

# Isolation of 1,1-Dialkoxysilylene-1,1-bis(2-phenylhydrazine); 1-Alkoxysilylyne-1,1,1-tris(2-phenylhydrazine) and 1,1,1,1-Tetrakis(2-phenylhydrazine) Silane\* as Adducts Through Lewis Acid Aided Disproportionation Reactions

SURAJ P. NARULA\*\*, NEETA KAPUR, CHHAJU R. RANA and RAJESH MALHOTRA

Department of Chemistry, Panjab University, Chandigarh, 160 014, India

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## Abstract

The title compounds with compositions (i)  $RR'Si(NHNHPh)_2 \cdot 2MCl_4$  [where  $R = R' = OEt$ ,  $OPr-n$ ,  $OBu-n$  or  $OPh$ ;  $R' = Me$ ,  $Et$  or  $Ph$ ;  $M = Sn$  or  $Ti$ ]; (ii)  $RSi(NHNHPh)_3 \cdot 2MCl_4$  [where  $R = OBu-n$ ,  $Ph$  or  $Et$ ]; or (iii)  $Si(NHNHPh)_4 \cdot MCl_4$  were obtained through one pot Lewis acid aided disproportionation reactions of 1-triorganoxy/organo-organoxy silyl 2-phenylhydrazines [ $RR'R''SiNHNHPh$ ; where  $R$  and  $R'$  are the same as above and  $R'' = OCH_2CF_3$ ] at low temperature. The nature of these adducts has been studied by elemental analyses, IR and  $^1H$  NMR spectral data. A deligation of these adducts results in the preparation of di/tri/tetra(2-phenylhydrazine) silanes in low yields (8–10%). Some light is also thrown on the possible mechanism of these reactions.

## Introduction

Literature records various methods for the preparation of compounds containing Si–N bond(s) [1–3]. However, compounds with the silicon atom bonded to two, three or four nitrogen-containing moieties are relatively less studied. The redistribution/disproportionation reactions in organosilicon chemistry have been extensively studied and factors controlling these reactions have been determined [4–7]. The synthetic utility of these reactions has given new routes for the preparation of some organosilicon compounds [8]. However, there is no such report (except those published by us) for the isolation of compounds which have multiple nitrogens bonded to a silicon atom. We have demonstrated the isolation of 1,1,1,1-tetrakis(2-fluoro/2,4-difluorophenyl) silane tetramine or 1-organoxy/organo, 1,1,1-tris(2-chlorophenyl) silanetriamine etc. as adducts in good yield in one pot reactions [9, 10]. With a view

to extending the scope of these reactions, isolation of di/tri/tetra(2-phenylhydrazine) silanes is attempted here. These compounds have been isolated and characterised and some light is thrown on the possible mechanism of these reactions reported here.

## Results and Discussion

The title compounds (Table 1) are white or brown to brick red, insoluble (except in DMSO), hygroscopic solids with the compositions (i)  $RR'Si(NHNHPh)_2 \cdot 2MCl_4$  (where  $R = R' = OEt$ ,  $OPr-n$ ,  $OBu-n$  or  $OPh$ ;  $R' = Me$  or  $Ph$ ;  $M = Sn$  or  $Ti$ ); (ii)  $RSi(NHNHPh)_3 \cdot 2MCl_4$  (where  $R = OBu-n$ ,  $Ph$  or  $Et$ ); (iii)  $Si(NHNHPh)_4 \cdot MCl_4$ . The bis/tris or tetrakis(2-phenylhydrazine) silanes can be obtained in low yields from these adducts by ligand exchange reactions in the heterogeneous phase as described [9, 11].

## Spectral Data

Infrared spectra of these complexes clearly indicate the conversion of the parent base (*i.e.* symmetrical 1-triorganoxy/organo-organoxy silyl 2-phenylhydrazine) to the corresponding bis/tris/tetrakis(2-phenylhydrazine) silanes. For example the diagnostic modes;  $\nu SiO(C)$ ,  $\delta SiO(C)$  and  $\nu OPh$  (wherever present) undergo considerable reduction in intensity or vanish completely (as in the case of tetrakis(2-phenylhydrazine) silane). The  $\nu NH$  mode of the ligands ( $3340-3310\text{ cm}^{-1}$ ) undergoes negative spectral shift and appears at  $3290-3150\text{ cm}^{-1}$ . These data are indicative of the donation through nitrogen of the ligands.  $\nu TiCl$  and  $\nu SnCl$  modes could be identified at  $400-380$  and  $310-290\text{ cm}^{-1}$  respectively.

$^1H$  NMR chemical shift ( $\delta$ ) values and proton counts of the groups in the complexes are recorded in Table 2. The  $\delta$  values identify  $CH_3$ ,  $CH_2$ ,  $CH_2O$ ,  $C_6H_5$ ,  $C_6H_5NH$  and  $(RO)_3SiNH$  groups, while the proton count reveals the number of such groups present in the ligands of the complexes isolated.

\*IUPAC names.

\*\*Author to whom correspondence should be addressed.

TABLE 1. Analytical Data of Complexes of 1-Triorganoxy/organo-organoxy Silyl 2-Phenylhydrazine with Titanium(IV) and Tin(IV) Chlorides at 0 to  $-10^{\circ}\text{C}^{\text{a}}$ 

Serial no.	Compound	Yield <sup>b</sup> (%)	Found (calc.) (%)			
			Cl	Ti/Sn	Si	N
1	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2TiCl <sub>4</sub>	50	39.6(39.9)	13.2(13.5)	3.7(3.9)	7.7(7.9)
2	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2SnCl <sub>4</sub>	55	33.4(33.2)	27.2(27.9)	3.1(3.3)	6.2(6.5)
3	(C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2TiCl <sub>4</sub>	65	38.1(38.4)	12.6(13.0)	3.5(3.8)	7.2(7.6)
4	(C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2SnCl <sub>4</sub>	60	32.0(32.2)	26.8(27.0)	2.8(3.2)	6.1(6.3)
5	(C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2TiCl <sub>4</sub>	60	36.7(37.0)	12.6(12.5)	3.1(3.6)	7.4(7.3)
6	(C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2SnCl <sub>4</sub>	62	30.8(31.2)	25.7(26.1)	2.8(3.1)	5.8(6.1)
7	(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2TiCl <sub>4</sub>	60	34.8(35.1)	11.7(11.9)	3.1(3.5)	6.5(6.9)
8	(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2SnCl <sub>4</sub>	50	29.6(29.9)	24.7(25.0)	2.5(2.9)	5.7(5.9)
9	C <sub>6</sub> H <sub>5</sub> (C <sub>3</sub> H <sub>7</sub> O)Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2TiCl <sub>4</sub>	55	37.2(37.5)	12.4(12.7)	3.3(3.7)	7.2(7.4)
10	C <sub>6</sub> H <sub>5</sub> (C <sub>3</sub> H <sub>7</sub> O)Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2SnCl <sub>4</sub>	60	31.3(31.5)	26.2(26.4)	2.8(3.1)	5.9(6.2)
11	CH <sub>3</sub> (C <sub>3</sub> H <sub>7</sub> O)Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·2TiCl <sub>4</sub>	62	40.6(40.8)	13.9(13.8)	3.8(4.0)	7.8(8.0)
12	C <sub>2</sub> H <sub>5</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·2TiCl <sub>4</sub>	58	37.2(37.5)	12.3(12.7)	3.4(3.7)	10.9(11.1)
13	C <sub>2</sub> H <sub>5</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·2SnCl <sub>4</sub>	55	31.2(31.5)	26.3(26.4)	2.9(3.1)	9.1(9.3)
14	C <sub>6</sub> H <sub>5</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·2TiCl <sub>4</sub>	50	34.9(35.2)	11.7(11.9)	3.2(3.5)	10.2(10.4)
15	C <sub>6</sub> H <sub>5</sub> Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·2SnCl <sub>4</sub>	55	29.6(29.9)	24.8(25.1)	2.7(2.9)	8.5(8.9)
16	(C <sub>4</sub> H <sub>9</sub> O)Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ·2TiCl <sub>4</sub>	57	35.3(35.4)	11.7(12.0)	3.2(3.5)	10.2(10.5)
17	Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ·TiCl <sub>4</sub>	90	21.6(22.0)	7.1(7.4)	4.1(4.3)	17.1(17.3)
18	Si(NHNHC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ·SnCl <sub>4</sub>	88	19.6(19.8)	16.4(16.6)	3.6(3.9)	15.3(15.6)

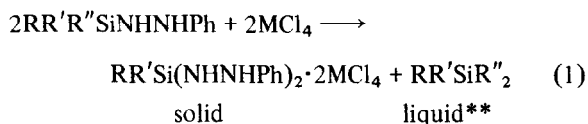
<sup>a</sup>C and H contents were estimated from the proton counts of the relevant groups in the <sup>1</sup>H NMR spectra or original bases as well as of the products. <sup>b</sup>The yield of the product is estimated from the amount of the original base taken.

TABLE 2. <sup>1</sup>H NMR Data of Complexes of 1-Triorganoxy/organo-organoxy Silyl 2-Phenylhydrazine with Titanium(IV) Chlorides Obtained at 0 to  $-10^{\circ}\text{C}$ 

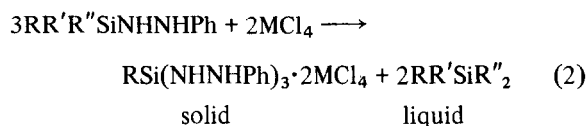
	CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>2</sub> O	≧SiNH	PhNH	C <sub>6</sub> H <sub>5</sub>
1, 2	1.0 (t, 6H)		3.8 (q, 4H)	3.5 (s, 2H)	4.9 (s, 2H)	7.4 (m, 10H)
3, 4	0.8 (t, 6H)	1.4 (q, 4H)	3.8 (q, 4H)	3.45 (s, 2H)	4.85 (s, 2H)	7.5 (m, 10H)
5, 6	0.7 (t, 6H)	1.2 (q, 8H)	3.95 (q, 4H)	3.5 (s, 2H)	4.9 (s, 2H)	7.4 (m, 10H)
7, 8				3.6 (s, 2H)	5.0 (s, 2H)	7.6 (m, 20H)
9, 10	0.8 (t, 3H)	1.4 (q, 2H)	3.7 (q, 2H)	3.6 (s, 2H)	4.9 (s, 2H)	7.45 (m, 15H)
11	0.8 (t, 6H)	1.4 (q, 2H)	3.6 (t, 2H)	3.7 (s, 2H)	4.95 (s, 2H)	7.4 (m, 10H)
12, 13	1.0 (t, 3H)	1.6 (q, 2H)		3.7 (s, 3H)	5.0 (s, 3H)	7.4 (m, 15H)
14, 15				3.7 (s, 3H)	4.9 (s, 3H)	7.4 (m, 20H)
16	0.85 (t, 3H)	1.4 (q, 2H)	3.6 (t, 2H)	3.8 (s, 3H)	5.0 (s, 3H)	7.5 (m, 15H)
17, 18				3.7 (s, 4H)	4.9 (s, 4H)	7.5 (m, 20H)

These data clearly show that in the compounds 1–11\*, 2-phenylhydrazino groups have increased two-fold and in the adducts 12–16\* these groups undergo a three-fold increase. In the case of complexes 17\* and 18\*, the original base [sym. 1-tris(2,2,2-trifluoroethoxy) silyl 2-phenylhydrazine] has been completely disproportionated to give 1,1,1,1-tetrakis(2-phenylhydrazine) silane.

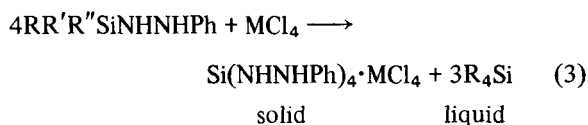
From the above data, the formation of products can be rationalised as:



[R = R' = R'' = OEt, OPr-n, OBU-n or OPh; R' = Me, Et or Ph; R'' = OCH<sub>2</sub>CF<sub>3</sub>; M = Sn or Ti]



[R = CH<sub>3</sub>, Ph or OBU-n; R' = R'' = OCH<sub>2</sub>CF<sub>3</sub>]



[R = R' = R'' = OCH<sub>2</sub>CF<sub>3</sub>]

A persual of the data reveals that Lewis acid aided disproportionation of sym. 1-triorganoxy/organo-organoxy silyl, 2-phenylhydrazines results in bis/tris/tetrakis(2-phenylhydrazine) silanes. The extent of dis-

proportionation in the present system is dependent upon the number of CF<sub>3</sub>CH<sub>2</sub>O groups on the silicon atom. Since this group is highly electronegative, the extent of disproportionation may be due to the inductive (-I) effects of R on silicon atoms. This observation is contrary to the one reported for dimethyl ethoxy alkoxy silanes in the presence of Lewis acids, where steric effect of such groups is considered responsible for the disproportionations of the molecule [7].

Hoping to throw light on the possible mechanism of these disproportionation reactions, the reactions were also carried out at -50 to -60 °C (Table 3). The products obtained are again white or orange-yellow to brick red coloured hygroscopic and insoluble (except in DMSO) solids. However, the elemental analytical data reveal them to be 1:1 adducts of the reactants. The infrared spectra show negative shift in the νNH mode. The other important absorptions such as νSiO(C), δSiO(C), C=C (skeletal), νTiCl and νSnCl appear at their usual positions (1080–1060, 470, 1590, 750, 380 and 310–280 cm<sup>-1</sup> respectively). In these cases, unlike in the disproportionated hydrazines, there is not much change in the absorption intensities of νSiO(C) and phenyl ring modes etc. <sup>1</sup>H NMR spectra show the presence of CH<sub>3</sub>, CH<sub>2</sub>, CH<sub>2</sub>O, >SiNH, PhNH and C<sub>6</sub>H<sub>5</sub> groups at 0.8, 1.2, 3.6, 3.8, 5.0 and 7.3 ppm respectively. Proton count ratios show the base in the adducts to be (RO)<sub>3</sub>SiNHNHPh. The recovery of the original silyl hydrazine through ligand exchange reaction [9–11] also suggests that the complexes are normal 1:1 adducts.

We have already reported that triorganoxy/organo-organoxy silanamines are sufficiently strong Lewis bases and undergo adduct formation involving nitrogen atoms [12, 13]. In the present cases, though there is choice between PhNH and (RO)<sub>3</sub>SiNH moieties acting as donors, the Lewis acids prefer organometalloidal nitrogen for bonding. This is evidenced by the change in the chemical shift (δ)

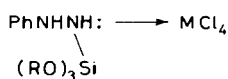
\*These are the serial numbers of the compounds in Table 1.

\*\*The liquid products were identified only from IR and <sup>1</sup>H and <sup>19</sup>F NMR spectra of the filtrates after solvent removal.

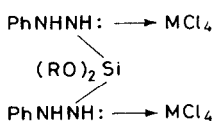
TABLE 3. Analytical Data of 1:1 Complexes of 1-Triorganoxy/organo-organoxy Silyl 2-Phenylhydrazine with Titanium(IV) and Tin(IV) Chlorides at -50 to -60 °C

Serial no.	Compound	Yield (%)	Found(calc.) (%)			
			Cl	Ti/Sn	Si	N
1	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> SiNHNHC <sub>6</sub> H <sub>5</sub> ·TiCl <sub>4</sub>	70	30.6(30.9)	10.3(10.4)	5.8(6.1)	6.0(6.1)
2	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> SiNHNHC <sub>6</sub> H <sub>5</sub> ·SnCl <sub>4</sub>	72	26.3(26.7)	22.2(22.4)	4.7(5.3)	4.9(5.3)
3	(C <sub>3</sub> H <sub>7</sub> O) <sub>3</sub> SiNHNHC <sub>6</sub> H <sub>5</sub> ·TiCl <sub>4</sub>	75	28.3(28.3)	9.2(9.6)	5.2(5.6)	5.3(5.6)
4	(C <sub>3</sub> H <sub>7</sub> O) <sub>3</sub> SiNHNHC <sub>6</sub> H <sub>5</sub> ·SnCl <sub>4</sub>	70	25.0(24.8)	20.5(20.8)	4.5(4.9)	4.7(4.9)
5	(C <sub>4</sub> H <sub>9</sub> O) <sub>3</sub> SiNHNHC <sub>6</sub> H <sub>5</sub> ·TiCl <sub>4</sub>	75	25.8(26.1)	8.7(8.8)	4.8(5.1)	4.8(5.1)
6	(C <sub>4</sub> H <sub>9</sub> O) <sub>3</sub> SiNHNHC <sub>6</sub> H <sub>5</sub> ·SnCl <sub>4</sub>	70	22.8(23.1)	19.1(19.3)	4.2(4.5)	4.3(4.5)
7	C <sub>6</sub> H <sub>5</sub> (C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> SiNHNHC <sub>6</sub> H <sub>5</sub> ·TiCl <sub>4</sub>	65	27.5(27.3)	8.9(9.2)	5.1(5.4)	5.3(5.4)
8	C <sub>6</sub> H <sub>5</sub> (C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> SiNHNHC <sub>6</sub> H <sub>5</sub> ·SnCl <sub>4</sub>	62	24.2(24.0)	19.7(20.1)	4.6(4.7)	4.4(4.7)
9	(CH <sub>3</sub> ) <sub>3</sub> SiNHNHC <sub>6</sub> H <sub>5</sub> ·SnCl <sub>4</sub>	78	31.8(32.2)	26.8(27.0)	5.9(6.3)	6.0(6.3)

value of the NH proton of the  $(RO)_3SiNH$  moiety from 3.4 up to 3.8 ppm on complexation. Also that these reactions carried out at higher temperature (30–40 °C) afford the cleaved products such as  $Cl_3Ti-NHNHPh$  etc. This observation may serve as chemical evidence for silicon bonded nitrogen to be the donor site. Similar observations have already been described by Peterson and Thé [14] for triorgano-silyl/germyl hydrazines with  $BF_3$  etc. The bonding in these adducts may therefore, be represented as:

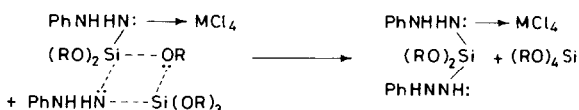


and

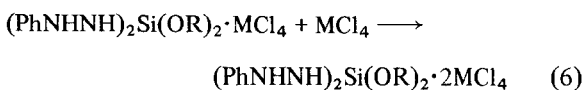
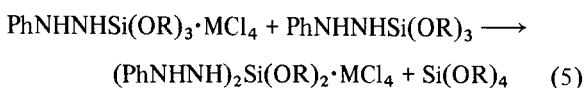
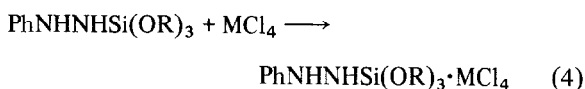


etc.

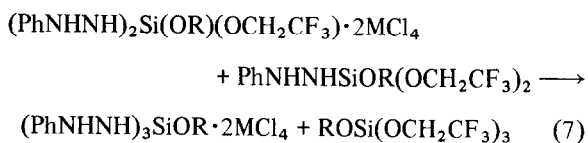
The acid catalysed disproportionation of organoxy silicon compounds is much faster than in the absence of the catalysts. Pola and Chvalovsky [7] have suggested the cyclic four-centre transition state between the adduct and the original organoxy silicon compound to be the rate determining step. Considering that the same applies here, the reaction can be represented as:



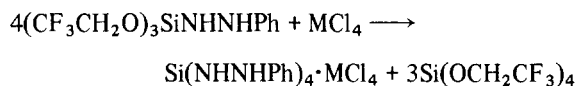
The overall mechanism may be represented as



However, if  $R = CH_2CF_3$ , the reaction proceeds further as



Interestingly, for sym. 1-tris(2,2,2-trifluoroethoxy)silyl 2-phenylhydrazine only one molecule of the Lewis acid is enough to completely disproportionate the base to 1,1,1,1-tetrakis(2-phenylhydrazine)silane as



This reaction is nearly quantitative and is useful to synthesise the tetrakis(2-phenylhydrazine)silane by removing one molecule of the Lewis acid by the ligand exchange reaction.

From all these studies it may be concluded that

(i) 1-Triorganoxy/organo-organoxy silyl 2-phenylhydrazines can undergo disproportionation to bis/tris and even tetrakis(2-phenylhydrazine)silanes. However, at temperatures of  $-50$  to  $-60$  °C no such disproportionation takes place.

(ii) 2,2,2-Trifluoroethoxy groups on the silicon atom are effective substituents for the enhanced disproportionation of the starting silyl hydrazine.

(iii) The reactions may be useful for the synthesis of multinitrogen bonded silicon compounds. However, it is accepted that an efficient deligation is a necessary precondition for this reaction to be of synthetic utility. In this connection a weak Lewis acid such as  $I_2$  or even  $SO_2$  may be more helpful. The work is in progress.

## Experimental

All operations were carried out under a dry nitrogen atmosphere. The solvents used were dried by the conventional method. Titanium(IV) and tin(IV) chlorides (Reidel, Pure) were distilled before use and stored under dry nitrogen atmosphere. Infrared spectra were recorded as nujol thin films on a Perkin-Elmer model 621 grating spectrophotometer using NaCl/KBr/polyethylene optics.  $^1H$  NMR and  $^{19}F$  NMR spectra were recorded in  $CDCl_3$  containing small amount of  $DMSO(d_6)$  on a Varian 390, 90 MHz using TMS as internal and Freon-11 as external references respectively. Low temperatures were maintained using Cryo-cool model CC-100II, Neslab, Italy.

### Preparation of Ligands

The ligands, 1-triorganoxy/organo-organoxy silyl 2-phenylhydrazines  $[RR'R''SiNHNHPh]$ , where  $R = R' = R'' = OEt$ ,  $OPr-n$ ,  $OBu-n$ ,  $PhO$  or  $CF_3CH_2O$ ;  $R = R' = CF_3CH_2O$ ;  $R = Et, Me$  or  $Ph$ ] were prepared by reactions of the corresponding chlorosilanes with phenylhydrazine in the molar ratio 1:2 in dry diethyl ether [1]. The purity of the compounds was checked by elemental analyses and infrared as well as  $^1H$  NMR spectral data.

*Preparation of 1,1-Dialkoxysilylene-1,1-bis(2-phenylhydrazine); 1-Alkoxysilylyne-1,1,1-tris(2-phenylhydrazine) and 1,1,1,1-Tetrakis(2-phenylhydrazine) Silane Adducts*

To a solution of 1-trialkoxysilyl 2-phenylhydrazine in petroleum ether (40–60 °C) kept at 0 to –10 °C, was added dropwise an equimolar amount of titanium(IV) chloride/tin(IV) chloride in the same solvent. This addition resulted in the precipitation of brown to brick red or white solids in each case respectively. The solid was filtered in a cold atmosphere of dry nitrogen, washed and dried under reduced pressure [15]. The analytical data are recorded in Table 1. In the filtrates, the products were identified through NMR spectra after solvent removal [15].

*Preparation of 1:1 Adducts of 1-Trialkoxysilyl 2-Phenylhydrazine and Titanium(IV) Chloride or Tin(IV) Chloride*

Identical quantities of the reactants were mixed under the same conditions at –50 to –60 °C. Solids of the same colour were precipitated which were isolated as above and analysed (Table 3).

The filtrates of these reactions after 1–2 h at room temperature afford another crop of the solid complexes. On the basis of elementary analyses and IR and <sup>1</sup>H NMR spectroscopy (see 'Discussion'), these adducts are the same as those obtained at 0 to –10 °C [*i.e.* RR'Si(NHNHPh)<sub>2</sub>·2MCl<sub>4</sub>].

*Ligand Exchange Reactions*

An adduct (10 mmol) was added to ethylenediamine (25 mmol) in a round bottomed flask (25 ml) fitted with a condenser and having a small moisture guard tube and dry nitrogen inlet tube or pyridine d<sub>5</sub> (25 mmol) and the adduct (10 mmol) in

a sealed tube. The mixtures were heated at 35–40 °C for 5–6 h. Thereafter dry carbon tetrachloride (5–10 ml) was added to the reaction mixture, the contents filtered and the filtrate concentrated (yield 8–10%). The liberated bases were identified by infrared and <sup>1</sup>H NMR spectral data.

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