BICYCLIC SILANES FROM CYCLOSILANE-METAL DERIVATIVES

F.K. MITTER, G.I. POLLHAMMER and E. HENGGE

Institute of Inorganic Chemistry of the Technical University Graz (Austria)

(Received April 23rd, 1986)

Summary

New cyclosilane derivatives with electropositive substituents (mercury, alkali metal) have been prepared from monohalo-undecamethylcyclohexasilane. The availability of these compounds opens up new routes for the preparation of polycyclic and other cyclosilane derivatives. Two bicyclic silanes, bi(undecamethylcyclohexasilanyl) and and bis(undecamethylcyclohexasilanyl)dimethylsilane have been prepared and characterized.

Introduction

Cyclosilane derivatives with various inorganic and organic substituents are well known, but except for halogen atoms, such derivatives containing functional groups, suitable for further reactions and therefore for the synthesis of new derivatives are rare [1]. Cyclosilanes bearing electropositive substituents such as alkali metals or mercury were previously unknown. Such compounds can be expected to be very useful in synthetic silicon chemistry. We describe here the preparation of the first representatives of this new class of compounds, bis(undecamethylcyclohexasilanyl)-mercury and undecamethylcyclohexasilanylpotassium, and their conversion into polycyclic silanes.

Results and discussion

The starting material for the preparation of cyclohexasilyl metal derivatives was monohalogenoundecamethylcyclohexasilane. Although it has been described previously, the synthesis of such monohalocyclosilanes on a preparative scale turned out to have a lot of difficulties. West et al. [2] describes the preparation of monophenyl-undecamethylcyclohexasilane from dimethyldichlorosilane and methylphenyldichlorosilane by a Wurtz coupling reaction with lithium, but we were could not reproduce their yields and always obtained only traces of the desired product. Cleaving off the phenyl group with HBr (in a sealed tube) did, however, give the monobromo derivative smoothly and in high yield.

The use of HCl in the presence of $AlCl_3$ is also satisfactory if the starting material is very pure; if it is not, some ring contraction reaction takes place.
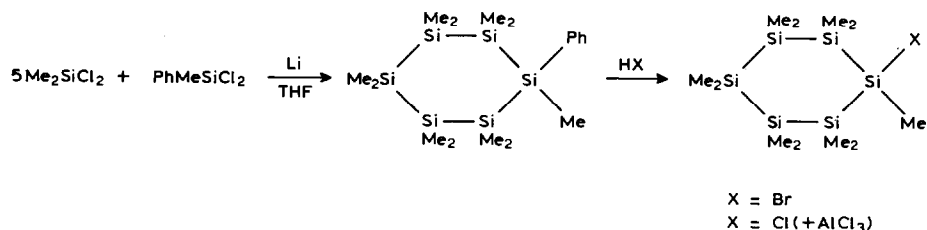

However, this method does not seem to be suitable for synthesizing larger amounts of monohaloundecamethylcyclohexasilanes because of the low yields in the initial preparation of the phenyl derivative. Another method has been described by Kumada et al. [3]. This treated dodecamethylcyclohexasilane with $HCl/AlCl_3$ and obtained along with some polychlorinated by-products, a mixture of the desired compound and a ring contraction product, a cyclopentasilane derivative:
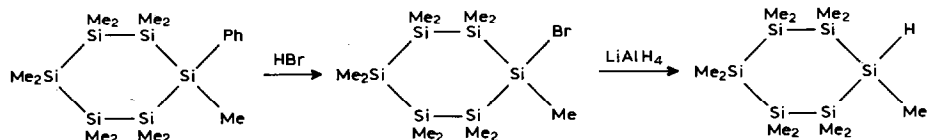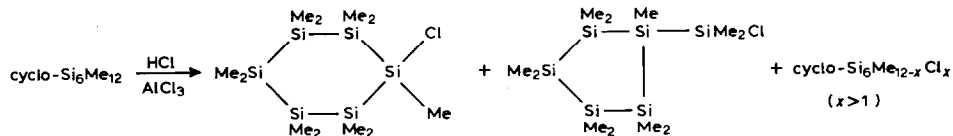
Direct separation of the product mixture is just possible by chromatography, but the sensitivity of the Si–Cl bond towards moisture and other nucleophilic reagents raises problems, and so we also used the work-up adopted by Kumada et al. involving phenylation of the crude product with phenylmagnesium bromide and separation of the resulting phenylcyclosilanes by fractional distillation. Subsequent reaction of the pure phenylundecamethylcyclohexasilane with HBr in a sealed tube gives the desired bromoundecamethylcyclohexasilane in high yields, making reasonable amounts of the compound accessible. However, is should be noted that this separation technique fails if the crude reaction mixture contains too much of the ring contraction product, the proportion of which depends greatly on the reaction conditions.

The next step on the way to the metal substituted cyclosilanes is the reduction of bromoundecamethylcyclohexasilane with $LiAlH_4$. The resulting undecamethylcyclohexasilane reacts very smoothly with bis(butyl)mercury to yield the corresponding silylmercury compound:

$$2 \text{ cyclo-}Si_6Me_{11}H + t\text{-}Bu_2Hg \rightarrow (\text{cyclo-}Si_6Me_{11})_2Hg + 2 \text{ } t\text{-}BuH$$
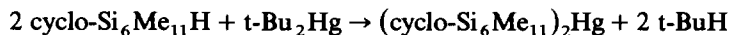
Such a reaction sequence was recently carried out successfully with open-chain silanes [4].

Bis(undecamethylcyclohexasilanyl)mercury is a yellow, crystalline substance, and has been characterized by elemental analysis, mass spectrometry and ^{29}Si NMR spectroscopy. It is soluble in benzene and other non-polar organic solvents and sensitive to moisture, oxygen, and light. If its solution in THF is stirred with Na/K-alloy, an amalgam is produced and the colour changes from yellow to reddish-brown, typical of silyl-alkali metal derivatives. After completion of the reaction the amalgam is solidified by addition of mercury and filtered off. To estimate the amount of the silyl-potassium compound produced, a small part of the solution is hydrolyzed and then titrated with HCl.

For further reactions the solution of undecamethylcyclohexasilanylpotassium is used directly without isolation of the pure compound. Thus treating this solution with dimethyldichlorosilane yields a bicyclic silane:

$$(\text{cyclo-Si}_6\text{Me}_{11})_2\,\text{Hg} \xrightarrow{\text{Na/K}} 2\,\text{cyclo-Si}_6\text{Me}_{11}\text{K} \;+\; \text{Hg}$$
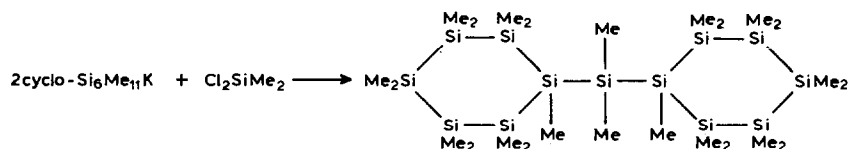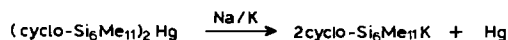
Bis(undecamethylcyclohexasilanyl)dimethylsilane is a colourless substance, very easily recrystallized from ethyl acetate.

Another bicyclic silane is produced by UV irradiation of bis(undecamethyl-cyclohexasilanyl)mercury. This compound (which was made earlier by Kumada [5], can also be made in good yields from bromoundecamethylcyclohexasilane by a Wurtz-coupling reaction with Na/K alloy:
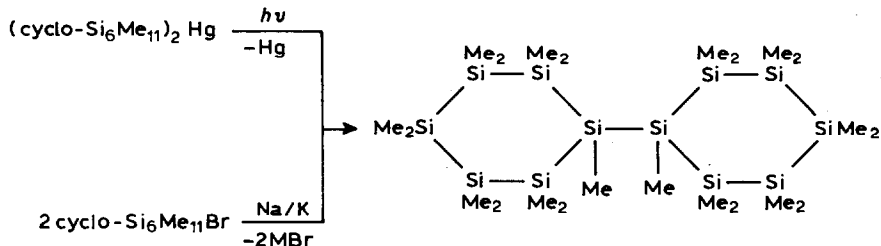
Both bicyclic silanes were characterized by elemental analysis, mass spectrometry, and ^{1}H and ^{29}Si NMR, IR, Raman, and UV spectroscopy.

The molecular structures of both bicyclic silanes were determined by X-ray diffraction. Details of the results will appear elsewhere together with a normal coordinate analysis and values of calculated force constants [6]. We note here only that the central Si–Si bond between the two ring systems is significantly elongated. This is in complete agreement with force constant calculations for disilane derivatives, which show the influence of substituents on the force constant of the Si–Si bond [1].

The new cyclosilane derivatives with electropositive substituents are valuable for the preparation of polycyclic silanes and other derivatives of cyclosilanes, and we are examining their potential.

Experimental

Bromoundecamethylcyclohexasilane $Si_6Me_{11}Br$

Monophenylundecamethylcyclohexasilane (20 g, 48.7 mmol) was reacted with a 3 molar proportion of HBr at room temperature in a sealed tube. After 48 h the tube was opened under nitrogen and the slurry rinsed out with dry benzene. Removal of the solvent and sublimation in vacuo at 80°C yielded 18 g (89.3%) of white crystals. M.p. 193–196°C. Anal. Found: Si, 40.68; Br, 19.18. $C_{11}H_{33}Si_6Br$ calcd.: Si, 40.22; Br, 19.38% ^{1}H NMR δ (ppm): 0.77 (1Me); 0.48 (4Me); 0.42 (4Me); 0.32 (2Me). ^{29}Si NMR δ (ppm): 9.93 (1Si); -39.28 (2Si); -41.74 (1Si); -41.99 (2Si). IR (cm^{-1}): 840s, 826s, 802vs, 790s, 768s, 720s, 679m, 645m, 520m, 453w, 418w, 390m, 352s, 323, 278w. Ra (cm^{-1}): 1000w, 830w, 815w, 742m, 730m,b, 685vs, 658vs, 640m, 465m, 355m, 328vs. MS (m/e): $M^+ = 414$; Experimental and calculated isotope patterns were in good agreement.

Bis(undecamethylcyclohexasilanyl) $(Si_6Me_{11})_2$

Method A. A flask containing 1 ml of Na/K alloy (1/3) in 60 ml n-heptane was placed in an ultrasonic bath. A solution of 7 g bromoundecamethylcyclohexasilane in 20 ml of n-heptane was added slowly. After 12 h the reaction was complete, and the dark blue precipitate was filtered off and washed with heptane. The resulting solution was acidified with HCl and the solvent was removed in vacuo. The residue of Si_6Me_{12} was sublimed at 85°C and 0.1 Torr. The product was sublimed in vacuo at 150°C and recrystallized from ethyl acetate, yielding 4.5 g (80%) of white crystals. m.p. 244–246°C.

Method B. A solution of bis(undecamethylcyclohexasilanyl)mercury in 100 ml of n-heptane was irradiated in a Pyrex flask with a UV lamp until the yellow colour of the mercury compound disappeared. The solution was decanted and worked up in the way described under method A. Anal. Found: Si, 50.46; C, 39.59; H, 9.97. $C_{22}H_{66}Si_{12}$ calcd.: Si, 50.45; C, 39.64; H, 9.99%. ^{1}H NMR δ (ppm): 0.42 (8Me), 0.38 (2Me), 0.27 (4Me), 0.25 (8Me). ^{29}Si NMR δ (ppm): -36.11 (4Si), -39.48 (4Si), -42.49 (2Si), -67.86 (2Si). IR (cm^{-1}): 795vs, 780s, 755s, 720vs, 678s, 643s, 622m, 495w, 455m, 396w, 388w, 378w, 300w, 280m. Ra (cm^{-1}): 822w, 806w, 745m,br, 722m, 670vs, 635s, 482s, 456w, 458m, 304vs. UV: 276 nm ($\epsilon = 3500$); 257 (nm ($\epsilon = 3200$); 237 nm ($\epsilon = 4700$).

Bis-(undecamethylcyclohexasilanyl)mercury $(Si_6Me_{11})_2Hg$

A solution of monohydroundecamethylcyclohexasilane (5 g, 14.9 mmol) and Hg(Bu-t)$_2$ (2.4 g, 7.5 mmol) in 20 ml of n-heptane was heated under reflux. The solution turned yellow and t-butane was evolved. After 3 h the solution was allowed to cool to room temperature and the product which separated was filtered off, dried in vacuo, and stored in the dark.

Yield: 5.8 g (86.5%). Anal. Found: Si, 38.67. $C_{22}H_{66}Si_{12}Hg$ calcd.: Si, 38.79%. ^{29}Si NMR δ (ppm): 1.44 (Si–Hg) -28.09, -38.74, -41.54. IR (cm^{-1}): 780b,s; 720m, 665m, 645m, 530w, 480w, 450w, 405w, 390w, 355w, 295w.

MS (m/e): $M^+ = 866$; Experimental and calculated isotope patterns were in good agreement.

Undecamethylcyclohexasilanylpotassium KSi$_6$Me$_{11}$

Bis-(undecamethylcyclohexasilanyl)dimethysilane Me$_2$Si(S$_6$Me$_{11}$)$_2$

A solution of 5 g (5.77 mmol) of bis-(undecamethylcyclohexasilanyl)mercury in 50 ml THF was stirred with 3 ml of Na/K alloy (1/3). The yellow solution turned reddish-brown. After 1 h 1 ml of the solution was hydrolyzed and titrated against 0.1 *M* HCl to determine the content of the silyl-potassium compound. When a stoichiometric amount of the compound had been formed the reaction was quenched by the addition of 1 ml of mercury. The solution was decanted into a dropping funnel and slowly added to an ice-cooled, stirred solution of Me$_2$SiCl$_2$ (0.37 g, 2.88 mmol) in 50 ml THF. The mixture was stirred for 12 h and then treated with 0.5 ml of conc. HCl. The solvent was removed in vacuo and the residual solid was recrystallized twice from ethyl acetate to give 2.5 g (59.8%) of colourless needles. m.p. 168–170°C.
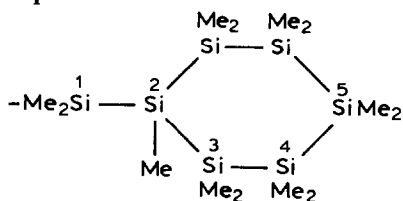
^{1}H NMR δ (ppm): 0.56 (Si(1)), 0.41 (Si(3)), 0.38 (Si(2)), 0.27 (Si(5)), 0.25 (Si(4)). ^{29}Si NMR δ (ppm): −23.4 (Si(1)), −36.5 (Si(3)), −40.3 (Si(4)), −42.4 (Si(5)), −73.7 (Si(2)). IR (cm^{-1}): 835s, 825s, 795vs, 780s, 760s, 730s, 680m, 645m, 460vw, 440w, 385w, 370w, 350vw, 230w. Ra (cm^{-1}): 820w, 735w, 670s, 630sh, 470m, 410w, 330vs. UV: 279 nm (ε = 4800); 250 nm (ε = 2200). MS (*m/e*): M^+ = 724; The experimental and calculated isotope patterns were in good agreement. ^{1}H NMR spectra were recorded either on a 60 MHz (Hitachi) or a Bruker WH-90 spectrometer; samples were dissolved in CCl$_4$ or in benzene-d_6 containing. TMS as internal standard. ^{29}Si NMR spectra were recorded on the Bruker WH-90 instrument with benzene-d_6 as solvent and Cr(acac)$_3$ as relaxation reagent. IR spectra were recorded with Nujol mulls on a Perkin–Elmer 325 infrared spectrophotometer. Raman spectra were recorded on a SPEX 1401 spectrophotometer. Mass spectra were obtained with a Finigan MAT 212 mass spectrometer by use of a direct insertion technique.

Acknowledgements

References

1 E. Hengge, Organomet. Chem. Rev., 9 (1980) 261.
2 B.J. Helmer and R. West, J. Organomet. Chem., 92 (1982) 2.
3 M. Ishikawa and M. Kumada, Synth. Inorg. Metalorg. Chem., 1 (1971) 191.
4 E. Hengge and F.K. Mitter, Z. Anorg. Allg. Chem., 529 (1985) 22.
5 M. Ishikawa, A. Nakamura and M. Kumada, J. Organomet. Chem., 59 (1973) C11.
6 E. Hengge, F.K. Mitter, C. Kratky and K. Hassler, to be published.