Inorganica Chimica Acta, 73 (1983) 183–187

Coordination Compounds of Organometallic Bases of Group IV Elements. Part VII*, **Reactions of Organoamino Triorganoxy/Di-n-butoxy Phenyl Silanes with Titanium(IV) Chloride

SURAJ P. NARULA and (MISS) NEETA KAPUR

Department of Chemistry, Panjab University, Chandigarh-160014, India

Received February 4, 1983

Benzylamino triethoxy/tri-n-propoxy/tri-n-butoxy/triphenoxy/di-n-butoxy phenyl silanes, anilino tri-n-propoxy/triphenoxy silanes or n-butylamino triphenoxy silane in carbon tetrachloride, petroleum ether or dichloromethane react with $TiCl_4$ in the same solvent at –20 to –5 °C to give compounds of composition $RSi(NHR')_3\cdot 2TiCl_4$ (where R = OEt, OPr-n, OBu-n, OPh or Ph and R' = CH_2Ph, Ph or Bu-n) and tetraalkoxy/tetraphenoxy/phenyl tri-n-butoxy silanes. Structure of the complexes is determined by elemental analyses, infrared and ^1H n.m.r. spectroscopy. These reactions are proposed to involve disproportionation of ligands.

Similar reaction with $(PhO)Et_2SiNHCH_2C_6H_5$ has resulted in the formation of $Et_2Si(NHCH_2C_6H_5)_2\cdot 2TiCl_4$ while $Me_3SiNHCH_2C_6H_5$ gives a 1:1 product ($Me_3SiNHCH_2C_6H_5\cdot TiCl_4$). This suggests that at least one alkoxy group is necessary for this type of reaction.

A few Lewis acids are now known to form coordination compounds with hexamethyl disilazane, cyclosilazanes and amino organo silanes [1–5]. With amino tri-t-butyl silane even protonic acids are found to form stable adducts [6]. Various coordination complexes of amino organoxysilanes have also been isolated and nitrogen is proposed to be the reaction site [7]. The relative strength of these bases has been determined thermochemically and is found to be dependent upon the inductive (+I) effect of substituents on silicon atoms [8]. However, detailed investigations of the reactions of common Lewis acids with organoamino triorganoxy/organo organoxy silanes are lacking. Presently, such reactions with titanium(IV) chloride have afforded new products. The results of these reactions are reported here.

Results and Discussion

The adducts are yellow or orange yellow solids insoluble in most common organic solvents, and are extremely sensitive to air and moisture. Elemental analyses conform to the composition, $RSi(NHR')_3\cdot 2TiCl_4$ (where R = OEt, OPr-n, OBu-n, OPh or Ph and R' = CH_2Ph, Ph or Bu-n). On hydrolysis, these complexes are quantitatively converted into the amines, alcohols/phenol, SiO_2 *etc.* However, all attempts to crystallise these adducts failed.

The filtrates obtained from these reactions, on removal of solvents, leave behind a liquid residue in each case. Elemental analyses, infrared and ^1H n.m.r. spectral data [1070–1020 s (ν_{as} Si–O–C)) 480–470 m (δSi–O(C)) cm^{-1}; δ = 0.9 (t, CH_3), 1.2 (q or m CH_2), 3.8 (t, OCH_2) ppm or 1250–1240 (ν_{as} OPh) cm^{-1} δ = 7.1 (m, C_6H_5) ppm] suggest them to be tetraalkoxy, tri-n-butoxy phenyl or tetraphenoxy silanes.

From the above data, the following reaction may be thought to occur:

$$3(RO)_{3-n}R_nSiNHR' + 2TiCl_4 \longrightarrow RSi(NHR')_3\cdot 2TiCl_4 + 2(RO)_{4-n}SiR_n \quad (n = 0 \text{ or } 1)$$

Spectral Studies of the Adducts

Infrared Spectra

νNH modes of the ligand are observed to undergo negative spectral shift from 3380–3320 to 3180–3110 cm^{-1}. Other prominent bands such as ν_{as} SiO–(C), δSiO(C), ν_{as} OPh (wherever applicable)

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*Part VI: *Inorg. Chim. Acta, 76,* L7 (1983).

**Part of the work was presented at the Xth International Conference on Organometallic Chemistry held at Toronto (Canada) on 9–14 August, 1981.

0020-1693/83/$3.00

TABLE I. Infrared Spectral Data of Adducts of Organoamino triorganoxy/di-n-butoxy phenyl/phenoxy diethyl Silanes with Titanium(IV) Chloride.[a]

$B \cdot 2TiCl_4$ (cm^{-1})	$B' \cdot 2TiCl_4$ (cm^{-1})	$B'' \cdot 2TiCl_4$ (cm^{-1})	$B''' \cdot 2TiCl_4$ (cm^{-1})	Assignments
3150–3120s	3175–3150s	3180s	3155–3150s	νNH
1590–1580s	1590–1575s	1570w	1565–1560s	C=C (skeletal)
–	–	–	1430m	νSi–Ph
–	1275–1270s	–	–	ν_{CN} (aromatic)
1240w	1255w	1245w	–	ν_{as} OPh
1220–1210s	–	1215s	1215–1210s	ν_{CN} (aliphatic)
1080–1065w	1075w	–	–	ν_{as} SiO(C)
–	–	–	840	νSi–C
480–465w	470w	–	–	δSiO(C)
390–380m	380m	385m	380–385m	νTiCl

[a] $B = (RO)Si(NHCH_2Ph)_3$ where R = Et, Pr-n, Bu-n, Ph; $B' = (n\text{-}PrO)Si(NHPh)_3$ or $(PhO)Si(NHPh)_3$, $B'' = (PhO)Si(NHBu\text{-}n)_3$ and $B''' = PhSi(NHCH_2Ph)_3$ or $Et_2Si(NHCH_2Ph)_2$.

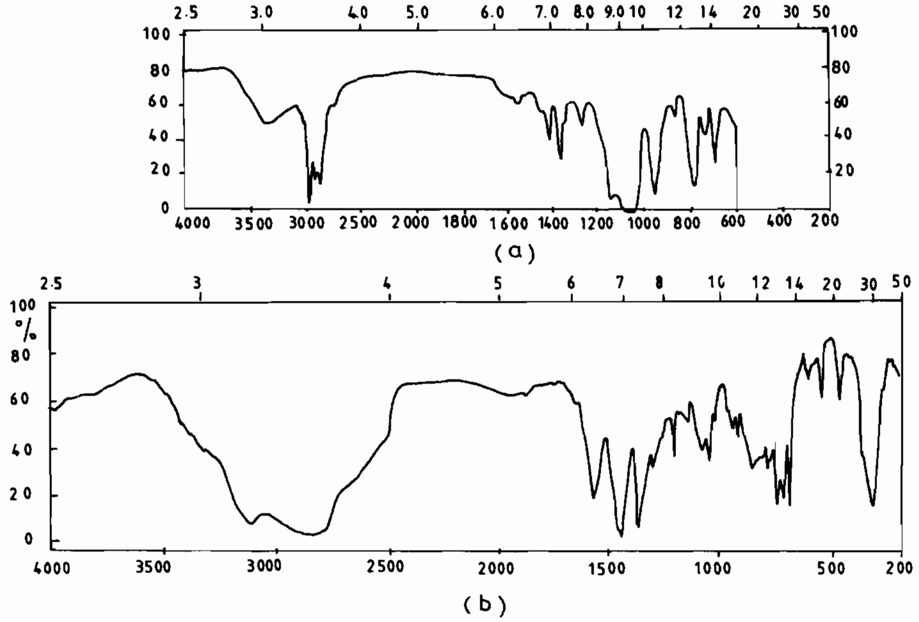

Fig. 1. Infrared spectra of (a) $(C_2H_5O)_3SiNHCH_2C_6H_5$, (b) $(C_2H_5O)\ Si(NHCH_2C_6H_5)_3 \cdot 2TiCl_4$.

C=C (skeletal) observed at 1080–1065, 480–465, 1255–1240 and 1590–1560 cm^{-1} of the ligands do not show spectral shift on reactions. However, ν_{as}-SiO(C) and ν_{as}OPh bands undergo diminution in intensity on adduct formation (Fig. 1). The complete infrared data of the adducts are given in Table I. The above observations may qualitatively suggest the change in the number of alkoxy/phenoxy groups of the ligands on complexation. νTiCl bands have been located at ~380 cm^{-1}. Amino triorganoxy/organo organoxy silanes are proposed to coordinate through nitrogen. On the basis of the arguments already reported [7], donation through nitrogen is also expected here.

^{1}*H N.m.r. Spectra*

The extreme insolubility of these complexes in the commonly available deuterated solvents have eluded direct evidence for the structure of the complexes through these spectra. Since the adducts are quantita-

TABLE II. ^{1}H N.m.r. Spectral Data of Adducts of Organoamino triorganoxy/di-n-butoxy phenyl/phenoxy diethyl Silanes with Titanium(IV) Chloride in D_2O.*

$L \cdot 2TiCl_4$	Chemical Shifts (δ)				
	a	b	c	d	e
$(CH_3CH_2O)Si(NHCH_2C_6H_5)_3$ a b c d	1.1 (3H,t)	3.3 (2H,q)	4.1 (6H,s)	7.4 (15H,s)	–
$(CH_3CH_2CH_2O)Si(NHCH_2C_6H_5)_3$ a b c d e	0.8 (3H,t)	1.3 (2H,q)	3.4 (2H,t)	4.0 (6H,s)	7.4 (15H,s)
$(CH_3CH_2CH_2CH_2O)Si(NHCH_2C_6H_5)_3$ a b b c d e	0.9 (3H,t)	1.5 (4H,m)	3.5 (2H,t)	4.1 (6H,s)	7.5 (15H,s)
$(C_6H_5O)Si(NHCH_2C_6H_5)_3$ a b c	7.0 (5H,m)	4.1 (6H,s)	7.4 (15H,s)	–	–
$(C_6H_5O)Si(NHCH_2CH_2CH_2CH_3)_3$ a b c c d	7.1 (5H,m)	3.0 (6H,t)	1.5 (12H,m)	0.9 (9H,t)	–
$(CH_3CH_2CH_2O)Si(NHC_6H_5)_3$ a b c d	0.9 (3H,t)	1.4 (2H,q)	3.5 (2H,t)	7.4 (15H,m)	–
$(C_6H_5O)Si(NHC_6H_5)_3$ a b	7.1 (5H,m)	7.4 (15H,m)			
**$C_6H_5Si(NHCH_2C_6H_5)_3$ a b	4.0 (6H,s)	7.4 (15H,s)			
**$(C_2H_5)_2Si(NHCH_2C_6H_5)_2$ a b	4.1 (4H,s)	7.4 (10H,s)			

*L = B, B′, B″ or B‴ (as in Table I). **In these complexes phenyl and ethyl protons could not be observed probably due to incomplete cleavage of Si–C bonds under these conditions. The signals due to NH protons are not observed due to $^1H-^2D$ exchange.

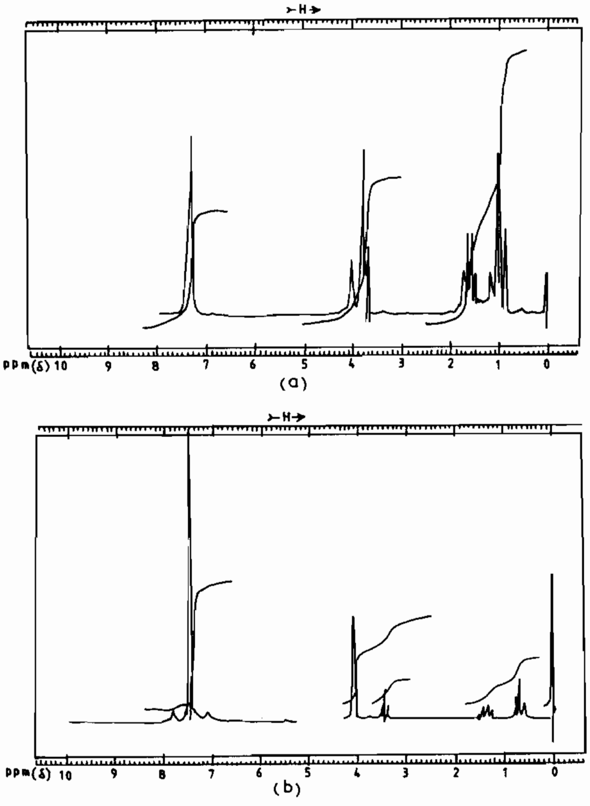

Fig. 2. ^{1}H n.m.r. spectra of (a) $(C_3H_7O)_3SiNHCH_2C_6H_5$, (b) $C_3H_7O\ Si(NHCH_2C_6H_5)_3 \cdot 2TiCl_4$.

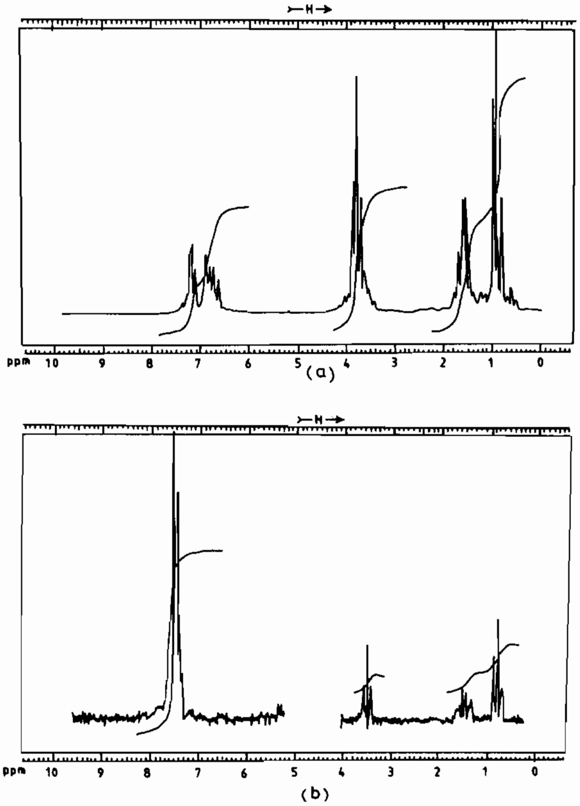

Fig. 3. ^{1}H n.m.r. spectra of (a) $(C_3H_7O)_3SiNHC_6H_5$, (b) $C_3H_7O\ Si(NHC_6H_5)_3 \cdot 2TiCl_4$.

TABLE III. Analytical Data of Adducts of Organoamino triorganoxy/di-n-butoxy phenyl and phenoxy diethyl Silanes with Titanium(IV) Chloride.

Reactants	Products	Analytical Data			
		%Cl Found (Calc)	%Ti Found (Calc)	%Si Found (Calc)	%N Found (Calc)
$(EtO)_3SiNHCH_2Ph + TiCl_4$	$(EtO)Si(NHCH_2Ph)_3 \cdot 2TiCl_4$	37.2 (36.8)	12.4 (12.5)	3.3 (3.6)	5.1 (5.4)
$(PrO)_3SiNHCH_2Ph + TiCl_4$	$(PrO)Si(NHCH_2Ph)_3 \cdot 2TiCl_4$	35.8 (36.1)	12.4 (12.2)	3.5 (3.5)	5.6 (5.3)
$(BuO)_3SiNHCH_2Ph + TiCl_4$	$(BuO)Si(NHCH_2Ph)_3 \cdot 2TiCl_4$	36.1 (35.5)	12.2 (12.0)	3.8 (3.5)	4.9 (5.2)
$(PhO)_3SiNHCH_2Ph + TiCl_4$	$(PhO)Si(NHCH_2Ph)_3 \cdot 2TiCl_4$	34.5 (34.6)	11.7 (11.7)	3.3 (3.4)	5.2 (5.1)
$(PrO)_3SiNHPh + TiCl_4$	$(PrO)Si(NHPh)_3 \cdot 2TiCl_4$	37.8 (38.2)	13.1 (12.9)	3.6 (3.7)	5.7 (5.6)
$(PhO)_3SiNHPh + TiCl_4$	$(PhO)Si(NHPh)_3 \cdot 2TiCl_4$	36.1 (36.4)	12.1 (12.3)	3.2 (3.5)	6.0 (5.3)
$(PhO)_3SiNHBu + TiCl_4$	$(PhO)Si(NHBu)_3 \cdot 2TiCl_4$	39.7 (39.7)	13.2 (13.4)	4.0 (3.9)	6.0 (5.8)
$(BuO)_2PhSiNHCH_2Ph + TiCl_4$	$PhSi(NHCH_2Ph)_3 \cdot 2TiCl_4$	35.9 (35.3)	12.6 (12.0)	3.5 (3.4)	5.6 (5.2)
$(PhO)Et_2SiNHCH_2Ph + TiCl_4$	$Et_2Si(NHCH_2Ph)_2 \cdot 2TiCl_4$	41.2 (41.2)	13.8 (13.9)	4.0 (4.0)	4.1 (4.0)
$Me_3SiNHCH_2Ph + TiCl_4$	$Me_3SiNHCH_2Ph \cdot TiCl_4$	38.3 (38.4)	12.8 (13.0)	7.3 (7.5)	3.6 (3.8)

tively degraded into amines and alcohols on hydrolysis (see above), some light can be thrown on the structure of these complexes indirectly by recording the spectra in D_2O. Chemical shift (δ) values obtained for various adducts are given in Table II.

These values are in good agreement with those of the pure amines and alcohols/phenol taken separately in D_2O. Moreover, the above data clearly demonstrate the ratio of alkoxy/phenoxy and benzylamino/anilino/n-butylamino moieties to be 1:3 (on the basis of the proton counts) (Figs. 2 and 3). The adducts may, therefore, be reconstructed to be $RSi(NHR')_3 \cdot 2TiCl_4$.

A confirmation about the nature of the adducts comes from the actual isolation of these complexes from the reactions of tris(benzylamino)/tris(n-butylamino)ethoxy/phenoxy silanes and $TiCl_4$ in dichloromethane, carbon tetrachloride or petroleum ether in molar ratio 1:2. The adducts so obtained have the composition $(RO)Si(NHR)_3 \cdot 2TiCl_4$, and are identical in all respects with the corresponding complexes obtained above.

Whereas $Ph(BuO)_2SiNHCH_2C_6H_5$ on reaction gives $PhSi(NHCH_2C_6H_5)_3 \cdot 2TiCl_4$, the reaction of $(PhO)Et_2SiNHCH_2C_6H_5$ afforded only the bis(benzylamino)diethyl silane adduct $[Et_2Si(NHCH_2C_6H_5)_2 \cdot 2TiCl_4]$. A similar reaction with $Me_3SiNHCH_2C_6H_5$ resulted in the formation of only a direct 1:1 adduct and no disproportionation product is observed.

It may thus be concluded that organoamino triorganoxy/organo organoxy silanes undergo disproportionation to form tris(organoamino)organoxy/organo silane adducts of the composition given above. The presence of at least one organoxy group on the silicon atom is deemed necessary to bring about this transformation.

Experimental

All operations were carried out under dry nitrogen atmosphere. The solvents used were dried by conventional methods. Titanium(IV) chloride (Reidel, Pure) was distilled before use.

Infrared spectra were recorded on a Perkin Elmer-621 double-beam grating spectrophotometer as nujol thin films. ^1H N.m.r. spectra were obtained from a Varian EM (90 MHz) spectrometer in D_2O using TMS as external reference. The convention used for expressing the proton resonance is that the low field absorption is positive. Some of the compounds were analysed in fully automatic microanalytical service at UMIST, Manchester, England.

Most of the organoamino silanes used here are not known in the literature. These aminosilanes were obtained by the reactions of the corresponding chlorosilanes with amines according to the method reported [9]. The purity of these compounds was checked by elemental analyses, infrared and ^{1}H n.m.r. spectral data.

Reactions of Benzylamino Triethoxy/Tri-n-propoxy/Tri-n-butoxy/Triphenoxy/di-n-butoxy Phenyl/Phenoxy diethyl/Trimethyl Silanes, n-Butylamino Triphenoxy Silane and Anilino Tri-n-propoxy/Triphenoxy Silanes with Titanium(IV) Chloride

Titanium(IV) chloride in carbon tetrachloride, dichloromethane or petroleum ether was added dropwise into a solution of benzylamino triethoxy/tri-n-propoxy/tri-n-butoxy triphenoxy/di-n-butoxy phenyl/phenoxy diethyl/trimethyl silane, n-butylamino triphenoxy silane, anilino tri-n-propoxy or triphenoxy silane separately, in the same solvent at −20 to −5 °C and in the molar ratio (acid:base) 1:1.5. A solid compound was obtained in each case which was filtered cold, washed, dried and analysed. The relevant data are given in Table III.

After attaining the room temperature, the filtrate gave traces of a white solid which was washed, filtered and dried. This compound was invariably the cleaved product of the aminosilanes *i.e.* $TiCl_3NHR'$, as evidenced by elemental analyses and spectral data. The amount of this compound increased with temperature of the reaction.

The filtrates from the above reactions, on evaporating the solvents, gave a liquid residue in each case which was analysed for silicon. The analysis was in agreement* with tetra alkoxy/tri-n-butoxy phenyl/tetraphenoxy silanes.

Tris benzylamino/n-butylamino phenoxy/ethoxy silanes were obtained from the reactions of ethoxy/phenoxy trichlorosilanes and the corresponding amines. They were characterised by elemental analyses, infrared and ^{1}H n.m.r. spectra. The adducts of these amines were also prepared in the same way, as described above, using an acid:base ratio of 2:1.

Acknowledgement

One of the authors (NK) is grateful to UGC, New Delhi for the award of a junior research fellowship under the special assistance program in the department.

References

1 H. Schmidbaur and M. Schmidt, *Angew. Chem. Int. Ed., 1,* 327 (1962).

2 H. Nöth and M. J. Sprague, *J. Organometal. Chem., 22,* 11 (1970).

3 Yu. V. Kolodyazhnyi, M. G. Gruntfest, M. M. Morgunova, Yu. M. Varezhkin, D. Ya. Zhinkin and O. A. Osipov, *Zh. Obshch. Khim., 46* (12), 2710 (1976); *C.A., 86,* 82976 (1977).

4 Yu. V. Kolodyazhnyi, M. G. Gruntfest. L. S. Baturina, M. M. Morgunova, N. I. Sizova, G. S. Gol'din and O. A. Osipov, *Zh. Obshch. Khim., 45,* 1046 (1975); *C.A., 83,* 27381 (1974).

5 J. M. Miller and R. K. Chadha, *J. Organometal. Chem., 216,* 177 (1981).

6 L. H. Sommer and P. M. Nowakowski, *J. Organometal. Chem., 178,* 95 (1979).

7 R. C. Paul, V. K. Aggarwal, S. C. Ahluwalia and S. P. Narula, *Inorg. Nucl. Chem. Lett., 6,* 487 (1970).

8 R. C. Paul, K. S. Dhindsa, S. C. Ahluwalia and S. P. Narula, *J. Inorg. Nucl. Chem., 34,* 1813 (1972).

9 U. Wannagat, in 'Adv. in Inorg. and Radiochem.', Vol. 6, Ed. H. J. Emeleus and A. G. Sharpe, Academic Press, New York and London, 1964.

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*Traces of chloride ions were also observed in these liquids. The amount of these ions increased with increase in $TiCl_3$-NHR′ contents.