3. New Synthetic Route to Polyhedral Organylsilsesquioxanes

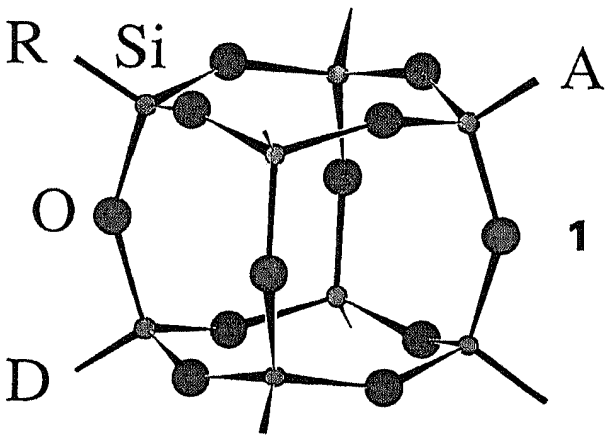
by **Daniel Herren, Heribert Bürgy,** and **Gion Calzaferri***

Institute of Inorganic and Physical Chemistry, University of Berne, CH-3000 Berne 9

(12.IX.90)

Hydrosilation of methylenecyclohexane and hex-1-ene by octa(hydridosilsesquioxane) catalysed by hexachloroplatinic acid is a new route to polyhedral organylsilsesquioxanes. Quantitative yield of octa(cyclohexylmethylsilsesquioxane) is reached. This reaction opens a vast field of yet unknown polyhedral silsesquioxanes.

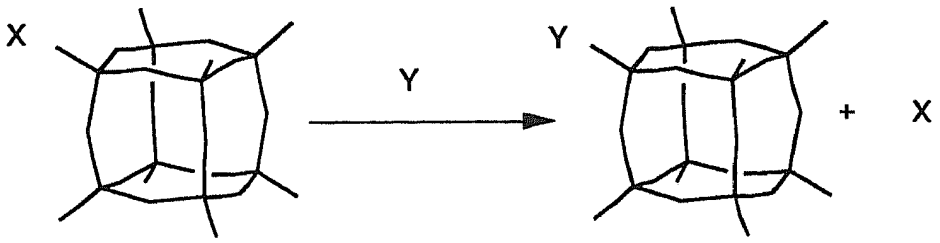
Polyhedral silsesquioxanes represent a versatile group of three-dimensional oligomeric organosilicon compounds of the general formula $(RSiO_{3/2})_n$ ($n = 8, 10, 12, \ldots$) [1]. The resemblance of the framework structure of octasilsesquioxanes to the double four ring in zeolites A and CoAPO-50 [2] has attracted our interest in using them as model compounds for investigating these systems [3]. They are appealing to look at as a framework for building donor/acceptor systems A/D of the type $A-Si(OSiO)_nSi-D$, $n = 1, 2$. Chemically linked donor/acceptor systems are used in studies on long-range through-space and through-bond interactions in the electronic ground and excited states [4] [5]. We are aiming at a way of synthesizing chemically stable silsesquioxanes with



donor/acceptor groups as shown in **1**. Very stable silsesquioxanes are those carrying Si–C substituents [1]. In **1**, R is a substituent, such as an alkyl group, attached to all Si-atoms except those occupied by A or D. A and D are linked to Si *via* a Si–C bond. We report the first example of an $(-O)_3Si-X + Y \rightarrow (-O)_3Si-Y + X$ substitution in symmetrical octasilsesquioxanes $(XSiO_{3/2})_8$ that leads directly to an $(-O)_3Si-C$ bond.

Only four examples of $(-O)_3Si-X + Y \rightarrow (-O)_3Si-Y + X$ substitution reactions (*Scheme 1*) have been reported for the symmetrical silsesquioxanes $(XSiO_{3/2})_8$. These

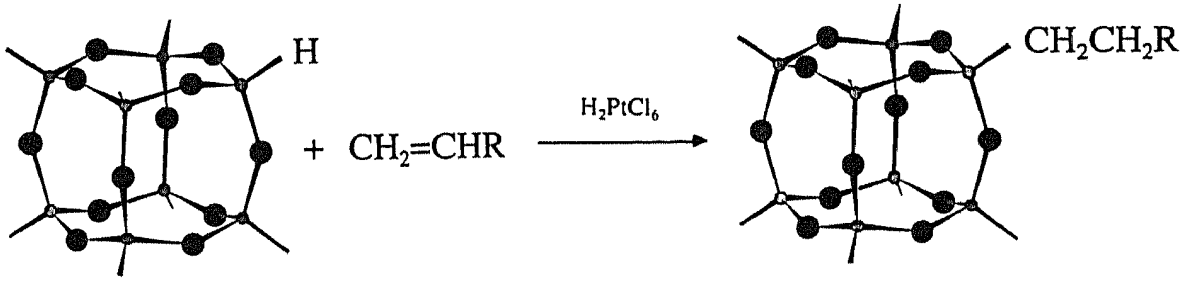
Scheme 1



include the photochlorination of $(HSiO_{3/2})_8$ leading to $(ClSiO_{3/2})_8$ and the methoxylation of this product resulting in $(CH_3OSiO_{3/2})_8$, both described in 1985 [6]. The third example is the trimethylsilylation of various hydridosilsesquioxanes [7], and we have recently described the Pd-catalyzed deuterium exchange of $(HSiO_{3/2})_8$ to $(DSiO_{3/2})_8$ [8]. It is reasonable to assume, that these reactions proceed *via* a radical-type mechanism.

An important radical-type reaction in silicon chemistry leading to the formation of a Si–C bond is the hydrosilation reaction. Provided that this reaction proceeds under retention, it would ideally suit our needs. Testing this hypothesis in the hydrosilation of hex-1-ene and of methylenecyclohexane by octa(hydridosilsesquioxane), we ended up with octa(hexylsilsesquioxane) and octa(cyclohexylmethylsilsesquioxane) being formed with a yield of at least 90%. This can be regarded as a proof that the hydrosilation does proceed under retention. It seems reasonable to assume, that the mechanism of this reaction is similar to that described for the Pd-catalyzed deuterium exchange of $(HSiO_{3/2})_8$ to $(DSiO_{3/2})_8$ [8] [9].

Scheme 2



The reaction presented in *Scheme 2* will lead to a great number of new oligosilsesquioxanes [10]. It appears to be suitable for designing supramolecular assemblies with silsesquioxanes as bridging components. A step-by-step route, separating unused intermediates after each reaction, is attractive [11].

Experimental. – *Synthesis of Octa(1-hexylsilsesquioxane).* Hydrosilation of hex-1-ene by octa(hydridosilsesquioxane): 0.25 ml (2 mmol) of hex-1-ene (*Fluka, p.a.*), 0.1 g (0.24 mmol) of octa(hydridosilsesquioxane) (prepared using the method by *Frye* and *Collins* [12], recrystallized twice from cyclohexane), 0.1 ml (1 μmol) of a 0.01M H_2PtCl_6 soln. in i-PrOH were put in a 10-ml round-bottom flask and heated at reflux for 5 h under N_2. A viscous yellowish liquid remained after evaporation of the solvent. Purification using size exclusion liquid chromatography [11] yielded a clear, viscous oil, from which a white solid precipitated after a few days. Yield: 90%. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.800–1.550 (*m*, 5H); 1.490 (*m*, 1H); 1.320–1.040 (*m*, 3H); 1.020–0.840 (*m*, 2H); 0.564 (*d*, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$): 32.354 (CH_2); 31.583 (CH_2); 22.759 (CH_2); 22.569 (CH_2); 14.111 (CH_3); 11.991 (CH_2). MS (70 eV, 200°): 1096 (0.5, M^+), 1011 (95, $[M - C_6H_{11}]^+$), 926 (4.5, $[M - 2C_6H_{11}]^+$). As far as comparable, spectroscopic results agree with those reported by *Andrianov* and *Izmailov* [13].

Synthesis of Octa(cyclohexylmethylsilsesquioxane). Hydrosilation of methylenecyclohexane by octa(hydridosilsesquioxane): 0.25 ml (2 mmol) of methylenecyclohexane (*Fluka, purum*), 0.1 g (0.24 mmol) of octa(hydridosilsesquioxane), 0.1 ml (1 μmol) of a 0.01M H_2PtCl_6 soln. in i-PrOH were put in a 10-ml round-bottom flask and heated at reflux for 5 h under N_2. A white solid precipitated after evaporation of the solvent. Recrystallization was performed from hexane. Yield: 90%. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.440–1.210 (*m*, 8H); 0.833 (*t*, 3H); 0.603 (*t*, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$): 36.198 (CH_2); 33.106 (CH); 26.585 (CH_2); 26.249 (CH_2); 21.029 (CH_2). MS (70 eV, 60°): 1192 (20, M^+), 1095 (75, $[M - C_7H_{13}]^+$), 999 (5, $[M^+ - 2(C_7H_{13})]^+$). The spectroscopic data are in excellent agreement with those previously published by *Feher* and *Budzichowski* [14].

We would like to thank Dr. *K. Hädener* for contributions. This work is part of project NF 2–5.542, financed by the *Swiss National Science Foundation* and the project BEW-EPA 217.307, financed by the *Schweizerische Bundesamt für Energiewirtschaft.*

REFERENCES

[1] M. G. Voronkov, V. I. Lavrent'yev, *Topics Curr. Chem.* **1982,** *102,* 199.
[2] W. M. Meier, D. H. Olson, 'Atlas of Zeolite Structure Types', 2nd edn., Butterworths, London, 1988.
[3] a) G. Calzaferri, L. Forss, *Chem. Phys. Lett.* **1984,** *103,* 296; b) G. Calzaferri, L. Forss, *Helv. Chim. Acta* **1987,** *70,* 465; c) P. Bornhauser, G. Calzaferri, *Spectrochim. Acta, A* **1990,** *7,* 1045.
[4] a) R. Hoffmann, *Acc. Chem. Res.* **1971,** *4,* 1; b) N. S. Hush, A. T. Wong, G. B. Bacskay, J. R. Reimers, *J. Am. Chem. Soc.* **1990,** *112,* 4192.
[5] a) J. R. Miller, *Nouv. J. Chim.* **1987,** *11,* 83; b) H. Oevering, M. W. Paddon-Row, M. Keppener, A. M. Oliver, E. Cotsaris, J. W. Verhoeven, N. S. Hush, *J. Am. Chem. Soc.* **1987,** *109,* 3258; c) F. Scandola, C. A. Bignozzi, C. Chirboli, M. T. Indelli, M. A. Rampi, *Coord. Chem. Rev.* **1990,** *97,* 299.
[6] V. W. Day, W. G. Klemperer, V. V. Mainz, D. M . Millar, *J. Am. Chem. Soc.* **1985,** *107,* 8262.
[7] P. A. Agaskar, V. W. Day, W. G. Klemperer, *J. Am. Chem. Soc.* **1987,** *109,* 5554.
[8] H. Bürgy, G. Calzaferri, *Helv. Chim. Acta* **1990,** *73,* 698.
[9] G. Calzaferri, R. Hoffmann, *J. Chem. Soc., Dalton Trans.*, in press.
[10] I. Ojima, 'The Chemistry of Organic Silicon Compounds', Eds. S. Patai and Z. Rappoport, Wiley, New York, 1989, Part II, pp. 1479–1526, and ref. cit. therein.
[11] H. Bürgy, G. Calzaferri, *J. Chromatogr.* **1990,** *507,* 481.
[12] C. L. Frye, W. T. Collins, *J. Am. Chem. Soc.* **1970,** *92,* 5586.
[13] K. A. Andrianov, B. A. Izmailov, *Zh. Obshch. Khim.* **1966,** *36,* 341.
[14] F. J. Feher, T. A. Budzichowski, *J. Organomet. Chem.* **1989,** *373,* 153.