ELSEVIER

Journal of Organometallic Chemistry 521 (1996) 401–403

Journal of Organometallic Chemistry

Preliminary communication

Reactions of an incompletely-condensed silsesquioxane with Ph_3PCH_2: a new procedure for derivatizing silsesquioxanes with important implications for the chemistry of silica surfaces [1]

Frank J. Feher *, Shawn H. Phillips

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

Received 2 April 1996

Abstract

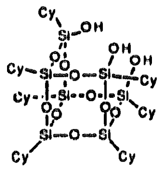
The reaction of $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$ (1) with Ph_3PCH_2 (one equivalent) occurs rapidly upon mixing to afford the $[Ph_3PMe]^+$ salt of $[(c\text{-}C_6H_{11})_7Si_7O_{10}(OH)_2]^-$ (2). Assignment of (2) as an ion pair, rather than a five-coordinate adduct of phosphorus, was based on compelling multinuclear NMR data. UV–vis studies indicate that trisilanol (1) is completely deprotonated by one equivalent of Ph_3PCH_2 and that further deprotonation does not occur. Strong hydrogen bonding appears to stabilize (2) and allow its use as a versatile monoanionic equivalent of (1). The reactions of (2) with chlorosilanes (e.g. PhMe(Vinyl)SiCl, $PhMe_2SiCl$ and Ph_3SiCl) result in the immediate formation of $[Ph_3PMe]Cl$ and afford the monosilylated derivatives of (1) in virtually quantitative yields. Aspects of this work relating to the chemistry of silica surfaces are discussed.

Keywords: Silicon; Silsesquioxanes; Silanol

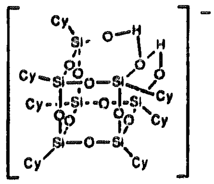
Incompletely-condensed silsesquioxanes (e.g. 1) are useful models for silica surfaces [1,2] and versatile ligands for a variety of elements [3,4]. They are also useful as comonomers in silsesquioxane–siloxane polymers [5]. A number of synthetic strategies have been devised for preparing Si–O and Si–O–M frameworks from incompletely-condensed silsesquioxanes. In all but a few instances, the products are completely condensed — i.e. there are no unreacted Si–OH groups. In this paper we describe a new and general approach for selectively attaching reagents to one silanol group of (1). The key to this approach is a surprisingly stable monoanion derived from the deprotonation of (1) with Ph_3PCH_2 [6]. Several aspects of our work have important implications for the chemistry of silica surfaces; these will be discussed in detail.

The reaction of (1) [1] with yellow C_6D_6 solutions of Ph_3PCH_2 (one equivalent) occurs rapidly upon mixing to afford the colorless $[Ph_3PMe]^+$ salt of (2).

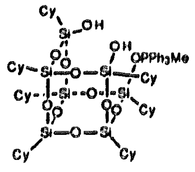
Assignment of (2) as an ion pair, rather than a five-coordinate adduct of phosphorus (i.e. 3), was based on compelling multinuclear NMR data. Most importantly, the ^{31}P NMR spectrum exhibits a sharp, single resonance at δ 22.46. This resonance occurs in the range observed for other $[Ph_3PMe]^+$ salts, and it is very far downfield from the resonances reported for five-coordinate R_4POR' complexes (the ^{31}P chemical shift for R_4POR' is typically −60 to −90 ppm [7]). The ^1H NMR spectrum of the product exhibits characteristic resonances for the Ph_3PMe cation, as well as a broad and strongly deshielded resonance (δ 12.05) for the two remaining SiOH groups. Finally, both the ^{13}C and ^{29}Si NMR spectra exhibit resonances consistent with a time-averaged C_3-symmetric Si–O framework.



1 Cy = c-C_6H_{11}



2



3

---

* Corresponding author.

[1] Dedicated to Professor Robert Corriu, whose outstanding contributions have forever changed the course of organosilicon chemistry.

PII S0022-328X(96)06370-X

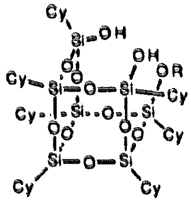
In order to examine the stoichiometry of the reaction between (**1**) and Ph_3PCH_2, C_6H_6 solutions containing a constant amount of Ph_3PCH_2 were treated with 0–2 equivalents of (**1**). (The ratio of Ph_3PCH_2:(**1**) varied from 0–4.) The amount of unreacted phosphorane (λ_{max} 340 nm; ε 2003 M^{-1} cm^{-1}) was quantitatively determined by UV–vis spectroscopy.

A plot of the absorbance at 340 nm vs. the number of equivalents of Ph_3PCH_2 used in the reaction indicates that one equivalent of Ph_3PCH_2 completely protonates one OH group of trisilanol (**1**). It also indicates that further deprotonation of (**2**) does not occur because the absorbance due to excess Ph_3PCH_2 corresponds to a Beer's law plot for Ph_3PCH_2 in C_6H_6.

Anion (**2**) is remarkably stable, and no noticeable decomposition was observed after 31 days in C_6D_6. This is somewhat surprising because silanols are known [8] to react with phosphoranes to give disiloxanes and phosphine oxide, and trisilanol (**1**) is prone to cyclodehydration reactions [1]. Strong hydrogen bonding appears to stabilize (**2**) and allow its use as a versatile monoanionic equivalent of (**1**).

The reactions of (**2**) with chlorosilanes result in the immediate formation of $[Ph_3PMe]Cl$.

In the case of PhMe(Vinyl)SiCl, $PhMe_2SiCl$ and Ph_3SiCl, the monosilylated derivatives of (**1**) (i.e. **4a**–**c**) are obtained in virtually quantitative yields, as indicated by NMR spectroscopy. Except for $PhMe_2SiCl$, none of these chlorosilanes react with (**1**), even in the presence of an amine base (e.g. Et_3N or pyridine). The reaction of (**2**) with mono-chlorosilanes therefore represents an important general method for preparing monosilylated derivatives of (**1**), including those containing chiral silyl groups.



4 **a** R = SiPhMe(vinyl)
b $SiPhMe_2$
c $SiPh_3$

The unexpected stability of (**2**) provides a powerful new method for preparing monofunctionalized derivatives of (**1**). It also supports our rationalization for the remarkable selectivities observed during the reactions of (**1**) with $Me_3SiCl/Et_3N/Et_2O$ [1] and Me_5Sb [1], as well as our earlier assertions about the chemistry of systems containing multiple hydrogen-bonded siloxy groups [1]. Extensive hydrogen-bonding increases the acidity of polyhydroxylic compounds by stabilizing their conjugate bases [9]. In the case of (**2**), the anion is so stable that it does not coordinate to a phosphonium ion — even in a hydrocarbon solvent. Stoichiometrically similar arrangements should be accessible and stable on silica, and they should exhibit enormous rate enhancements during reactions with chlorosilanes and other electrophilic reagents.

2. Experimental Details

2.1. Synthesis of (2)

Solid (**1**) (150 mg; 0.154 mmol) was added with stirring to a solution of Ph_3PCH_2 (42.6 mg; 0.154 mol) in toluene (2 ml). The yellow color due to Ph_3PCH_2 completely disappeared within 1 min. The product (**2**) was obtained as white needles (153 mg; 80%) by allowing acetonitrile to diffuse slowly into the toluene solution over a period of 3 days. For (**2**): ^1H NMR (500.06 MHz, C_6D_6, 21 °C): δ 12.05 (br, 2 H), 7.29 (m, 6 H), 7.13 (m, 9 H), 3.12 (d, 3 H, J = 13.1 Hz), 2.6–1.2 (br m, 70 H), 1.2–0.9 (br m, 7 H). ^{13}C NMR (125.75 MHz, C_6D_6, 21 °C): δ 134.29, 133.43 (d, J = 11.8 Hz), 130.02 (d, J = 11.7 Hz), 120.20 (d, J = 86.5 Hz), 28.62, 28.52, 28.32, 28.23, 28.07, 27.91, 27.78, 27.63, 27.51, 26.96 (s for CH_2), 25.56, 24.87, 24.37 (s, 3:3:1 for CH), 9.21 (d, J = 55.1 Hz). ^{31}P NMR (202 MHz, C_6D_6, 21 °C): δ 22.46. ^{29}Si NMR (99.36 MHz, C_6D_6, 21 °C): δ −58.87, −67.30, −68.31 (s, 3:1:3). Anal. Calc. (found) for $C_{61}H_{97}O_{12}PSi_7$: C, 58.61 (58.74); H, 7.82 (7.97). M.p.: 210–212 °C.

2.2. Reactions of (2) with chlorosilane

In a typical reaction, the chlorosilane (0.41 mmol) was added to a solution of (**2**) prepared by adding Ph_3PCH_2 (0.316 mmol) to trisilanol (**1**) (0.316 mmol) in CH_2Cl_2 (5 ml). The solution was stirred for 5 min, CH_3CN (5 ml) was added to precipitate the product partially, then the solvent was evaporated in vacuo (25 °C, 0.1 Torr) to a volume of ca. 5 ml. The precipitate was filtered, rinsed with CH_3CN (3 × 5 ml) then dissolved in hexanes. Filtration through a sintered glass frit and evaporation of the volatiles (25 °C, 0.1 Torr) afforded the crude product in nearly quantitative yield. For **4a**: the crude product was recrystallized from CH_2Cl_2–CH_3CN to afford 255 mg (72% yield) of white rectangular crystals. ^1H NMR (500.06 MHz, $CDCl_3$, 21 °C): δ 7.260 (m, 2 H), 7.42–7.34 (m, 3 H), 6.325 (m, 1 H), 6.098 (m, 1 H), 5.862 (m, 1 H) 3.65 (br, 1 H), 3.50 (br, 1 H), 1.73 (br, 35 H), 1.23 (br, 35 H), 0.75 (br, 7 H), 0.503 (s, 3 H). ^{13}C NMR (125.75 MHz, C_6D_6, 21 °C): δ 137.58, 137.40, 134.23, 129.70, (s, C_6H_5), 133.73, 127.93 (s, C_2H_3), 27.63, 27.57, 27.53, 27.48, 26.82, 26.77, 26.62, 26.54, 26.26 (s, CH_2), 24.42, 23.94, 23.48, 23.13, 23.03 (s, 1:2:2:1:1 for CH), −1.56 (s, CH_3). ^{29}Si NMR (99.36 MHz, C_6D_6, 21 °C): δ −12.26, −59.25, −67.69, −67.79, −68.80, −69.91. Anal.

Calc. (found) for $C_{51}H_{90}O_{12}Si_7$: C, 54.70 (54.71); H, 8.10 (8.14). M.p.: 143–144.5 °C. For **4b**: the crude product was recrystallized from CH_2Cl_2–CH_3CN to afford 303 mg (87% yield) of colorless blocks. ^1H NMR (500.06 MHz, C_6D_6, 21 °C): δ 7.63 (m, 2 H), 7.38 (m, 3 H), 3.52 (br, s, 2 H), 1.73 (v br, m, 35 H), 1.23 (v br, m, 35 H), 0.76 (v br, m, 7 H), 0.41 (s, 6 H). ^{13}C NMR (125.75 MHz, C_6D_6, 21 °C): δ 133.23, 129.54, 128.31, 127.94, 27.53, 27.47, 26.79, 26.63, 26.54, 26.41 (s, CH_2), 24.49, 23.90, 23.45, 23.11, 23.01 (s, 1:2:2:1:1 for CH), 0.41 (s, CH_3). For **4c**: the crude product was recrystallized from CH_2Cl_2–CH_3CN to afford 288 mg (74% yield) of white rectangular crystals. ^1H NMR (500.06 MHz, C_6D_6, 21 °C): δ 7.62 (m, 2 H), 7.44 (m, 1 H), 7.38 (m, 2 H), 3.09 (br, 2H), 1.80–1.60 (br, 35 H), 1.45–1.10 (br, 35 H), 0.80–0.65 (br, 7 H). ^{13}C NMR (125.75 MHz, C_6D_6, 21 °C): δ 135.43, 135.24, 129.97, 127.86 (s, C_6H_5), 27.63, 27.60, 27.56, 27.48, 27.45, 26.85, 26.77, 26.74, 26.68, 26.59, 26.52 (s, CH_2), 24.58, 24.03, 23.54, 23.10, 23.03 (1:2:2:1:1 for CH). ^{29}Si NMR (99.36 MHz, C_6D_6, 21 °C): δ −20.74, −59.43, −67.63, −67.76, −69.54, −69.97. Anal. Calc. (found) for $C_{60}H_{92}O_{12}Si_8$: C, 58.49 (58.96); H, 7.69 (7.87). M.p.: 187.5–188.5 °C.

Acknowledgements

These studies were supported by the National Science Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References

[1] (a) F.J. Feher, D.A. Newman and J.F. Walzer, *J. Am. Chem. Soc.*, *111* (1989) 1741. (b) F.J. Feher and D.A. Newman, *J. Am. Chem. Soc.*, *112* (1990) 1931. (c) F.J. Feher, T.A. Budzichowski, R.L. Blanski, K.J. Weller and J.W. Ziller, *Organometallics*, *10* (1991) 2526. (d) F.J. Feher, T.A. Budzichowski, K. Rahimian and J.W. Ziller, *J. Am. Chem. Soc.*, *114* (1992) 3859.

[2] (a) T.W. Hambley, T. Maschmeyer and A.F. Masters, *Appl. Organomet. Chem.*, *6* (1992) 253. (b) L.D. Field, C.M. Lindall, T. Maschmeyer and A.F. Masters, *Aust. J. Chem.*, *47* (1994) 1127. (c) I.E. Buys, T.W. Hambley, D.J. Houlton, T. Maschmeyer, A.F. Masters and A.K. Smith, *J. Mol. Catal.*, *86* (1994) 309.

[3] (a) F.J. Feher and R.L. Blanski, *J. Am. Chem. Soc.*, *114* (1992) 5886. (b) F.J. Feher and R.L. Blanski, *J. Chem. Soc. Chem. Commun.*, (1990) 1614. (c) F.J. Feher, J.F. Walzer and R.L. Blanski, *J. Am. Chem. Soc.*, *113* (1991) 3618. (d) J.-C. Liu, S.R. Wilson, J.R. Shapley and F.J. Feher, *Inorg. Chem.*, *29* (1990) 5138. (e) F.J. Feher and J.F. Walzer, *Inorg. Chem.*, *30* (1991) 1689. (f) F.J. Feher, *J. Am. Chem. Soc.*, *108* (1986) 3850. (g) T.A. Budzichowski, S.T. Chacon, M.H. Chisholm, F.J. Feher and W. Streib, *J. Am. Chem. Soc.*, *113* (1991) 689. (h) F.J. Feher and J.F. Walzer, *Inorg. Chem.*, *29* (1990) 1604. (i) F.J. Feher, S.L. Gonzales and J.W. Ziller, *Inorg. Chem.*, *27* (1988) 3440. (j) F.J. Feher, T.A. Budzichowski and K.J. Weller, *J. Am. Chem. Soc.*, *111* (1989) 7288. (k) F.J. Feher and K.J. Weller, *Organometallics*, *9* (1990) 2638. (l) F.J. Feher and K.J. Weller, *Inorg. Chem.*, *30* (1991) 880. (m) F.J. Feher, K.J. Weller and J.W. Ziller, *J. Am. Chem. Soc.*, *114* (1992) 9686. (n) F.J. Feher, T.A. Budzichowski and J.W. Ziller, *Inorg. Chem.*, *31* (1992) 5100. (o) F.J. Feher and T.L. Tajima, *J. Am. Chem. Soc.*, *116* (1994) 2145.

[4] (a) N. Winkhofer, H.W. Roesky, M. Noltmeyer and W.T. Robinson, *Angew. Chem. Int. Ed. Engl.*, *31* (1992) 599. (b) W.A. Herrmann, R. Anwander, V. Dufaud and W. Schere, *Angew. Chem. Int. Ed. Engl.*, *33* (1994) 1285. (c) N. Winkhofer, A. Voigt, H. Dorn, H.W. Roesky, A. Steiner, D. Stalke and A. Reller, *Angew. Chem. Int. Ed. Engl.*, *33* (1994) 1352. (d) H.-J. Gosink, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, E. Irmer and R. Herbst-Irmer, *Organometallics*, *13* (1994) 3420.

[5] (a) J.D. Lichtenhan, N.Q. Vu, J.A. Carter, J.W. Gilman and F.J. Feher, *Macromolecules*, *26* (1993) 2141. (b) J.D. Lichtenhan, *Comments Inorg. Chem.*, *17* (1995) 115. (c) J.D. Lichtenhan, R.A. Mantz, P.F. Jones and M.J. Carr, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, *35* (1994) 523. (d) T.S. Haddad and J.D Lichtenhan, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, *35* (1994) 708. (e) J.D. Lichtenhan, Y.A. Otonari and M.J. Carr, submitted to Macromolecules. (f) J.D. Lichtenhan, Silsesquioxane-based polymers, in *The Polymeric Materials Encyclopedia: Synthesis, Properties and Applications*, CRC Press, Boca Raton, FL, in press. (g) T.S. Haddad and J.D. Lichtenhan, *J. Inorg. Organomet. Polym.*, *5* (1995) 237.

[6] (a) R. Koster, D. Simic and M.A. Grassberger, *Justus Liebigs Ann. Chem.*, *739* (1970) 211. (b) S.M. Grim and J.H. Ambrus, *J. Org. Chem.*, *33* (1968) 2993. (c) K.A.O. Starzewski and H. Bock, *J. Am. Chem. Soc.*, *98* (1976) 8486.

[7] J.G. Verkade and L.D. Quin, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, Florida, 1987.

[8] (a) M.G. Voronkov, E.A. Maletina and V.K. Roman, *Heterosiloxanes*, Vol. 2, *Derivatives of Nitrogen and Phosphorus*, Harwood Academic, New York, 1991. (b) D.E.C. Corbridge, *Phosphorus: An Outline of its Chemistry, Biochemistry, and Technology*, Elsevier, New York, 1980.

[9] (a) H. Musso and H.G. Matthies, *Chem. Ber.*, *94* (1961) 356. (b) J.A.W. Beenackers, B.F.M. Kuster and H.S. VanderBaan, *Carbohyd. Res.*, *140* (1985) 169. (c) J.A. Rendleman, *Adv. Chem. Ser.*, *117* (1973) 51. (d) E.J. Roberts, C.P. Wade and S.P. Rowland, *Carbohyd. Res.*, *17* (1971) 393.