2:1:1, in keeping with effective C_{2v} symmetry. The ν(CO) IR spectra are closely similar, exhibiting high-frequency bands at 2139 and 2154 cm^{-1} for **1** and **2**, respectively, which are among the highest reported for group VIII metal carbonyls.

The isolation and characterization of the singly bridged cationic complexes **1** and **2** offer an opportunity to probe a number of fundamental aspects of the chemistry of binuclear phosphido complexes. Given their enhanced susceptibility to nucleophilic attack, they may serve as simple models for the examination of reaction mechanisms leading to bridge cleavage[3a,e15] and/or ligand substitution.[1,2a,b] In addition, they should be useful synthons for cluster chemistry. We are currently exploring these possibilities.

Acknowledgment. We acknowledge the support of the Natural Sciences and Engineering Research Council of Canada.

Supplementary Material Available: A full description of the synthesis of **1** and listings of X-ray crystal data, atomic positions, anisotropic thermal parameters, and bond lengths and angles for **2** (11 pages); a listing of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

---

(15) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984,** *3,* 814.

Polyhedral Aluminosilsesquioxanes as Models for Aluminosilicates: Unique Synthesis of Anionic Al/Si/O Frameworks

Frank J. Feher* and Keith J. Weller

Department of Chemistry, University of California, Irvine, California 92717

Received May 8, 1990

Summary: An efficient procedure for the synthesis of polyhedral aluminosilsesquioxanes has been developed and applied to the synthesis of **7**, an anionic aluminosilsesquioxane that is formally derived from two corner-sharing D4R subunits of Linde type A zeolite. The salient feature of this procedure is the use of tetramethylstibonium siloxides as mild sources of siloxide anions. Tetramethylstibonium siloxides can be prepared from silanols by using standard means or from the oxidation of hydridosilsesquioxanes with Me_3NO.

We recently reported the synthesis of **2**, an excellent latent source of **3** and a versatile precursor for the syntheses of polyhedral aluminosilsesquioxanes.[1a] In this paper we describe an interesting procedure for the synthesis of anionic aluminosilsesquioxanes. The utility of this procedure, which exploits a unique property of tetramethylstibonium siloxides (and alkoxides), is demonstrated by synthesizing **7**, an anionic aluminosilsesquioxane that is formally derived from two corner-sharing D4R subunits of Linde type A zeolite.

The most obvious approach to anionic aluminosilsesquioxanes, the reaction of **2** with alkali-metal siloxides (e.g., $MOSiMe_3$, M = Li, Na, K), produces complex mixtures of intractable products. Even in nonpolar media, where strong contact ion pairing greatly reduces anion nucleophilicities, alkali-metal siloxides (and alkoxides) quickly destroy most silsesquioxane frameworks. The nucleophilicity of siloxide anions can, however, be tempered by using tetramethylstibonium siloxides (e.g., $Me_4SbOSiMe_3$), which are actually hydrocarbon-soluble molecular species with five-coordinate antimony centers. These interesting "pseudosalts" are excellent sources of siloxide anions under very mild conditions.[2]

The reaction[3] of **2** with $Me_4SbOSiMe_3$[2b] in C_6H_6 (80 °C, 12 h) affords a virtually quantitative yield of **4**, which was easily identified on the basis of ^1H, ^{13}C, and ^{29}Si NMR spectral data. Both the ^{29}Si NMR spectrum and the methine region of the ^{13}C NMR spectrum of **4** exhibit three resonances with the expected relative intensities of 3:3:1, while the ^{13}C NMR spectrum exhibited a singlet resonance (δ −0.72) characteristic of the four-coordinate $[Me_4Sb]^+$ ion.[4]

The thermodynamic stability of **4** and efficiency of its synthesis suggested that a variety of interesting aluminosilsesquioxanes (e.g., **7**) could be synthesized from **2**, if a convenient source of anhydrous tetramethylstibonium siloxides and/or silicates could be discovered. Unfortunately, the usual methods[5] for synthesizing stibonium si-

---

(1) (a) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989,** *111,* 7288–9. (b) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989,** *111,* 1741–8.

(2) (a) Schmidbauer, H.; Weidlein, J. Z.; Mitschke, K.-H. Ber. **1969,** *102,* 4136–46. (b) Schmidbaur, H.; Arnold, H.-S.; Beinhofer, E. Ber. **1964,** *97,* 449–66. (c) Eberwein, B. B.; Ott, R.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1977,** *431,* 95–104. (d) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1965,** *4,* 201–11.

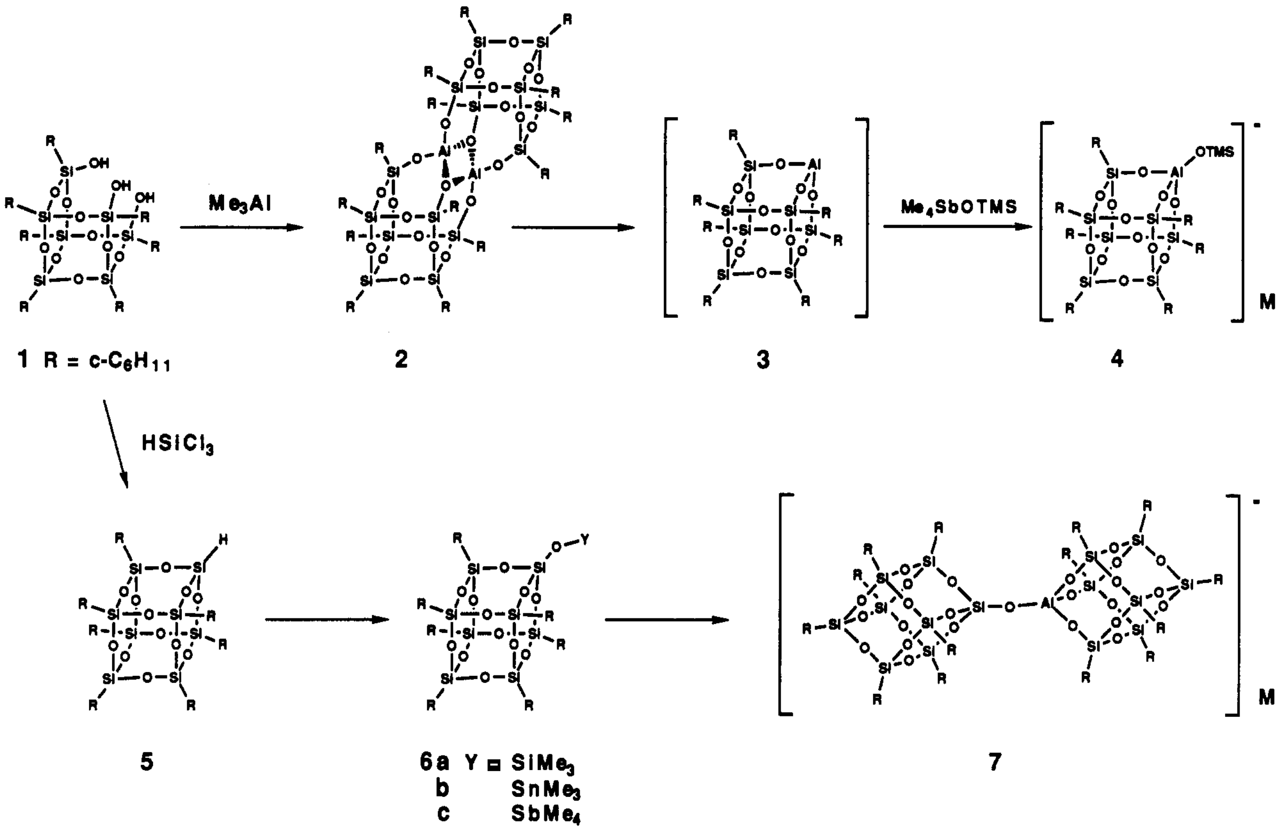
(3) In a typical reaction, $Me_4SbOSiMe_3$ (1.00 mmol) was added to a solution of **2** (576 mg, 0.288 mM) in benzene. The solution was refluxed for 12 h and then evaporated (25 °C, 0.1 mTorr) to give **4** in virtually quantitative yield (by ^1H and ^{13}C NMR spectroscopy). Analytically pure **4** was obtained by recrystallization from C_6H_6/hexane. Spectroscopic and analytical data for **4** are as follows. ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ 2.26–2.18 (m, 14 H), 1.90–1.67 (complex, m, 35 H), 1.41–1.22 (complex m, 21 H), 1.10–1.06 (complex m, 4 H), 1.05 (s, 12 H), 0.96–0.85 (m, 3 H), 0.327 (s, 9 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 25 °C): δ 28.62, 28.53, 28.47, 28.36, 28.21, 28.14, 28.04, 27.90, 27.79, 27.62, 27.48 (CH_2), 25.93, 24.72, 24.28 (3:3:1 for CH), 3.82 ($SiMe_3$), −0.72 ($SbMe_4$). $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6, 25 °C): δ 0.035, −66.59, −68.35, −69.52 (1:3:1:3). Anal. Calcd (found) for $C_{49}H_{98}AlO_{13}Si_8Sb$: C, 46.39 (46.54); H, 7.78 (8.07). Mp: >400 °C.

(4) In C_6D_6 at 25 °C, resonances for the Me_4Sb groups in five-coordinated complexes (e.g., $Me_4SbOSiMe_3$, $Me_4SbOCMe_3$, Me_5Sb) typically occur downfield from 10 ppm in ^{13}C NMR spectra. Resonances for the Me_4Sb groups in four-coordinate complexes (e.g., $[Me_4Sb][Al(OSiMe_3)_4]$) typically occur upfield from 0 ppm.

(5) The two most common methods for synthesizing stibonium siloxides are the reactions of alkali-metal siloxides with $[Me_4Sb]Cl$[2b] and the reactions of silanols with Me_5Sb.[2a,c]

0276-7333/90/2309-2638$02.50/0 © 1990 American Chemical Society

Scheme I



loxides are not attractive routes to stibonium silsesquioxides or multifunctional siloxides and silicates. Recent syntheses of silylsilicates by Klemperer[6] did, however, suggest that hydridosilsesquioxanes might be excellent precursors for tetramethylstibonium silicates. In order to explore this possibility, **5** was prepared by the reaction of **1**[1b] with HSiCl$_3$ in Et$_3$N/Et$_2$O.[7]

The reaction[8] of **5** with Me$_3$NO/(TMS)Cl[6] affords a quantitative (NMR) yield of **6a**. Under conditions that do not induce gross decomposition, the O–SiMe$_3$ group in **6a** is surprisingly resistant to cleavage by anionic nucleophiles. The analogous trimethyltin derivative (**6b**)[9] is, however, much more reactive and can be easily cleaved (3 h, 25 °C, C$_6$H$_6$) by Me$_4$SbOSiMe$_3$ and Me$_4$SbOCMe$_3$ to give quantitative (NMR) yields of **6c** and the corresponding stannyl ethers (i.e., Me$_3$SnOSiMe$_3$ or Me$_3$SnOCMe$_3$). Compound **6c** can also be prepared directly by the reaction of **5** with Me$_3$NO (2 equiv) and [Me$_4$Sb]Cl.[9]

The structure of **6c** was straightforwardly established on the basis of multinuclear NMR data. Of particular relevance was the presence of a strongly shielded resonance in the ^{29}Si NMR spectrum of **6c**. The chemical shift of this resonance (δ −108.93) was within the range expected for Q-type silicon atoms in a [Si$_8$O$_{12}$] framework (−100 to −110 ppm)[6,10] and was upfield from the region where an-

---

[6] Agaskar, P. A.; Day, V. W.; Klemperer, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 5554–6.

[7] (a) The synthesis of **5** has been previously described.[7b] A much more efficient synthetic procedure and complete characterization data for **5** are provided in ref 7c. (b) Brown, J. F.; Vogt, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 4313–7. (c) In a typical reaction, freshly distilled HSiCl$_3$ (0.995 g, 7.35 mM) was added to a solution of **1** (7.155 g, 7.35 mM) and Et$_3$N (2.41 g, 23.25 mM) in 35 mL of Et$_2$O. The mixture was stirred overnight and then filtered to remove Et$_3$NHCl. Evaporation of the volatiles (25 °C, 0.1 mTorr) gave 6.50 g (88%) of **5**. The product is spectroscopically pure (^{1}H, ^{13}C, ^{29}Si NMR) but can be recrystallized from C$_6$H$_6$/acetonitrile. Spectroscopic and analytical data for **5** are as follows. ^{1}H NMR (500.1 MHz, C$_6$D$_6$, 25 °C): δ 4.689 (s, 1 H), 2.09–1.99 (complex m, 14 H), 1.75–1.57 (complex m, 35 H), 1.26–1.20 (complex m, 21 H), 0.950 (m, 7 H). ^{13}C{^{1}H} NMR (125.03 MHz, C$_6$D$_6$, 25 °C): δ 27.73, 27.68, 27.28, 27.26, 27.21, 27.07 (CH$_2$), 23.78, 23.53 (4:3 for CH). ^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 25 °C): δ −68.05, −68.12, −68.15, −83.16 (3:1:3:1). Mass spectrum (20 eV, 200 °C): *m/e* (relative intensity) 998 (M$^+$, 10%), 915 (M$^+$ − C$_6$H$_{11}$, 100%), 833 (M$^+$ − 2 C$_6$H$_{11}$, 20%). Anal. Calcd (found) for C$_{42}$H$_{78}$O$_{12}$Si$_8$: C, 50.46 (49.90); H, 7.86 (7.77). Mp: >400 °C dec.

[8] In a typical reaction, **5** (519 mg, 0.519 mM) was added to a solution of Me$_3$NO (78 mg, 1.04 mM) and Me$_3$SiCl (112 mg, 1.04 mM) in 10 mL of THF. The solution was refluxed for 44 h and then filtered to remove [Me$_3$NOH]Cl and [Me$_3$NSiMe$_3$]Cl. Evaporation of the solvent (25 °C, 0.1 mTorr) gave **6a** in virtually quantitative (NMR) yield. Analytically pure material was obtained by recrystallization (46%) from CH$_2$Cl$_2$/acetone. Spectroscopic and analytical data for **6a** are as follows. ^{1}H NMR (500.1 MHz, C$_6$D$_6$, 25 °C): δ 2.10–2.05 (complex m, 14 H), 1.73–1.55 (complex m, 35 H), 1.25–1.20 (complex m, 21 H), 1.03 (m, 7 H), 0.278 (s, 9 H). ^{13}C{^{1}H} NMR (125.03 MHz, C$_6$D$_6$, 25 °C): δ 27.75, 27.70, 27.29, 27.22, 27.16 (CH$_2$), 23.80, 23.76, 23.66 (1:3:3 for CH), 1.60 (SiMe$_3$). ^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 25 °C): δ 11.29, −67.54, −68.09, −68.12, −107.81 (1:3:3:1:1). Mass spectrum (20 eV, 200 °C): *m/e* (relative intensity) 1086 (M$^+$, 15%), 1071 (M$^+$ − CH$_3$, 25%), 1003 (M$^+$ − C$_6$H$_{11}$, 100%). Anal. Calcd (found) for C$_{45}$H$_{86}$O$_{13}$Si$_9$: C, 49.68 (49.71); H, 7.97 (7.76). Mp: >400 °C.

[9] (a) In contrast to the oxidation silylation reaction,[6,8] which requires 2 equiv of Me$_3$NO and 2 equiv of Me$_3$SiCl per Si–H moiety, oxidative stannylation and stibnation only require 1 equiv of Me$_3$SnCl or [Me$_4$Sb]Cl. (b) Compounds **6b** and **6c** were prepared in 87% and 83% yields, respectively, by the oxidation of **5** with 2:1 Me$_3$NO/Me$_3$SnCl and 2:1 Me$_3$NO/[Me$_4$Sb]Cl. Spectroscopic and analytical data for **6b** are as follows. ^{1}H NMR (500.1 MHz, C$_6$D$_6$, 25 °C): δ 2.25–1.95 (m, 14 H), 1.94–1.44 (complex m, 35 H), 1.44–1.15 (complex m, 21 H), 1.15–0.95 (complex m, 7 H), 0.307 (s, 9 H). ^{13}C{^{1}H} NMR (125.03 MHz, C$_6$D$_6$, 25 °C): δ 27.82, 27.79, 27.35, 27.34, 27.29, 27.27, 27.23 (CH$_2$), 23.93, 23.87, 23.84 (3:1:3 for CH), −2.84 (*Me*$_3$Sn) ($J_{\text{Sn–C}}$ = 2500, 2710 Hz). ^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 25 °C): δ −68.00, −68.09, −68.14, −102.99 (3:3:1:1). Mass spectrum (20 eV, 200 °C): *m/e* (relative intensity) 1178 (M$^+$, 1%), 1163 (M$^+$ − Me, 30%), 1095 (M$^+$ − C$_6$H$_{11}$, 50%), 931 (M$^+$ − SnMe$_3$ − C$_6$H$_{11}$, 100%). Anal. Calcd (found) for C$_{45}$H$_{86}$Si$_8$O$_{13}$Sn: C, 45.86 (45.69); H, 7.36 (7.42). Mp: 318–322 °C. Spectroscopic and analytical data for **6c** are as follows. ^{1}H NMR (500.1 MHz, C$_6$D$_6$, 25 °C): δ 2.25–2.00 (m, 14 H), 1.82–1.45 (complex m, 35 H), 1.15–1.42 (m, 21 H), 1.10–0.95 (complex m, 7 H), 0.914 (s, 12 H). ^{13}C{^{1}H} NMR (125.03 MHz, C$_6$D$_6$, 24 °C): δ 27.96, 27.86, 27.83, 27.49, 27.43, 27.41, 27.37, 27.32, 27.29 (CH$_2$), 24.21, 23.96, 23.94 (3:3:1 for CH), 10.39 (*Me*$_4$Sb). ^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 25 °C): δ −68.08, −68.16, −68.58, −108.93 (3:1:3:1). Anal. Calcd (found) for C$_{46}$H$_{89}$Si$_8$O$_{13}$Sb: C, 46.17 (45.85); H, 7.50 (7.34). Mp: >400 °C dec.

ionic T-type silicate nuclei are typically observed (–94 to –97 ppm).[10] The ^{13}C NMR spectrum of **6c** also exhibited a characteristic singlet resonance (δ 10.39) for five-coordinate Me$_4$SbOR ethers.[4]

The reaction[11] of **6c** with **2** gave high yields of **7**, which was identified on the basis of multinuclear (^{1}H, ^{13}C, ^{29}Si) NMR data. A single-crystal X-ray diffraction study on one of many well-formed but poorly diffracting crystals confirmed the identity of **7**. Unfortunately, a serious discussion of metrical data is not warranted due to the marginal quality of the diffraction data and the severely disordered nature of the cyclohexyl groups.[12]

The preparation of **6c** and its use for the synthesis of **7** clearly suggests that a number of other interesting silicate clusters could be synthesized from **6c**. More tantalizing, though, are the prospects for achieving syntheses of very large, structurally well-defined clusters and/or entirely new framework silicates by using multifunctional precursors (e.g., [HSiO$_{1.5}$]$_n$; n = 8, 10, 12, 14).[6,13] We are currently exploring these possibilities and will present the details of this work in due course.

Acknowledgment. We express our thanks to Theodore A. Budzichowski for assistance with the X-ray structural study of **7** and for suggesting the use of Me$_4$SbOSiMe$_3$ as a mild source of siloxide anions. These studies were supported by the National Science Foundation (Grant No. CHE-8703016) and an NSF-Presidential Young Investigator Award (Grant No. CHE-8657262). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support from the UCI Academic Senate Committee on Research is also gratefully acknowledged. Funds for the purchase of the X-ray diffraction equipment were made available from NSF Grant No. CHE-85-14495.

Registry No. **1**, 47904-22-3; **2**, 122487-88-1; **4**, 129193-59-5; **5**, 3809-29-8; **6a**, 129174-78-3; **6b**, 129174-79-4; **6c**, 129193-57-3; **7**, 129193-61-9; Me$_4$SbOSiMe$_3$, 18279-58-8; HSiCl$_3$, 10025-78-2.

Supplementary Material Available: An ORTEP drawing, a summary of the crystal structure determination, and listings of atomic coordinates, interatomic distances and angles, and hydrogen atomic coordinates for **7** (10 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

---

(10) (a) Marsmann, H. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1980; Vol. 17, and references cited therein. (b) Williams, E. A. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 235 and referenced cited therein. (c) Williams, E. A. *Annu. Rep. NMR Spectrosc.* **1979**, *9*, 221 and referenced cited therein.

(11) In a typical reaction dimer **2** (81 mg, 0.0404 mM) and **7c** (98 mg, 0.0819 mM) were refluxed in benzene (3 mL) for 12 h. Evaporation of the solvent gave a quantitative (NMR) yield of **7** (based on **2**), which was recrystallized from C$_6$H$_6$/MeCN to give large colorless crystals. Spectroscopic and analytical data for **7** are as follows. ^{1}H NMR (500.1 MHz, C$_6$D$_6$, 25 °C): δ 2.30–2.04 (complex m, 28 H), 2.04–1.55 (complex m, 70 H), 1.55–1.17 (complex m, 42 H, with sharp singlet (12 H) at 1.35 for SbMe$_4$), 1.17–0.85 (complex m, 14 H). ^{13}C{^{1}H} NMR (125.03 MHz, C$_6$D$_6$, 25 °C): δ 28.76, 28.36, 28.25, 28.13, 28.03, 27.93, 27.88, 27.85, 27.82, 27.66, 27.61, 27.48, 27.44, 27.41, 27.37, 27.29 (CH$_2$), 25.75, 24.75, 24.26, 25.15, 23.92 (3:3:1:3:4 for CH), –0.43 (SbMe_4). ^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 25 °C): δ –66.94, –68.44, –68.52, –68.57, –68.74, –70.07, –106.21 (3:3:1:3:1:3:1). Anal. Calcd (found after removal of benzene and MeCN of crystallization in vacuo) for C$_{82}$H$_{155}$AlO$_{25}$SbSi$_{13}$: C, 47.93 (47.42); H, 7.60 (7.61). Mp >400 °C dec.

(12) Compound **7** crystallizes as a benzene–(CH$_3$CN)$_3$ solvate in the space group $P6_3$ (a = 14.734 (1) Å, c = 35.498 (6) Å; V = 6674 (1) Å^3; D_{calcd} = 1.270 g/cm^3 (Z = 2)). A total of 2930 independent reflections with 4.0 < 2θ < 45.0° were collected on a Nicolet R3m/V diffractometer at –100 °C using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL PLUS), and all non-hydrogen atoms were located by a series of difference-Fourier syntheses. The crystallographic 3-fold rotational axis is aligned along the Si–O–Al linkage joining both silsesquioxane frameworks. (The dihedral angle for the gauche O$_3$Al(–O–)SiO$_3$ conformation is 35°.) All of the cyclohexyl groups are severely disordered. Although efforts to model the disordered cyclohexyl groups as 1-adamantyl groups were moderately successful, the final R factor for isotropic refinement of all non-hydrogen atoms was 10.2%.

(13) Frye, C. L.; Collins, W. T. *J. Am. Chem. Soc.* **1970**, 492, 5586–8.

A New Class of Silicon Compounds with Interesting Nonlinear Optical Effects

G. Mignani,[*,†] A. Krämer,[†] G. Puccetti,[‡] I. Ledoux,[‡] G. Soula,[†] J. Zyss,[‡] and
R. Meyrueix[†]

Centre de Recherches des Carrières, Rhône-Poulenc Recherches, 85 avenue des Frères Perret,
BP 62, 69192 Saint-Fons Cedex, France, and Centre National d'Etudes des Télécommunications,
196 avenue Henry Ravera, 92120 Bagneux, France

Received June 4, 1990

Summary: The synthesis and characterization of a new class of silicon compounds with high transparency and nonlinear optical properties have been carried out.

The growing interest in new organic products for quadratic nonlinear optics, related to intramolecular electronic charge transfer (CT), has led to numerous studies of various classes of molecules.[1] In most compounds, previously published, this CT between an electron-donor and an electron-acceptor group takes place through a conjugated π system. For many applications (optical processing, integrated optics, ...) new compounds combining high nonlinear optical activities (NLO) with good transparency are needed. In this study, we have examined a new class of silicon compounds, whose general

---

[†] Rhône-Poulenc Recherches.

[‡] Centre National d'Etudes des Télécommunications.

(1) (a) Chemla, D. S.; Zyss, J. Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando, FL, 1987. (b) Hann, R. A., Bloor, D., Eds. *Organic Materials for Non-linear Optics*; Royal Society of Chemistry: London, 1989.

0276-7333/90/2309-2640$02.50/0 © 1990 American Chemical Society