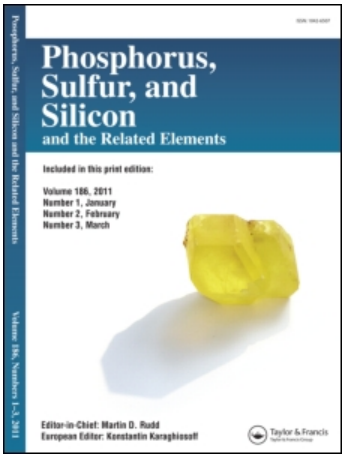


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# HIGH YIELD ROOM TEMPERATURE SYNTHESIS AND SPECTRAL STUDIES OF TRI(AMINO)SILANES: $(R_2N)_3SiH$

K. N. Radhamani[a]; Anil J. Elias[a]; D. K. Padma[a]
[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

**To cite this Article** Radhamani, K. N. , Elias, Anil J. and Padma, D. K.(1992) 'HIGH YIELD ROOM TEMPERATURE SYNTHESIS AND SPECTRAL STUDIES OF TRI(AMINO)SILANES: $(R_2N)_3SiH$', Phosphorus, Sulfur, and Silicon and the Related Elements, 66: 1, 297 — 300
**To link to this Article: DOI:** 10.1080/10426509208038359
**URL:** http://dx.doi.org/10.1080/10426509208038359

*Phosphorus, Sulfur, and Silicon*, 1992, Vol. 66, pp. 297–300
Reprints available directly from the publisher
Photocopying permitted by license only



## *Communication*

# HIGH YIELD ROOM TEMPERATURE SYNTHESIS AND SPECTRAL STUDIES OF TRI(AMINO)SILANES: $(R_2N)_3SiH$

K. N. RADHAMANI, ANIL. J. ELIAS and D. K. PADMA*
*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India*

*(Received June 6, 1991; in final form August 30, 1991)*

Tri(amino)silanes were prepared by the condensation of trichlorosilane with secondary amines in 1:6 molar ratio. Reactions of trichlorosilane with pyrrolidine, piperidine, hexamethyleneimine, morpholine, N-methylpiperazine and diethylamine afford the tri(amino)silanes in nearly quantitative yields. Their physical and spectroscopic properties are discussed. All these compounds are highly sensitive to moisture and hydrolyse to silica and the respective amine with the evolution of hydrogen. The compounds have been characterised by IR, $^1H$ NMR, $[^1H]^{29}Si$ NMR spectroscopic methods and CHN elemental analysis.

*Key words:* Pyrrolidine; piperidine; hexamethyleneimine; morpholine; N-methylpiperazine; diethylamine.



## INTRODUCTION

Tri(amino)silanes are well known starting materials for the production of various substituted silanes.[1,2] They are versatile catalysts for the addition of $SiHCl_3$ to acrylonitrile to give $\beta$-cyanoethyltrichlorosilane,[3] and have been used for the preparation of catalysts for urethane foams and elastomers.[4] The weak nature of Si—N bonds[5] in aminosilanes have been exploited for transesterification[6,7] and halogenation[8,9] reactions. Preliminary studies of Aylett and Peterson[10] have shown that these compounds are potential precursors for the preparation of silane ($SiH_4$), similar to trialkoxy silanes.[11] The use of tri(amino)silanes as reducing agents has not been attempted so far, although the hydrolytic dissociation leads to the liberation of amine and hydrogen.[10] Although a few examples of N-substituted tri(amino)silanes have been described,[12] very little is known about their physical and spectral properties as well as the chemistry of these compounds. We herein report the synthesis and spectral studies of six N-substituted tri(amino)silanes, where three nitrogens are directly linked to silicon.

## RESULTS AND DISCUSSION

The IR spectroscopic data of the compounds in Table I show strong absorptions in the region 670–700 $cm^{-1}$ which has been assigned to Si—N vibrations.[9,13] On hydrolysis by atmospheric moisture, the intensities of these bands decrease and after some time the bands can no longer be discerned in the spectra, thereby showing

TABLE I

Nuclear magnetic resonance (proton and silicon) and infrared spectral data of $(R_2N)_3SiH$

| Sl. No. | Tri(amino)silane | bp/mp °C | IR ($cm^{-1}$) $\nu$Si—H | $\nu$Si—N | $\delta$Si—H | $^1$H NMR# $\delta$(in ppm) | $^{29}$Si NMR* $\delta$(in ppm) |
|---|---|---|---|---|---|---|---|
| 1. | $(C_4H_8N)_3SiH$ | 92.5[a] | 2102 | 669 | 821 | 4.45 (s, 1H)Si—H<br>2.98 (t, 12H)N—$CH_2$<br>1.67 (m, 12H)C—$CH_2$ | −35.76 |
| 2. | $(C_5H_{10}N)_3SiH$ | 109[a] | 2105 | 696 | 820 | 4.09 (s, 1H)Si—H<br>2.82 (t, 12H)N—$CH_2$<br>1.37 (m, 18H)C—$CH_2$ | −30.27 |
| 3. | $(C_6H_{12}N)_3SiH$ | 140[a] | 2100 | 690 | 834 | 4.22 (s, 1H)Si—H<br>2.89 (m, 12H)N—$CH_2$<br>1.55 (s, 24H)C—$CH_2$ | −26.94 |
| 4. | $(OC_4H_8N)_3SiH$ | 107[c] | 2107 | 694 | 815 | 4.21 (s, 1H)Si—H<br>3.56 (t, 12H)O—$CH_2$<br>2.92 (t, 12H)N—$CH_2$ | −29.81 |
| 5. | $(CH_3NC_4H_8N)_3SiH$ | 48[c] | 2106 | 700 | 822 | 4.19 (s, 1H)Si—H<br>2.93 (m, 12H)C—N—$CH_2$<br>2.27 (t, 12H)Si—N—$CH_2$<br>2.24 (s, 9H)N—$CH_3$ | −29.95 |
| 6. | $[(C_2H_5)_2N]_3SiH$ | 73[a] | 2104 | 670 | 837 | 4.25 (s, 1H)Si—H<br>2.82 (q, 12H)N—$CH_2$<br>0.99 (t, 18H)C—$CH_3$ | −28.45 |
| 7. | $Cl_3SiH$ | 31[b] | 2245 | — | 805 | 6.10 (s, 1H)Si—H | −9.75 |

[a]bp at 0.7 mm of mercury; [b]bp at 760 mm of mercury; [c]melting point.

*Spectra were recorded (400 MHz) in the proton coupled and decoupled mode in $CDCl_3$ solutions with respect to TMS external standard.

#Data obtained on a 270 MHz instrument in $CDCl_3$ solutions with respect to TMS internal standard.



the cleavage of the Si—N bonds during hydrolysis. The residue left behind after complete hydrolysis of the compound shows IR absorption peaks corresponding to that of silica.[14] It is interesting to point out that the Si—N frequency reported for tris(dimethylamino)silane at 700–740 $cm^{-1}$ is shifted to the region 670–700 $cm^{-1}$ for the compounds (**1–6**). This perhaps may be due to the vibrational interactions of the various groups attached to nitrogen which in turn influences the Si—N bond.

It is known that in the IR spectra of compounds which have —$SiH_3$ groups, the Si—H deformation gives rise to two bands of almost equal intensity.[9,13,15] However, in the spectra of organoaminosilanes containing $(R_2N)_3Si$—H groupings, only one band is observed corresponding to the Si—H bending vibration, in the range 837–815 $cm^{-1}$ (Table I). The Si—H stretching vibration in these synthesized derivatives occurs in a narrow range 2104 ± 3 $cm^{-1}$. The nature of the amino groups has only a marginal effect on the Si—H vibrations. In trichlorosilane these bands occur at 805 and 2258 $cm^{-1}$, respectively.[16,17]

The $^1$H NMR spectra of compounds (**1–6**) (Table I) reveal that the Si—H protons are shielded in comparison with $Cl_3SiH$ ones as expected, with resonances in the range 3.98 to 4.45 ppm. The chemical shifts of the hydrogens on the amino residues of compounds (**1–6**) are in the same region as reported in the case of aminophosphines.[18] The [$^1$H]$^{29}$Si NMR spectra of the aliphatic tri(amino)silanes fall in the narrow range −26 to −35 ppm (Table I), comparable with the value reported

TABLE II

$^{29}Si—^{1}H$ coupling constants and Si—H bond stretching frequencies ($cm^{-1}$) of tri(amino)silanes

| Sl.No. | $(R_2N)_3SiH$ | $\nu$Si—H | $^{1}J_{Si—H}$ |
|---|---|---|---|
| 1 | $(C_4H_8N)_3SiH$ | 2102 | 224.18 |
| 2 | $(C_5H_{10}N)_3SiH$ | 2105 | 229.74 |
| 3 | $(C_6H_{12}N)_3SiH$ | 2100 | 228.28 |
| 4 | $(OC_4H_8N)_3SiH$ | 2107 | 238.06 |
| 5 | $(CH_3NC_4H_8N)_3SiH$ | 2106 | 234.51 |
| 6 | $[(C_2H_5)_2N]_3SiH$ | 2104 | 226.55 |
| 7 | $Cl_3SiH$ | 2245 | 365.68 |

for tris(dimethylamino)silane (−25.4 ppm).[19] The spin-spin coupling constants $^{1}J_{Si—H}$ give valuable information on the nature of chemical bonds.[20] E. Kuppce *et al.*,[19] have shown that for nitrogen derivatives a linear correlation between $^{1}J_{Si—H}$ and $\nu_{Si—H}$ exists. In the case of aminosilanes also such a linear correlation is found to exist except for compound (**3**) (Table II). It is evident from the $[^{1}H]^{29}Si$ NMR spectra that the three nitrogen atoms bonded to silicon give rise to a significant upfield shift when compared to trichlorosilane, indicating shielding of silicon.



## EXPERIMENTAL

All operations were performed under a dry oxygen free nitrogen atmosphere using standard schlenk techniques. Reagents were of AR grade, purified and dried by standard procedures. n-Hexane and benzene (Caution! Potential carcinogen) were distilled and stored over sodium wire. The spectral instruments used were as follows: IR (in nujol): Hitachi 270-50 spectrophotometer; NMR:Bruker WH 270 and Bruker AMX-400; MS:Finnigan Matt 8230.

In a typical reaction, trichlorosilane (5 ml, 0.046 mol) in 50 ml benzene—hexane (v/v 1:1) mixture was added to a solution of the secondary amine (0.276 mol) in the same solvent mixture in a side-arm flask. An instantaneous reaction was observed with the formation of a white precipitate, which on analysis was found to be the corresponding amine hydrochloride. After 12 hours of vigorous stirring at room temperature, the solvent mixture was removed 'in vacuo' to yield the corresponding tri(amino)silanes (yield 90–95%) which were further purified by repeated recrystallization from benzene hexane mixtures or by vacuum distillation under reduced pressure.

The overall reaction proceeds as follows:

$$HSiCl_3 + 6R_2NH \rightarrow (R_2N)_3SiH + 3R_2NH \cdot HCl$$

[$R_2N$ = 1) pyrrolidino, 2) piperidino, 3) hexamethyleneimino, 4) morpholino, 5) N-methylpiperazino and 6) diethylamino].

*Spectral and analytical data.* Tables I and II summarizes and compares the IR as well as the $^{1}H$— and $^{29}Si$—NMR data on compounds (**1–6**) with that of trichlorosilane. With a view to provide additional evidence for the identity of this set of compounds, analytical and mass spectral data on a selected example $(OC_4H_8N)_3SiH$ (**4**) was also obtained. Anal. Calcd. for **4**: C, 50.14; H, 8.77; N, 74.82%: Found: C, 49.67; H, 8.77; N, 74.20%. Mass Spectra (EI, 70 eV) *m/e* (rel. abundance): 287 ($M^+$, 61%), 200 ($M^+$—$OC_4H_9N$, 41%), 143 (33%), 116 (50%), 115 ($M^+$—2 $OC_4H_8N$, 47%), 86 ($OC_4H_8N$, 47%), 58 (70%), 43 (100%).

Presently efforts are under way to explore the potential use of these compounds in various reactions and to synthesize other tri(amino)silanes.

## ACKNOWLEDGEMENTS

We thank M/s Metkem Silicon Ltd, Mettur Dam, Tamilnadu, India for supply of free samples of pure trichlorosilane. Spectral facilities of the Sophisticated Instrumentation Facility, I. I. Sc, Bangalore is gratefully acknowledged.

REFERENCES

1. (a) B. Kanner, C. L. Schilling and S. P. Hopper, U.S. Pat. 4400526 (1983); C.A. **99,** No. 176052 (1983); (b) B. Kanner, J. M. Quirk, A. P. DeMonte and K. R. Mehta, U.S. Pat. 4558146 (1985); C.A. **104,** No. 207443 (1986).
2. (a) B. Kanner, J. M. Quirk, A. P. De Monte and S. P. Hopper, U.S. Pat. 4556725 (1985); C.A. **104,** No. 207441 (1986). (b) J. M. Quirk, L. K. Kozak and B. Kanner, Eur. Pat. 184692 (1986); C.A. **105,** No. 153676 (1986).
3. R. A. Pike and R. L. Schank, *J. Org. Chem.*, **27,** 2190 (1962).
4. F. O. Baskent and J. D. Reddy, Eur. Pat. 84183 (1983); C.A. **100,** No. 35616 (1984).
5. S. D. Barton and W. David Ollis, Comprehensive Organic Chemistry (Pergamon Press, Oxford, 1979), Vol. 3, Part 13, pp. 544.
6. B. Kanner and S. P. Hopper, U.S. Pat 4384131 (1983); C.A. **99,** No. 70982 (1983).
7. B. Kanner and S. P. Hopper, U.S. Pat. 4395564 (1983); C.A. **99,** No. 176049 (1983).
8. H. J. Campbell-Ferguson, E. A. V. Ebsworth, A. G. MacDiarmid and T. Yoshioka, *J. Phys. Chem.*, **71,** 723 (1967).
9. C. Glidewell and D. W. H. Rankin, *J. Chem. Soc.*, **(A),** 279 (1970).
10. B. J. Aylett and L. K. Peterson, *J. Chem. Soc.*, 3429 (1964).
11. S. Inaba and H. Nagaham, Jap. Pat. 63195107 (1988); C.A. **109,** No. 233654 (1988).
12. E. Lukevits, R. Ya. Sturkovich, E. Liepin'sh and I. V. Dipan, *Zh. Obshch. Khim.*, **46,** 2536 (1976).
13. B. J. Aylett and J. Emsley, *J. Chem. Soc.*, **(A),** 1918 (1967).
14. J. J. Hauser, G. A. Pasteur, A. Staudinger and R. S. Hutton, *J. Non-Crystalline Solids*, **46,** 71 (1981).
15. N. B. Colthup, L. H. Daly and S. C. Wiberley, Introduction to Infrared and Raman Spectroscopy (Academic Press, Inc., New York, 1975), 2nd ed., Chap. 12. pp. 339.
16. S. N. Sahau, T. S. Shi, P. W. Gee, J. W. Corbett, A. Hiriki, T. Imura, M. Tashiro and Vijay A. Singh, *J. Chem. Phys.*, **77,** 4330 (1982).
17. C. J. Pouchert, Aldrich Library of infrared spectra (Aldrich Chem. Co., Wisconsin, 1981), 3rd ed., pp. 1539.
18. L. Altaf Hussian, Anil. J. Elias and M. N. Sudhendra Rao, *Tetrahedron Lett.*, **29,** 5983 (1988).
19. K. Kupce, E. Liepins, A. Lapsina, G. Zelcans and E. Lukevics, *J. Organomet. Chem.*, **333,** 17 (1987).
20. G. A. Webb, Annual reports on NMR spectroscopy (Academic Press, Inc., New York, 1979), Vol. 9, pp. 276–281.