Biomimetic Polyorganosiloxanes: Model Compounds for New Materials

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Abstract

The chemistry of N-organosilylalkyl-substituted heterocyclic bases (thymine, adenine and cytosine) is described, covering the structures of model compounds, the synthesis of substituted oligo-siloxanes and a preliminary report of the synthesis of a poly-(organosiloxane) with pendant N-alkyl(heterocycle) functionalities. N-alkenylthymines \( \text{CH}_2=\text{CH}((\text{CH}_2)_n\text{T} \quad \text{T} = \text{thymine}, \quad n = 1 \quad (1), \quad 2 \quad (2), \quad 3 \quad (3)) \) have been prepared and 2 hydrosilylated to form \( \text{PhMe}_2\text{Si(CH}_2)_4\text{T} \quad (5) \). Alternatively, 5 was prepared by reaction of \( \text{PhMe}_2\text{Si(CH}_2)_4\text{Br} \quad (6) \) with \( (\text{O},\text{O}-\text{SiMe}_3)_2\text{T} \), a method which has also been used to prepare \( \text{PhMe}_2\text{Si(CH}_2)_4\text{A} \quad (7) \) and \( \text{PhMe}_2\text{Si(CH}_2)_4\text{C} \quad (8) \) (A = adenine, C = cytosine). Model di- and tri-siloxanes \( [\text{Br(CH}_2)_4\text{Si)}_2\text{O}]_2 \quad (10) \), \( \text{Me}_3\text{SiOSi(Me)}_2\text{(CH}_2)_4\text{Br} \quad (11) \), \( \text{PhMe}_2\text{SiOSi(Me)}_2\text{(CH}_2)_4\text{Br} \quad (12) \) and \( (\text{Me}_3\text{SiO})_2\text{(Me)}_2\text{Si(CH}_2)_4\text{Br} \quad (13) \) have been prepared by hydrosilylation of \( \text{H}_2\text{C=C(H)}((\text{CH}_2)_4\text{Br} \quad \text{with an appropriate hydrosiloxane and used to prepare} \quad \text{Me}_3\text{SiO(Me)}_2\text{Si(CH}_2)_4\text{T} \quad (14), \quad \text{Me}_3\text{SiO(Me)}_2\text{Si(CH}_2)_4\text{A} \quad (15) \) (both from 11), and

\[ \text{Me}_3\text{SiO(Me)}_2\text{Si(CH}_2)_4\text{T} \quad (16), \quad (\text{Me}_3\text{SiO})_2\text{(Me)}_2\text{Si(CH}_2)_4\text{A} \quad (17) \] (both from 13). 10 reacts with thymine to give a mixture of the pyrimidocyclophanes \( \text{cyclo-T-N-N-[}((\text{CH}_2)_4\text{Me)}_2\text{Si]}_2\text{O} \quad (19) \) and \( [\text{T(CH}_2)_4\text{Si(Me)}_2]\_2\text{O} \quad (20) \), while cytosine reacts similarly to form \( \text{cyclo-C-N-N-[}((\text{CH}_2)_4\text{Me)}_2\text{Si]}_2\text{O} \quad (21) \); as an imine) and

\[ [\text{C(CH}_2)_4\text{Si(Me)}_2]\_2\text{O} \quad (22); \quad \text{adenine only generates} \quad [\text{A(CH}_2)_4\text{Si(Me)}_2]\_2\text{O} \quad (18) \] in an analogous synthesis. Using a related protocol, polymeric \( [(\text{MeSi(O)(CH}_2)_4\text{Br})_2\text{[Me}_2\text{SiO]}_{88}]_n \quad (23) \) has been converted to

\[ [(\text{MeSi(O)(CH}_2)_4\text{T})_2\text{[Me}_2\text{SiO]}_{88}]_n \quad (24) \] and \( [(\text{MeSi(O)(CH}_2)_4\text{A})_2\text{[Me}_2\text{SiO]}_{88}]_n \quad (24) \). The structures of 4, 5, 8, 19 and 21, along with a 2:1 adduct of 5 with Ni(dithiobiuret)$_2$ (9) are reported.

Keywords: siloxane, thymine, cytosine, adenine, polymer, X-ray
Introduction

The use of hydrogen bonds to direct the self-assembly of novel materials is one of the most exploited routes to nanostructures of defined composition. The most sophisticated of such systems – DNA – in which complimentary purine / pyrimidine base pairs provides a framework for self-replication is arguably the most simple, yet most structurally appealing, example of nature's work. In recent years, the interplay of T/A and C/G base pairs (T = thymine, A = adenine, C = cytosine, G = guanine) has been used to construct numerous nanomaterials, with applications including nanomechanical devices.\textsuperscript{1}

Furthermore, there has been interest in the functionalization of polymer chains with biomimetic substituents, in attempts to produce synthetic polymers with the same properties as their naturally occurring counterparts. Polymers analogous to nucleic acids have been made from easily-synthesised vinyl, polypeptide or methacrylate polymers or oligomers with biologically functional pendant groups combined with controlled radical polymerization methods to produce well defined structures.\textsuperscript{2, 3} Materials based on poly(\textepsilon-caprolactone)\textsuperscript{4} and polylactides\textsuperscript{5} have been produced, as well as block copolymers with, for example, poly(ethylene glycol).\textsuperscript{6} Exploitation of the nucleobase interactions in the block materials led to enhanced aggregation over the individual copolymers. The exploitation of these complementary interactions in forming supramolecular polymers has been reviewed by Sessler \textit{et al}.\textsuperscript{7}

Such polymers have potential biomedical applications\textsuperscript{8-10} and have also been proposed as thermoresponsive materials.\textsuperscript{11} Rowan and co-workers have used the complementary nucleobase interactions between T/A\textsuperscript{12} or C/A\textsuperscript{11} to prepare stable, thermotropic liquid crystalline polymers which displayed thermoreversible phase behaviour.

However, as far as we are aware, there has only been very limited attention given to silicon-based materials functionalised by the nucleobases. Délérès \textit{et al}. carried out the most significant studies, with the aim of producing anti-HIV agents,\textsuperscript{13} or improving the lipophilicity of oligodeoxynucleotides,\textsuperscript{14, 15} but none of these studies specifically addressed the formation of siloxane polymers. More recent work has focussed on the synthesis of nanostructured organosilica materials by hydrolysis of (EtO)\textsubscript{3}Si(CH\textsubscript{2})\textsubscript{n}-substituted bases,\textsuperscript{16} and the resulting solids were characterised by solid-state NMR.\textsuperscript{17} Amino acid-functionalised siloxanes are, however, better known.\textsuperscript{18} Meijer and co-workers\textsuperscript{19, 20} prepared siloxanes terminated with
quadruple hydrogen-bonding ureido-pyrimidone units which assembled into high molecular weight polymer networks with reversible rheology.

Our own interest in silicon-based polymers,\textsuperscript{21} and in particular polysiloxanes,\textsuperscript{22, 23} has led us to look more closely at the chemistry of the latter polymer backbones functionalised by nucleobases, which might ultimately afford novel, self-organising materials. While our synthetic methodology builds on the earlier work of Déléris,\textsuperscript{13-15} our emphasis is on the synthesis and structural chemistry of both precursors and model compounds as well as the polymers themselves, with a view to understanding more fundamentally the nature of any self-assembly processes.

**Experimental**

**Experimental Procedures**

Starting materials adenine, thymine, cytosine, guanine, phenyldimethylsilane, (3-aminopropyl)-diethoxymethylsilane, chlorodimethylsilane, chloroplatinic acid, allylamine, allyl bromide, 4-bromo-1-butene, hexamethyldisilazane, 3-bis-(3-aminopropyl)tetramethyldisiloxane, PDMS (Mw ~ 50,000) and PDMS (Mw ~ 25,000) were obtained from Sigma-Aldrich and used without further purification.

Pentamethyldisiloxane and 1,1,1,3,5,5,5-heptamethyltrisiloxane were obtained from Gelest. All reactions were carried out under nitrogen unless otherwise specified. O,O-Bis(trimethylsilyl)thymine, N,N-bis(trimethylsilyl)adenine and O,N-bis(trimethylsilyl)cytosine were prepared as described elsewhere,\textsuperscript{24} as was nickel bis(dithiobiuret).

Infra-red spectra were recorded on NaCl plates using a Nexus Nicolet 510P FT-IR spectrometer in the region 4000-400 cm\(^{-1}\). \(^1\)H, \(^{13}\)C and \(^{29}\)Si spectra were recorded on Bruker Avance (300 MHz) Fourier transform spectrometer, using TMS as an internal reference. Elemental analyses were performed using a Carbo Erba Strumentazione E.A. model 1106 analyser. The results were duplicated and the mean of the duplicated measurements was the final result. Gel permeation chromatography (GPC) was carried out in chloroform at 30 °C using a flow rate of 1 ml min\(^{-1}\) through two 30 cm ‘PL Gel 10 μm Mixed’ columns. Data was collected from a refractive index detector on a Viskotek ‘Trisek 2000’ chromatograph and analysed using ‘Trisec 3.0’ software. Molecular weights are reported relative to polystyrene calibration.

1-allyl-5-methylpyrimidine-2,4(1H,3H)-dione (1).
A THF (50 cm³) solution of bis-(trimethylsilyl)thymine (11.0 g, 41 mmol) and an excess of allyl bromide (13.0 cm³, 150 mmol) were refluxed until the IR spectrum displayed no further generation of the product, monitored by charting the growth of the peak at ca. 1750 cm⁻¹ due to the carbonyl groups on thymine (ca. 72 h). The THF and excess allyl bromide were then removed under reduced pressure leaving the product as a yellow oil from which the product 1-allylthymine (1) spontaneously crystallised. Two recrystallizations from toluene liberated the pure product as white platelets (5.5 g, 81 %, m.p. 109-111 °C, lit. 112, 1496-99 °C). Also prepared by the same method were:

1-(but-3-en-1-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (2).
From bis-(trimethylsilyl)thymine (3.0 g 11 mmol) and 4-bromo-1-butene (3.0 cm³, 30 mmol) over 72 h. The resulting brown oil was chromatographed on silica with a mixture of dichloromethane and methanol (98:2), yielding one band from which the crude product was obtained on solvent evaporation. Two recrystallizations from toluene yielded the pure product (2) as white platelets (1.17 g, 59 %, m.p. 119-121 °C, lit. 133-135 °C). ¹H NMR (300 MHz, CDCl₃): 9.68 (bs, 1H, NH), 6.98 (s, 1H, CH), 5.76 (m, 1H, CH=CH₂), 5.10 (m, 2H, CH=CH₂), 3.71 (t, J = 7.3 Hz, 2H, NCH₂), 2.47 (m, 2H, NCH₂CH₂), 1.92 (s, 3H, CH₃); ¹³C NMR (300 MHz, CDCl₃): 164.6 (C=O), 151.0 (C=O), 140.7 (CH), 133.5 (CH=CH₂), 118.5 (CH=CH₂), 110.4 (CCH₂), 48.0 (NCH₂), 33.3 (NCH₂CH₂), 12.3 (CCH₃); analysis, calcd for C₅H₁₂N₂O₂: C 60.0, H 6.71, N 15.6 %, found C 60.0, H 6.58, N 15.6 %.

5-methyl-1-(pent-4-en-1-yl)pyrimidine-2,4(1H,3H)-dione (3)
From bis-(trimethylsilyl)thymine (3.0 g 11 mmol) and 4-bromo-1-pentene (2.6 cm³, 22 mmol) over 144 h. Work-up as for 2 yielded the product (3) as brown needles (0.38 g, 18 %, m.p. 134-6 °C, lit 105-6 °C). ¹H NMR (300 MHz, CDCl₃): 9.84 (bs, 1H, NH), 6.98 (s, 1H, CH), 5.79 (m, 1H, CH=CH₂), 5.05 (m, 2H, CH=CH₂), 3.71 (t, J = 7.3 Hz, 2H, NCH₂), 2.11 (m, 2H, NCH₂CH₂), 1.92 (s, 3H, CH₃), 1.80 (m, 2H, NCH₂CH₂CH₂); ¹³C NMR (300 MHz, CDCl₃): 164.7 (C=O), 151.2 (C=O), 140.5(CH), 133.7 (CH=CH₂),
115.8 (CH=CH), 110.6 (CCH), 48.0 (NCH), 30.4 (NCHCH), 28.0 (m, 2H, NCHCH), 12.3 (CCH); analysis calcd for C$_{10}$H$_{14}$N$_{2}$O$_{2}$: C 61.8, H 7.27, N 14.4 %, found C 61.4, H 7.18, N 14.1 %.

1-allyl-5-methyl-4-((trimethylsilyl)oxy)pyrimidin-2(1H)-one (4)

A mixture of hexamethyldisilazane (20 cm$^3$, 91 mmol), 1-allyl-5-methylpyrimidine-2,4(1H,3H)-dione (1) (2.00 g, 12 mmol) and a few crystals of ammonium sulphate was refluxed for 18 h. After this time, the solid had dissolved and a colourless solution remained. The excess disilazane was removed under reduced pressure, affording the clear oily product (2.68 g, 93%). 4 spontaneously crystallised upon cooling under nitrogen. $^1$H NMR (300 MHz, CHCl$_3$): 6.98 (q, J = 1.0 Hz, CH), 5.90 (m, 1H, CH=CH), 5.27 (m, 2H, CH=CH), 4.27 (d, J = 6.0 Hz, 2H, NCCH), 1.92 (d, J = 1.0 Hz, 3H, CH$_3$), 0.38 (s, 9H, Si(CH$_3$)$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$): 170.3 (COSi), 156.5 (C=O), 143.9 (CH), 132.6 (CH=CH), 118.9 (CH=CH), 106.1 (CH), 51.5 (NCH), 12.5 (CCH); analysis, calcd for C$_{11}$H$_{20}$N$_{2}$O$_{2}$Si: C 55.0, H 8.39, N 11.7 %, found C 55.1, H 8.29, N 11.8 %.

1-(4-(dimethyl(phenyl)silyl)butyl)-5-methyl-4-((trimethylsilyl)oxy)pyrimidin-2(1H)-one (5)

A mixture of 1-(but-3-en-1-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (2) (0.50 g, 2.74 mmol) and excess of hexamethyldisilazane and a few crystals of ammonium sulphate were refluxed for 18 h, after which the opacity due to solid 2 had cleared. The volatiles were removed under reduced pressure, and to the remaining colourless oil (4a) was added THF (10 cm$^3$), phenyldimethylsilane (0.37 g, 2.74 mmol) and a catalytic amount of chloroplatinic acid in propan-2-ol. The solution was heated to 80 °C for 72 h, after which the IR spectrum (neat liquid) revealed an absence of starting material. The volatiles were removed, affording a brown solid, which was chromatographed on silica using a mixture of dichloromethane and methanol (98:2) as eluent. The chromatography yielded two bands. The first was eluted with the solvent front and afforded unreacted phenyldimethylsilane. The second was eluted at $r = 0.45$ and afforded the crude product as a white powder. Recrystallization from a mixture of chloroform and hexane yielded (4-phenyldimethylsilyl)butylthymine (5) as colourless tabular crystals (0.43 g, 51 %). $^1$H NMR (300 MHz, 8CDCl$_3$): 8.92 (bs, 1H NH), 7.49 (m, 2H, C$_6$H$_5$), 7.32 (m, 3H, C$_6$H$_5$), 3.67 (t, J = 7.0 Hz, 2H, NCH$_2$), 1.91 (s, 3H, CH$_3$), 1.68 (m, 2H, NCH$_2$CH$_2$), 1.33 (m, 2H, SiCH$_2$CH$_2$), 0.78 (m, 2H, SiCH$_2$), 0.27 (s, 6H, Si(CH$_3$)$_2$);
\( ^{13} \text{C NMR} \) (75 MHz, CDCl\(_3\)): 164.3 (C=O), 150.9 (C=O), 140.4 (CH), 110.5 (CCH\(_3\)), 47.9 (NCH\(_2\)), 21.0 (SiCH\(_2\)), 14.8 (SiC\(_2\)H), -3.1 (Si(CH\(_3\))\(_2\)); \( ^{29} \text{Si NMR} \) (60 MHz, CDCl\(_3\)) -3.0; analysis, calcd for C\(_{17}\)H\(_{24}\)N\(_2\)O\(_2\)Si: C 64.5, H 7.64, N 8.85 \%, found C 63.9, H 7.64, N 8.61 \%.

Alternative synthesis of 5.

A solution of (4-bromobutyl)phenyldimethylsilane (6, 1.00 g, 3.69 mmol), bis-(trimethylsilyl)thymine (1.00 g, 3.69 mmol) and tetrabutylammonium fluoride (0.96 g, 3.69 mmol) in THF (50 cm\(^3\)) was refluxed for 72 h. After removal of the volatiles, the solid remaining was purified by chromatography on silica, using a mixture of dichloromethane and methanol as eluent (98:2). The chromatography yielded three bands. The first eluted with the solvent front and was found to be unreacted 6. The second band eluted at approximately \( r = 0.7 \) and was found to be TBAF. The third eluted as a broad smear at between \( r = 0.75 \) and 0.45 and was found to be the target product. The product was washed with water to extract any further traces of remaining TBAF, and then recrystallised from a mixture of dichloromethane and hexane, yielding the pure product (5) as colourless, tabular crystals (0.86 g, 74 \%).

(4-bromobutyl)phenyldimethylsilane (6)

A mixture of phenyldimethylsilane (4.3 cm\(^3\), 18.3 mmol), 4-bromo-1-butene (2.0 cm\(^3\), 19.89 mmol) and a catalytic amount of chloroplatinic acid in propan-2-ol was heated to 80 °C for 72 h, after which IR spectroscopy revealed a lack of starting material by an absence of a peak at 2150 cm\(^{-1}\) corresponding to the Si-H stretching vibration. The excess 4-bromo-1-butene was removed under reduced pressure, and the remaining solution was chromatographed using chloroform as eluent. The chromatography yielded one band, eluting with the solvent front and affording the product (4-bromobutyl)phenyldimethylsilane (6, 3.7 g, 74 \%). Variations on the experiment were made by varying the time of reaction between 18 h and 96 h but no improvements to the yield were made. \(^1\text{H NMR} \) (300 MHz, CDCl\(_3\)): 7.42 (m, 5H, C\(_6\)H\(_5\)), 3.35 (t, J = 6.9 Hz, 2H, CH\(_2\)Br), 1.84 (m, 2H, CH\(_2\)CH\(_2\)Br), 1.45 (m, 2H, SiCH\(_2\)CH\(_2\)H), 0.74 (m, 2H, SiCH\(_2\)H), 0.27 (s, 6H, Si(CH\(_3\))\(_2\)); \( ^{13} \text{C NMR} \) (75 MHz, CDCl\(_3\)): 139.1 (C\(_6\)H\(_5\)), 133.5 (C\(_6\)H\(_5\)), 133.0 (C\(_6\)H\(_5\)), 129.2 (C\(_6\)H\(_5\)), 128.9 (C\(_6\)H\(_5\)), 127.8 (C\(_6\)H\(_5\)), 36.2 (CH\(_2\)Br), 33.4 (CH\(_2\)CH\(_2\)Br), 22.5 (SiCH\(_2\)CH\(_2\)H), 14.8 (SiCH\(_2\)H), -3.1 (Si(CH\(_3\))\(_2\)); \( ^{29} \text{Si NMR} \) (60 MHz, CDCl\(_3\)) -3.0; analysis, calcd for C\(_{15}\)H\(_{19}\)BrSi: C 55.1, H 7.06 \%, found C 55.7, H 6.91 \%. 

\( ^{13} \text{C NMR} \) (75 MHz, CDCl\(_3\)): 164.3 (C=O), 150.9 (C=O), 140.4 (CH), 110.5 (CCH\(_3\)), 47.9 (NCH\(_2\)), 21.0 (SiCH\(_2\)), 15.4 (CCH\(_3\)), 12.3 (SiCH\(_2\)), -3.1 (Si(CH\(_3\))\(_2\)); \( ^{29} \text{Si NMR} \) (60 MHz, CDCl\(_3\)) -3.0; analysis, calcd for C\(_{17}\)H\(_{24}\)N\(_2\)O\(_2\)Si: C 64.5, H 7.64, N 8.85 \%, found C 63.9, H 7.64, N 8.61 \%. 

Alternative synthesis of 5.

A solution of (4-bromobutyl)phenyldimethylsilane (6, 1.00 g, 3.69 mmol), bis-(trimethylsilyl)thymine (1.00 g, 3.69 mmol) and tetrabutylammonium fluoride (0.96 g, 3.69 mmol) in THF (50 cm\(^3\)) was refluxed for 72 h. After removal of the volatiles, the solid remaining was purified by chromatography on silica, using a mixture of dichloromethane and methanol as eluent (98:2). The chromatography yielded three bands. The first eluted with the solvent front and was found to be unreacted 6. The second band eluted at approximately \( r = 0.7 \) and was found to be TBAF. The third eluted as a broad smear at between \( r = 0.75 \) and 0.45 and was found to be the target product. The product was washed with water to extract any further traces of remaining TBAF, and then recrystallised from a mixture of dichloromethane and hexane, yielding the pure product (5) as colourless, tabular crystals (0.86 g, 74 \%).

(4-bromobutyl)phenyldimethylsilane (6)

A mixture of phenyldimethylsilane (4.3 cm\(^3\), 18.3 mmol), 4-bromo-1-butene (2.0 cm\(^3\), 19.89 mmol) and a catalytic amount of chloroplatinic acid in propan-2-ol was heated to 80 °C for 72 h, after which IR spectroscopy revealed a lack of starting material by an absence of a peak at 2150 cm\(^{-1}\) corresponding to the Si-H stretching vibration. The excess 4-bromo-1-butene was removed under reduced pressure, and the remaining solution was chromatographed using chloroform as eluent. The chromatography yielded one band, eluting with the solvent front and affording the product (4-bromobutyl)phenyldimethylsilane (6, 3.7 g, 74 \%). Variations on the experiment were made by varying the time of reaction between 18 h and 96 h but no improvements to the yield were made. \(^1\text{H NMR} \) (300 MHz, CDCl\(_3\)): 7.42 (m, 5H, C\(_6\)H\(_5\)), 3.35 (t, J = 6.9 Hz, 2H, CH\(_2\)Br), 1.84 (m, 2H, CH\(_2\)CH\(_2\)Br), 1.45 (m, 2H, SiCH\(_2\)CH\(_2\)H), 0.74 (m, 2H, SiCH\(_2\)H), 0.27 (s, 6H, Si(CH\(_3\))\(_2\)); \( ^{13} \text{C NMR} \) (75 MHz, CDCl\(_3\)): 139.1 (C\(_6\)H\(_5\)), 133.5 (C\(_6\)H\(_5\)), 133.0 (C\(_6\)H\(_5\)), 129.2 (C\(_6\)H\(_5\)), 128.9 (C\(_6\)H\(_5\)), 127.8 (C\(_6\)H\(_5\)), 36.2 (CH\(_2\)Br), 33.4 (CH\(_2\)CH\(_2\)Br), 22.5 (SiCH\(_2\)CH\(_2\)H), 14.8 (SiCH\(_2\)H), -3.1 (Si(CH\(_3\))\(_2\)); \( ^{29} \text{Si NMR} \) (60 MHz, CDCl\(_3\)) -3.0; analysis, calcd for C\(_{15}\)H\(_{19}\)BrSi: C 55.1, H 7.06 \%, found C 55.7, H 6.91 \%. 

\( ^{13} \text{C NMR} \) (75 MHz, CDCl\(_3\)): 164.3 (C=O), 150.9 (C=O), 140.4 (CH), 110.5 (CCH\(_3\)), 47.9 (NCH\(_2\)), 21.0 (SiCH\(_2\)), 15.4 (CCH\(_3\)), 12.3 (SiCH\(_2\)), -3.1 (Si(CH\(_3\))\(_2\)); \( ^{29} \text{Si NMR} \) (60 MHz, CDCl\(_3\)) -3.0; analysis, calcd for C\(_{17}\)H\(_{24}\)N\(_2\)O\(_2\)Si: C 64.5, H 7.64, N 8.85 \%, found C 63.9, H 7.64, N 8.61 \%.
9-(4-(dimethyl(phenyl)silyl)butyl)-9H-purin-6-amine (7)

Reaction of \(N,N\)-bis(trimethylsilyl)adenine (0.56 g, 2.02 mmol), 6 (0.55 g, 2.03 mmol) and TBAF (0.53 g, 2.04 mmol) yielded 7 as fine white needles (0.34 g, 55%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): 8.36 (s, 1H, CH), 7.69 (s, 1H, CH), 7.45 (m, 2H, \(C_6H_5\)), 7.30 (m, 3H, \(C_6H_5\)), 5.65 (bs, 2H, NH\(_2\)), 4.15 (t, \(J = 7.0\) Hz, 2H, NCH\(_2\)), 1.89 (m, 2H, NCH\(_2\)C\(_H\)), 1.37 (m, 2H, SiCH\(_2\)C\(_H\)), 0.80 (m, 2H, SiC\(_H_2\)), 0.25 (s, 6H, Si(C\(_H_3\))\(_2\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)): 155.3 (CNH\(_2\)), 152.9 (CH), 140.4 (CH), 133.5 (C\(_6H_5\)), 129.0 (C\(_6H_5\)), 127.8 (C\(_6H_5\)), 43.4 (NCH\(_2\)), 33.6 (NCH\(_2\)C\(_H\)), 21.0 (SiCH\(_2\)C\(_H\)), 15.2 (SiCH\(_2\)) -3.2 (Si(C\(_H_3\))\(_2\)), two NCN too weak to be observed; \(^29\)Si NMR (60 MHz, CDCl\(_3\)): -3.1; analysis, calcd for C\(_{17}\)H\(_{23}\)N\(_5\)Si: C 62.7, H 7.12, N 21.5 %, found C 61.9, H 7.13, N 21.3 %.

4-amino-1-(4-(dimethyl(phenyl)silyl)butyl)pyrimidin-2(1H)-one (8)

Reaction of O, N-bis(trimethylsilyl)cytosine (1.15 g, 4.05 mmol), 6 (1.22 g, 4.05 mmol) and TBAF (1.55 g, 4.55 mmol) yielded 8 as tabular crystals (0.61 g, 45%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): 8.02 (bs, 2H, NH\(_2\)), 7.48 (m, 2H, \(C_6H_5\)), 7.35 (m, 3H, \(C_6H_5\)), 7.13 (d, \(J = 1.0\) Hz, 1H, NCH), 5.86 (d, \(J = 1.0\) Hz, 1H, \(C\)C\(_H\)), 3.60 (t, \(J = 7.0\) Hz, 2H, NCH\(_2\)), 1.59 (m, 2H, NCH\(_2\)C\(_H\)), 1.35 (m, 2H, SiCH\(_2\)C\(_H\)), 0.76 (m, 2H, SiCH\(_2\)), 0.26 (s, 6H, Si(CH\(_3\))\(_2\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)): 162.5 (CNH\(_2\)), 152.9 (CH), 140.4 (CH), 133.4 (C\(_6H_5\)), 129.0 (C\(_6H_5\)), 127.8 (C\(_6H_5\)), 99.0 (CH), 49.9 (NCH\(_2\)), 32.7 (NCH\(_2\)C\(_H\)), 21.0 (SiCH\(_2\)C\(_H\)), 15.2 (SiCH\(_2\)) -3.1 (Si(CH\(_3\))\(_2\)); \(^29\)Si NMR (60 MHz, CDCl\(_3\)): -3.1; analysis, calcd for C\(_{16}\)H\(_{23}\)N\(_3\) Si: C 63.8, H 7.69, N 13.9 %, found C 63.6, H 7.8, N 13.6 %.

Nickel bis(dithiobiuret) adduct (1:2) with 5 (9)

(5) (0.070 g, 0.22 mmol) and Ni(dtb)\(_2\)\(^{25}\) (0.074 g, 0.22 mmol) were dissolved in a minimum of warm methanol (25 mL), sealed with a subaseal punctured with a syringe needle and left to cool to room temperature. Pink crystals of Ni(dtb)\(_2\).2(5) (9) grew slowly over a period of days. Yield 20%, m.p. 224 °C; no further analysis of these crystals was carried out.

1,3-bis(4-bromobutyl)-1,1,3,3-tetramethyldisiloxane (10)
A mixture of 4-bromo-1-butene, chlorodimethylsilane and a catalytic amount of chloroplatinic acid in propan-2-ol was heated at 110 °C until the neat-liquid IR spectrum revealed an absence of starting material, denoted by lack of Si-H stretching vibration at 2150 cm⁻¹ (ca. 72 h). The volatiles were removed and the remaining grey liquid was hydrolysed, washed with water, extracted with chloroform and dried over MgSO₄. Column chromatography on silica with chloroform as eluent afforded the 1,3-bis-(4-bromobutyl)-disiloxane product as an air stable, colourless oil, recovered with the solvent front. ¹H NMR (300 MHz, CDCl₃): 3.42 (t, J = 7.0 Hz, 2H, CH₂Br), 1.88 (m, 2H, CH₂CH₂Br), 1.48 (m, 2H, SiCH₂CH₂), 0.52 (m, 2H, SiCH₂), 0.15 (s, 6H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃): 35.7 (CH₂Br), 33.3 (CH₂CH₂Br), 21.6 (SiCH₂CH₂), 17.0 (SiCH₂), 0.7 (Si(CH₃)₂); ²⁹Si NMR (60 MHz, CDCl₃): 7.0.

Also prepared by the same method were:

1-(4-bromobutyl)-1,1,3,3,3-pentamethyldisiloxane (11)

From 1,1,3,3,3-pentamethyldisiloxane (2.40 g, 16.0 mmol) and 4-bromo-1-butene (2.0 cm³, 19.9 mmol); yield 2.80 g, 61%. ¹H NMR (300 MHz, CDCl₃): 3.35 (t, J = 7.0 Hz, 2H, CH₂Br), 1.83 (m, 2H, CH₂CH₂Br), 1.45 (m, 2H, SiCH₂CH₂), 0.52 (m, 2H, SiCH₂), 0.15 (s, 6H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃): 35.3 (CH₂Br), 32.8 (CH₂CH₂Br), 21.1 (SiCH₂CH₂), 16.5 (SiCH₂), 0.7 (Si(CH₃)₂), 0.6 (Si(CH₃)₂); ²⁹Si NMR (60 MHz, CDCl₃): 7.6 (Me₃SiO), 7.0 (OSiMe₂); analysis, calcd for C₉H₂₃Si₂OBr: C 38.2, H 8.18 %, found C 38.0, H 8.01 %.

1-(4-bromobutyl)-1,1,3,3-tetramethyl-3-phenyldisiloxane (12)

From 1,1,3,3-tetramethyl-3-phenyldisiloxane (3.70 g, 16.0 mmol) and 4-bromo-1-butene (2.0 cm³, 19.9 mmol); yield 3.10 g, 56%. ¹H NMR (300 MHz, CDCl₃): 7.45 (m, 5H, C₆H₅), 3.35 (t, J = 6.9 Hz, 2H, CH₂Br), 1.83 (m, 2H, CH₂CH₂Br), 1.45 (m, 2H, SiCH₂CH₂), 0.52 (m, 2H, SiCH₂), 0.33 (s, 6H, Si(CH₃)₂), 0.05 (s, 6H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃): 139.0 (C₆H₅), 132.2 (C₆H₅), 132.1 (C₆H₅), 128.5 (C₆H₅), 128.4 (C₆H₅), 127.0 (C₆H₅), 35.2 (CH₂Br), 32.6 (CH₂CH₂Br), 21.0 (SiCH₂CH₂), 16.5 (SiCH₂), 0.6 (Si(CH₃)₂), 0.4 (PhSi(CH₃)₂); ²⁹Si NMR (60 MHz, CDCl₃): 8.6 (PhMe₂SiO), 7.3 (O-SiMe₂CH₂); analysis, calcd for C₁₅H₂₅Si₂OBr: C 48.7, H 7.30 %, found C 49.0, H 7.30 %.
3-(4-bromobuty)-1,1,3,5,5,5-heptamethyltrisiloxane (13)

From 1,1,3,5,5,5-heptamethyltrisiloxane (3.00 g, 13.5 mmol) and 4-bromo-1-butene (1.4 cm³, 15.5 mmol); yield 3.80 g, 79%. $^1$H NMR (300 MHz, CDCl₃): 3.31 (t, J = 7.0 Hz, 2H, CH₂Br), 1.77 (m, 2H, CH₂CH₂Br), 1.38 (m, 2H, SiCH₂CH₂), 0.38 (m, 2H, SiCH₂), -0.08 (s, 18H, Si(CH₃)₃), -0.09 (s, 3H, O₂Si(CH₃)); $^{13}$C NMR (75 MHz, CDCl₃): 34.1 (CH₂Br), 31.6 (CH₂CH₂Br), 19.9 (SiCH₂CH₂), 14.6 (SiCH₂), -2.2 (O₂Si(CH₃)), -2.4 (Si(CH₃)₃); $^{29}$Si NMR (60 MHz, CDCl₃): 7.5 (Me₃Si/O), -22.5 (O₂SiMe); analysis, calcd for C₁₁H₂₉Si₂O₂Br: C 37.0, H 8.18 %, found C 37.4, H 8.18 %.

5-methyl-1-(4-(1,1,3,3,3-pentamethyltrisiloxanyl)butyl)pyrimidine-2,4(1H,3H)-dione (14)

From a DMSO solution (40 cm³) of thymine (1.20 g, 9.54 mmol), potassium carbonate (1.57 g, 11.30 mmol) and 1-(4-bromobuty)-1,1,3,3,3-pentamethyltrisiloxane (11; 0.50 g, 1.77 mmol). Yield: 0.08 g, 14%. $^1$H NMR (300 MHz, CDCl₃): 8.62 (bs, 1H, NH), 7.01 (s, 1H, CH), 3.68 (t, J = 7.0 Hz, 2H, NCH₂), 1.96 (s, 3H, CH₃), 1.70 (m, 2H, NCH₂CH₂), 1.35 (m, 2H, SiCH₂CH₂), 0.54 (m, 2H, SiCH₂), 0.04 (s, 6H, SiCH₃), -0.01 (s, 9H, SiCH₃); $^{13}$C NMR (75 MHz, CDCl₃): 162.1 (C=O), 148.7 (C=O), 138.4 (CH), 108.5 (CCH₃), 46.3 (NCH₂), 30.6 (NCH₂CH₂), 18.3 (SiCH₂CH₂), 15.9 (CH₃), 10.4 (SiCH₂), -1.7 (SiCH₃), -2.0 (SiCH₃); $^{29}$Si NMR (60 MHz, CDCl₃): 7.0, 7.6 (OSMe₂, OSMe₃); analysis, calcd for C₁₄H₂₉N₂O₃Si₂: C 51.2, H 8.59, N8.62 %, found C 50.7, H 8.32, N 8.62 %.

9-(4-(1,1,3,3,3-pentamethyltrisiloxanyl)butyl)-9H-purin-6-amine (15)

From a DMSO solution (40 cm³) of adenine (1.29 g, 9.54 mmol), potassium carbonate (0.48 g, 3.52 mmol) and 1-(4-bromobuty)-1,1,3,3,3-pentamethyltrisiloxane (11; 0.50 g, 1.77 mmol). Yield: 0.07 g, 12%. $^1$H NMR (300 MHz, CDCl₃): 8.44 (s, 1H, CH), 7.93 (s, 1H, CH), 7.09 (bs, 2H, NH₂), 4.14 (t, J = 7.0 Hz, 2H, NCH₂), 1.81 (m, 2H, NCH₂CH₂), 1.24 (m, 2H, SiCH₂CH₂), 0.47 (m, 2H, SiCH₂), 0.15 (s, 6H, Si(CH₃)₃), 0.07 (s, 9H, SiCH₃); $^{13}$C NMR (75 MHz, CDCl₃): 155.8 (CNH₂), 152.2 (CH), 149.4 (NCN), 140.6 (CH), 118.6 (NCN), 42.3 (NCH₂), 32.6 (NCH₂CH₂), 19.5 (SiCH₂CH₂), 16.9 (SiCH₂), 1.7 (Si(CH₃)₂), 0.1 (Si(CH₃)); $^{29}$Si NMR (60 MHz, CDCl₃): 7.1, 7.6 (OSMe₂, OSMe₃); analysis, calcd for C₁₄H₂₉N₃O₃Si₂: C 49.8, H 8.06, N 20.8 %, found C 49.3, H 7.93, N 21.7 %.
1-(4-(1,1,3,5,5-heptamethyltrisiloxan-3-yl)butyl)-5-methylpyrimidine-2,4(1H,3H)-dione (16)
From a DMSO solution (40 cm³) of thymine (0.46 g, 3.65 mmol), potassium carbonate (0.62 g, 4.50 mmol) and 3-(4-bromobutyl)-1,1,3,5,5-heptamethyltrisiloxane (13; 0.50 g, 1.40 mmol). Yield: 0.06 g, 11%. ¹H NMR (300 MHz, CDCl₃): 8.58 (bs, 1H, NH), 6.96 (s, 1H, CH), 3.68 (t, J = 7.0 Hz, 2H, NCH₂), 1.91 (s, 3H, CH₃), 1.70 (m, 2H, NCH₂CH₂), 1.35 (m, 2H, SiCH₂CH₂), 0.54 (m, 2H, SiCH₂), 0.10 (s, 18H, Si(CH₃)₃), 0.09 (s, 3H, SiCH₃); ¹³C NMR (75 MHz, CDCl₃): 155.7 (CNH₂), 153.0 (CH), 149.2 (NCN), 140.0 (CH), 118.6 (NCN), 41.8 (NCH₂), 31.5 (NCH₂CH₂), 18.5 (SiCH₂CH₂), 15.2 (SiCH₂), 1.83 (SiCH₃), 1.02 (Si(CH₃)₃); ²⁹Si NMR (60 MHz, CDCl₃): 7.3 (Me₃SiO), -22.0 (O(SiMe)); analysis calcd for C₁₆H₃₄N₂O₄Si₃: C 47.7, H 8.51, N 6.96 %, found C 46.9, H 8.24, N 6.96 %.

9-(4-(1,1,3,5,5-heptamethyltrisiloxan-3-yl)butyl)-9H-purin-6-amine (17)
From a DMSO solution (40 cm³) of adenine (0.40 g, 2.96 mmol), potassium carbonate (0.48 g, 3.52 mmol) and 3-(4-bromobutyl)-1,1,3,5,5-heptamethyltrisiloxane (13; 0.39 g, 1.09 mmol). Yield: 0.08 g, 11%. ¹H NMR (300 MHz, CDCl₃): 8.30 (s, 1H, CH), 7.74 (s, 1H, CH), 6.66 (br, 2H, NH₂), 4.14 (t, J = 7.0 Hz, 2H, NCH₂), 1.86 (m, 2H, NCH₂CH₂), 1.32 (m, 2H, SiCH₂CH₂), 0.46 (m, 2H, SiCH₂), 0.07 (s, 18H, Si(CH₃)₃, 0.06 (s, 3H, SiCH₃); ¹³C NMR (75 MHz, CDCl₃): 155.1 (CNH₂), 153.0 (CH), 149.2 (NCN), 140.0 (CH), 118.6 (NCN), 41.8 (NCH₂), 31.5 (NCH₂CH₂), 18.5 (SiCH₂CH₂), 15.2 (SiCH₂), 1.83 (SiCH₃), 1.02 (Si(CH₃)₃); ²⁹Si NMR (60 MHz, CDCl₃): 7.3 (Me₃SiO), -22.0 (O(SiMe)); analysis, calcd for C₁₆H₃₄N₆O₂Si₃: C 46.7, H 8.08, N 17.0 %, found C 45.5, H 7.92, N 17.0 %.

9,9′-[1,1,3,3-tetramethyldisiloxane-1,3-diyl]dibutane-4,1-diyl]bis(9H-purin-6-amine) (18)
From a DMSO solution (40 cm³) of adenine (0.91 g, 6.72 mmol), potassium carbonate (1.11 g, 7.99 mmol) and 1,3-bis(4-bromobutyl)-1,1,3,5,5-heptamethyltrisiloxane (10; 0.50 g, 1.24 mmol). Yield: 0.10 g, 16%. ¹H NMR (300 MHz, CDCl₃): 8.33 (s, 1H, CH), 7.74 (s, 1H, CH), 7.16 (br, 2H, NH₂), 4.13 (t, J = 7.0 Hz, 2H, NCH₂), 1.79 (m, 2H, NCH₂CH₂), 1.45 (m, 2H, SiCH₂CH₂), 0.45 (m, 2H, SiCH₂), -0.08 (s, 6H, Si(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): 155.7 (CNH₂), 152.1 (CH), 149.3 (NCN), 140.6 (CH), 118.5 (NCN), 42.2
(NCH₂), 32.5 (NCH₂CH₂), 19.5 (SiCH₂CH₂), 16.8 (SiCH₂), -0.1 (Si(CH₃)₂); ²⁹Si NMR (60 MHz, CDCl₃): 7.0, 6.4 (SiMe₂); analysis, calcd for C₂₂H₅₈N₂₀OSi₂: C 51.5, H 7.08, N 27.3 %, found C 49.8, H 6.94, N 28.4 %.

6,6,8,8,15-Pentamethyl-7-oxa-1,13-diaza-6,8-disila-bicyclo[11.3.1]heptadec-15-ene-14,17-dione (19) and 1,1'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)dibutane-4,1-diylbis(5-methylpyrimidine-2,4(1H,3H)-dione) (20).

A DMSO solution (40 cm³) of thymine (0.85 g, 6.72 mmol), potassium carbonate (1.11 g, 7.99 mmol) and 1,3-bis(4-bromobutyl)-1,1,3,3-tetramethyldisiloxane (10; 0.50 g, 1.44 mmol) was stirred at room temperature for 72 h, after which a white precipitate of potassium bromide formed, considerably thickening the solution. The solution was filtered and the residue washed with further DMSO. 19 crystallised first from solution on standing at room temperature for 48 h (0.04 g, 8%). ¹H NMR (300 MHz, CDCl₃): 6.99 (s, 1H, CH), 4.16 (t, J = 7.0 Hz, 4H, NCH₂), 1.99 (s, 3H, CH₃), 1.74 (m, 4H, NCH₂CH₂), 1.35 (m, 4H, SiCH₂CH₂), 0.52 (m, 4H, SiCH₂), 0.07 (s, 12H, SiCH₃); ¹³C NMR (75 MHz, CDCl₃): 163.1 (C=O), 151.9 (C=O), 137.2 (CH), 109.4 (CCH₃), 46.7 (²NCH₂), 39.9 (³NCH₂), 32.9 (³NCH₂CH₃), 30.9 (³NCH₂CH₂), 19.3 (³NCH₂CH₂CH₂), 18.8 (³NCH₂CH₂CH₃), 17.4 (CH₃), 12.5 (SiCH₂), 0.0 (Si(CH₃)₂); ²⁹Si NMR (60 MHz, CDCl₃): 7.1, 6.5 (SiOSi); analysis calcd for C₁₁₁H₃₂N₂₀OSi₂: C 55.4, H 8.75, N 7.60 %, found C 55.4, H 8.82, N 7.67 %.

After isolation of 19 by filtration, the DMSO was removed under reduced pressure followed by washing three times with water (50 cm³). Thin layer chromatography of the resulting white powder, using a mixture of dichloromethane and hexane (98:2), suggested a mixture of three remaining species, at r = 1.00-0.95, 0.70 and 0.65-0.40. Chromatography on silica using the same eluent yielded three bands in each case. The first, eluted with the solvent front, was found to be trace amounts of unreacted siloxane (10). The second was found to be trace amounts of DMSO, and the third yielded the desired product 20 as a white powder (0.06 g, 8%). A white powder remaining uneluted was assumed to be the unreacted thymine.

Recrystallization was attempted from dichloromethane, chloroform, ethyl acetate and a mixture of dichloromethane and hexane, but crystals of the product were not obtained. ¹H NMR (300 MHz, CDCl₃): 8.57 (br, 1H, NH), 6.98 (s, 1H, CH), 3.70 (t, J = 7.0 Hz, 2H, NCH₃), 1.92 (s, 3H, CH₃), 1.70 (m, 2H, NCH₂CH₂), 1.34 (m, 2H, SiCH₂CH₂), 0.54 (m, 2H, SiCH₂), 0.03 (s, 6H, Si(CH₃)₂); ¹³C NMR (75 MHz,
Bromobutyl

\[ 7.50 \text{ (NCH)}_2 \text{, 4.24 (t, J = 6.9 Hz, 2H, NCH)}_2 \text{, 18.8 (NCH}_2\text{CH}_2\text{CH}_2 \text{), 17.4 (CH)}_3 \text{, 12.5 (SiCH)}_3 \text{, -0.03 (Si(CH)}_3\text{)}_2 \text{; } ^{29}\text{Si NMR (60 MHz, CDCl}_3 \text{): 7.1, 6.4 (SiOSi); analysis calcld for C}_{29}\text{H}_{38}\text{N}_2\text{O}_5\text{Si}_2 \text{: C 53.4, H, 7.74, N 11.3 %, found C 52.3, H 7.65, N 10.9 %.)}

Also prepared by the same method were:

16-Imino-6,6,8,8-tetramethyl-7-oxa-1,13-diaza-6,8-disila-bicyclo[11.3.1]heptadec-14-en-17-one (21) and 1,1'-[(1,1,3,3-tetramethyldisiloxane-1,3-diyl)dibutane-4,1-diyl]bis(4-aminopyrimidin-2(1H)-one) (22)

From a DMSO solution (40 cm\(^3\)) of cytosine (0.75 g, 6.72 mmol), potassium carbonate (1.11 g, 7.99 mmol) and 1,3-bis(4-bromobutyl)-1,1,3,3-tetramethyldisiloxane (10; 0.50 g, 1.24 mmol). 21 crystallised from solution over a 48h period (as with 19), yield: 0.03 g, 7%. \(^1\text{H NMR (300 MHz, CDCl}_3 \text{): 7.66 (d, J = 7.0 Hz, 1H, CH)}, \text{ 6.45 (br s, 1H, C=NH)}, \text{ 5.92 (d, J = 7.0 Hz, 1H, CH)}, \text{ 4.19 (t, J = 7.0 Hz, 4H, NCH}_2\text{CH}_2 \text{), 1.74 (m, 4H, NCH}_2\text{CH}_2 \text{), 1.41 (m, 4H, SiCH}_2\text{CH}_2 \text{), 0.60 (m, 4H, SiCH}_2 \text{)}, \text{ 0.01 (s, 12H, Si(CH)}_3\text{)}_2 \text{; } ^{13}\text{C NMR (75 MHz, CDCl}_3 \text{): 165.4 (C=NH), 156.1 (C=O), 145.3 (CH), 93.2 (CH), 54.3 (NCH}_2 \text{), 48.7 (NCH}_2 \text{), 34.0 (NCH}_2\text{CH}_2 \text{), 32.3 (NCH}_2\text{CH}_2 \text{), 21.5 (NCH}_2\text{CH}_2\text{CH}_2 \text{), 20.2 (NCH}_2\text{CH}_2\text{CH}_2 \text{), 16.9 (SiCH}_2 \text{), 0.2 (Si(CH)}_3\text{)}_2 \text{; } ^{29}\text{Si NMR (60 MHz, CDCl}_3 \text{): 7.2, 6.6 (SiOSi); analysis calcld for C}_{18}\text{H}_{33}\text{N}_2\text{O}_5\text{Si}_2 \text{: C 54.4, H 8.44, N 11.9 %, found C 54.1, H 9.33, N 11.9 %.)}

\text{After removal of 21 by filtration, 22 was isolated in the same manner at 20, yield: 0.05 g, 9%. (22): } ^1\text{H NMR (300 MHz, CDCl}_3 \text{): 8.01 (s, 2H, NH}_2 \text{), 7.10 (d, J = 6.9 Hz, 1H, CH)}, \text{ 5.78 (d, J = 6.9 Hz, 1H, CH)}, \text{ 4.24 (t, J = 6.9 Hz, 2H, N-CH}_2 \text{), 1.74 (m, 2H, NCH}_2\text{CH}_2 \text{), 1.35 (m, 2H, SiCH}_2\text{CH}_2 \text{), 0.51 (m, 2H, SiCH}_2 \text{), 0.04 (s, 6H, Si(CH)}_3\text{)}_2 \text{; } ^{13}\text{C NMR (75 MHz, CDCl}_3 \text{): 165.9 (CNH}_2 \text{), 156.6 (C=O), 146.0 (CH), 93.7 (CH), 50.1 (NCH}_2 \text{), 32.6 (NCH}_2\text{CH}_2 \text{), 20.4 (SiCH}_2\text{CH}_2 \text{), 18.0 (SiCH}_2 \text{), 0.6 (Si(CH)}_3\text{)}_2 \text{; } ^{29}\text{Si NMR (60 MHz, CDCl}_3 \text{): 7.1, 6.5 (SiOSi); analysis calcld for C}_{29}\text{H}_{38}\text{N}_2\text{O}_5\text{Si}_2 \text{: C 51.7, H 7.81, N 18.1 %, found C 50.8, H 8.49, N 16.9 %.)}

Bromobutyl-functionalised poly(dimethylsiloxane) (23)
Targeting a polymer with 0.2% bromobutyl functionality, a mixture of 3-(4-bromo)butylheptamethyltrisiloxane (13; 0.1 g) and poly(dimethylsiloxane) (PDMS; 20.4 g) with molecular weight ca. 50,000 was stirred at 70 °C with a catalytic amount of glacial acetic acid and water for 120 h during which time the viscosity increased markedly. The viscous oil was dissolved in dichloromethane, washed with sodium hydrogen carbonate solution until no further effervescence was observed, dried over anhydrous MgSO₄ and filtered. Removal of the volatiles afforded a viscous, air stable, colourless oil. Yield 84%, Mₓ (GPC) 23700, PDI 3.7. PDMS (0.2% bromobutyl) (23): ¹H NMR (300 MHz, CDCl₃): 3.40 (t, J = 6.7 Hz, 2H, CH₂Br), 1.88 (m, 2H, CH₂CH₂Br), 1.39 (m, 2H, SiCH₂CH₂), 0.40 (m, 2H, SiC₂H₃), 0.07 (s, Si(C₂H₅)₂); ²⁹Si NMR (60 MHz, CDCl₃): -22.0.

Thymine-functionalised PDMS (24)
A mixture of 23 (1.0 g) and 50 mg of each of thymine and potassium carbonate was stirred at room temperature in DMSO (50cm³) for 18 h. A white, water soluble precipitate formed in the reaction which was removed by filtration. Removal of volatiles under reduced pressure resulted in a viscous, cloudy oil which was twice dissolved in chloroform and washed repeatedly with water before the organic layers were combined and dried over anhydrous magnesium sulphate. Removal of the volatiles afforded a very viscous, air stable, colourless oil. Yield 55%. Mₓ (GPC) 22100, PDI 4.1. PDMS (0.2% butylthymine) (24): ¹H NMR (300 MHz, CDCl₃): 6.97 (s, 1H, CH), 3.70 (m, 2H, NCH₂), 1.92 (s, 3H, CCH₃), 1.70 (m, 2H, NCH₂CH₂), 1.39 (m, 2H, SiCH₂CH₂), 0.88 (m, 2H, SiCH₂), 0.07 (s, Si(CH₃)₂); ²⁹Si NMR (60 MHz, CDCl₃): -22.0.

Adenine-functionalised PDMS (25)
A mixture of 23 (1.0 g) and 50 mg of each of adenine and potassium carbonate was stirred at room temperature in DMSO (50cm³) for 18 h. A white, water soluble precipitate was removed by filtration. Removal of volatiles under reduced pressure resulted in a viscous, cloudy oil which was twice dissolved in chloroform and washed repeatedly with water before the organic layers were combined and dried over anhydrous magnesium sulphate. Removal of the volatiles afforded a viscous, air stable, colourless oil. Yield 48%. Mₓ (GPC) 21300, PDI 5.6. PDMS (0.2% butyladenine) (25): ¹H NMR (300 MHz, CDCl₃): 8.02
(br, 2H, NH$_3$), 6.96 (s, 1H, CH), 6.91 (s, 1H, CH), 4.11 (t, J = 6.0 Hz, 2H, NCH$_2$N), 1.70 (m, 2H, NCH$_2$CH$_2$), 1.34 (m, 2H, SiCH$_2$CH$_3$), 0.88 (m, 2H, SiCH$_2$), 0.07 (s, Si(CH$_3$)$_2$); $^{29}$Si NMR (60 MHz, CDCl$_3$): -22.0.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. Data for 4, 5, 9, 19 and 21 were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å), while that for 8 was collected at 150(2) K using the synchrotron radiation ($\lambda = 0.846$ Å) at Daresbury Station 9.8. Structure solution was followed by full-matrix least squares refinement and was performed using the WinGX-1.70 suite of programmes. Unless stated otherwise, all non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added in calculated positions save those involved in hydrogen bonding, which were located and freely refined. Specific details are as follows: 4 has two independent molecules in the asymmetric unit while in 8 the two molecules in the asymmetric unit are connected to each other via hydrogen bonding. 9: The asymmetric unit consists of half a nickel complex (in which the metal centre is located at a crystallographic inversion centre) and one heavily disordered silylated thymine unit. The flexible arm of the thymine functionality [C(9) – C(19) and the silicon] exhibited extensive disorder which is modelled over 3 sites in a 40:30:30 ratio. Only the phenyl component attached to the 40% occupancy silicon [Si(1)] could be located with any reliability, and this is included subject to the restraint of being treated as a rigid hexagon. In the cases of Si(1A) and Si(1B), only the ipso carbon of the phenyl component is included in the refinement, as the disorder proximate to these centres has resulted in substantial smearing of the electron density. Anisotropic refinement was confined to the fractional occupancy silicons and C(12) – C(13) in this disordered region. 21: There is disorder in the hetero-aromatic ring over two sites in the ratio 70:30, the major component of which was refined anisotropically. Hydrogen atoms on
N(2) [and its disordered analogue N(2A)] and C(8) (which is involved in hydrogen bonding) could not be located and had to be placed on calculated positions.
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Results and Discussion

The synthetic strategy we have followed is summarised in outline in Scheme 1 for thymine. There are two complimentary routes to the target polymers, each starting from a trimethylsilyl-protected base, which affords better regiospecificity of the subsequent reactions. The first protocol involves $N$-alkenylation of the base followed by protection and hydrosilylation, while the alternative is to form an $\alpha$-silyl-$\omega$-bromoalkane by hydrosilylation of an appropriate alkene $a$ priori, with attachment of the nucleobase as a final step. Where possible we have attempted similar reactions on all four nucleoside bases, but in general the chemistry of guanine (and to a slightly lesser extent, adenine) has proved the least tractable due to solubility considerations, while thymine has given the broadest range of characterisable products.
Synthesis and structural chemistry of N-1-alkenyl- and N-1-(organosilyl)alkyl thymines

The N-1-alkenylthymine derivatives 1 – 3 have been synthesised from the reaction of silyl-protected thymine with the appropriate alkenylbromide. An excess of alkenyl bromide was refluxed with the silylated base until the IR spectrum of the reaction mixture displayed no further generation of the product, measured by monitoring the evolution of a peak at 1720 cm\(^{-1}\) due to the carbonyl group in thymine. After removal of the volatiles, thick liquids remained from which 1 crystallised in good yield (81%), while 2 and 3 were first separated by chromatography from excess reagent before crystallization; yields fell markedly with increasing chain length (59, 18% for 2, 3 respectively). 1,\(^{14,26}\) 2,\(^{27,30}\) 3\(^{28,30}\) and analogues with longer alkenyl chains (n = 9; C\(_{11}\)\(^{16,17}\)) have been prepared by others, usually using NaH as base to deprotonate the thymine, though there appears to be a wide variation in literature melting points cited for these products. Furthermore, the use of an unprotected base leads to a mixture of regio-isomers with substitution at both N-1 and N-3,\(^{31}\) something that was not seen in our synthesis where the steric protection offered by the Me\(_3\)Si groups directs substitution to N-1 rather than the more acidic (but now more hindered) N-3 site. NMR data for 1 and 3 are similar to those reported by others, while spectral characterization of 2 is reported for the first time.

As a representative example, 1 was then re-protected by O-silylation using (Me\(_3\)Si)\(_2\)NH / (NH\(_4\))\(_2\)SO\(_4\) to yield 4 in almost quantitative yield; protection occurs only at the unhindered C-4 carbonyl. Given the success of this reaction, 2, with a longer chain and more exposed alkenyl group, was then re-protected (4a; n = 2; not isolated) and hydrosilylated using PhMe\(_2\)SiH in the presences of a catalytic amount of chloroplatinic acid to afford the N-phenyldimethylsilylbutyl derivative of thymine (5) in 51% yield. The reaction was monitored by the loss of the Si-H stretch at 2160 cm\(^{-1}\) in the IR spectrum. Chromatography indicates only one product is formed, implying \(\beta\)-silylation is minimal at best, presumably as a result of
bulky thymine substituent close to the $\beta$-carbon of the olefin. Deprotection of the O-SiMe$_3$ group takes place on the silica column. The $^1$H NMR of 5 includes resonances at 3.67, 1.68, 1.33 and 0.78 ppm corresponding to the saturated N(CH$_2$)$_4$Si group and loss of the signals in 2 at 5.76 and 5.10 ppm due to the alkenyl hydrogens. The $^{29}$Si NMR of 5 is a single peak at -3.0 ppm, typical of a C$_4$Si environment and reflecting the purity of the sample.

The structures of 4 (Figure 1) and 5 (Figure 2) are of interest for the insights they provide on the self-assembly of the pyrimidine base.

Figure. 1. The structure of 4 showing the atom labelling scheme; ellipsoids are at the 60% level. Selected geometric data for the molecule based on Si(1) as representative: Si(1)-O(2) 1.6893(18), N(1)-C(4)
1.363(4), N(1)-C(8) 1.395(3), N(1)-C(3) 1.474(2), N(2)-C(7) 1.305(4), N(2)-C(8) 1.371(4), O(1)-C(8) 1.237(3), O(2)-C(7) 1.344(3), C(1)-C(2) 1.291(5), C(2)-C(3) 1.501(4), C(4)-C(5) 1.348(4), C(5)-C(7) 1.418(4), C(5)-C(6) 1.503(4) Å; O(2)-Si(1)-C(10) 110.20(13), O(2)-Si(1)-C(9) 111.27(13), C(10)-Si(1)-C(9) 111.87(17), O(2)-Si(1)-C(11) 99.98(13), C(10)-Si(1)-C(11) 111.17(16), C(9)-Si(1)-C(11) 111.77(17), C(4)-N(1)-C(8) 121.4(2), C(7)-N(2)-C(8) 118.7(2), C(7)-O(2)-Si(1) 126.31(17), C(1)-C(2)-C(3) 123.0(3), N(1)-C(3)-C(2) 111.5(2), C(5)-C(4)-N(1) 121.4(2), C(4)-C(5)-C(7) 114.6(2), N(2)-C(7)-C(5) 125.8(2), N(2)-C(8)-N(1) 117.8(2)°. Hydrogen bond data: H(24)-O(1) 2.29, H(4'')-O(3) 2.34 Å, ∠C(24)-H(24)-O(1) 158.8, ∠C(4)-H(4)-O(3) 164.0°. Symmetry operations: ' 3/2-x,1/2+y,z-1/2; '' 3/2-x,1/2-y,1/2+z.

The asymmetric unit of 4 is formed of two independent molecules held together by a C-H...O hydrogen bond. The silyl group has protected the less sterically hindered of the carbonyl moieties [Si(1)-O(2) 1.6893(18) Å, O(4)-Si(2) 1.6862(6) Å], with the silicon atom in the plane of the heterocycle. The Si-O bond length compares well to the complementary group in bis(trimethylsilyl)thymine [1.6951(16) Å], though it is long in comparison to similar bonds in compounds such hexa-(trimethylsiloxy)benzene [Si-O 1.655(3) Å, 1.673(4) Å].33 The heterocyclic ring is moderately distorted [C(7)-N(2) 1.305(4), C(7)-C(5) 1.418(4) Å] due to the steric bulk of the SiMe₃ group relative to that of thymine [C(7)-N(2) 1.401(5), C(7)-C(5) 1.453(4) Å].34 In order to accommodate the bulk of the SiMe₃ group, the C-O-Si bond angle widens from the tetrahedral [C(7)-O(2)-Si(1) 126.31(17), C(27)-O(4)-Si(2) 126.77(18)°], to a marginally greater extent than in bis(trimethylsilyl)thymine [C-O-Si 125.46(14)°].24 The molecule forms a polymeric chain in the b-direction, interacting via another C-H...O hydrogen bonds [H(4)...O(3) 2.34 Å, ∠C(4)-H(4)...O(3) 164.0°; H(24)...O(1) 2.29 Å, ∠C(24)-H(24)...O(1) 158.8°], of comparable length with those in bis(trimethylsilyl)-cytosine [H(1)...O(2) 2.26(3) Å], though longer than similar examples of C-O...H hydrogen bonds, such as in 1-methylcytosine [H(1)...O(2) 2.04(2) Å].35
Selected geometric data: Si-C(9) 1.8772(18), O(1)-C(1) 1.2378(19), O(2)-C(4) 1.2198(19), N(1)-C(1) 1.381(2), N(1)-C(4) 1.3862(19), N(2)-C(3) 1.374(2), N(2)-C(4) 1.374(2), N(2)-C(6) 1.4778(19), C(1)-C(2) 1.445(2), C(2)-C(3) 1.353(2), C(2)-C(5) 1.499(2) Å; C(1)-N(1)-C(4) 126.83(14), C(4)-N(2)-C(3) 121.48(13), N(1)-C(1)-C(2) 115.64(13), C(3)-C(2)-C(1) 117.59(14), C(2)-C(3)-N(2) 123.80(15), N(2)-C(4)-N(1) 114.63(13)°.

Hydrogen bond data: H(1)-O(1') 1.97(2) Å, ∠N(1)-H(1)-O(1') 173(2)°. Symmetry operation: 2-x,1-y,1-z.

Hydrogenation of 4a took place at the exocyclic olefin in the favoured α-orientation to form a C-Si single bond [C(9)-Si(1) 1.8772(18) Å] in 5. There appears to be no distortion of the bond distances in the heterocyclic ring [C(4)-N(1) 1.3862(19), C(1)-N(1) 1.381(2), C(1)-C(2) 1.445(2) Å] relative to thymine [C(4)-N(1) 1.361(4), C(1)-N(1) 1.401(5), C(1)-C(2) 1.453(4) Å], 34 and the N-CH₂ bond distance in 5 [N(2)-C(6) 1.4778(19) Å] compares well with the analogous distance in 4 [1.474(2) Å]. The alkyl moiety does not appear to have caused the heterocyclic ring to distort [C(3)-N(2)-C(4) 121.48(13), N(1)-C(4)-N(2) 114.63(13), C(1)-N(1)-C(4) 126.83(14)°] relative to the same angles in thymine [C(3)-N(2)-C(4) 122.5(3), N(1)-C(4)-N(2) 115.5(2), C(1)-N(1)-C(4) 126.3(3)°]. 34 In contrast to 4, loss of the O-silyl protection in 5 allows the bases to form pairs through more conventional NH...O=C hydrogen bond pairs. [H(1)...O(1) 1.97(2) Å, ∠N(1)-H(1)...O(1') 173(2)°], which are short compared to the analogous bonds in similar compounds, such as 1-methylcytosine [H(1)...O(2) 2.04(2) Å] 35 and bis-(trimethylsilyl)cytosine (2) [2.26(3) Å]. 24

The alternative route to silylalkyl-substituted bases (Scheme 1) involves formation of R₃Si(CH₂)ₙ₋₂Br by a priori hydrosemilization of H₂C=C(H)(CH₂)ₙBr followed by alkylation of the protected bases in a manner analogous to Eqn. 1, using a stoichiometric quantity of tetrabutylammonium fluoride as co-reagent.
Accordingly, PhMe$_2$Si(CH$_2$)$_3$Br (6) was prepared in 74% yield by chloroplatinic acid-catalysed hydrosilylation of H$_2$C=C(H)CH$_2$CH$_2$Br. 6, which is a known compound, was characterised by NMR, including $\delta(^{29}\text{Si})$ at -3.0 ppm, before reaction with the silylated thymine, adenine and cytosine bases (Scheme 2).

![Scheme 2](image)

Compound 5 is prepared in better yield (74%) by this route than via hydrosilylation of N-butenylthymine (2; 51%). Similar reactions with silyl-protected adenine and cytosine afforded 7 and 8 in modest yield (55, 45%, respectively), with single-site substitution at the adenine N-9 and cytosine N-1 positions. The NMR data for 7, 8 are unexceptional; both show similar $^{29}\text{Si}$ chemical shifts (-3.1 ppm) to 5, 6 (3.0 ppm).

The asymmetric unit of 8 is formed of two independent molecules of 8 (Figure 3). The substitution is confirmed as having taken place N-1, to form an N-alkyl moiety [N(1)-C(5) 1.477(3), N(4)-C(21) 1.474(3) Å] with the N-C bond comparable to those of (4) [1.474(2) Å] and (5) [1.4778(19) Å], as is the H$_2$C-Si bond distance [8: C(1)-Si(1) 1.881(3), C(24)-Si(2) 1.870(3); 5: C(9)-Si 1.8772(18) Å]. The bond angles around the N-1 position [C(3)-N(1)-C(4) 120.1(2), C(3)-N(1)-C(5) 120.5(2), C(4)-N(1)-C(5) 119.3(2), C(19)-N(4)-C(20) 120.4(2), C(19)-N(4)-C(21) 120.2(2), C(20)-N(4)-C(21) 119.6(2)°] are very close to 120°, and are less distorted than those in 5. The molecule forms a dimer held together by two N-H...N hydrogen bonds.
[H(3A)...N(5) 2.102(17) Å, \( \angle \)N(3)-H(3a)...N(5) 178(2)°; H(6A)...N(2) 2.112(17) Å, \( \angle \)N(6)-H(6a)...N(2) 174(2)°], considerably shorter than those in bis-(trimethylsilyl)adenine [2.38(1) Å].\(^2\)\(^4\) but of comparable length with those in bis-(trimethylsilyl)cytosine [2.26(3), 2.24(3) Å].\(^2\)\(^4\) Furthermore, additional H-bond donors allows dimers to further aggregate into a laddered structure via two symmetry-related N-H...O hydrogen bonds [H(3b)...O(2'') 2.026(1) Å, \( \angle \)N(3)-H(3b)...O(2'') 164(3)°; H(6B)...O(1') 2.022(18) Å, \( \angle \)N(3)-H(3b)...O(2') 163(3)°], though these are longer than those in 5 [1.97(2) Å].

Figure 3. The structure of 8 showing the atom labelling scheme; ellipsoids are at the 65% level. Selected geometric data based on the molecule containing Si(1) as representative: Si(1)-C(8) 1.881(3), O(1)-C(4) 1.242(3), O(2)-C(20) 1.239(3), N(1)-C(3) 1.358(3), N(1)-C(4) 1.393(3), N(1)-C(5) 1.477(3), N(2)-C(1) 1.333(3), N(2)-C(4) 1.362(3), N(3)-C(1) 1.340(3), C(1)-C(2) 1.423(3), C(2)-C(3) 1.350(3) Å; C(3)-N(1)-C(4) 120.1(2), C(1)-N(2)-C(4) 119.7(2), N(2)-C(1)-C(2) 122.1(2), C(3)-C(2)-C(1) 117.0(2), C(2)-C(3)-N(1) 121.5(2), N(2)-C(4)-N(1) 119.5(2)°. Hydrogen bond data: H(3A)...N(5) 2.102(17) Å, \( \angle \)N(3)-H(3a)...N(5) 178(2)°; H(6A)...N(2) 2.112(17) Å, \( \angle \)N(6)-H(6a)...N(2) 174(2)°; H(3b)...O(2'') 2.026(18) Å, \( \angle \)N(3)-H(3b)...O(2') 164(3)°; H(6B)...O(1') 2.022(18) Å, \( \angle \)N(3)-H(3b)...O(2') 163(3)°. Symmetry operations: \(^{'}\) 1-x,-y,-z; \("\) 2-x,-y,-z-2.
The ability of compounds such as 5 and 8 to form more complex hydrogen-bonded networks was explored by co-crystallising the thymine derivative 5 with nickel dithiobiuret. 25 5 was added to Ni(S₂C₃N₃H₄)₂ in warm MeOH in 1:1 ratio, from which Ni(S₂C₃N₃H₄)₂.2(5) [9; 20% yield, m.p. 224 °C, pink crystals] crystallised, despite the reagent stoichiometry. The structure of 9 is shown in Figure 4.

Figure 4. The structure of 9 showing the atom labelling scheme; ellipsoids are at the 60% level. Only the major occupancy component of the three disordered (CH₃)₃SiMe₂Ph moieties is shown for clarity; labels associated with the carbon atoms of the phenyl ring [C(14) – C(19)] have also been omitted for the same reason. Selected geometric data: Ni-S(1) 2.1464(11), Ni-S(2) 2.1665(11) Å, S(1)-Ni-S(1') 180.0, S(1)-Ni-S(2) 94.71(4); S(1)-Ni-S(2') 85.29(4) °. Hydrogen bond data: H(1a)...O(1) 1.927(4) Å, ∠N(1)-H(1a)...O(1) 170.2(2) °; H(1b)...O(2') 2.142(2) Å, ∠N(1)-H(1b)...O(2') 165.9(2) °; H(3a)...O(2) 2.069(3) Å, ∠N(3)-H(3a)...O(2) 170.2(2) °; H(3b)...S(2') 2.921(1) Å, ∠N(3)-H(3b)...S(2') 159.37(4) °; H(4)...N(2) 2.207(3) Å,
The structure of 9 shows the three-fold hydrogen bonding between the complex and the base with the silylated alkyl chains at the periphery of the molecule on either side. The metal is itself square planar with Ni-S distances [Ni-S(1) 2.1466(9), Ni-S(2) 2.1671(9) Å] consistent with those in the two other nickel dithiobiuret reported previously [2.150 – 2.168 Å]. The two biuret ligands are not coplanar but form a flattened chair conformation about the metal. The pattern of hydrogen bonds between biuret and thymine shows two strong NH...O and a weaker NH...N interaction, as has been observed by others in the complex between dithiobiuret and uracil, despite the general preference for thymine to form just two hydrogen bond interactions with its partner. It also follows a similar pattern to other complexes in which thymine forms a triple ADA:DAD hydrogen bond pair (D = donor, A = acceptor). There is a further network of intermolecular NH...O and notably weaker NH...S interactions which generate a chain of hydrogen-bonded donor:acceptor complexes propagating along b. This is in contrast to the Ni(biuret)₂·2uracil·2H₂O which forms a sheet structure via hydrogen bonding between N(5)-H (the hydrogen replaced by the alkylsilyl group), O(1) and water (numbering as in Figure 4).

Synthesis of model siloxanes and their compounds with pendant purine / pyrimidine bases

In order to gain insights into the attachment and resulting structures of purine and pyrimidine bases linked to siloxane chains, we have synthesised several model siloxanes (10 - 13; Scheme 3) for further elaboration.
4-bromobut-1-ene, the silane and a catalytic amount of $H_2PtCl_6$ were heated in propan-2-ol at 110 °C until $\nu$(Si-H) at ca. 2050 cm$^{-1}$ had disappeared from the IR spectrum. After hydrolysis, the mixture was extracted into CHCl$_3$, dried and purified by column chromatography; the product eluted with the solvent front as a single isomer ($\alpha$-addition) of $10 - 13$ in 59 – 79% yield.

Thymine, adenine and cytosine were, in various combinations, reacted with $10, 11$ and $13$ in DMSO in the presence of $K_2CO_3$ as base, since the TBAF used in the coupling reactions to form $10 - 13$ would cause fission of the siloxane component. The reactions carried out are summarised in Schemes 4 and 5.

For siloxanes $11$ and $13$ which each contain only one butyl side-chain, both thymine and adenine form one product in each case though the isolated yields of purified product are low (ca. 10%). The two products incorporating adenine ($15, 17$) have clean NMR spectra suggesting only one region-isomer has been formed, and the $^1H/^13C$ NMR shifts of the CH$_2$N methylene group is consistent with this being at the expected N-9 position ($\delta$(H) = 4.14, $\delta$(C) 42.3, 41.8 ppm, respectively; cf 4.15, 43.4 ppm in N-9 substituted 7). In the case of the two thymine-containing products ($14, 16$) however, the $^1H/^13C$ NMR shifts of the CH$_2$N methylene group give evidence for both dominant N-1 and secondary N-3 substitution in a ratio ca. 4:1. The latter substitution is indicated by $\delta$(H) at ca. 3.91 ppm (ca. 3.70 ppm for N-1) and $\delta$(C) at ca. 39 ppm (ca. 46 ppm for N-1). For comparison, the $^1H$ NMR spectrum of 1,3-dibutylthymine has
CH$_3$N signals at 3.66 and 3.90 ppm for N-1 and N-3 butyl groups, respectively. The lack of a single product in these cases is in contrast to the observed reactions using silyl-protected bases in these reactions, as discussed earlier.
The reaction chemistry involving 10, which bears two 4-bromobutyl substituents, is more complex. In the case of adenine, a single product (18) is formed, with N-9 attachment of two bases at the termini of the two butyl chains. The CH$_2$N NMR signals [$\delta (^1H) = 4.13; \delta (^{13}C) = 42.2$ ppm] are very similar to those in 15 and 17, while data for the compound analogous to 18 but embodying two propyl, rather than butyl, chains prepared by others has NMR chemical shifts of 4.09, 45.7 ppm, respectively. Although the two halves of the molecule are indistinguishable in the

![Diagram of the reaction]

Scheme 5

For both thymine and cytosine, two quite distinct products are formed in each case. First to crystallise from solution are the pyrimidinocyclophanes 19 and 21, respectively, in which a single base has been substituted at both N-1 and N-3 positions by the two alkyl chains of the disiloxane (10). In the case of 19, 

![Diagram of the reaction]
the -(CH₂)$_3$- chains can clearly be distinguished in the $^{13}$C NMR spectrum between N-1 bound [$\delta$($^{13}$C): 46.7, 32.9, 19.3 ppm] and N-3 bound [$\delta$($^{13}$C): 39.9, 30.9, 18.8 ppm] for the three carbon centres closest to the heterocycle, though in the $^1$H NMR spectrum the associated multiplets overlap, are poorly resolved and appear as a single signals at 4.16, 1.74 and 1.35 ppm. Similarly, the signals for 21 appear in the $^{13}$C NMR at 54.3, 34.0, 21.5 ppm (N-1 bound) and 48.7, 32.3, 20.2 (N-3 bound) for the two -(CH₂)$_3$- chains.

For 21, the second deprotonation of cytosine required for formation results in generation of an exocyclic imine, evidenced by the short N(2)-C(7) distance [1.272(4) Å].

After crystallization of the two pyrimidycyclophanes, two further products, 20 and 22, can be isolated, in which pyrimidine bases have attached at the ends of both butyl chains, in an analogous manner to the formation of 18. Although different regio-isomers could not be separated chromatographically, NMR evidence points to a major N-1,N-1-substituted product, with a secondary N-1,N-3 isomer and traces of a third, presumably N-3,N-3 substituted product; $^1$H NMR integrals suggest a 25:7:1 ratio of these products. The different isomers are again most easily identified by differences in the $^1$H / $^{13}$C chemical shifts of the NCH$_2$ group [N-1, $\delta$($^1$H) 3.70; $\delta$($^{13}$C) 46.7 ppm; N-3, $\delta$($^1$H) 3.96; $\delta$($^{13}$C) 40.0 ppm]. However, for 22, only one set of resonances is visible, consistent with dominant N-1, N-1 substitution. In both 20 and 22, two $^{29}$Si resonances could be seen for the SiOSi residue, similar to those seen in 18.

In all the reactions shown in Schemes 4 and 5, the yields of products 14 – 22 are low (thymine: 8 – 14%; adenine: 11 – 16 %; cytosine: 7 – 9%).

The structures of 19 and 21 are shown in Figures 5 and 6, respectively. The metrical parameters for each are unexceptional, save that the Si-O-Si angle [19: 150.53(15); 21 150.38(10)] reflects the wide conformational flexibility associated with this connectivity. In addition, the short C(7)-N(2) bond in 21 [1.272(4) Å] confirms the amine to imine rearrangement required to allow cyclophane formation. Both structures incorporate a 14-membered macrocycle which includes the siloxane and spans the N-1 and N-3 positions on the base. There are, however, differences between the supramolecular structures of the two species.
Figure 5. The structure of 19 showing the atom labelling scheme; ellipsoids are at the 40% level. Selected geometric data: Si(1)-O(1) 1.623(2), Si(2)-O(1) 1.629(2), O(2)-C(9) 1.219(3), O(3)-C(10) 1.254(5), N(1)-C(9) 1.385(3), N(1)-C(10) 1.391(4), N(1)-C(8) 1.475(4), N(2)-C(9) 1.376(4), N(2)-C(13) 1.393(4), N(2)-C(14) 1.479(4), C(10)-C(11) 1.386(5), C(11)-C(13) 1.386(4) Å; Si(1)-O(1)-Si(2) 150.53(15), C(9)-N(1)-C(10) 123.6(2), C(9)-N(2)-C(13) 123.5(2), N(2)-C(9)-N(1) 115.2(2), C(11)-C(10)-N(1) 119.2(3), C(13)-C(11)-C(10) 118.9(3), C(11)-C(13)-N(2) 119.4(3) °. Symmetry operation: 1-x,1-y,1-z.

In the case of 19, arising from the lack of any suitably acidic hydrogens to promote hydrogen bonding, two symmetry-related molecules stack in a slightly offset π-π manner [centroid-centroid distance between
proximate rings 3.34 Å] wherein the thymine rings face each other in a head-to-tail orientation. Similarly, the cytosine derivative 21 also aggregates through π-π stacking [centroid-centroid distance between proximate rings 3.33 Å], but these pairs further interact via O(2)...H(8) hydrogen bonds to form parallel chains running approximately in the c-direction. Surprisingly, the exocyclic NH₂ group plays no part in the supramolecular assembly.

Figure 6. The structure of 21 showing the atom labelling scheme; ellipsoids are at the 60% level. Only the major component of the disordered heterocyclic ring is shown for clarity. C(10) is hidden and lies behind C(6). Selected geometric data: Si(1)-O(1) 1.6321(15), Si(2)-O(1) 1.6375(15), N(1)-C(10) 1.408(6), N(1)-C(7) 1.421(5), N(3)-C(10) 1.358(8), N(3)-C(11) 1.371(7), N(3)-C(9) 1.372(6), C(7)-C(8) 1.423(5), C(8)-C(9) 1.337(5), N(2)-C(7) 1.272(4) Å; Si(1)-O(1)-Si(2) 150.42(10), C(10)-N(1)-C(7) 124.8(4), C(10)-N(3)-C(9) 121.6(5), N(1)-C(7)-C(8) 115.0(3), C(9)-C(8)-C(7) 119.4(3), C(8)-C(9)-N(3) 123.8(4), N(3)-C(10)-N(1) 115.3(5)°. Hydrogen bond data: O(2)...H(8') 2.33 Å, ∠O(2)...H(8')-C(8') 154.8°. Symmetry operation: 1+x,y,z.
The structures of other pyrimidocyclophanes incorporating a single thymine have been reported,\textsuperscript{46} largely with macrocycle-,\textsuperscript{47} aza-\textsuperscript{47,49} and thio-methylene\textsuperscript{47} bridges between points on the pyrimidine base. To the best of our knowledge, \textbf{21} is the first such species incorporating cytosine.

\textit{Polymer chemistry}

As a preliminary exploration of the potential to prepare nucleobase-substituted polysiloxane chains, we have prepared siloxane polymers carrying pendant thymine and adenine groups using methodology adapted from that shown in Scheme 4.

Reaction of 3-(4-bromo)butylheptamethyltrisiloxane (\textbf{13}) with a poly(dimethylsiloxane) with known molecular weight yielded polysiloxanes with 0.2 \% of pendant bromobutyl functionality (Scheme 6). The single peak in the \textsuperscript{29}Si spectrum of \textbf{23} at -22.0 ppm, which compares well with the \textsuperscript{29}Si NMR chemical shift for octamethyltrisiloxane [-20.8 ppm],\textsuperscript{50} and the lack of an observable \textsuperscript{29}Si resonance at ca. 7.5 ppm due to trimethylsiloxyl end groups of \textbf{13} indicate that the latter has re-equilibrated with the PDMS to form a new polysiloxane containing pendant bromobutyl groups. The peaks in the \textsuperscript{1}H NMR spectra compare well with those of the trisiloxane starting material (\textbf{13}).

Reaction with thymine and adenine (selected as the two DNA bases that had shown the most consistent results in the small molecule chemistry) under similar conditions to those described above gave rise to the nucleobase-substituted polysiloxanes \textbf{24} (thymine) and \textbf{25} (adenine) as viscous, air stable, colourless oils in good yield.

The resonances due to the methylene protons \(\alpha\) to the nitrogen in the \textsuperscript{1}H NMR spectra of \textbf{24} compared with those in \textbf{23} show a change to a more deshielded environment, as expected from substitution with the secondary amine. All the resonances compare very favourably with the analogous ones in \textbf{13} which indicate that the same reaction has taken place between bromoalkyl-functionalised siloxanes and thymine as in the small molecule chemistry. Substitution occurred exclusively at the more basic 1-position\textsuperscript{37} assigned by comparison with the peaks due to N-1 and N-3 addition in the \textsuperscript{1}H NMR spectrum of small molecule analogues. The relative integrals of the peaks due to the methylene protons and the siloxane
methyl protons suggest the molecular weight of the polymer was not affected during the reaction. The small changes in values measured by GPC are likely due to the effect of the added base on the conformation and hence hydrodynamic volume in solution, the values being reported relative to polystyrene calibration.

\[ \text{Me}_3\text{Si} \left( \frac{\text{Si-O-SiMe}_3}{\text{(CH}_2\text{Br} \text{)}} \right) + \text{HO-Si-O-SiMe}_3 \xrightarrow{\text{K}_2\text{CO}_3, \text{DMSO}} \left( \frac{\text{O-Si-O-SiMe}_3}{\text{(CH}_2\text{Br} \text{)}} \right)_{\text{n}} \]

\[ \text{(13)} \]

\[ \text{(23)} \]

The NMR spectra for the adenine-substituted polymer 25 also show sufficient similarity to the small molecule compounds for us to be confident of the structure of the polymers, with comparison of the position of the N^9-CH_2 peak indicating that substitution took place at the most basic 9-position.\(^{37}\) The change in \(M_n\) for the polymer 21250 to 23700 is not significant.

In an initial attempt to investigate the potential interactions between the polymer chains via hydrogen bonding, equal amounts of these 0.2% functionalised polymers (24, 25) were mixed and analysed by \(^1\text{H}\)
NMR and GPC. Unfortunately, the $^1$H NMR spectra of the mixture gave no indication of the potential bonding while the molecular weight distributions correspond to a simple mixture with no interaction between components. This suggests that little or no hydrogen bonding interaction takes place in solution between the thymine and adenine functionalised siloxane polymers at the low loadings in these materials. It may be that higher loadings of base pairs are needed to achieve strong interactions in solution, particularly with the A – T combination which has only the two hydrogen bonding sites; using complementary bases with three or four sites has been used previously to provide siloxanes with useful material properties. To date, however, we have not achieved complete conversion to pure base-functionalised polymers from starting bromobutyl-substituted polymers with higher than 0.2% functionalised loadings to test this assertion.

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References


Crystal data for 9: $C_{14}H_{20}Ni_{10}O_{4}S_{4}$, formula weight 579.35, triclinic, $P \overline{1}$, $a = 7.5968(5)$, $b = 8.2841(5)$, $c = 9.0845(6)$ Å, $\alpha = 104.418(3)$, $\beta = 98.826(3)$, $\gamma = 95.465(3)^\circ$, $V = 541.80(6)$ Å$^3$, $\rho_{calc} = 1.776$ Mg/m$^3$, $\mu$(Mo-\(k_{\alpha}\)) = 1.328 mm$^{-1}$, $F(000) = 298$, goodness-of-fit on $F^2 = 1.093$, final $R_1$, $wR_2$ indices [$I > 2\sigma(I)$] 0.0450, 0.1099, $R_1$, $wR_2$ (all data) 0.0594, 0.1186, max., min. peak and hole 0.495, -0.755 eÅ$^{-3}$. CCDC No. 956094.


