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Coordination Compounds of Organometallic Bases of Group IV Elements: Part III†—Unusual Reactions of Benzylamino/*n*-butylamino-triethoxy/triphenoxy-silanes with Antimony(III) Halides

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Benzylamino/*n*-butylamino-triethoxy/triphenoxy-silanes and SbX_3($X = Cl$, Br) in chloroform at 0°C and SbI_3 in carbon tetrachloride at room temperature, react to give solid adducts of compositions $ROSi(NHR)_3.nSbX_3$ ($n = 1$ or 2) and $(C_2H_5O)_2Si(NHC_4H_9)_2.2SbCl_3$. The structure of these complexes has been established by elemental analyses, infrared and PMR spectroscopy. The bases are proposed to undergo disproportionation in these reactions.

A few Lewis acids are known to form coordination compounds with hexamethyldisilazane[1-5], cyclosilazane[6] and amino-tri-*t*-butylsilane[7] and structures of some of these adducts are established. With amino-tri-*t*-butylsilane even some protonic acids are found to give stable adducts[7]. Coordination compounds of amino-tri-*n*-butoxysilane with tin(IV), titanium(IV), arsenic(III) chlorides etc. have been obtained and nitrogen is suggested to be the donor site[8]. The relative strength of these types of bases has been determined thermochemically and is found to be dependent upon inductive (+*I*) effect of the substituents on silicon atoms[9]. However, there is no report on the behaviour of antimony(III) halides towards organoamino-triorganoxysilanes, $(RO)_3SiNHR'$. Herein, the results of the reactions of *n*-butylamino/benzylamino-triethoxy/triphenoxy-silanes towards SbX_3 ($X = Cl$, Br, I) are reported.

Materials and Methods

All operations were carried out under dry nitrogen atmosphere. The solvents used were dried by conventional methods. Antimony(III) chloride and bromide (E. Merck) were recrystallised from chloroform and antimony(III) iodide (Hopkins and Williams) was resublimed before use.

Benzylaminotriethoxy-, benzylaminotriphenoxy-, *n*-butylaminotriethoxy- and *n*-butylaminotriphenoxy-silanes, hitherto not reported in literature were obtained by the reactions of the corresponding chlorosilanes with amines according to the reported method[10], and their purity checked by elemental analyses, infrared and PMR spectral data.

Reactions of benzylamino/n-butylamino-triphenoxy/triethoxy-silanes with antimony(III) chloride, bromide and iodide

Antimony(III) chloride or bromide (1 mol) in chloroform was added dropwise to an ice-cold solution of benzylaminotriethoxysilane, benzylaminotriphenoxysilane, *n*-butylaminotriethoxysilane or *n*-butylaminotriphenoxysilane (1.5 mol) in chloroform. A solid compound was precipitated in each case which was filtered, washed, dried and analysed (Table 1).

The solvent was removed from the filtrate to furnish a liquid in each case which was analysed: (i) Found: Si, 13.8. $C_8H_{20}O_4Si$ requires Si, 13.4%; (ii) Found: Si, 7.2. $C_{24}H_{20}O_4Si$ requires Si 7.0%.

Because of the insolubility of antimony(III) iodide in common organic solvents, its reactions with Lewis bases in the molar ratio 1:2 (acid:base) were carried out by stirring a suspension of the reactants in carbon tetrachloride for 24 hr. There was change in colour from red to yellow on adduct formation. The progress of the reaction was also checked through intermittent isolation of the complex from the reaction mixture and subsequent elemental and spectral analyses. The filtrate from this reaction was not studied.

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

Results and Discussion

The adducts obtained are slightly hygroscopic solids, insoluble in the common organic solvents, thus precluding their molecular weight determination cryoscopically. The composition of the compounds is $ROSi(NHR')_3.nSbX_3$ ($R = C_2H_5$, C_6H_5; $R' = CH_2C_6H_5$, n-C_4H_9; $n = 1$ or 2 and $X = Cl$, Br or I). However, the adduct of $SbCl_3$ and $(EtO)_3SiNHC_4H_9$ has the composition $(EtO)_2Si(NHC_4H_9)_2.2SbCl_3$. The conductances of the solutions (10^{-3} *M*) of these complexes in nitrobenzene suggest them to be 1:1 electrolytes (Table 1). These adducts deteriorate on standing.

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Table 1—Molar Conductance and Analytical Data of Adducts of Organoaminotriorganoxy-silanes with Antimony(III) Halides

Reactants	Products	Found (Calc.), % N	Found (Calc.), % Cl/Br/I	Found (Calc.), % Sb	Found (Calc.), % SI	Λ_M (ohm^{-1} cm^2 mol^{-1})
1 $(PhO)_3SiNHCH_2C_6H_5 + SbCl_3$	$PhOSi(NHCH_2C_6H_5)_3.2SbCl_3$	3.9 (4.6)	23.7 (23.7)	27.8 (27.2)	3.1 (3.1)	36.1
2 $(PhO)_3SiNHCH_2C_6H_5 + SbBr_3$	$PhOSi(NHCH_2C_6H_5)_3.2SbBr$	3.6 (3.6)	41.6 (41.3)	20.2 (20.9)	2.4 (2.4)	35.3
3 $(PhO)_3SiNHCH_2C_6H_5 + SbI_3$	$PhOSi(NHCH_2C_6H_5)_3.SbI_3$	4.5 (4.4)	40.7 (40.5)	13.0 (12.9)	3.0 (2.9)	27.0
4 $(PhO)_3SiNHC_4H_9 + SbCl_3$	$PhOSi(NHC_4H_9)_3.2SbCl_3$	5.1 (5.3)	26.6 (26.9)	30.5 (30.8)	3.2 (3.5)	29.0
5 $(PhO)_3SiNHC_4H_9 + SbI_3$	$PhOSi(NHC_4H_9)_3.2SbI_3$	3.0 (3.1)	56.9 (56.7)	17.8 (18.1)	1.9 (2.1)	31.0
6 $(EtO)_3SiNHCH_2C_6H_5 + SbCl_3$	$EtOSi(NHCH_2C_6H_5)_3.2SbCl_3$	4.3 (4.9)	25.2 (25.1)	28.6 (28.8)	3.1 (3.3)	32.0
7 $(EtO)_3SiNHCH_2C_6H_5 + SbI_3$	$EtOSi(NHCH_2C_6H_5)_3.2SbI_3$	2.7 (3.0)	54.5 (54.5)	17.5 (17.4)	1.8 (2.0)	31.0
8 $(EtO)_3SiNHC_4H_9 + SbCl_3$	$(EtO)_2Si(NHC_4H_9)_2.2SbCl_3$	4.2 (3.9)	30.0 (29.7)	33.7 (34.0)	3.8 (3.9)	25.8
9 $(EtO)_3SiNHC_4H_9 + SbI_3$	$EtOSi(NHC_4H_9)_3.2SbI_3$	3.7 (3.3)	59.0 (58.9)	19.2 (18.9)	1.9 (2.1)	26.0
10 $(EtO)_3SiNHC_4H_9 + SbBr_3$	$EtOSi(NHC_4H_9)_3.2SbBr_3$	4.0 (4.1)	47.0 (47.1)	23.5 (23.9)	2.8 (2.7)	29.0

Table 2—PMR Data of Benzylaminotriethoxy-, benzylaminotriphenoxy-, *n*-butylaminotriethoxy-, *n*-butylamino-triphenoxy-silanes

Compound	Chemical shifts (δ) a	b	c	d	e	f
$(CH_3CH_2O)_3SiNHCH_2C_6H_5$ a b c d e	0.9 (9H, *t*)	3.8 (6H, *q*)	1.0 (1H, *s*)	3.9 (2H, *s*)	7.0 (5H, *s*)	—
$(C_6H_5O)_3SiNHCH_2C_6H_5$ a b c d	7.3 (15H, *m*)	1.0 (1H, *s*)	4.0 (2H, *s*)	7.0 (5H, *s*)	—	—
$(CH_3CH_2O)_3SiNHCH_2CH_2CH_2CH_3$ a b c d e e f	1.1 (9H, *t*)	3.95 (6H, *q*)	1.2 (1H, *s*)	2.8 (2H, *t*)	1.4 (4H, *m*)	0.9 (3H, *t*)
$(C_6H_5O)_3SiNHCH_2CH_2CH_2CH_3$ a b c d e e	7.1 (15H, *m*)	1.1 (1H, *s*)	2.9 (2H, *t*)	1.3 (4H, *m*)	0.9 (3H, *t*)	—
$CH_3CH_2OSi(NHCH_2C_6H_5)_3$ a b c d e	0.9 (3H, *t*)	3.8 (2H, *q*)	1.1 (3H, *s*)	3.9 (6H, *s*)	7.0 (15H, *s*)	—
$C_6H_5OSi(NHCH_2CH_2CH_2CH_3)_3$ a b c d d e	7.3 (5H, *m*)	1.1 (3H, *s*)	3.9 (6H, *s*)	1.4 (12H, *m*)	0.9 (9H, *t*)	—

The liquid residue obtained from the filtrate in each case, as evidenced by elemental analyses, infrared and PMR spectral data. [IR: 1080-1020 *vs* (νSiO(C)), 480 (δ SiO(C)) cm^{-1}; PMR: 0.9 (*t*, CH_3), 3.8-3.9 (*t*, OCH_2) for $(C_2H_5O)_4Si$; and IR: 1570-1595 s (C=C ring), 1250-1240 s (νSi−OPh) cm^{-1}; PMR: δ 7.3 (*m*, OC_6H_5) for $(C_6H_5O)_4Si$] is found to be mainly‡ tetraethoxy or tetraphenoxy silane.

Infrared spectra

The spectra (λ_{max} in cm^{-1}) were recorded in nujol on a Perkin-Elmer, model 621 double beam grating spectrophotometer. The νNH modes of the free ligands at 3380-3350 shift to lower wavenumber (3180-3110) in the adducts. Other prominent bands of the ligands due to −C=C− (ring skeletal) at 1595-1585, νOPh at 1245-1250 (wherever applicable), ν_{as} SiO(C) and δSiO(C) modes at 1075-1020 and 480-470 respectively, remain unchanged on adduct formation, though there is a definite change in the intensity of these absorptions. The νSbCl and νSbBr modes in the adducts appear at 320-280 while νSbI has not been located because of the limited range of the instrument. On the basis of the earlier observations[8] donation through nitrogen is expected here also.

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‡In a few cases some unreacted base has been detected by PMR.

PMR spectra

PMR spectra of the adducts were recorded on a Varian EM 390 (90 MHz) instrument using TMS as an external reference; chemical shifts are expressed in δ-scale. The PMR spectra of the adducts in DMSO-d_6 exhibit clear signals for the ring protons and weak signals due to the alkoxy/phenoxy protons (Table 2). The spectra of the adducts solvolysed in D_2O[§] exhibit sharp peaks of the relevant groups of the amines and alcohols obtained from adduct molecules. The spectra also demonstrate alkoxy/phenoxy and benzylamino/*n*-butylamino groups to be in the ratio 1:3 (on the basis of the proton counts of the complexes).

A further confirmation of the structure of the adducts is provided by their actual isolation from the reactions of tris(benzylamino)/tris(*n*-butylamino)-ethoxy/phenoxy-silanes and SbX_3 in the molar ratio of 1:2.

It may thus be concluded that the benzylamino/*n*-butylamino triethoxy/triphenoxy-silanes undergo disproportionation in the presence of Lewis acids to form tris(benzylamino)/tris(*n*-butylamino)-ethoxy/phenoxy-silane adducts according to the equation:

$$3(RO)_3Si\,NHR' + nSbX_3 \rightarrow ROSi(NHR')_3.nSbX_3 + 2(RO)_4Si$$

(where $n = 1$ or 2; X = Cl, Br or I)

Wade and Wiley[11] have also reported disproportionation reactions of $Me_2(Cl)SiNMe_2$ by tin(IV) and titanium(IV) chlorides.

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[§] In a separate experiment, the adducts on hydrolysis in the presence of small amount of conc. HCl are found to be quantitatively converted into corresponding amines, alcohols and SiO_2 etc.