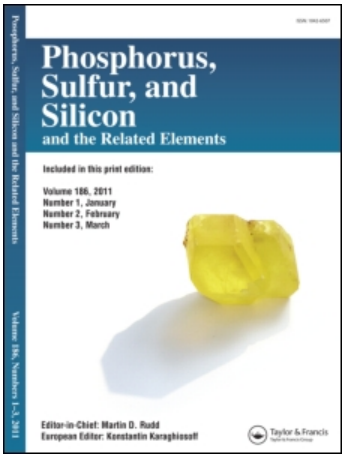

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SYNTHESIS AND CHARACTERIZATION OF NEW (CHLOR0)AMINOSILANES: X-RAY CRYSTAL STRUCTURE OF [(2,6-$Me_2C_6H_3NH)_2SiCl_2$]

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SYNTHESIS AND CHARACTERIZATION OF NEW (CHLORO)AMINOSILANES: X-RAY CRYSTAL STRUCTURE OF $[(2,6\text{-}Me_2C_6H_3NH)_2SiCl_2]$

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Starting from racemic α-methylbenzyl amine or α-methylbenzyl bromide, new (amino)trichlorosilanes $(MePhC(H))(SiMe_3)NSiCl_3$(**1**) and $(MePhC(H))(2,6\text{-}Me_2C_6H_3)NSiCl_3$ (**2**) have been synthesized in good yields. The products have been characterized by analytical and IR, mass, and NMR (^1H and ^{29}Si) spectroscopic techniques. The diamino-dichlorosilane $(2,6\text{-}Me_2C_6H_3NH)_2SiCl_2$ (**3**) obtained as the side product during the synthesis of **2** has been characterized by a single crystal X-ray diffraction study.

Keywords: silazanes; chlorosilanes; X-ray crystal structure; ^{29}Si NMR

INTRODUCTION

Recent work by several groups has shown that the silanols are excellent starting materials for the preparation of model compounds for metallosilicates and metal complexes anchored on silica surfaces [1–4]. It has been recently shown by us and others that the silanetriols serve as ideal starting materials for assembling model compounds for this purpose [4]. Several synthetic routes are known in the literature for the synthesis of silanetriols [5]. However, in our hands, the most facile and clean route for the preparation of silanetriols is the aniline assisted hydrolysis of (amino)trichlorosilanes (prepared from a multi-step procedure; see Scheme 1) in dry diethyl ether under very mild conditions [6].

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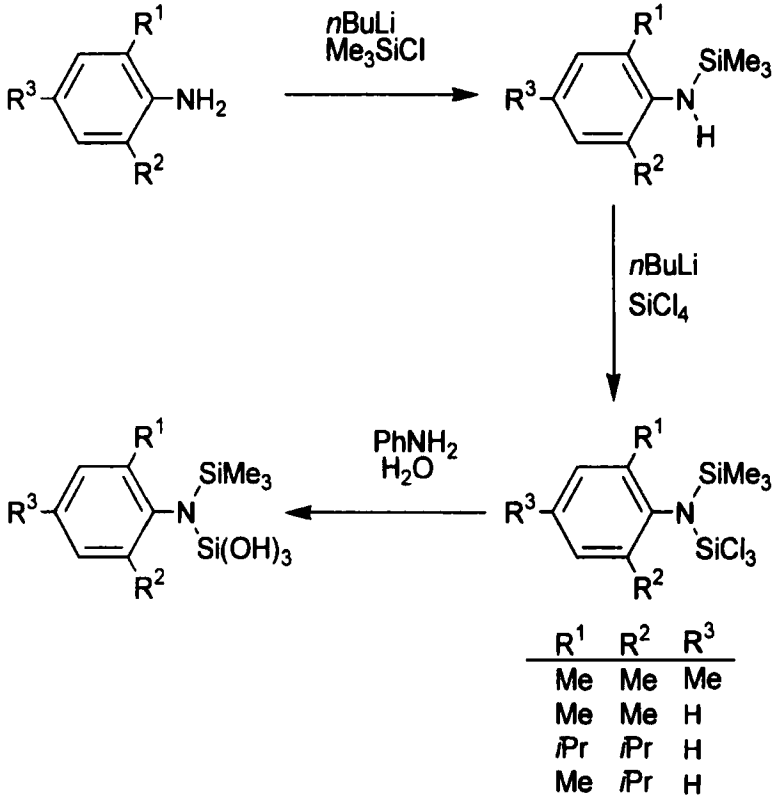


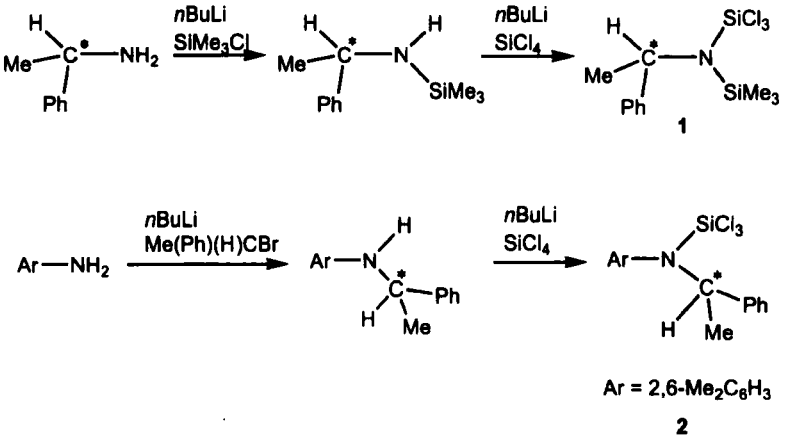
SCHEME 1

Silanols and metallasiloxanes derived from them have been shown to be useful catalysts in several organic transformations [3,4]. Owing to the possible use of silanols and / or their metal derivatives with chiral centers in asymmetric catalysis, we have now synthesized two new chiral (amino)trichlorosilanes and characterized them. During the course of this investigation, we have also isolated a (diamino)dichlorosilane and characterized it by spectroscopic and single crystal X-ray diffraction studies. The results of these investigations are reported in this paper.

RESULTS AND DISCUSSION

Synthesis of Chiral Aminotrichlorosilanes

Starting from a racemic mixture of α-methylbenzylamine or 2,6-dimethylaniline, the (amino)silyltrichlorides (MePhC(H))($SiMe_3$) $NSiCl_3$ (**1**) and (MePhC(H))(2,6-$Me_2C_6H_3$)$NSiCl_3$ (**2**) have been synthesized by employing a two-step procedure in fairly good yields as shown in Scheme 2. Both the compounds have been obtained as high boiling liquids and purified by fractional distillation under vacuum.



SCHEME 2

Compounds **1** and **2** have been characterized with the aid of analytical and spectroscopic techniques. Due to the formation of SiC during the combustion process, the experimentally found carbon values are rather low. Both the compounds yield molecular ion peaks in the EI mass spectra. In the ^1H NMR spectrum, the hydrogen atom attached to the chiral carbon resonates as a quartet at around δ 4.5 ppm. The resonance due to the methyl group of the α-methylbenzylamine moiety appears as a doublet (δ 1.83 for **1** and 1.64 for **2**). The observed silicon NMR shifts for the $SiCl_3$ moiety (*ca.* δ −25 ppm) are comparable with the values found for several N-bonded trichlorosilanes *e.g.* (2,6-$Me_2C_6H_3$)N($SiMe_3$)$SiCl_3$ (δ-28.2 ppm) [6], see also Table I.

TABLE I ^{29}Si NMR chemical shifts for (amino)trichlorosilanes[a]

Compound	$\delta(SiCl_3)$	$\delta(SiMe_3)$	*Ref.*
$(MePhC(H))(SiMe_3)NSiCl_3$ (**1**)	−24.8	11.9	this work
$(MePhC(H))(2,6\text{-}Me_2C_6H_3)NSiCl_3$ (**2**)	−25.7	–	this work
$(C_6H_5)(SiMe_3)NSiCl_3$	−25.8	12.8	6
$(2,6\text{-}Me_2C_6H_3)(SiMe_3)NSiCl_3$	−28.2	12.5	6
$(2,4,6\text{-}Me_3C_6H_3)(SiMe_3)NSiCl_3$	−28.3	12.3	6
$(2\text{-}Me\text{-}6\text{-}iPrC_6H_3)(SiMe_3)NSiCl_3$	−27.9	12.2	6

a. all spectra were recorded in $CDCl_3$.

In spite of several modifications in the hydrolysis procedure (see Experimental), it has not been possible to convert the trichlorosilanes **1** and **2** into the corresponding silanetriols (using the methodology depicted in Scheme 1) due to the hydrolysis of the Si-N bonds resulting in the formation of silica and amine hydrochloride. This observation indicates that the R group present in these molecules does not exert the required steric protection against the polycondensation and as well as Si-N bond hydrolysis side reactions. However, it should be possible to synthesize chiral silanetriols either by introducing still bulkier groups on nitrogen or by employing even milder hydrolysis conditions.

Synthesis and Structure of $((2,6\text{-}Me_2C_6H_3)NH)_2SiCl_2$ (3)

The diaminodichlorosilane $((2,6\text{-}Me_2C_6H_3)NH)_2SiCl_2$ (**3**) was obtained in *ca.* 5% yield during the synthesis of **2**, due to presence of a slight excess of 2,6-dimethylaniline in the reaction mixture. The mass spectrum of **3** under electron impact conditions yields the molecular ion peak at *m/z* 338 with an isotope pattern containing two chlorine atoms. The observed ^1H and ^{29}Si NMR chemical shifts are in accordance with its molecular structure. Even under the conditions of vacuum distillation (see experimental), it is surprising to note that, there is no further HCl elimination reaction of **3** to produce further condensed products.

In order to establish the solid state conformation in **3**, the X-ray crystal structure was determined. The compound crystallizes in centrosymmetric monoclinic space group C2/c with four molecules in the unit cell. Figure 1

depicts the molecular structure of **3** along with the selected structural parameters. This molecule is a rare example of a chlorosilane, which contains two free N-H groups. Probably owing to the bulkiness of the two aryl groups on the silicon, there is no further reaction, even at elevated temperatures, resulting in cyclic Si-N products (*vide supra*). There are also no N-H...Cl or N-H...N hydrogen bonds due to steric factors. The Si-N bonds (1.680 Å) are somewhat shorter than the corresponding distances observed for the silanetriol $(2,6\text{-}Me_2C_6H_3)N(SiMe_3)Si(OH)_3$ (1.71 Å) [6].

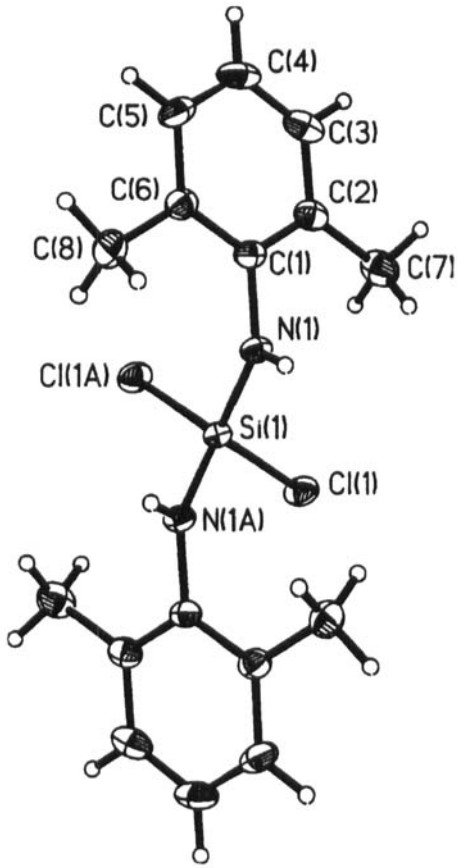


FIGURE 1 Molecular structure of **3** (thermal ellipsoids are drawn at 50 % probability level). Selected bond distances (Å): Si(1)-Cl(1) 2.0582(7), Si(1)-N(1) 1.680(2), N(1)-C(1) 1.436(2). Selected bond angles (°) Cl(1)-Si(1)-Cl(1A) 103.9(1), N(1)-Si(1)-N(1A) 110.5(1), N(1)-Si(1)-Cl(1) 105.1(1), N(1)-Si(1)-Cl(1A) 116.2(1)

EXPERIMENTAL

General

All experimental manipulations were carried out under oxygen-free dinitrogen atmosphere using standard Schlenk glassware. Solvents were rigorously dried and routinely freshly distilled by standard methods prior to their use. Elemental analyses were performed on a Carlo Eraba (Italy) Elemental Analyzer. The ^{1}H and ^{29}Si spectra were recorded on a Bruker AM 200 MHz spectrometer using Me_4Si as reference. Infrared spectra were recorded on a Nicolet Impact 400 spectrometer. Mass spectra were obtained on a Finnigan MAT system 6230 or a Varian MAT CH5 mass spectrometer. The EI mass spectra of all silyl chlorides yielded the expected chlorine isotope pattern.

Synthesis of (MePhC(H))($SiMe_3$)$NSiCl_3$ (1)

Freshly distilled α-methylbenzylamine (163 mmol, 19.74 g) in diethyl ether (140 mL) was cooled to −78 °C. To this solution, *n*BuLi (180 mmol in *n*-hexanes) in diethyl ether (50 mL) was dropped slowly under constant stirring. The reaction mixture was allowed to attain room temperature. After 4 h of stirring, $SiMe_3Cl$ (163 mmol, 20.7 mL) was added slowly under vigorous mixing. The onset of reaction is observed with formation of white lithium chloride precipitate. After overnight stirring the precipitated LiCl was filtered off and the filtrate was concentrated under vacuum to 100 mL colorless solution. To this solution, *n*BuLi (163 mmol in *n*-hexanes) in diethyl ether (50 mL) was added dropwise and stirred. To the resulting lithium salt, $SiCl_4$ (18.7 mL, 163 mmol) was added using cannula and the stirring was continued for 12 h. The precipitated LiCl was filtered off and the solvent was removed under reduced pressure. Purification of **1** was achieved by fractional distillation of the resultant oil under vacuum.

Yield: 26.63 g (50%). Bp. 79 – 81 °C at 26.6 Pa (0.2 mmHg), Anal. Calcd for $C_{11}H_{18}Cl_3NSi_2$ (326.8): C, 40.4; H, 5.6; N, 4.3. Found C, 40.1; H, 5.8; N, 4.7. MS (EI, 70 eV): 326 (2%, M^+), 312 (90%, M^+ – Me), 105 (100%, MePhC(H)NH_2-Me), 73 (80%, $SiMe_3$), IR (Nujol): 1496, 1448, 1384, 1257, 1204, 1099, 1058, 1018, 989, 956, 904, 844, 763, 697, 659, 612, 592, 565, 507, 481, 443 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ0.27 (s,

9H, Si*Me*$_3$), 1.83 (d, 3H, C*H*$_3$, $^3J_{HH}$ = 7.0 Hz), 4.85 (q, 1H, CH, $^3J_{HH}$ = 7.0 Hz), 7.2 – 7.5 (m, 5H, *aromatic*). ^{29}Si NMR (C_6D_6; 79.5 MHz) δ –24.84 (*Si*Cl$_3$), 11.87 (*Si*Me$_3$).

Synthesis of (MePhC(H))(2,6-Me$_2$C$_6$H$_3$)NSiCl$_3$ (2)

Freshly distilled 2,6-dimethylaniline (59 mmol, 7.21 g) was dissolved in diethyl ether (75 mL) and the resulting solution was cooled to –78 °C. To this solution, *n*BuLi 17.4 mL (60 mmol in *n*-hexanes) in diethyl ether (50 mL) was dropped slowly under constant stirring. The reaction mixture was allowed to attain room temperature. After 4 h of stirring, α-methylbenzyl bromide (59 mmol, 11.0 mL) was added slowly under constant stirring. After stirring overnight the precipitated LiCl was filtered off and the filtrate was concentrated under vacuum to 100 mL colorless solution. This solution containing the secondary amine (43 mmol, 9.66 g) was diluted with diethyl ether (75 mL) and *n*BuLi (43 mmol, 12.6 mL) was added. After 4 h of stirring $SiCl_4$ (5.9 mL) was added dropwise. The reaction was allowed to reach completion over a period of 12 h. and the LiCl was filtered off. Removal of the solvent under reduced pressure leaves a thick brown oil which was purified by distillation under vacuum to yield **2** in spectroscopically pure form.

Yield: 9.53 g (45%). Bp. 105 – 110°C at 53.3 Pa (0.4 mmHg), Anal. Calcd for $C_{16}H_{18}Cl_3NSi$ (358.8): C, 53.6; H, 5.1; N, 3.9. Found: C, 47.0; H, 5.0; N, 4.2 (low carbon value may be due to the formation of SiC). MS (EI, 70 eV): *m/z* 359 (1%, M^+), 344 (1%, M^+-Me), 105 (100%, MePhC(H)NH$_2$-Me). IR (Nujol): 1595, 1493 1474, 1454, 1375, 1261, 1219, 1209, 1158, 1121, 1099, 1028, 983, 897, 764, 745, 699, 628, 606, 543, 510, 468 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 1.64 (d, 3H, CH$_3$, $^3J_{HH}$ = 6.7 Hz), 2.27 (s, 6H, aromatic C*H*$_3$), 4.42 (q, 1H, C*H*, $^3J_{HH}$= 6.7 Hz), 6.74 – 7.4 (m, 8H, *aromatic*). ^{29}Si NMR ($CDCl_3$, 49.7 MHz) δ-25.7.

Isolation of ((2,6-Me$_2$C$_6$H$_3$)NH)$_2$SiCl$_2$ (3)

Compound **3** has been isolated in low yields (< 5%) during the synthesis of **2**. It crystallizes out as a colorless solid from the oil, which was obtained as the last fraction during the purification of **2** by vacuum distillation (b.p. ~130°C at the pressure described above for the purification of **2**).

Yield: 1.0 g. Anal. Calcd for $C_{16}H_{20}Cl_2N_2Si$ (339.3): C, 56.6; H, 5.9; N, 8.2. Found C, 55.8; H, 6.0; N, 8.0. MS (EI, 70 *eV*): *m/z* 338 (5%, M^+), 121 (100%, 2,6-$Me_2C_6H_3NH_2$). ^{1}H NMR ($CDCl_3$, 200 MHz,): δ2.29, 2.48, (s, 12H, *Me*), 6.8 – 7.2 (m, 6H, *aromatic*), 10.31 (s, 2H, N*H*). ^{29}Si NMR ($CDCl_3$; 49.7 MHz) δ –30.7.

Attempted hydrolysis of 1 and 2

Following the procedure established earlier,[6] the hydrolysis of the N-bonded silyltrichlorides **1** and **2** (1 equiv) were attempted by treating them with a mixture of H_2O (3 equiv) and aniline (3 equiv) in diethyl ether at 0 °C. In both the cases, a voluminous white precipittate, containing amine hydrochloride and silica, was obtained at the end of hydrolysis. Hence, the hydrolysis reactions were reattempted using other amines (such as pyridine or triethylamine) as HCl scavengers. Reactions were also repeated at still lower temperatures. However, in all cases, no silanetriol or any other organic-soluble product could be isolated.

X-ray structure determination of 3

Crystals of **3** suitable for X-ray diffraction studies were obtained directly by distilling the mixture containing **2** and **3** at reduced pressure. Intensity data were collected on a Siemens STOE-AED2 diffractometer equipped with graphite monochromatized MoKα radiation (λ = 0.71073 Å). A regular shaped crystal of dimensions 0.8 × 0.6 × 0.4 mm^3 was used for data collection. The structure was solved by direct methods (SHELXS-90) [8] and refined by full-matrix least-squares method against F^2 using SHELXL-96 [9] program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed on calculated positions using a riding model and refined isotropically. Other details pertaining to data collection and structure refinement are listed in Table II. Other crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151486. Copies of the data can be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: Int. code +(1223) 336–033; e-mail: deposit@chemcrys.cam.ac.uk).

TABLE II Crystal data and structure refinement for **3**

Empirical formula	$C_{16}H_{20}Cl_2N_2Si$
Formula weight	339.33
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/c
Unit cell dimensions	a = 14.214(3) Å
	b = 8.873(2) Å
	c = 13.495(3) Å
	$\alpha = 90°$
	$\beta = 90.00(3)°$
	$\gamma = 90$
Volume	1701.9(6) $Å^3$
Z	4
Density (calculated)	1.324 Mg/m^3
Absorption coefficient	0.447 mm^{-1}
F(000)	712
Crystal size	0.80 × 0.60 × 0.40 mm
θ range for data collection	4.06 – 25.04°
Index anges	$-16 \le h \le 16, -10 \le k \le 10, -16 \le l \le 16$
Reflections collected	1805
Independent reflections	962 [R(int) = 0.0159]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	962 / 0 / 98
Goodness-of-fit on F^2	1.093
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0243, $wR2$ = 0.0635
R indices (all data)	$R1$ = 0.0259, $wR2$ = 0.0650
Largest difference peak and hole	0.162 and –0.146 e•$Å^{-3}$

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References

[1] M. G. Voronkov, E. A. Maletina and V. K. Roman, *Heterosiloxanes*, Soviet Scientific Review Supplement, Series Chemistry, M. E. Vol'pin, (Ed.), Academic, London, 1988; Vol. 1.
[2] F. J. Feher and T. A. Budzichowski, *Polyhedron* 1995, **14**, 3239.
[3] R. Murugavel, A. Voigt, M. G. Walawalkar and H. W. Roesky, *Chem. Rev.* 1996, **96**, 2205.
[4] R. Murugavel, V. Chandrasekhar and H. W. Roesky, *Acc. Chem. Res.* 1996, **29**, 183.
[5] P.D. Lickiss, *Adv. Inorg. Chem.* 1995, **42**, 147.
[6] R. Murugavel, V. Chandrasekhar, A. Voigt, H. W. Roesky, H.-G. Schmidt and M. Noltemeyer, *Organometallics*, 1995, **14**, 5298.
[7] M.G. Walawalkar, Ph. D. Thesis, University of Goettingen, Germany, 1997.
[8] G. M. Sheldrick, SHELXS-90, *Program for Structure Solution, Acta Crystallogr. Sect. A* 1990, **46**, 467.
[9] G. M. Sheldrick, SHELXL-93, *Program for Crystal Structure Refinement*, Universität Göttingen 1993.