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The synthesis and characterization of norbornylsilasesquioxanes

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Norbornene reacts with trichlorosilane to generate norbornyltrichlorosilane in high yield. The slow hydrolysis of norbornyltrichlorosilane in acetone yields incompletely condensed norbornylsilasesquioxanes. The compound $C_{42}H_{70}O_{11}Si_6$ can be isolated from this reaction. On the basis of elemental analyses, ^1H, ^{13}C and ^{29}Si NMR, mass spectroscopy, infrared spectroscopy, and crystallographic analysis, $C_{42}H_{70}O_{11}Si_6$ is formulated as $[(C_7H_{11})_6Si_6O_7(OH)_4]$, with the Si_6O_7 framework being composed of two perpendicular Si_4O_4 planes sharing an edge. $[(C_7H_{11})_6Si_6O_7(OH)_4]$ is a putative model of vicinal $[Si(OH)]_2$ sites on the surface of partially dehydroxylated silica.

Keywords: Silasequioxanes, synthesis, characterization, NMR spectra, infrared spectra, mass spectra

INTRODUCTION

Considerable effort world-wide is being devoted to preparing materials in which organometallic complexes are reacted with the surface of a metal oxide support. The resultant materials find applications in catalysis, sensor technologies, electrode and thin film fabrication, etc.[1] One incentive is to prepare improved catalysts either by using the organometallic substrate as a precursor of well-dispersed small particles of uniform and controllable size and composition, or by combining the benefits of homogeneous and heterogeneous catalysis by chemically anchoring a soluble organometallic complex to an insoluble support. Both the industrially-significant high-volume Phillips and Union Carbide polymerization process employ catalysts prepared in this way, and the definition can be extended to include Ziegler–Natta catalysts.[2,3]

Despite the enormous research activity in the area, and the powerful surface spectroscopy techniques now available, a rational understanding of the fundamental organometallic chemistry involved in the interactions of organometallics with surfaces does not exist and there are consequently few, if any, predictive principles to guide directed syntheses using surfaces as reagents. Rational interpretations of, and improvements in, catalytic behaviour have therefore been extremely difficult. That a surface can display unique chemistry is clear from the enhanced catalytic performance of some supported materials, and the use of surfaces to direct the high-yield syntheses of species obtainable only in low yield by conventional homogeneous synthetic routes.[4,5]

Attempts have been made to model the reactions between organometallics and surfaces by using, for example, alcohols[6,7] and siloxanes[8,9] as homogeneous analogues of surfaces. However, these reagents are clearly poor models of a surface, a point underscored in those cases where the resultant well-characterized molecular complex has none of the activity of the supported material.

In the particular case of partialy dehydroxylated silica surfaces, a fundamental problem which has contributed significantly to this lack of understanding of surface organometallic chemistry is the inadequacy of the species used to date (e.g., alcohols, silanols, disilanols, etc.) to mimic the reactivity of surface functionalities such as different Si—OH groups. Partially dehydroxylated silica surfaces are thought to consist of well-dispersed $[Si(OH)]_n$ ($n = 1$–3) groups, with the bulk of the surface containing supposedly unreactive Si—O—Si linkages.

The concentrations of these $[Si(OH)]_n$ sites are thought to vary with an inverse power of n, and organometallic compounds are supposed to react almost exclusively with the $[Si(OH)]_n$, and not with most of the [Si—O—Si] sites. Moreover, the silica surface is considered to be constructed from domains with the surface morphologies which resemble partially dehydroxylated [100] and [111] surfaces of crystalline silica phases such as

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β-crystobalite.[10–12] Geminal $Si(OH)_2$ groups are produced by hydroxylation of the [100] surfaces,[9,10] whilst siloxane bridges are formed by dehydroxylation of the [100] surface.[9] The $[Si(OH)]_n$ sites in different surface domains have different steric demands.[12] In addition to the steric demands, there is evidence that some *silicon/oxygen ensembles* can be as electron-withdrawing as a CF_3 group.[13] Thus, the different $[Si(OH)]_n$ ($n = 1–3$) sites can conceivably have different reactivity patterns. A variety of supported organometallic species may exist on the surface in different concentrations, and the spectroscopic response of one, high-concentration catalytically-inactive, surface species may mask that of another, low-concentration catalytically-active, surface species.

In light of the foregoing, the functional and spectroscopic inadequacy of 'models' derived by using alcohols or siloxanes as analogues of surface Si—OH groups is hardly surprising. The lack of success of much of the early work does not, therefore, invalidate the use of the modelling approach. What are required, however, are more realistic models of surface $[Si(OH)]_n$ ($n = 1–3$) sites which more accurately model the various surface sites.

Fortunately, reasonable, soluble, molecular models of surface silica fragments have recently become available.[13–15] These are oligosilasesquioxanes, such as $[Cy_6Si_6O_9]$, $[Cy_8Si_8O_{11}(OH)_2]$ and $[Cy_7Si_7O_9(OH)_3]$ (Cy = cyclohexyl, C_6H_{11}). These materials contain zero, two isolated and three adjacent Si—OH groups, respectively, and provide extremely attractive soluble molecular models of some elements of a silica surface. However, analogous models of the important vicinal $(Si—OH)_2$ and geminal $Si(OH)_2$ sites are not yet available. We report here further examples of incompletely condensed silasequioxanes, including a model of the important and potentially significant[12] vicinal $(Si—OH)_2$ surface site.

EXPERIMENTAL

All manipulations were carried out under an atmosphere of dry nitrogen (Matheson high-purity grade) using conventional Schlenk techniques unless otherwise stated.[16] Analytical-grade solvents were dried and freshly distilled under dry nitrogen. Diethyl ether (Ajax) was distilled from sodium benzophenone ketyl. Pyridine (Merck) was distilled from magnesium shavings. Trichlorosilane, norbornene, triethylamine and hexachloroplatinic acid (all Aldrich) were used as received. Acetone (Ajax, AR) was used as received. $[Cy_6Si_6O_9]$ was prepared by the method of Feher *et al.*[15]

Fourier transform infrared spectra were obtained using a Digilab 20/80 FTS spectrometer. Solid samples were presented as potassium bromide discs. ^{29}Si NMR spectra were recorded on Bruker AC 200F and JEOL 200 NMR spectrometers and were externally referenced to tetramethylsilane (taken as δ 0.0 ppm). All samples contained 0.02 mol dm^{-3} $[Cr(acac)_3]$. ^1H NMR spectra were recorded on a Bruker AC 200F NMR spectrometer and were referenced internally to tetramethylsilane (taken as δ 0.0 ppm). ^{13}C NMR spectra were recorded on Bruker AC 200F and Bruker AMX 400 NMR spectrometers and were referenced internally against the solvent, $CDCl_3$ (taken as δ 77.00 ppm). The ^{13}C NMR distortionless enhancement by polarization transfer (DEPT) experiments were performed at 50.03 MHz with a filtering pulse angle of 135°. Mass spectra were obtained using a direct insertion probe with a 200 °C source temperature, 70 eV ionization voltage and 8 kV acceleration voltage on a modified MS 9 geometry mass spectrometer.

Preparation of norbornyltrichlorosilane

CAUTION: Trichlorosilane is an extremely volatile lachramator, which is readily hydrolysed in air and should be handled with care.

Hexachloroplatinic acid (120 mg, 0.3 mmol; **care**—light-sensitive, very hygroscopic) and freshly distilled and degassed norbornene (37.4 g, 0.4 mol) were added to a three-necked three-litre round-bottom flask fitted with a thermometer and a 90 cm reflux condenser topped with a three-way tap connected to the vacuum/nitrogen manifold. A 3:1 ethanol/water mixture was pumped through the condenser from a high-efficiency recirculating low-temperature bath set to −35 °C. The reaction apparatus was assembled in a heating mantle and was well insulated against light and heat by successive layers of aluminium foil, cotton wool and aluminium foil. After the temperature of the reflux condenser had stabilized at about −20 °C, trichlorosilane (85 cm^3, 0.8 mol)

was added cautiously dropwise. The reaction mixture was refluxed at 60 °C with the condenser maintained at −20 °C. After four days the thermometer was replaced with a distillation head and the reaction mixture fractionally distilled under argon at atmospheric pressure.

Trichlorosilane (16 cm^3, 0.16 mol) distilled between 28 °C and 39 °C. Silicon tetrachloride (1 cm^3) distilled between 54 °C and 64 °C. Norbornyltrichlorosilane (80 cm^3, 71 g, 0.3 mol, 98% based on the amount of norbornene used) distilled at 180 °C/0.1 Torr.

Synthesis of norbornyl-substituted silasesquioxane

Colourless norbornyltrichlorosilane (71 g, 0.3 mol as isolated) was added dropwise with stirring to degassed acetone (1500 cm^3) under nitrogen in a three-litre round bottom flask. During the addition the colour of the solution became pale yellow, but no warming of the solution was observed. Once all the silane had been added, distilled and degassed water (625 cm^3) was added cautiously dropwise to the well-stirred reaction mixture. During this procedure, the solution became bright yellow and noticeably warm. Towards the addition of the last one-third of the water, the bright yellow colour started to fade and the water droplets left a sharp white trace where they entered the solution. During this stage of the addition the reaction mixture was cooled by the added water, became almost colourless again and started to cloud slightly. The stirred mixture gradually became cloudier and a very fine precipitate began to form. After five days, stirring was discontinued and the reaction was stored under a continuous positive pressure of nitrogen. Over a period of three months the solution turned yellow while continuing to precipitate crystalline material. A thick, dark yellow resinous layer also formed on the bottom of the flask.

The isolation and recrystallization of the norbornyl-substituted silasesquioxanes were performed in air.

After 14 weeks the yellow supernatant was decanted under nitrogen into another three-litre flask. The resinous layer was removed by washing with degassed AR acetone (100 cm^3). Acetone (300 cm^3) was added to slurry out the white precipitate which was then collected by filtration, washed with acetone (2 × 100 cm^3) and dried. The dried solid was pulverized, stirred for one hour with acetone (300 cm^3), collected by filtration and dried overnight at 50 °C *in vacuo*. The acetone washings were combined with the reaction supernatant in another three-litre flask. Additional crops of crude material could subsequently be isolated from the combined washings and supernatant.

Isolation of pyridine-insoluble products

The dried white solid was extracted by stirring in pyridine (50 cm^3) for 30 min. The residue was collected by filtration, washed with pyridine (2 × 20 cm^3), and dried for 12 h at 50 °C/0.1 Torr. The dried crude material (2.3 g) was recrystallized from boiling triethylamine. IR ν_{max} (KBr, cm^{-1}) 3418w; 3233w,br; 3093w,br; 2947vs; 2916sh; 2867s; 1629w,br; 1447 w,br; 1309w; 1301w; 1292w; 1273w; 1252m; 1235w; 1207vw; 1191m; 1141sh; 1131sh; 1122vs; 1117vs; 1098vs; 1023m; 975m; 951vw,br; 921sh; 911m; 882m; 875sh; 838w; 787vw,br; 763vw,br; 694w. MS: m/z(%) = 1081 (1), 942 (100), 882 (3), 849 (4), 765 (2), 95 (25). M.p.: 310–325 °C (dec.).

Isolation of pyridine-soluble products

The pyridine washings and filtrate were combined and the solution was decanted slowly and carefully into ice-cold aqueous hydrochloric acid (350 cm^3, 1 cm^3 HCl (13 mol dm^{-3})/1 cm^3 pyridine). A white lumpy precipitate formed immediately. This precipitate was broken up as finely as possible, collected by filtration and dried for 12 h at 50 °C/0.1 Torr. The white solid was then pulverized and stirred with water (500 cm^3). The water was removed, the residue was washed with water (2 × 40 cm^3), and was then dried overnight at 50 °C *in vacuo*. The material was extracted into hot diethyl ether (100 cm^3) and separated from a very small ether-insoluble fraction by filtration. The diethyl ether was stripped and a white crystalline material was obtained. The crude norbornylsilasesquioxane was recrystallized from diethyl ether by slow diffusion of acetone yielding 1.2 g of crystalline material. IR ν_{max} (KBr, cm^{-1}) 3403m,br; 3243m,br; 2949vs; 2916sh; 2869s; 1954w; 1849w; 1628vw; 1452w; 1311w; 1294w; 1274w; 1256m; 1240w; 1209vw; 1192m; 1143sh; 1121vs; 1103vs; 1057sh; 1030m; 997w; 975w; 949vw; 918sh; 912m; 893m; 875m; 837w; 806vw; 788vw; 765w; 606w; 580w; 535vw; 482w. ^{29}Si NMR: (49.69 MHz, $CDCl_3$): δ −59.5 (s, 4 Si),

−68.8 (s, 2 Si). ^{1}H NMR: (200.13 MHz, $CDCl_3$): δ 7.10 (br, s, ~4 H), 2.34 (s, 6 H), 2.23 (s, 6 H), 1.60 (s, 6 H), 1.54 (s, 6 H), 1.50 (m, 6 H), 1.40 (m, 12 H), 1.18 (m, 18 H), 0.67 (br,m, 6 H). ^{13}C {^{1}H} NMR (50.03 MHz, $CDCl_3$): δ 37.87(s), 37.71(s), 37.35(m), 36.6(s), 33.51(s), 33.40(s), 31.48(m), 28.99(s), 26.03(s), 25.70(s); (100.06 MHz, $CDCl_3$) δ 37.85(m), 37.70(s), 37.41(d), 37.35(m), 36.61(s), 36.55(s), 33.49(s), 33.39(s), 31.47(s), 31.00(s), 28.99(s), 26.04(s), 25.74(s) MS *m/z*(%): 943 (30), 882 (89, $M^+ - 2H_2O$), 854 (32), 841 (45), 787 (60, $M^+ - 2H_2O - C_7H_{11}$), 649 (36), 95 (86), 67 (100), 28 (90). M.p.: 338–345 °C (dec). Analysis: Calcd for $C_{42}H_{70}O_{11}Si_6$: C, 54.9; H 7.7; Si, 18.3. Found: C, 56.0; H, 7.6; Si, 18.8% (Calcd. for $C_{42}H_{68}O_{10}Si_6$: C, 55.8; H, 7.4; Si, 18.7%).

RESULTS AND DISCUSSION

Polyhedral oligosilasesquioxanes have been known for over 40 years.[17,18] However, the high-yield syntheses of pure materials has proved to be difficult. The silasesquioxanes $[Cy_6Si_6O_9]$, $[Cy_8Si_8O_{11}(OH)_2]$ and $[Cy_7Si_7O_9(OH)_3]$, derived by incomplete condensation of cyclohexyltrichlorosilane, are notable and potentially significant exceptions.[15] Additional species with similar and complementary frameworks are produced by the incomplete condensation of norbornyltrichlorosilane. The norbornyl group is an attractive substituent in these systems, not only because of its bulk and solubility properties, but because of the potential utility of ^{1}H and ^{13}C NMR as aids to structural elucidation in rigid bicyclic systems.[19] The controlled hydrolysis of norbornyltrichlorosilane yields a white powder which consists of a pyridine-soluble and a pyridine-insoluble fraction. The mass spectra suggest that there are several species present in each crude fraction. These species may include the fully condensed species $[nor_8Si_8O_{12}]$ (MW 1176; m/z 1081 = $M^+ - C_7H_{11}$] and $[nor_6Si_6O_6]$ (m/z 882 = M^+) and/or the norbornylsilasesquioxane analogue of Feher's silasesquioxanes (**3a**),[15] i.e. $[nor_8Si_8O_{11}(OH)_2]$ (MW 1194; m/z 1081, $M^+ - C_7H_{11} - H_2O$) and (**1**), i.e. $[nor_7Si_7O_9(OH)_3]$ (MW 1056; m/z 942, $M^+ - C_7H_{12} - H_2O$). Perhaps surprisingly, the latter are isolated from the pyridine-insoluble fraction in the present work, whereas their cyclohexylsilasesquioxane analogues are soluble in pyridine.[15]

We have isolated a crystalline material from the pyridine-soluble fraction. This material has the empirical formula $C_{42}H_{70}O_{11}Si_6$, i.e. $[nor_6Si_6O_7(OH)_4]$ (nor = norbornyl = C_7H_{11}). The elemental analysis and mass spectra do not differentiate between the formulations $[nor_6Si_6O_7(OH)_4]$ and $[nor_6Si_6O_8(OH)_2]$. However, the material can be formulated as $[nor_6Si_6O_7(OH)_4]$ on the basis of a combination of a crystallographic analysis and the ^{29}Si NMR spectrum. Although the crystals slowly decomposed in the X-ray beam, a near-complete data set could be obtained. Application of direct methods[20] yielded a solution which revealed the Si_6O_7 framework and most of the immediately bonded carbon and oxygen atoms (Fig. 1). Difference Fourier maps revealed the remaining immediately bonded carbon atoms, but no chemically sensible sites were observed for the remaining norbornyl carbon atoms. The most logical explanation for this is rotational disorder of the norbornyl groups, and possibly isomeric (*endo/exo*) disorder. Disorder problems are not uncommon in silsesquioxane chemistry.[15] However, the silicon nuclearity, relative silicon stereochemistry and connectivities were established.* This analysis showed the Si_6O_7 framework to have C_{2v} symmetry, being composed of two perpendicular Si_4O_4 planes sharing an edge. An alternative, useful description of the structure is an Si_8O_{12} cube from which one Si–O–Si edge has been removed. The four resultant 'dangling' oxygens are protonated to form four strongly hydrogen-bonded Si—OH groups. With the *caveat* that structural assignments from NMR data alone can be ambiguous because of the paucity of well-characterized model compounds, the ^{1}H and ^{29}Si NMR and infrared spectra can be shown to be consistent with this structure as follows.

The highest-molecular-weight ion initially detected in the mass spectrum is observed at m/z 882 ($M^+ - 2H_2O$), consistent with a Si_6 framework. At longer scan times, additional higher-molecular-weight peaks (m/z 943, 1081, 1238) appear, probably as a result of oligomerization reactions in the mass spectrometer. The mass spectral data reported are those obtained after

* Crystal data: orthorhombic, space group $C222_1$, a = 19.952(4) Å, b = 24.105(4) Å, c = 22.363(4) Å, V = 10755(4) Å^3; R = 29 % for 1855F.

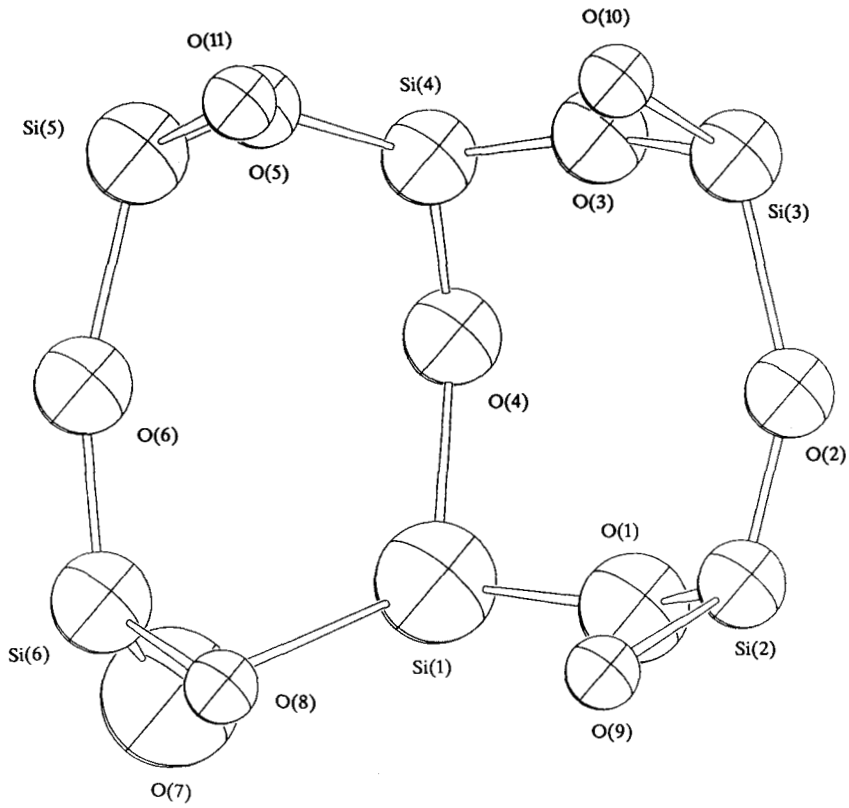

Figure 1 ORTEP representation of the $Si_6O_7O_4$ framework of $[(nor)_6Si_6O_7(OH)_4]$.

7 min. No difference could be detected between the infrared spectra of solid samples in KBr discs or of the compound in chloroform ($CHCl_3$) solution. The very strong infrared absorption at 1117 cm^{-1} is readily assigned as a ν(Si—O) vibration, by analogy with the infrared spectrum of $[H_8Si_8O_{12}]$ [ν(Si—O) 1140 cm^{-1}].[21] Infrared absorptions at 580 cm^{-1} and 482 cm^{-1} can similarly be assigned as ν(O—Si—O) and ν(Si—O) vibrations by analogy with the spectrum of $[H_8Si_8O_{12}]$ and related cyclic siloxanes.[21–24] The strong infrared absorption at 1117 cm^{-1} in the infrared spectrum of $[nor_6Si_6O_7(OH)_4]$ is thus consistent with the presence of two edge-shared cyclic tetramers. Absorptions at 908 and 888 cm^{-1} in the infrared spectrum of partially dehydroxylated silica have been assigned as ν(Si—O—Si) absorptions of highly strained and reactive siloxane bridges.[25] We have not detected corresponding absorptions in the spectrum of $[nor_6Si_6O_7(OH)_4]$. The presence of the hydroxyl groups is confirmed by the broad absorption at 3403 cm^{-1} in the infrared spectrum and by the broad ^1H NMR resonance at δ 7.10 ppm. These spectra suggest further that the OH groups are strongly hydrogen-bonded. Thus, the ν(OH) infrared absorption of isolated silonal groups on silica surfaces is observed at 3750 cm^{-1},[1,26] whereas an infrared absorption at ~3400 cm^{-1} in the spectrum of afwillite has been assigned as the ν(OH) absorption associated with a long hydrogen bond between adjacent silanol groups.[27] Similarly, Armistead *et al.* have assigned an absorption at 3550 cm^{-1} in the infrared spectrum of partially dehydroxylated silica as ν(OH) of a hydrogen-bonded surface species,[10] and the strongly hydrogen-bonded[15] OH groups of $[Cy_7Si_7O_9(OH)_3]$ exhibit a single strong, broad infrared absorption at 3230 cm^{-1} (CS_2 or CCl_4 solution), which is some 460 cm^{-1} from the position of free siloxanol OH groups in CS_2.[28] The proximity of the Si—OH groups is also consistent with the ^1H NMR resonance at δ7.10 ppm. A ^1H NMR resonance at δ 6.97 ppm ($CDCl_3$) has been reported in the spectrum of $[Cy_7Si_7O_9(OH)_3]$, which has three adjacent silanol groups, separated by 4.0 Å.[15] This resonance is lost upon derivatization of $[Cy_7Si_7O_9(OH)_3]$, to form

$[Cy_7Si_7O_9(O_3M)]$ (M = GeMe, SnMe, Zr(C_5Me_5) (NMR spectra in $CDCl_3$)), $[Cy_7Si_7O_9(OH)(OSiMe_3)_2$ [δ (OH) 2.79 ppm ($CDCl_3$)] or $[Cy_7Si_7O_9(OSiMe_3)_3]$ ($CDCl_3$), or dehydration of $[Cy_7Si_7O_9(OH)_3]$ to form $[Cy_7Si_7O_{10}(OH)]$ [δ (OH) 2.997 ppm (C_6D_6)].[14,15,29] The isolated Si—OH groups in $[Cy_8Si_8O_{11}(OH)_2]$ exhibit an ^1H NMR resonance at δ 2.09 ppm ($CDCl_3$).[15] The position of the δ 7.10 ppm absorption did not appear to be concentration-dependent.

The ^{29}Si NMR spectrum ($CDCl_3$) exhibits two resonances at δ −59.5 ppm and δ −68.8 ppm in the ratio 2:1, respectively. The ^{29}Si NMR spectra of $[R_8Si_8O_{12}]$ cubes exhibit resonances at δ −109.33 ppm (R = $OSiMe_2CH_2Cl$),[30] −109.03 ppm (R = $OSiMe_2CH{=}CH_2$),[30] −104.33 ppm (R = $OSbMe_4$),[31] −101.55 ppm (R = $OSnMe_3$),[31] −101.40 ppm (R = OMe),[32] −91.16 ppm (R = Cl),[32] and −69.80 ppm (R = Cy).[15] Similarly, the unique siloxane silicons of $[Cy_7Si_7O_9(OM)_3]$ can be assigned on intensity grounds as resonating at δ −67.99 ppm (M = H),[15] −68.24 ppm (M = $(SnMe)_{1/3}$),[15] −68.40 ppm (M = $GeMe)_{1/3}$),[15] −68.486 ppm (M = $(Zr(\eta^5\text{-}C_5Me_5))_{1/3}$),[14] −68.60 ppm (M = $AlONMe_3)_{1/3}$),[29] and −68.85 ppm (M = $(AlOPPh_3)_{1/3}$).[28] These data suggest that the siloxane silicons of silasesquioxane $RSi(O_{1/2})_3$ moieties resonate at δ ~67 ppm in the ^{29}Si NMR spectra. With that assignment, resonances at ∂ −58.46 ppm, −58.53 ppm and −60.16 ppm in the ^{29}Si NMR spectra of $[Cy_8Si_8O_{11}(OH)_2]$, $[Cy_7Si_7O_9(OH)_2(OSiMe_3)]$ and $[Cy_7Si_7O_9(OH)_3]$, respectively, can be assigned to silanol silicons. These assignments are consistent with increasing substitution of $Si(O_{1/2})_4$ by electron-withdrawing groups shifting the ^{29}Si NMR resonance to lower field. Thus, the hydrolysis of $SiCl_4$ produces a series of oligomers containing $SiCl_{4-h}(O_{1/2})_n$ (n = 1–4) moieties which exhibit ^{29}Si NMR resonances at δ ~−100 ppm, ~−80 ppm, ~−60 ppm and ~−45 ppm assigned to species with n = 4, 3, 2 and 1, respectively.

The resonance at δ −59.5 ppm in the ^{29}Si NMR spectrum of $[nor_6Si_6O_7(OH)_4]$ can then be assigned to the four silanol silicons, and that at δ −68.8 ppm to the two siloxane silicons, consistent with the structure.

This assignment is somewhat complicated by the observation of a single silanol resonance at δ −56.23 ppm ($CDCl_3/Et_3N$) in the spectrum of the trigonal prismatic $[Cy_6Si_6O_9]$ which contains siloxane silicons only.[15] We have observed this latter resonance at δ −56.56 ppm in $CDCl_3$, but have found other silsesquioxane ^{29}Si NMR resonances to be rather solvent-dependent. The resonance at δ ~−56 ppm is likely to be a characteristic of the strained Si_3O_3 ring. Such a ring is also found in $[Cy_7Si_7O_{10}(OH)]$ for which ^{29}Si NMR resonances at δ −55.28 ppm and −56.91 ppm (both with relative intensity 1) may be assigned to the silanol silicon and a Si_3O_3-ring-siloxane silicon. A resonance at δ −57.08 ppm (relative intensity 2) can then be assigned to the equivalent siloxane silicons which complete the Si_3O_3 ring.[15] Downfield shifts have previously been correlated with decreasing Si—O—Si bond angles[29,37,38] (cf. $[(SiO_2)_3O_3]^{6-}$, the cyclic trimeric anion at δ −10 ppm and $[(SiO_2)_4O_4]^{8-}$, the cyclic tetrameric anion at δ −25.58 ppm from SiO_4^{2-}).[39] These considerations underscore the need for data from a more comprehensive set of well-characterized silasesquioxanes to facilitate structural assignments by NMR.

The ^{13}C NMR spectrum, with near or exact degeneracies at δ 37.4 ppm, 31.5 ppm and 28.99 ppm, can be interpreted in terms of two sets of seven resonances in the approximate ratio 2:1. Of these seven pairs of resonances, three can be assigned from the DEPT spectrum as CH resonances, and four as CH_2 resonances, as required by the presence of the norbornyl group. The ^{13}C NMR spectrum is consistent with two different norbornyl groups—those on the siloxane silicons, and those of the silanol silicons. In particular, the resonances at δ 25.70 and 26.03 are assigned to the Si—C(2)H carbons on the basis of the DEPT spectrum and by comparisons with the spectra of $[Cy_6Si_6O_9]$ [in which the Si—CH carbon (i.e. that bound to a siloxane silicon) resonates at δ 22.67 ppm][15] and of 2-trimethyltin-norbornanes [in which the Sn—CH carbons resonate at δ 27.6 ppm (*exo*) and 28.7 ppm (*endo*)].[40,41] The relative intensities of these $[nor_6Si_6O_7(OH)_4]$ resonances suggest further that the one at δ 25.70 ppm be assigned to carbons bound to siloxane silicons, and the resonance at δ 26.03 ppm be assigned to carbons bound to silanol silicons. This is again consistent with the spectrum of $[Cy_7Si_7O_9(OH)_3]$, in which a resonance at δ 23.11 ppm can be unambiguously assigned to carbons bound to siloxane silicons, with the carbons bound to silanol silicons resonating at higher field.[15] The spectrum can then be assigned from the DEPT spectrum, and by comparison with the spectra of 2-trimethyltin-norbornanes.[40,41] Multiplets at δ ~37.35 ppm and δ ~36.61 ppm, identified as

CH carbons from the DEPT spectrum, are assigned to C(1) and C(4), respectively. A single strong CH_2 resonance at δ 28.99 ppm is assigned to C(5), with the signals from C(5) atoms of norbornyl groups on siloxane and silanol silicons assumed to be accidentally degenerate. The CH_2 resonances at δ 37.87 ppm and 37.71 ppm are assigned to C(7) carbons, their relative intensities suggesting that they are situated on norbornyl groups on silanol and siloxane silicons, respectively. CH_2 resonances at δ 33.51 ppm and δ 33.40 ppm are tentatively assigned to C(3) carbons. They are similarly assigned to norbornyl groups on silanol and siloxane silicons, respectively, on the basis of their relative intensities. The multiplet at δ 31.5 ppm is thus tentatively assigned to C(6) carbons.

An alternative interpretation is that the two sets of ^{13}C NMR resonances derive from *endo* and *exo* conformations of the Si/O framework relative to the norbornyl groups. However, the ^{13}C NMR spectral pattern appears to indicate an almost exclusive *exo*-Si conformation. In particular, a difference of some 3 ppm in the C(7) resonances might be expected for an *exo*,*endo* mixture.

The ^1H NMR spectrum, although somewhat difficult to interpret because of the broad envelopes of overlapping spectra, is consistent with this interpretation. Thus, two multiplets of relative intensities ~2:1 at δ ~0.7 ppm and δ ~0.9 ppm, respectively, have shapes appropriate for *endo* H(2) resonances,[42] and are therefore tentatively assigned to norbornyls on silanol and siloxane silicons, respectively. Broad resonances at δ 2.35 ppm at δ 2.24 ppm can be assigned to the H(1) and H(4) protons respectively. At 400 MHz, the H(1) absorption is partially resolved into two resonances at δ 2.35 ppm and δ 2.32 ppm, with relative intensities 2:1, consistent with the structure.

Both the ^1H and ^{13}C NMR spectra are therefore consistent with a nearly exclusive *exo*-Si 2-norbornyl conformation for both the siloxane and silanol silicons. There is no evidence of any fluxionality on the NMR time scales, suggesting that the molecule is locked into a single conformation.

Vicinal Si—OH groups in $[nor_6Si_6O_7(OH)_4]$ are also suggested by the facile loss of water in the mass spectrum to generate $[nor_6Si_6O_9]^+$, the analogue of $[Cy_6Si_6O_9]$. The elimination of water appears to be less favourable in the mass spectrum of $[Cy_8Si_8O_{11}(OH)_2]$, in which the Si—OH groups are farther apart.[15]

The evidence for vicinal Si—OH groups also makes the alternative hexanuclear doubly bridged cyclic tetramer[35] an unlikely structure for $[nor_6Si_6O_7(OH)_4]$. Moreover, the ^{29}Si NMR resonances of the $norSiO_{3/2}$ groups in such a structure might be expected at higher field than δ −66 ppm.[36]

CONCLUSIONS

The reaction of norbornene with trichlorosilane produces norbornyltrichlorosilanes in high yield. Incomplete condensation of norbornyltrichlorosilane results in the formation of several norbornylsilasesquioxanes. The compound $[nor_6Si_6O_7(OH)_4]$ has been isolated from this reaction as a white crystalline product, soluble in pyridine, diethyl ether and chloroform, and insoluble in acetone. This compound is readily prepared and purified and is tentatively assigned a conformation with two edge-sharing perpendicular Si_4O_4 planes on the basis of analytical, crystallographic and spectroscopic data.

The species $[nor_6Si_6O_7(OH)_4]$ is an important compound in the search for models of silica surfaces. The surface of partially dehydroxylated silica is believed to contain well-dispersed aggregates of $(Si—OH)_n$ groups. Single Si—OH groups (**A**) predominate, with vicinal $(Si—OH)_2$ groupings (**B**) occurring less frequently and aggregates of three adjacent Si—OH groups (**C**) being comparatively rare. These $(Si—OH)_n$ aggregates are separated by domains of fully condensed $(Si—O—Si)_n$ linkages (**D**). The surface features **C** and **D** are modelled by silasesquioxanes $[Cy_7Si_7O_9(OH)_3]$ and $[Cy_6Si_6O_9]$, respectively.[15] Surface feature **A** might be modelled by a silanol (e.g. triphenylsilanol), by the silasesquioxane $[Cy_8Si_8O_{11}(OH)_2]$ or by the silasesquioxane $[Cy_7Si_7O_{10}(OH)]$.[15]

The norbornylsilasesquioxane $[nor_6Si_6O_7(OH)_4]$ provides a model by which the reactivity of the important functionality, vicinal surface Si—OH groups (**B**), can be examined. It is an alternative model of vicinal surface Si—OH groups to those derived by silylation or functionalization of, for example, $[Cy_7Si_7O_9(OH)_3]$, in which the steric demands of the derivatizing group, M, in $[Cy_7Si_7O_9(OM)(OH)_2]$ may be the predominant influence on the chemistry. Additionally, $[(nor)_6Si_6O_7(OH)_4]$ may provide a model for a hydroxylated surface defect site on silicon. The reactivity of $[nor_6Si_6O_7(OH)_4]$ and the syntheses

of further silasesquioxane derivatives are under examination.

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