RESEARCH ARTICLE

ScienceAsia 25 (1999) : **113-119**

A Novel Route to Tris(silatranyloxy-*i*-propyl)amine Directly from Silica and Triisopropanolamine, Part I

Pensri Piboonchaisit [a], Sujitra Wongkasemjit [a,*] and Richard M Laine [b]

[a] The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand.

[b] The Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA.

[*] Corresponding author. Tel +66-2-218 4133, Fax +66-2-215 4459, E-mail: dsujitra@chula.ac.th

Received 5 April 1999

ABSTRACT New convenient and inexpensive method of tris(silatranyloxy-*i*-propyl)amine synthesis directly from silica and triisopropanolamine (TIS) has been elaborated using ethylene glycol solvent. The silatrane product is obtained in one step via the the "Oxide One Pot Synthesis (OOPS)" process. In the presence of catalytic amounts of triethylenetetramine (TETA), the reaction easily takes place. The product is characterized by DSC, TGA, ^{1}H-, ^{13}C-, ^{29}Si-NMR and FAB$^+$-MS. The FTIR result indicates the presence of N→Si transannular bonding. The chemical and physical properties of these compounds are described specially with respect to their polymeric properties.

KEYWORDS: tris(silatranyloxy-i-propyl)amine, silica, triisopropanolamine, silatrane.

INTRODUCTION

The limited number of simple silicon-containing starting materials restricts the potential role of inorganic and organometallic silicon compounds in the development of new chemical reagents, polymeric glasses and ceramics. The reason is that silicon-containing chemicals are almost exclusively prepared from elemental silicon, obtained from the carbothermal reduction of silica at around 1200°C.[1] The utilization of crude silica to form silicon-containing compounds directly, in order to circumvent this energy-intensive step, has been the aim of a number of research groups by a variety of strategies.

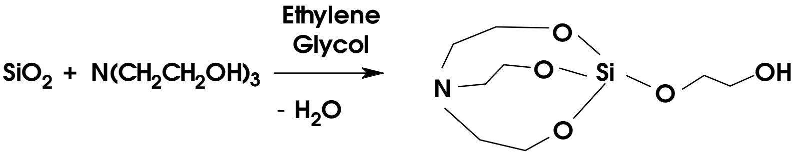
Silatranes, for example, as a class of pentacoordinated silicon compounds are known for more than three decades, and their specific biological,[2-3] physico-chemical[4-5] and structural[6-7] properties still attract research interests. Although the investigation results were published in many papers,[8-10] most of them deal solely with the intriguing properties study of these compounds.

The most popular methods for the silatrane synthesis are the reactions of halo-, hydro- and alkoxysilanes with triethanolamine or its derivatives[11] (see eq 1). The original way of silatrane synthesis from ethoxysilanes and boratrane in the presence of Al(O$\underline{i}$-Pr)$_3$ or Al$_2$Cl$_6$ has also been described.[12-13]

$$\begin{aligned}&XSi(OC_2H_5)_3 + (HOCH_2CH_2)_3N \rightarrow\\&\quad XSi(HOCH_2CH_2)_3N + 3C_2H_5OH \qquad (1)\\&X \quad = \quad C_2H_5O, C_6H_5\end{aligned}$$

Recently, Laine and colleagues have found a way to synthesize organosilicon compounds directly from a very inexpensive starting material, silica (SiO$_2$), and ethylene glycol in only one step.[14-16] They also found a way to synthesize tris(silatranyloxy-ethyl)amine from silica and triethanolamine[17] *via* the "OOPS" process, as shown in eq 2.

We have been further investigating this reaction with different kind of trialkoxylamine, namely TIS, to determine whether similar silatrane product can be obtained. This paper describes the production and characterization of tris(silatranyloxy-*i*-propyl)amine via the "OOPS" process directly from silica, which is a widespread and inexpensive starting material, as compared to triethoxysilanes which are far more expensive, and TIS.



(2)

EXPERIMENT

Materials

All reactions were carried out under a N_2 atmosphere with careful exclusion of extraneous moisture and air since the product is slightly sensitive to moisture and air. The glassware used for these experiments was oven dried. Amorphous, precipitated silicon dioxide, SiO_2, with a multi-point BET surface area of 182 m^2/g, was donated by PPG Siam Silica Co., Ltd. and used as received. It was stored in a dry environment prior to use to prevent moisture adsorption. Ethylene glycol, EG, (99.5% Farmitalia Carlo Erba) used as solvent in the reaction was distilled before used by fractional distillations at 200°C. Triethylenetetramine, TETA, (Union Carbide, Thailand, Ltd) used as a base catalyst was distilled under vacuum prior to use. TIS was obtained from Fluka Chemika Company and used as received. Anhydrous diethyl ether and dichloromethane (JT Baker Inc) used as purification solvents were purified by standard techniques under N_2 atmosphere. Dichloromethane was distilled from anhydrous calcium chloride, and anhydrous diethyl ether was dried by adding anhydrous calcium chloride and kept in a clear dry Winchester bottle.

Characterization

FTIR spectra were obtained using a Bio-Rad FT-45A spectrometer with a resolution of 4 cm^{-1}. A solid sample was thoroughly ground using 1.0% sample to 99% by weight of pure and dry crystalline KBr, followed by mixing and pressing hydraulically into pellet. ^1H-, ^{13}C-, ^{29}Si-NMR spectra were obtained using a 500 MHz JEOL spectrometer at room temperature in DMSO-d_6 as solvent and TMS as internal reference. Mass spectra were obtained on a Fison Instrument (VG Autospec-ultima 707E) with VG data system using a direct probe of the positive fast atom bombardment technique (FAB^+ mode) and cesium iodide (CsI) as a standard for peak calibration.

Thermal transition properties were determined using a Netzsch DSC 200 at a heating rate of 10°C / min under nitrogen atmosphere. The thermal stability of the synthesized products was obtained using Netzsch TGA 209 at a heating rate

and flow rate of 20°C and 10 mL per min, respectively.

Synthetic Method

Synthesis of silatrane complex was carried out with and without catalyst TETA by placing 6.09 g (100 mmol) of silica, 19.12 g (100 mmol) of TIS, and 100 mL of ethylene glycol into a 250 mL two-neck reaction flask. In case of running the reaction with catalyst, then 0.15 g. (1 mmol) of TETA was also added into the mixture. The solution mixture was magnetically stirred and heated to the boiling point of EG under N_2 atmosphere to distill off EG and by-product, water. During the course of reaction, the same amount of fresh EG as distillate was added. This process of EG distillation and addition was repeated until the mixture turned clear, indicating that the reaction was complete which took approximately 5 and 10 h for the reaction containing with and without TETA, respectively. The remaining EG was removed by vacuum distillation (10^{-2} torr) using an oil-bath temperature of 100±5°C. The resulting product turned very viscously at this point. It was then purified by precipitating with dried 10% dichloromethane in diethyl ether. The powder product was filtered off, dried in vacuum oven at 50°C for 10 h., and finally characterized by TGA, DSC, FAB^+-MS, FTIR and NMR.

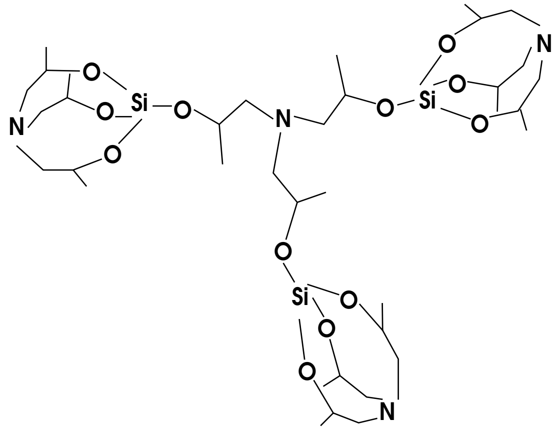
RESULTS AND DISCUSSION

Silatrane complex, tris(silatranyloxy-*i*-propyl) amine, (<u>I</u>), was synthesized *via* the "Oxide One Pot Synthesis (OOPS)" process using widely available SiO_2 in the presence and absence of TETA catalyst under identical conditions. The reaction without TETA took twice longer than the one with TETA. Characterization of isolated products from both reactions indicated that their structures were almost identical, except that the product obtained from the reaction with TETA was bis(silatranyloxy-*i*-propyl)-hydroxyl- *i*-propyl amine, (<u>II</u>), as discussed in detail below.

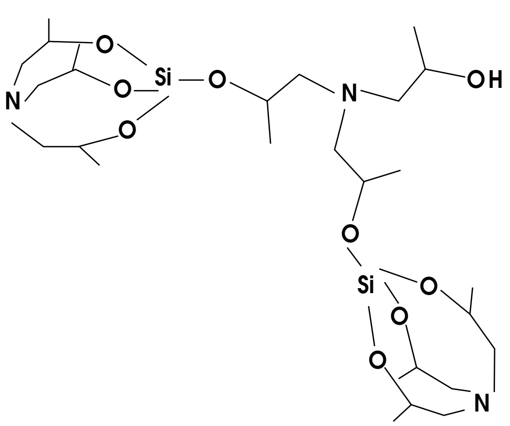
Thermogravimetric Analysis (TGA)

The silatrane product without TETA show three regions of mass loss, 150°-250°C, 290°-370°C and 390°-620°C, see Figure 1(a). The first one corresponds to the loss of traces of residual EG and TIS. The second and the last mass loss correspond to organic ligand decomposition and the oxidation of residual carbon char, respectively. The final %ceramic yield is 22%, as compared to 21.5% for the theoretical ceramic yield.

In case of the product obtained with TETA (Fig 1(b)), it show similar mass losses to that from the reaction without TETA, except the mass loss between 260°-320°C. This region is likely belong to the TETA mixed in the product which is supported by NMR data indicating that approximately 15% TETA is present in the product. As a result, the % ceramic



I



II

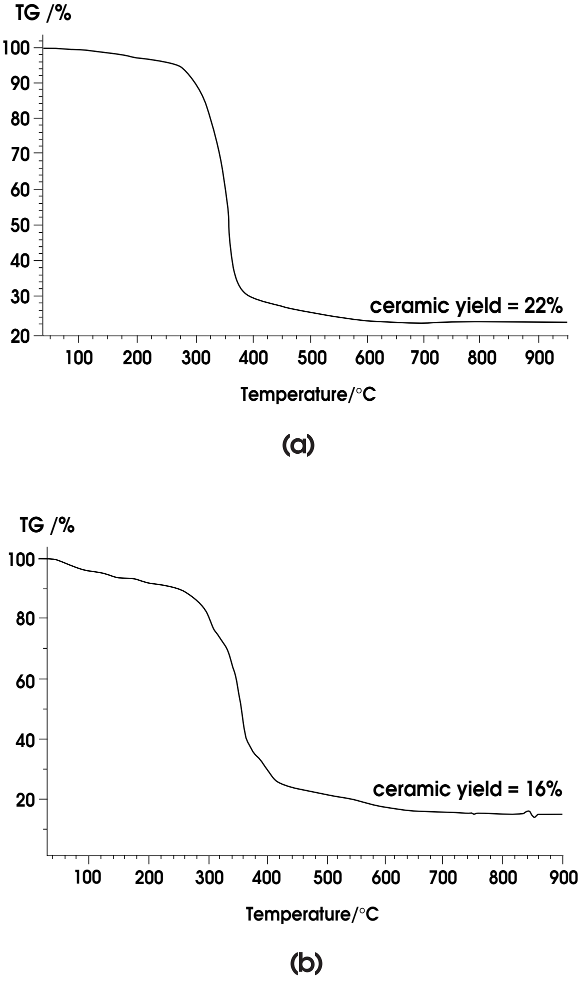


Fig 1. TGA of Precipitated Silatrane Complexes, (a) without TETA and (b) with TETA.

yield was only 16%, which is lower than the theoretical ceramic yield, 19.2%.

Differential Scanning Calorimeter (DSC)

DSC data of both products (Figure 2) show similar results to the TGA profiles. Both exotherms at about 140 C correspond to decomposition of EG, TIS and TETA. The peaks at 220° and 180°C in Figures 2(a) and 2(b), respectively, corresponding to the melting point of silatrane complexes, confirm that using catalyst in a reaction always results in shorter oligomers, as supported by FAB$^+$-MS, than the product obtained from the one without TETA.

Positive Fast Atom Bombardment Mass Spectroscopy (FAB$^+$-MS)

The FAB$^+$-MS spectrum fragmentation pattern can be employed to confirm the silatrane structures, as can be seen in Table 1 showing the proposed structures of the complexes obtained from the reaction without and with TETA. These structures support the fragmentation patterns in Figure 3.

From the results of FAB$^+$-MS spectroscopy, Figure 3 and Table 1 indicate that the product without TETA mainly consists of the oligomer that has the molecular ion peak at m/e 838, and the base peak is the monomer silatrane. The second highest intensity is the fragment with m/e 407 which has an intensity of 63%.

The fragmentation pattern of the product with TETA is similar to the pattern of the product from the reaction without TETA, except that the m/e 838 is absent. This is probably because TETA acts like an accelerator in the reaction, which results in the shorter chain of oligomers.

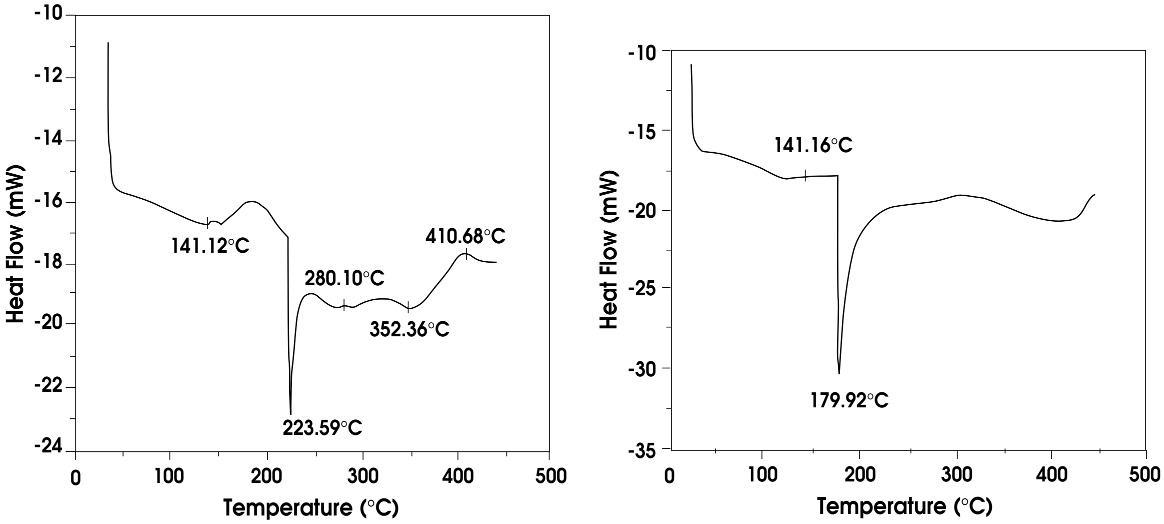
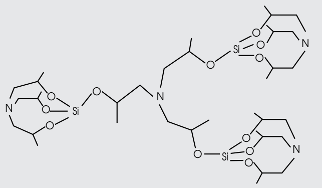
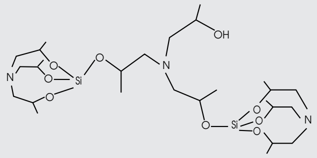
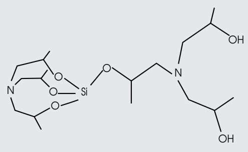
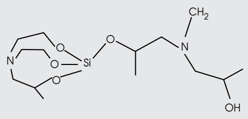
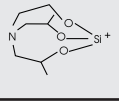


Fig 2. DSC of Precipitated Silatrane Complexes, (a) without TETA and (b) with TETA.

Table 1. The proposed structures and the pattern of fragmentation of the products obtained from the reactions w/o and w/ TETA.

m/e	Intensity		Species
	w/o TETA	w/ TETA	
838 (836 + $2H^+$)	8	-	
623 (621 + $2H^+$)	22	8	
407 (405 + $2H^+$)	63	18	
361 (360 + H^+)	24	10	
216 (215 + H^+)	100	100	

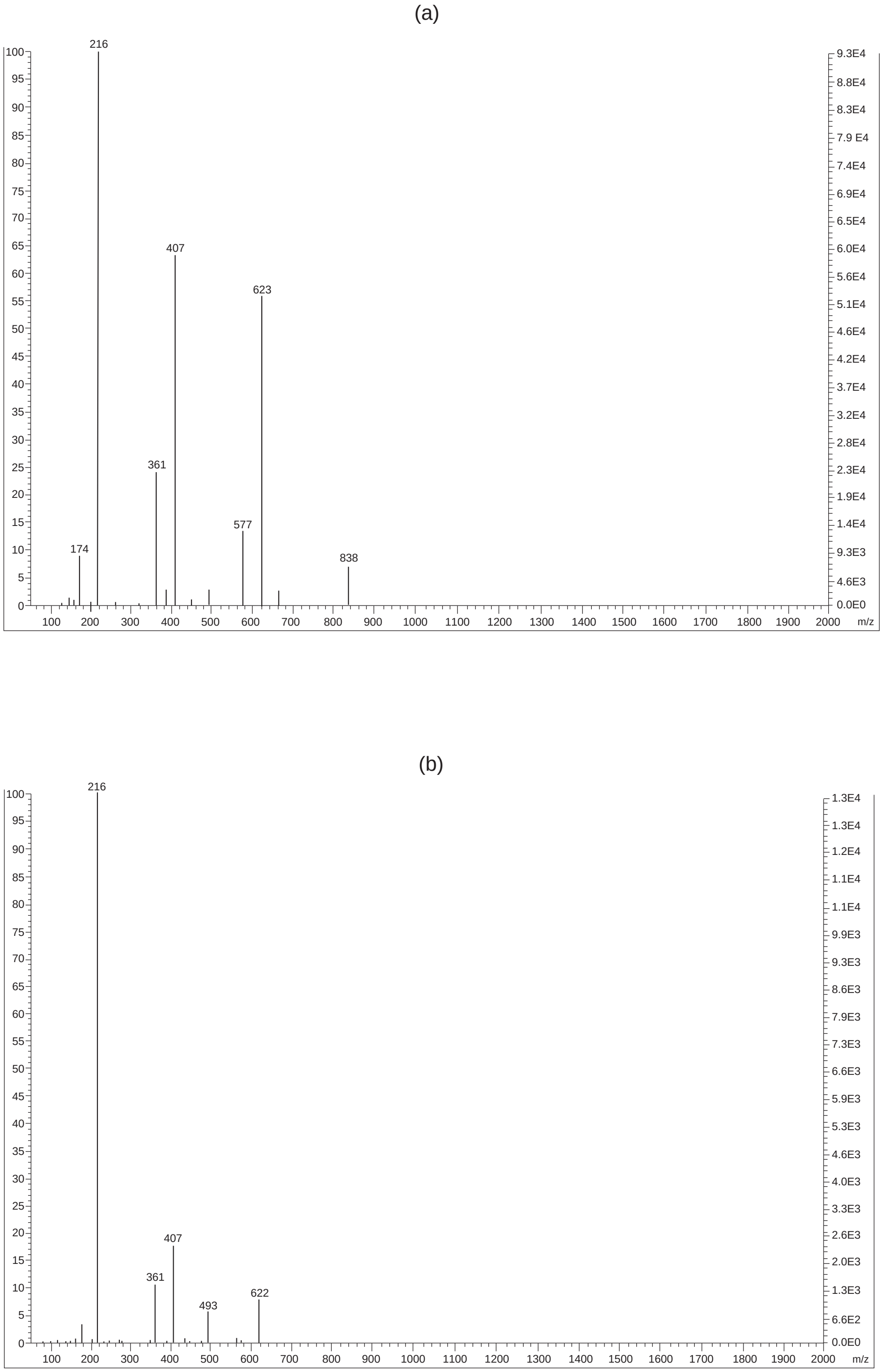


Fig 3. FAB$^+$-MS Fragmentation Patterns of Silatrane Complexes, (a) without TETA and (b) with TETA.

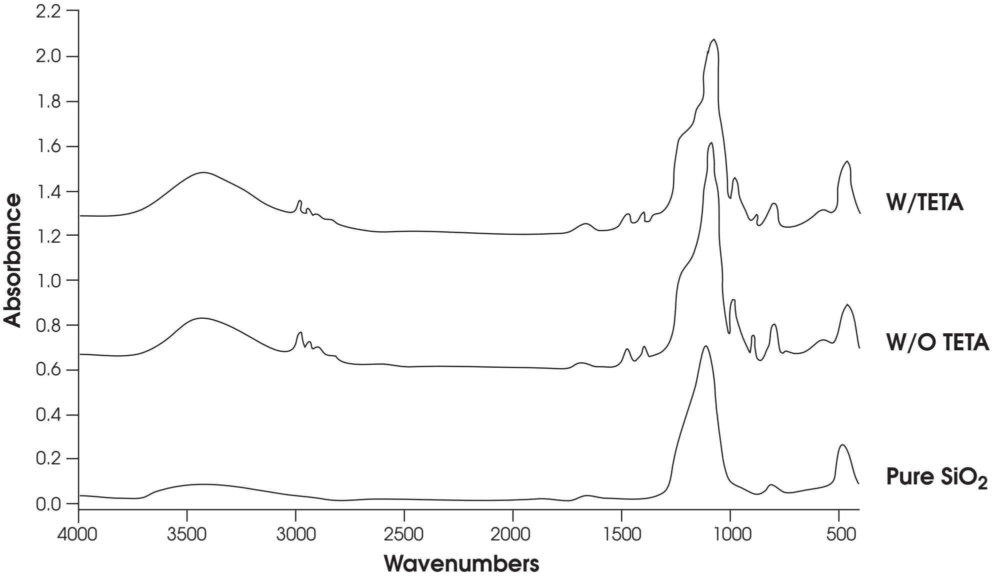


Fig 4. FT-IR Spectra of Pure Silica and Silatrane Complexesw/o and w/ TETA.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra show that the precipitated product of the reaction with TETA gives the same peaks found in the reaction without TETA. Both products indicate the presence of strong Si-O-C stretching bands at about 1015-1085 cm^{-1}. The peak at 2800-2976 cm^{-1} corresponds to the C-H stretching, whereas the peak at 1380-1460 cm^{-1} is resulted from the C-H bending. The peak at 1270 cm^{-1} comes from the C-N stretching. The strong peak at 1030-1070 cm^{-1} corresponds to the C-O stretching and the peak at 560-590 cm^{-1} refers to the $Si \rightarrow N$ dative bond.

Nuclear Magnetic Resonance Spectroscopy (NMR)

The ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra are used to confirm the structure of silatrane complexes. For the product without TETA ^{1}H-NMR spectrum in d_6-DMSO shows peaks at 0.96-1.12, 2.86-2.91, 3.3, 3.4-3.5, and 4.0 ppm, which are assigned to $CH\text{-}C\underline{H}_3$, $N\text{-}C\underline{H}_2$, $C\underline{H}_2\text{-}O$, $CH_2O\underline{H}$ of EG, and $C\underline{H}\text{-}CH_3$, respectively. The ^{13}C-NMR spectrum shows peaks at 20-21, 23, 57.7, 59.2, and 62.5-65 ppm which can be attributed to $H_2C\text{-}CH\text{-}\underline{C}H_3$, $H_2C\text{-}\underline{C}H\text{-}CH_3$, $N\text{-}\underline{C}H_2$, $\underline{C}H_2\text{-}O$, $\underline{C}H_2OH$ of EG, respectively.

^{1}H- and ^{13}C-NMR spectra of the silatrane complexes with TETA show similar peaks to those obtained from the reaction without TETA, except that ^{1}H-NMR spectrum shows the peaks at 2.6-2.7, which is the group of $NH_2\text{-}C\underline{H}_2$ in TETA. ^{13}C-NMR spectrum also shows peaks at 39-41 ppm indicating the $NH_2\text{-}\underline{C}H_2$ group of TETA. All results are summarized in Table 2.

Table 2. Compared Peak Positions of Products.

Position	Groups	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
a	$N\text{-}C\underline{H}_2$	2.86-2.91	57.7
b	$C\underline{H}\text{-}CH_3$	4.0	23
c	$CH\text{-}C\underline{H}_3$	0.96-1.12	20-21
d	$C\underline{H}_2\text{-}O$	3.3	59.2
e	$CH_2O\underline{H}$ of EG	3.4-3.5	62.5-65
f	$NH_2\text{-}C\underline{H}_2$ of TETA	2.6-2.7	39-41
g	$NH\text{-}C\underline{H}_2$ of TETA	2.9-3.1	60.4-60.7

^{29}Si NMR spectra of precipitated products of the reactions without and with TETA show the peaks at 96 and 98 ppm, respectively, identifying a pentacoordinate Si with dative bond,[18] as shown in Figure 5. One silica atom is bonded not only with 4 oxygen atoms, but also has a transannular dative bond, which interacts with N atom of TIS. Transannular dative bond is not like a "normal" silicon-nitrogen bond because internuclear distance ($r_{Si\text{-}N}$) is considerably shorter than the vander waal but longer than Si-N covalent bond. This is confirmed by the detailed X-ray crystalliographic studies by Boer and Turley in 1968.[19]

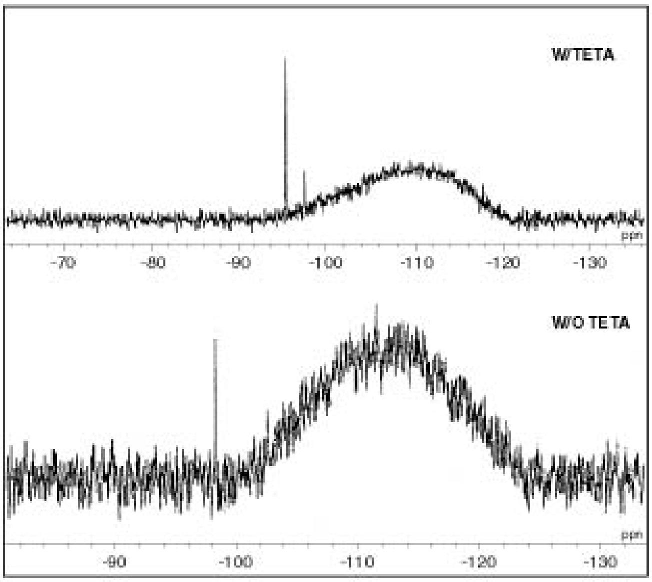


Fig 5. ^{29}Si-NMR Spectra of Silatrane Complexes w/ and w/o TETA.

CONCLUSIONS

The silatrane complexes can be synthesized directly from widespread available SiO_2 and TIS via the "Oxide One Pot Synthesis" process in the presence and absence of TETA. When TETA is present, the reaction time is twice faster. Thus, TETA could be used as an accelerator for this reaction. The purified products from the reaction with and without TETA are white solid powder which give molecular ion peaks at m/e=623 and 838, respectively. Other characterization studies show that both products display similar properties.

ACKNOWLEDGEMENTS

This study was supported by Royal Thai Government for research funding.

REFERENCES

1. Kirk-Othmer Encyclopedia of Chemical Technology (1979), 3rd Ed. *Silica*, Vol. 20, p 750
2. R Tacke and H Linoh (1989) Bioorganosilicon Chemistry. In S Patai and Z Rappoport, *The Chemistry of Organic Silicon Compounds*, Wiley-Interscience, New York.
3. E Lukevics and L Ignatovich (1992) Comparative Study of the Biological Activity of Organosilicon and Organogermanium Compounds, *Appl Organomet Chem* **6**, 113
4. MG Voronkov, MS Sorokin, VA Klyuchnikov, GN Shvetz and VJ Pepekin (1989) Thermochemistry of Organosilicon Compounds, *J Organomet Chem* **359** , 301
5. G Cerveau, C Chuit, E Colomer, RJP Corriu and C Reye (1990) Ferrocenyl Compounds Containing Two Hypervalent Silicon Species, *Organometallics* **9** , 2415
6. M Nasim, LJ Livantsova, PD Krutko, GS Zaitseva, J Lorbertth and M Otto (1991) Synthesis of 2-Silatranyl-and 2-(3,7,10-trimethylsilatranyl) acetaldehydes, *J Organomet Chem* **402** , 313
7. P Hencsei (1991) Mass-spectrometric Study of Ring Substituted Silatranes, *Struct Chem* **2** , 21
8. RJP Corriu and JC Young (1989) ìHypervalent Silicon Compounds. In: S Patai and Z Rappoport, *The Chemistry of Organic Silicon Compounds*, Wiley-Interscience, New York
9. C Chuit, RJP Corriu, C Reye and JC Young (1993) Reactivity of Penta- and Hexacoordinate Silicon Compounds and Their Role as Reaction Intermediates, *Chem Rev* **93**, 1371
10. V Gevorgyan, L Borisova, A Vjater, J Popelis, S Belyakov and E Lukevics (1994) Synthesis and Structure of Silylmethylsilatranes RR'R"SICH$_2$SI(OCH$_2$CH$_2$)$_3$)N", *J Organomet Chem* **482** , 73
11. MG Voronkov, VM Dyakov and SV Kirpichenko (1982) Silatranes, *J Organomet Chem* **233** , 1-147
12. MG Voronkov (1966) Silatranes:Intra-Complex Heterocyclic Compounds of Pentacoordinated Silicon, *Pure Appl Chem* **13**, 35
13. J Dirk Nies, JM Bellama, BZ Nava (1985) Multiphoton Infrared Laser-induced Degradation of Polydimethylsiloxane and Hexamethyldisilane, *J Organomet Chem* **296**, 315
14. Rangsitphol, J (1995) Aryloxysilane Synthesis Directly from silica and Catechol, Master Thesis, The Petroleum and Petrochemical College, Chulalongkorn University.
15. R Laine, K Blohowiak, T Robinson, M Hoppe, P Nardi, J Kampf and J Uhm (1991) Synthesis of Pentacoordinate Silicon Complexes from SiO_2, *Nature* **353** , 642-4
16. K Blohowiak, D Tradewell, R Mueller, M Hoppe, S Jouppi, P Kansal, K Chew, C Scotto, F Babonneau, J Kampf and R Laine (1994) SiO_2 as a Starting Material for the Synthesis of Pentacoordinate Silicon Complexes, *Chem Mater* **6**, 2177-92
17. C Bickmore and R Laine (1996) Synthesis of Oxynitride Powders via Fluidized-Bed Ammonolysis, Part I: Large, Porous, Silica Particles, *J Am Ceram Soc* **79**, 2865-77
18. L Sommer and O Bennett (1957) Anomalous Spin-Spin Splitting in NMR Spectra of Cyclobutenes, *J Am Chem Soc* **79** , 1008
19. J Turley and F Boer (1968) Structural Studies of Pentacoordinated Silicon. I-Phenyl-(2,2',2"-nitrilotriethoxy)silane, *ibid* **90**, 4026