Inorganica Chimica Acta, *86* (1984) 37–40

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

SURAJ P. NARULA and NEETA KAPUR

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

Received October 7, 1983

The reactions of 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 with $SnCl_4$ *in the same solvent at −20 to −5 °C give solid compounds of composition* $(RO)/PhSi(NHR')_3 \cdot 2SnCl_4$ *and liquids* $Ph_n(RO)_{4-n}Si$ *[where R = Et, n-Pr, n-Bu or Ph; R′ = Ph,* CH_2Ph*, or n-Bu and n = 0 or 1] Elemental analyses, molar conductances, infrared and* ^1H *NMR spectra, ligand exchange reactions as well as the adduct formation by a different route point towards ligand disproportionation in these reactions and that the adducts are 1:1 electrolytes. The reaction of* $(PhO)Et_2SiNHCH_2C_6H_5$ *gives* $Et_2Si(NHCH_2C_6H_5)_2 \cdot 2SnCl_4$ *and* $(PhO)_2Et_2Si$ *while* $Me_3SiNHCH_2C_6H_5$ *gives a simple 1:1 adduct (non-electrolyte). Here also at least one alkoxy group is necessary for the reactions to occur.*

Introduction

Various coordination complexes of amino triorganoxy/organo-organoxy silanes of common Lewis acids have been isolated and nitrogen is proposed to be the donation site [1]. The relative strength of these bases has also been determined thermochemically [2]. Recently, we reported [3] the reactions of titanium(IV) chloride with benzylamino/anilino/n-butylamino triorganoxy/di-n-butoxy phenyl silanes, which have resulted in the isolation of some novel adducts. The formation of these complexes has been rationalised on the basis of disproportionation of the ligands, and it is proposed that at least one alkoxy group on silicon is necessary to bring about these reactions. With a view to check the general validity of these postulates, the work is extended to the reactions of tin(IV) chloride with the above mentioned amino silanes. This paper also reports ligand exchange reactions as an additional support for the disproportionation reaction already proposed [3].

Results and Discussion

The adducts are white hygroscopic solids, insoluble in most of the common organic solvents except for millimolar solubility in nitrobenzene. The molar conductances of these solutions suggest them to be 1:1 electrolytes. Elemental analyses reveal their compositions as $RO/PhSi(NHR')_3 \cdot 2SnCl_4$ (where R = Et, n-Pr, n-Bu or Ph and R′ = CH_2Ph, Ph or n-Bu). On hydrolysis, these complexes are quantitatively converted into the amines, alcohols/phenol, SiO_2, SnO_2, *etc.*

The removal of solvent from the filtrates of the reactions in question leaves behind a liquid residue in each case. Tetraalkoxy, tri-n-butoxy phenyl or tetraphenoxy silane so obtained have been identified by the methods already reported [3].

The reaction may be given as:

$$3Ph_n(RO)_{3-n}SiNHR' + 2SnCl_4 \longrightarrow RO/PhSi(NHR')_3 \cdot 2SnCl_4 + 2Ph_n(RO)_{4-n}Si$$

(n = 0 or 1)

Spectral Studies of the Adducts

Infrared Spectra

νNH modes of the ligands [3] undergo negative spectral shifts to 3175–3120 cm^{-1} on complexation. The bands such as $\nu_{as}SiO(C)$, $\delta SiO(C)$, $\nu_{as}OPh$

---

*Part VII., *Inorg. Chim. Acta, 73,* 183 (1983).

0020-1693/84/$3.00

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

$B\cdot 2SnCl_4$ (cm^{-1})	$B'\cdot 2SnCl_4$ (cm^{-1})	$B''\cdot 2SnCl_4$ (cm^{-1})	$B'''\cdot 2SnCl_4$ (cm^{-1})	Assignments
3150–3120s	3175–3150s	3180s	3133–3150s	νNH
1590–1580s	1590–1575s	1570w	1565–1560s	C=C (skeletal)
			1430m	νSi–Ph
	1275–1270s			νCN (aromatic)
1240w	1255w	1245w		$\nu_{as}OPh$
1220–1210s		1215s	1215–1210s	νCN (aliphatic)
1080–1065w	1075w			$\nu_{as}SiO(C)$
			840	νSi–C
480–465w	470w			δSiO(C)
310–290m	280m	285m	280–285m	νSnCl

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

TABLE II. ^1H NMR Spectral Data of Adducts of Organoamino triorganoxy/di-n-butoxy phenyl/phenoxy diethyl Silanes with Tin(IV) Chloride in D_2O.

$L\cdot 2SnCl_4$[a]	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)			
$(C_6H_5Si(NHCH_2C_6H_5)_3$[b] *a b*	4.0 (6H,s)	7.5 (15H,s)			
$(C_2H_5)_2Si(NHCH_2C_6H_5)_2$[b] *a b*	4.1 (4H,s)	7.4 (10H,s)			

[a] L = B, B' B'' or B''' (as in Table I). [b] 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.

(wherever applicable), *C=C* (skeletal) *etc.* of the ligands do not show spectral shift on adduct formation. As explained before [3], the diminution in intensity of $\nu_{as}SiO(C)$ or $\nu_{as}OPh$ bands may qualitatively suggest change in the number of alkoxy/phenoxy groups attached to silicon atom of the ligands on complexation. νSn–Cl bands have been located between 310–280 cm^{-1}. As indicated earlier [1, 3], donation through nitrogen is expected. The spectral data of the complexes are given in Table I.

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

Reactants	Product	Analytical data % Found/(Calc)				Molar Cond. (ohm^{-1} cm^2 mol^{-1})
		Cl	Sn	Si	N	
$(EtO)_3SiNHCH_2Ph + SnCl_4$	$(EtO)Si(NHCH_2Ph)_3 \cdot 2SnCl_4$	31.5 (31.1)	25.4 (26.0)	2.5 (3.0)	5.0 (4.6)	23.2
$(PrO)_3SiNHCH_2Ph + SnCl_4$	$(PrO)Si(NHCH_2Ph)_3 \cdot 2SnCl_4$	31.0 (30.6)	25.6 (25.4)	3.1 (3.0)	4.3 (4.5)	29.0
$(BuO)_3SiNHCH_2Ph + SnCl_4$	$(BuO)Si(NHCH_2Ph)_3 \cdot 2SnCl_4$	31.2 (30.3)	26.4 (25.2)	3.1 (2.9)	4.9 (4.5)	33.8
$(PhO)_3SiNHCH_2Ph + SnCl_4$	$(PhO)Si(NHCH_2Ph)_3 \cdot 2SnCl_4$	29.1 (29.5)	24.0 (24.5)	2.7 (2.9)	4.0 (4.3)	32.0
$(PrO)_3SiNHPh + SnCl_4$	$(PrO)Si(NHPh)_3 \cdot 2SnCl_4$	31.9 (32.0)	26.8 (26.8)	3.3 (3.2)	4.5 (4.7)	30.4
$(PhO)_3SiNHPh + SnCl_4$	$(PhO)Si(NHPh)_3 \cdot 2SnCl_4$	31.2 (30.8)	25.0 (25.5)	2.7 (3.0)	4.6 (4.5)	31.0
$(PhO)_3SiNHBu + SnCl_4$	$(PhO)Si(NHBu)_3 \cdot 2SnCl_4$	32.9 (33.0)	27.6 (27.8)	2.8 (3.2)	5.2 (4.9)	29.0
$(BuO)_2PhSiNHCH_2Ph + SnCl_4$	$PhSi(NHCH_2Ph)_3 \cdot 2SnCl_4$	29.3 (30.0)	24.6 (25.1)	2.5 (2.9)	4.1 (4.4)	28.0
$(PhO)Et_2SiNHCH_2Ph + SnCl_4$	$Et_2Si(NHCH_2Ph)_2 \cdot 2SnCl_4$	34.9 (34.6)	28.6 (29.0)	3.0 (3.4)	3.2 (3.4)	29.0
$Me_3SiNHCH_2Ph + SnCl_4$	$Me_3Si(NHCH_2Ph) \cdot SnCl_4$	32.0 (32.2)	26.6 (26.9)	6.1 (6.3)	3.0 (3.1)	

^{1}H NMR Spectra

Due to extreme insolubility of the complexes in commonly available deuterated solvents, the evidence of the structure of these complexes could be obtained only indirectly [3]. The chemical shift (δ) values of the complexes (degraded quantitatively into amines and alcohols) in D_2O are given in Table II. They are in excellent agreement with those of the amines and alcohols/phenol taken separately in D_2O. The amounts of amines and alcohols/phenol, as obtained from proton counts, are in the ratio 3:1. Thus the bases can be construed to be present in the adducts as $RO/PhSi(NHR')_3$.

The nature of the bases in the adducts can be further supported by the actual isolation of these adducts from tris (benzylamino/n-butylamino), ethoxy/phenoxy silanes 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 confirmation of the compositions of the adducts is obtained from ligand replacement reactions with 2,2'-bipyridyl and ethylene diamine, separately in carbon tetrachloride at 35–40 °C. Tris(benzylamino/n-butylamino/anilino) organoxy/phenyl silanes were obtained from the filtrates and identified by infrared and ^{1}H NMR spectroscopy.

Whereas the reaction with $Ph(BuO)_2SiNHCH_2Ph$ formed the $PhSi(NHCH_2Ph)_3 \cdot 2SnCl_4$ adduct, $(PhO)Et_2SiNHCH_2Ph$ gives only bis(benzylamino)diethyl silane complex $[Et_2Si(NHCH_2Ph)_2 \cdot 2SnCl_4]$ while $Me_3SiNHCH_2Ph$ results in the formation of simple non-electrolyte 1:1 adduct $[Me_3SiNHCH_2Ph \cdot SnCl_4]$ and no disproportionation product was isolated.

It is thus concluded that tin(IV) chloride also disproportionates the organoamino triorganoxy/di-n-butoxy phenyl silanes and at least one organoxy group is required to bring about this change. The adducts obtained here are ionic in nature in solution.

Experimental

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

Elemental analyses, infrared and ^{1}H NMR spectroscopic measurements were made as reported before [3].

The organoamino triorganoxy/di-n-butoxy phenyl silanes as well as tris(benzylamino/n-butylamino), ethoxy/phenoxy silanes were synthesised as described [4]. The purity of these compounds was checked by elemental analyses, infrared and ^{1}H NMR 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 Tin(IV) Chloride:

Tin(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, filtered cold, washed, dried and analysed. The relevant data are given in Table III.

After keeping the filtrate at room temperature for 2–3 h another white solid was obtained (30–40%, on the basis of $SnCl_4$ used) which was washed, filtered and dried. Elemental analyses and spectral data invariably suggested it to be the cleaved product of the amino silanes ($SnCl_3 \cdot NHR$). The amount of this product increased with rise in the reaction temperature.

The filtrates thus obtained, on evaporating solvents, gave a liquid residue in each case which was analysed for silicon. The elemental analyses and infrared and ^1H NMR spectra were in agreement with the compounds to be tetraalkoxy/tri-n-butoxy phenyl/tetraphenoxy and diphenoxy diethyl silanes.

The reactions of tris(benzylamino/n-butylamino), phenoxy/ethoxy silanes with tin(IV) chloride in molar ratio 1:2 were carried out in the manner already described. The adducts were isolated as mentioned above.

Ligand Exchange Reactions

The adducts (10 mmol) were added to ethylenediamine (25 mmol) or molten 2,2′-bipyridyl (25 mmol) in a round-bottom flask fitted with a reflux condenser having silica gel moisture guard tube and a dry nitrogen inlet tube. The reaction mixture was kept at 35–40 °C for 5–6 hours. Thereafter dry carbon tetrachloride (~30 ml) was added and the contents of the flask were filtered. The filtrate was concentrated and ^1H NMR spectra were taken. The tris(organoamino) organoxy/phenyl silane obtained was identified by the chemical shifts and proton counts.

Acknowledgement

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

References

1 R. C. Paul, V. K. Aggarwal, S. C. Ahluwalia and S. P. Narula, *Inorg. Nucl. Chem. Lett., 6,* 487 (1970).
2 R. C. Paul, K. S. Dhindsa, S. C. Ahluwalia and S. P. Narula, *J. Inorg. Nucl. Chem., 34,* 1823 (1972).
3 S. P. Narula and N. Kapur, *Inorg. Chim. Acta, 73,* 183 (1983).
4 U. Wannagat, in 'Adv. in Inorg. and Radiochem.', Vol. 6, Ed. H. J. Emeléus and A. G. Sharpe, Academic Press, New York and London, 1964.