Si(NHC ₆ H ₄ Cl- <i>o</i>) ₃ .2SnCl ₄	28.4 (28.73)	23.79 (24.07)	2.57 (2.83)	4.12 (4.25)
9.	(BuO)Si(NHC ₆ H ₄ Cl- <i>o</i>) ₃ .2TiCl ₄	32.72 (33.0)	10.9 (11.16)	3.0 (3.25)	4.75 (4.88)
10.	(BuO)Si(NHC ₆ H ₄ Cl- <i>o</i>) ₃ .2SnCl ₄	28.19 (28.32)	23.59 (23.74)	2.60 (2.79)	4.10 (4.19)
11.	(PrO)Si(NHCH ₂ C ₆ H ₅) ₃ .2TiCl ₄	36.0 (36.18)	12.10 (12.23)	3.45 (3.51)	5.25 (5.35)
12.	(PrO)Si(NHCH ₂ C ₆ H ₅) ₃ .2SnCl ₄	30.57 (30.64)	26.35 (25.67)	2.94 (3.02)	4.44 (4.53)
13.	(PrO) ₂ Si[N(C ₂ H ₅) ₂] ₂ .TiCl ₄	29.72 (29.58)	10.14 (10.00)	5.62 (5.83)	5.79 (5.83)
14.	(BuO) ₂ Si[N(C ₂ H ₅) ₂] ₂ .TiCl ₄	27.72 (27.95)	9.52 (9.45)	5.39 (5.51)	5.47 (5.51)
15.	(PrO) ₂ Si[N(C ₂ H ₅) ₂] ₂ .SnCl ₄	25.57 (25.77)	21.51 (21.60)	4.98 (5.08)	5.01 (5.08)
16.	(BuO) ₂ Si[N(C ₂ H ₅) ₂] ₂ .SnCl ₄	24.69 (24.52)	20.42 (20.55)	4.67 (4.84)	4.87 (4.84)

ethylenediamine (25 mmol), molten 2,2'-bipyridyl (25 mmol) or pyridine-*d*₅ (25 mmol) under dry nitrogen atmosphere and kept at 35-40°C for 5-6 hr. Thereafter dry carbon tetrachloride was added, filtered, and the solids obtained identified by the chemical shifts and proton counts.

Results and Discussion

Analytical data (Table 1) of the adducts conform to the composition [(RO)Si(NHR')₃.2MCl₄] except in the case of the ligands N,N'-*p*-methylphenyl-1,1-di-*n*-propoxy/*n*-butoxysilanediamines and N,N'-diethyl-1,1-di-*n*-propoxy/*n*-butoxysilanediamines. Whereas the former affords adducts of the type Si(NHC₆H₄CH₃-*p*)₄.3MCl₄, the latter forms normal 1:1 adducts and no rearrangement is observed in the ligands. All the adducts are extremely hygroscopic and insoluble in common organic solvents except DMSO.

Infrared spectra

Infrared spectra of adducts [(RO)₂Si(NR')₂.2MCl₄], [(RO)Si(NHR')₃.2MCl₄] and [Si(NHR')₄.3MCl₄] are similar to those already reported⁶. However, the IR spectra of 1:1 adducts [*n*-C₃H₇O/*n*-C₄H₉O]₂Si(NCH₂CH₃)₂.MCl₄ display νCO and νSiO(C) modes at 1080 and 1020-30 cm⁻¹ respectively. The νCN (aliphatic) modes at 1290 cm⁻¹ in these ligands undergo shift to lower wavenumbers (Δν = 15-20 cm⁻¹) indicating coordination through nitrogen atom. The bands at 300 and 375 cm⁻¹ have been assigned to coordinated νSnCl and νTiCl modes of the Lewis acids used.

PMR spectra

The chemical shift (δ) values along with the number of protons for each group are recorded in Table 2. From a comparison of proton counts of the parent ligand with those of the ligands in the

Table 2—PMR Spectral Data of Complexes of N,N'-(Phenyl/*o*-chlorophenyl/*p*-methylphenyl/benzyl/diethyl)-1,1-diorganoxy-silanediamines with Tin(IV) and Titanium(IV) Chlorides

Complexes*	CH ₃	CH ₂	CH ₂ O	CH ₂ N	NH	C ₆ H ₅ /C ₆ H ₄ ring CH ₃
1,2	0.85 (t, 3H)	1.2 (m, 2H)	3.6 (t, 2H)	—	4.2 (s, 3H)	7.4 (m, 15H)
3,4	0.90 (t, 3H)	1.2 (m, 4H)	3.5 (t, 2H)	—	4.1 (s, 3H)	7.45 (m, 15H)
7,8	0.85 (t, 3H)	1.15 (m, 2H)	3.5 (t, 2H)	—	4.3 (s, 3H)	7.4 (m, 12H)
9,10	0.8 (t, 3H)	1.2 (m, 4H)	3.55 (t, 2H)	—	4.2 (s, 3H)	7.35 (m, 12H)
5,6	—	—	—	—	4.35 (s, 4H)	7.5 (m, 16H) 2.25 (s, 12H)
11,12	0.8 (t, 3H)	1.4 (q, 2H)	3.55 (t, 2H)	4.05 (s, 6H)	1.5 (s, 3H)	7.35 (s, 15H)
13,15	0.8 (t, 6H)	1.4 (m, 12H)	3.6 (t, 4H)	2.85 (q, 8H)	—	—
14,16	0.85 (t, 6H)	1.4 (m, 14H)	3.6 (t, 4H)	2.90 (q, 8H)	—	—

*Sl nos refer to complexes listed in Table 1

adducts, it is apparent that the proton count due to alkylamino/anilino moieties in the ligands of the adducts have undergone three to four fold increase. On the other hand the proton count due to alkoxy groups in the adducts have suffered corresponding decrease. This shows that on reaction the ligands are disproportionated to alkoxy-silane-tetramines or silane-tetramines, which are precipitated as the adducts. However, no such change is observed in the adducts of the tertiary amines such as (*n*-C₃H₇O/*n*-C₄H₉O)₂Si [N(CH₂CH₃)₂]₂. This observation indicates that no base rearrangement occurs for the ligand in tertiary silanamine which is contrary to the observations in secondary silanamine reactions.

Base exchange reaction

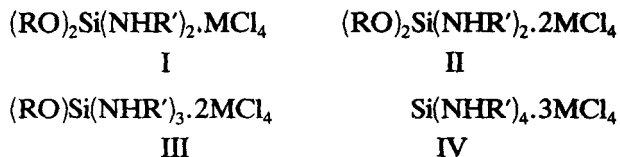
Further evidence in support of the compositions of the adducts is provided by the results of the base exchange reactions. Using the stronger electron donors such as 2,2'-bipyridyl, pyridine-*d*₅ and ethylenediamine in carbon tetrachloride separately, the silanamines could be regenerated and their identity confirmed through IR and PMR spectra.

From the foregoing data, it is apparent that under the same experimental conditions, the silane-diamines like, silanamines¹⁻⁶ are converted into silane-triamines. N,N'-(*p*-Methylphenyl)-1,1-dialkoxy-silane-diamines are rearranged to silane-tetramines⁷. The liberated silanamine from (*n*-C₃H₇O/*n*-C₄H₉O)₂Si[N(CH₂CH₃)₂]₂.MCl₄ is the original base molecule, which supports the view that tertiary silanamines do not undergo disproportionation in these donor-acceptor reactions.

Complexes isolated from filtrates

The filtrates of the above reactions at room temperature after 48-72 hr, afford another solid (15-20%), in each case. The composition of these compounds as evidenced by elemental analyses (Table 3), IR spectra [νNH 3200; νCO 1100-1080; νSiO(C) 1060 cm⁻¹], PMR spectra [CH₃, CH₂, CH₂O, C₆H₅, C₆H₅Cl and CH₃(Ph) proton signals at 0.8 to 0.9, 1.3 to 1.4, 3.6 to 3.8, 6.8 to 7.5 and 2.4 ppm respectively along with proton integration] corresponds to (OR)₂Si(NHR')₂.2MCl₄. These adducts have also been isolated from the filtrates of the similar reactions of N-organo-1-chloro-1,1 dialkoxy-silane-amines⁶. In the case of N,N'-diethyl-1,1-dialkoxy-silane-diamines, only the residual normal 1:1 adducts were obtained.

The donor-acceptor reactions of organoxy-silane-amines studied so far¹⁻⁷, give adducts I-IV as the major reaction products.



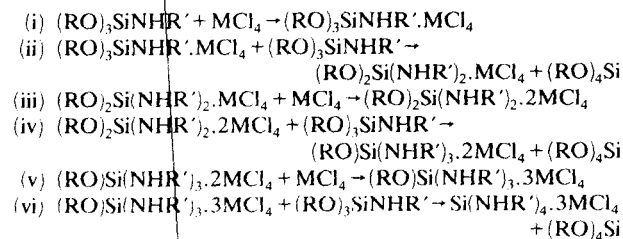
Adducts (I) are obtained⁴ from the ligands [(RO)₃SiNHR'] (R = ClC₂H₄; R' = C₆H₅/C₆H₅CH₂ and R = CF₃CH₂; R' = C₆H₄F/C₆H₃F₂). Adducts (II) are formed⁴ from the ligand having mixed 2-chloroethoxy and *n*-propoxy/*n*-butoxy groups on silicon atom and R' = C₆H₅/C₆H₅CH₂. Adducts (III) are most common of the complexes isolated and are obtained from ligands having different R and

Table 3—Analytical Data of Complexes Isolated from Filtrates

Compound	Found (Reqd) %			
	Cl	Ti/Sn	Si	N
(PrO) ₂ Si(NHC ₆ H ₅) ₂ .2TiCl ₄	39.72 (40.0)	13.4 (13.52)	3.7 (3.94)	3.8 (3.94)
(PrO) ₂ Si(NHC ₆ H ₅) ₂ .2SnCl ₄	33.16 (33.33)	27.7 (27.93)	3.0 (3.29)	3.2 (3.29)
(BuO) ₂ Si(NHC ₆ H ₅) ₂ .2TiCl ₄	38.3 (38.48)	12.85 (13.01)	3.7 (3.79)	3.65 (3.79)
(BuO) ₂ Si(NHC ₆ H ₅) ₂ .2SnCl ₄	32.02 (32.27)	27.16 (27.04)	2.9 (3.18)	3.22 (3.18)
(PrO) ₂ Si(NHC ₆ H ₄ Cl-o) ₂ .2TiCl ₄	36.29 (36.45)	12.24 (12.34)	3.7 (3.59)	3.65 (3.59)
(PrO) ₂ Si(NHC ₆ H ₄ Cl-o) ₂ .2SnCl ₄	30.95 (30.84)	25.7 (25.84)	2.8 (3.04)	3.16 (3.04)
(BuO) ₂ Si(NHC ₆ H ₄ Cl-o) ₂ .2TiCl ₄	35.05 (35.19)	11.7 (11.89)	3.27 (3.47)	3.42 (3.47)
(BuO) ₂ Si(NHC ₆ H ₄ Cl-o) ₂ .2SnCl ₄	29.85 (29.93)	25.12 (25.08)	2.9 (2.95)	3.01 (2.95)
(PrO) ₂ Si(NHC ₆ H ₄ CH ₃ -p) ₂ .2TiCl ₄	38.35 (38.48)	12.90 (13.01)	3.68 (3.79)	3.12 (3.79)
(PrO) ₂ Si(NHC ₆ H ₄ CH ₃ -p) ₂ .2SnCl ₄	32.14 (32.27)	27.15 (27.04)	3.02 (3.18)	3.12 (3.18)
(BuO) ₂ Si(NHC ₆ H ₄ CH ₃ -p) ₂ .2TiCl ₄	36.91 (37.07)	12.40 (12.53)	3.39 (3.65)	3.59 (3.65)
(BuO) ₂ Si(NHC ₆ H ₄ CH ₃ -p) ₂ .2SnCl ₄	31.15 (31.27)	26.07 (26.21)	3.21 (3.08)	3.01 (3.08)
(PrO) ₂ Si(NHCH ₂ C ₆ H ₅) ₂ .2TiCl ₄	38.39 (38.48)	12.89 (13.01)	3.58 (3.79)	3.65 (3.79)
(PrO) ₂ Si(NHCH ₂ C ₆ H ₅) ₂ .2SnCl ₄	32.35 (32.27)	26.92 (27.04)	3.0 (3.18)	3.11 (3.18)

R' groups¹⁻⁶. Adducts (IV) are rare and are obtained as in the present case as well as when R=CF₃CH₂; R'=C₆H₄F. However, the present report and the literature observations also record the precipitation of adducts (II) as the minor products from the filtrates during the formation of III and IV. Even adduct III has been found in small amounts in the reaction giving IV as the main product⁸.

Thus adducts (II) and (III) may be presumed to be the unconsumed intermediate products leading to the formation of the appropriate silane polyamines. The tentative mechanism may therefore, be written as shown in the Scheme 1.



Scheme (1)

As mentioned above, adducts I-IV are stable and isolable under appropriate experimental conditions. However, the adducts (RO)₃SiNHR'.MCl₄ and (RO)₃Si(NHR')₃.3MCl₄ have not yet been isolated and/or identified. In the case of tertiary silanamines the reaction stops after the first reaction and affords only 1:1 adducts.

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