Monosaccharides as Silicon Chelators: Pentacoordinate Bis(diolato)(phenyl)silicates with the *cis*-Furanose Isomers of Common Pentoses and Hexoses**

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Abstract: Five-coordinate phenylsilicates are formed from the reaction of trimethoxy(phenyl)silane with monosaccharides in methanol in the presence of a stoichiometric amount of base. Five complexes have been isolated and characterized with two ketoses and three aldopentoses. The silicon central atom in [K([18]crown-6)][PhSi(β-D-Fru*f*2,3H$_{-2}$)$_2$]·MeOH (**1**, Fru = fructose) is part of two chelate rings, with the ligands being β-D-fructofuranose-O^2,O^3 dianions. The β-furanose isomer is best suited for silicon ligation because it exhibits a torsion angle close to 0° for the most acidic diol function, thus assuring a flat chelate ring. The same structural principles are also found in [K([18]crown-6)][PhSi(β-D-Ara*f*1,2H$_{-2}$)$_2$]·2 MeOH (**2**, Ara = arabinose), [K([18]crown-6)][PhSi(α-D-Rib*f*1,2H$_{-2}$)$_2$] (**3**, Rib = ribose), [K([18]crown-6)][PhSi(α-D-Xyl*f*1,2H$_{-2}$)$_2$]·acetone (**4**, Xyl = xylose), and [K([18]crown-6)][PhSi(α-D-Rul*f*2,3H$_{-2}$)$_2$] (**5**, Rul = ribulose).

Keywords: carbohydrates · chelates · monosaccharides · pentacoordinate silicate · silicon

Introduction

Monosaccharide ligands: Although monosaccharides are both ubiquitous molecules in living organisms and an inexhaustible source of raw material for chemical industry, there is little solid knowledge of their complexation reactions with various metals and semimetals—a statement that is valid in particular from the viewpoint of structural chemistry. For metals and semimetals of the p block of the periodic system, for example, there is, to the best of our knowledge, a single work that deals with a crystal-structure determination on a monosaccharide chelate complex, a work describing β-D-mannofuranose complexes with aluminium and gallium.[1] This lack of structural data is most astonishing since knowledge about monosaccharide complexes and their structures is of significant practical impact. A better understanding of the interaction of catalytically active metal centers and original carbohydrates would provide tools to overcome the "over-functionalization" of the sugars in the carbohydrate-based branch of green chemistry. A better understanding of the interaction of oxophilic metals and semimetals with the polyfunctional and oxygen-rich carbohydrates would also be useful. This latter aspect has implications for transport forms of oxophilic centers in organisms. A prominent example is silicon, whose interaction with biomolecules reveals many unanswered questions.

To contribute to the discussion of one of these questions—should oxygen-rich monosaccharides be considered as ligands for the oxophilic element silicon?—we have used the recent finding that furanoidic *cis*-diols, that is, 1,2-diol functions attached *cis* to an oxolane ring, are particularly promising silicon chelators, whose anions are able to establish hydrolytically stable Si–O–C linkages.[2] Due to the α/β anomerism, each of the monosaccharides is able to provide such a *cis*-diol fragment by adjusting its anomeric hydroxy group to be oriented *cis* to the epimeric one. The metal-coordinating properties of the simple *cis*-oxolanediol structure, as found in anhydroerythritol (*cis*-oxolane-3,4-diol) or the ribonucleosides, should thus, in principle, be shared by each of the monosaccharides. A particular monosaccharide is expected to act as a good ligand if its *cis*-furanose form is of considerable stability, so that the stability constant of the complex is not charged with the isomerization energy of the ligand. In terms of equilibrium concentrations of the respective furanose isomers, particularly promising candidates for most efficiently enriching a silicate solution with stable complexes may be expected to be at the top of Table 1.

In fact, almost all of the monosaccharides enrich alkaline aqueous silicate solutions with five- and six-coordinate silicon species to some extent. However, the determination of

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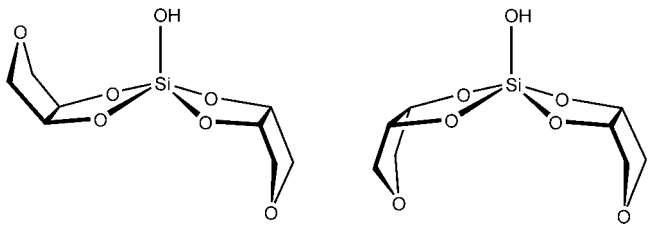
Table 1. Percentage share, in descending order, of the *cis*-furanose form, including the anomeric hydroxy group of the 16 D-pentoses and D-hexoses, in aqueous solution at equilibrium. The second column denotes the respective *cis*-configured anomer. The more abundant monosaccharides are printed in bold.

Aldose/ketose*	*cis-f*	%[a]	%[b]
ribulose*	α-2,3	62.8	n.d.[c]
xylulose*	β-2,3	62.3	n.d.[c]
psicose*	α-2,3	39.0	n.d.[c]
fructose*	β-2,3	25.0	n.d.[c]
idose	β-1,2	14.0	16.1
altrose	β-1,2	13.0	13.4
talose	β-1,2	13.0	11.1
tagatose	β-2,3	7.5	n.d.[c]
ribose	α-1,2	6.5	7.4
allose	α-1,2	3.5	3.0
galactose	α-1,2	2.5	2.3
arabinose	β-1,2	2.0	3.6
sorbose*	β-2,3	1.0	n.d.[c]
xylose	α-1,2	<1.0	0.9
lyxose	β-1,2	0.5	0.6
mannose	β-1,2	0.3	0.3
gulose	α-1,2	n.d.[c]	0.9
glucose	α-1,2	n.d.[c]	0.1

[a] As given in ref. [11]. [b] As given in ref. [12]. [c] n.d. = not determined.

the compositions and structures of the involved species is largely complicated by the mere number of the species in equilibrium. This has recently been demonstrated for D-ribose solutions by Kinrade et al., who detected a vast amount of various five- and six-coordinate species in such solutions.[3] For monosaccharides other than D-ribose, the situation is not any better. To get a chance to isolate individual monosaccharide–silicon species in order to gain insight into the principles of their structure and bonding, a strategy has to be developed both to decrease the large number of species and, at the same time, not to drift into areas of silicon chemistry that lack structural relationships with the aqueous carbohydrate–silicate solutions. A rationale for this goal arises from the fact that ^{29}Si and ^{13}C NMR spectra of the five-coordinate monosaccharide–silicon species closely resemble the spectra of the known bis(diolato)(hydroxo)silicate ion derived from *cis*-oxolane-3,4-diol (anhydroerythritol, AnEryt), $[(HO)Si(AnErytH_{-2})_2]^-$ (Scheme 1), two salts of which have been characterized by single-crystal work.[2] This observation led to the obvious idea of decreasing the functionality of the silicon center by substituting the (reactive) hydroxo ligand by an (inert) phenyl residue. Thus, a connection is established to the well-known *O*,*O*-chelated phenylsilicates, which in turn satisfy the demand for closely related chemistry; five-coordination of the silicon central atom is shared with the monosaccharide species of interest here. As a silicon starting material for the synthesis of monosaccharide–silicon complexes we used trimethoxy(phenyl)silane, a compound successfully used as a starting material for the synthesis of pentacoordinate bis(phenylenediolato) and bis(alkylenediolato)(phenyl)silicates. These investigations,[4] which include crystal-structure determinations on a catecholato complex[4c] as well as a diolato complex,[4d] have been reviewed.[4e] The diolato complex has been crystallized by using the $[K([18]crown-6)]^+$ counterion, which has been successfully used throughout this work as well. To allow for monosaccharide isomerization, methanol was used as a protic solvent similar to water.

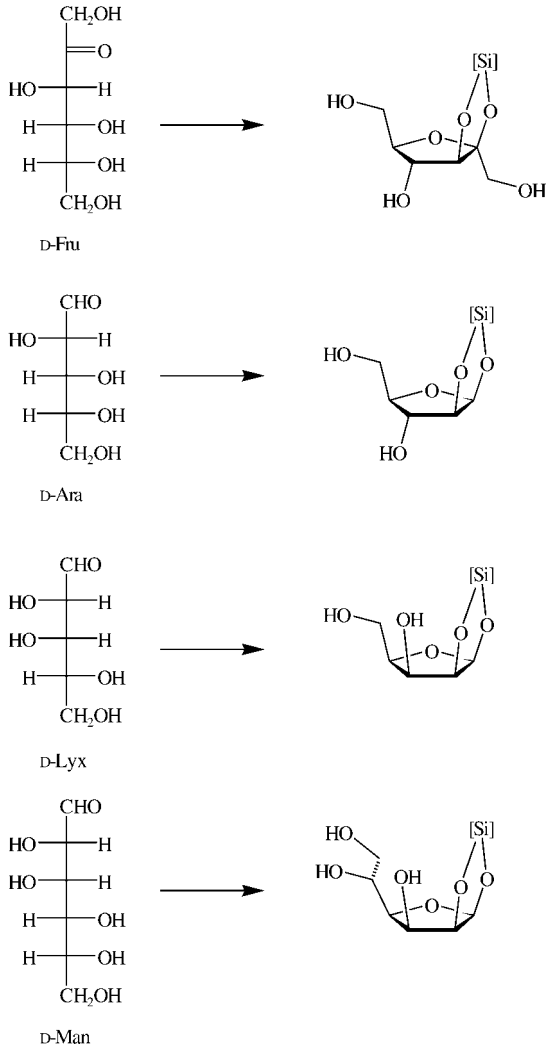


Scheme 1. Left: the *syn*/*anti* arrangement of two oxolanediolato ligands at a hydroxosilicon center as found in $Li[(HO)Si(AnErytH_{-2})_2]\cdot H_2O$,[2a] $Na[(HO)Si(AnErytH_{-2})_2]$,[9] and $K[(HO)Si(AnErytH_{-2})_2]$.[2a] Right: The *anti*/*anti* isomer of the same silicate as found in $Rb[(HO)Si(AnErytH_{-2})_2]$ and $Cs[(HO)Si(AnErytH_{-2})_2]$.[9] *syn* and *anti* refer to the orientation of the oxolane ring to the hydroxo ligand.

Results

The β-D-furanose series: fructose, arabinose, lyxose, mannose: If Table 1 is used as a guideline, D-fructose (D-Fru, Scheme 2) appears as the first candidate for silicon chelation among the common monosaccharides. In methanol, the reaction of trimethoxy(phenyl)silane with a double molar amount of fructose and an equimolar amount of base in fact yielded a single main product. According to ^{29}Si and ^{13}C NMR spectra, a five-coordinate silicate species with β-D-fructofuranose ligands had formed. If we assume the bonding of two fructose ligands at the silicon center, these appear equivalent in terms of ^{13}C NMR signal count. This means that the orientation of the oxolane rings relative to the phenyl substituent should be *syn*/*syn* or *anti*/*anti* to assure the required C_2 symmetry. With [18]crown-6/KOMe used as the base, colorless crystals of $[K([18]crown-6)][PhSi(\beta\text{-D-Fru}f2,3H_{-2})_2]\cdot MeOH$ (**1**) have been grown. X-ray crystal-structure analysis confirms the spectroscopic findings (Figure 1). The coordination number of the silicon central atom is five, due to the phenyl substituent and two diolato (2−) moieties from two 2,3-deprotonated fructofuranose ligands. Deprotonation includes the most acidic hydroxy group of fructose (O2–H). The substituents of silicon are arranged almost midway between a trigonal-bipyramidal (tbp) and a square-pyramidal (sp) structure (Table 2). As intended, the *cis*-furanose isomer assures a flat chelate ring, which is characterized by the small torsion angles of its ligating diol groups. In addition, the silicate complex appears to be enforced by a total of three intramolecular hydrogen bonds. Both furanose rings are oriented *anti* with respect to the phenyl substituent; hence, a (time-averaged) C_2-symmetric conformation may be adopted in solution. It should be noted that in the case of a *syn*-oriented fructose moiety the polar hydroxymethyl group at position 6 would be close to the hydrophobic phenyl substituent; an *anti*/*anti* configuration, on the other hand, is a prerequisite for one of the three hydrogen bonds.

The β-furanose isomer next in terms of abundance is the aldopentose D-arabinose (D-Ara, Table 1, Scheme 2). For



Scheme 2. The monosaccharides of the β-furanose series, in order of furanose abundance (Table 1), and their bonding sites for silicon. From top to bottom: D-fructose, D-arabinose, D-lyxose, and D-mannose.

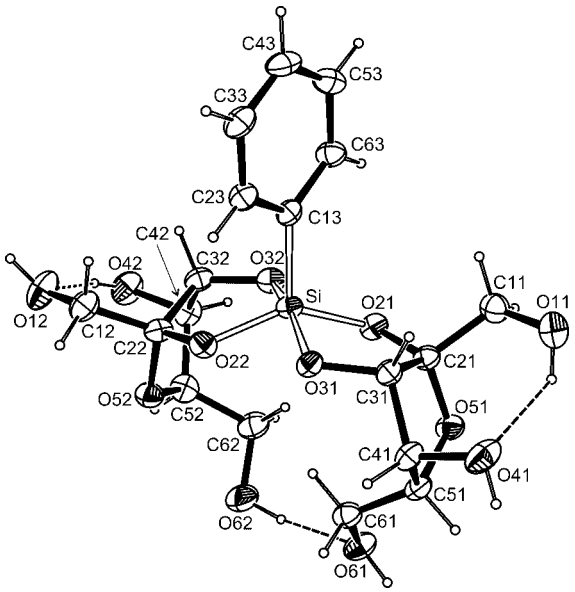


Figure 1. The structure of the crystallographically C_1-symmetrical $[PhSi(\beta\text{-D-Fru}f2,3H_{-2})_2]^-$ ions in crystals of **1** (30% probability ellipsoids). Intramolecular hydrogen bonds are shown as dashes. Distances [Å] and angles [°] (with standard deviations in parentheses): from Si to: O22 1.707(1), O21 1.710(1), O31 1.748(1), O32 1.755(1), C13 1.882(2); C11–O11 1.425(3), C21–O21 1.396(2), C21–O51 1.426(2), C31–O31 1.413(2), C41–O41 1.435(2), C51–O51 1.447(2), C61–O61 1.433(2), C12–O12 1.434(3), C22–O22 1.390(2), C22–O52 1.449(2), C32–O32 1.402(2), C42–O42 1.420(3), C52–O52 1.444(2), C62–O62 1.433(2); fructose bond angles with largest deviation from the tetrahedral angle: C31-C41-C51 103.0(2), C32-C42-C52 102.6(2); torsion angles in the coordinating diol groups: O21-C21-C31-O31 13.1(2), O22-C22-C32-O32 16.1(2); intramolecular hydrogen bonds: O11–H 0.87(3), H···O41 2.24(3), O11···O41 2.908(2), O11–H···O41 133(3); O42–H 0.87(3), H···O12 1.93(3), O42···O12 2.762(2), O42-H···O12 159(3); O62–H 0.95(4), H···O61 1.90(4), O62···O61 2.836(2), O62–H···O61 167(3); puckering parameters[10] of the furanose rings: O51–C21: $Q_2 = 0.339(2)$ Å, $\varphi_2 = 125.7(3)°$; O52–C22: $Q_2 = 0.345(2)$ Å, $\varphi_2 = 113.3(3)°$; the conformations are thus close to $^{C4}T_{C3}$ and E_{C3} (ideal φ_2 values: 126 and 108°, respectively).

Table 2. Summary of silicon coordination geometries.

	1	**2** (Si1)	**2** (Si2)	**3**	**4** (Si1)	**4** (Si2)	$\mathbf{5}_{anti}$	$\mathbf{5}_{syn}$
noncrystalline symmetry	C_2	C_2	C_2	C_2	C_2	C_2	C_1	
% from tbp[a]	38.6	42.5	46.0	77.4	78.3	95.9	27.3	
O_{axial}[b]	epi	ano	ano	(epi)	(ano)	–	epi	ano
$Si–O_{ano}$[c]	1.709	1.772	1.776	1.722	1.728	1.723	1.704	1.742
$Si–O_{epi}$[c]	1.752	1.680	1.682	1.733	1.727	1.726	1.760	1.711

[a] Percentage distance from trigonal-bipyramidal coordination along the Berry pseudorotation coordinate (see ref. [13]). [b] O_{axial} = axial position in a trigonal bipyramid, ano = hemiacetal O atom (aldoses: O1, ketoses: O2), epi = second O atom of chelate ring (aldoses: O2, ketoses: O3). [c] Mean Si–O distances in Å.

fructose and arabinose, silicon complexes very similar in structure may be expected; the arabinose complex is formally derived by removing the hydroxymethyl group at position 1 in **1** (Scheme 2). Although two hydrogen bonds, which are obviously not essential, are missing in the tentative complex, the spectra taken from the reaction mixtures are consistent with a C_2-symmetric five-coordinate silicate with β-D-arabinofuranose ligands binding through their *cis*-1,2-diol groups. Structure analysis on crystals of the formula [K([18]crown-6)][PhSi(β-D-Ara-f1,2H$_{-2}$)$_2$]·2MeOH (**2**) confirms the spectroscopic assignment. Figure 2 shows the solid-state silicate structure, which is unexpectedly free of any intramolecular hydrogen bonds; these are obviously not essential. As with **1**, the silicon central atom adopts a conformation midway between tbp and sp (Table 2).

Switching the 3-hydroxy group turns D-arabinose into D-lyxose (D-Lyx, Table 1, Scheme 2). Solutions of the same composition as above are enriched with the β-D-lyxofuranose form. Contrary to the results with the two monosaccharides dealt with above, the spectra show a major species in the ^{13}C NMR spectra but the signals of about half a dozen five-coordinate species are present in the ^{29}Si NMR spectra. In view of the unsuitably large number of species, crystallization has failed up to now. The same situation was observed with D-mannose (D-Man, Table 1, Scheme 2), the

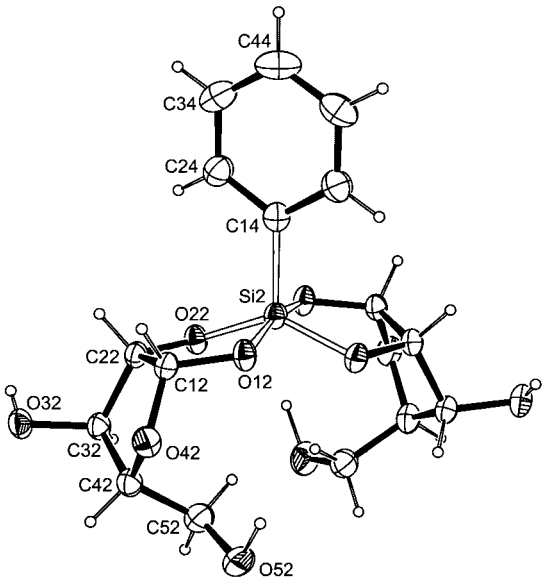
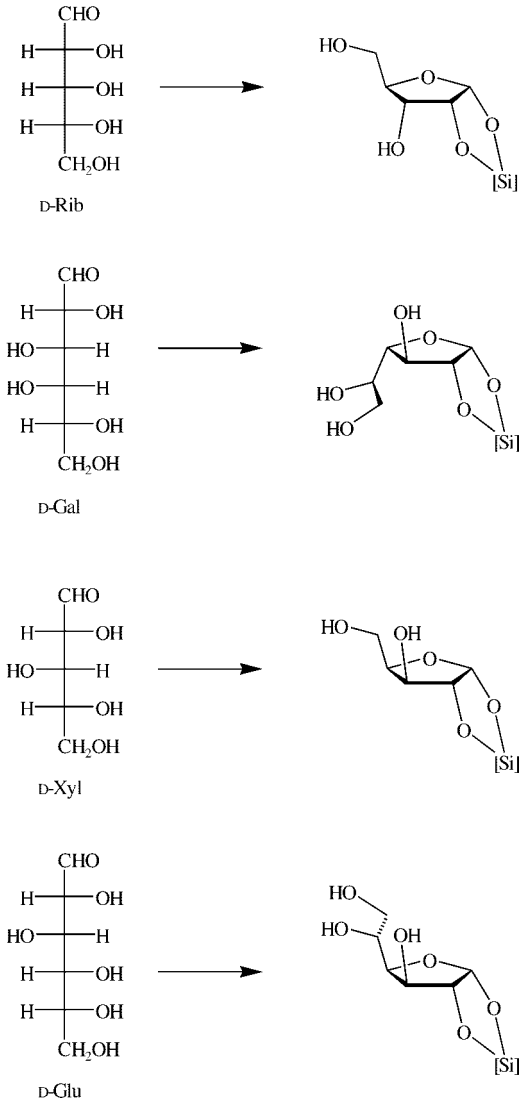


Figure 2. The structure of one of two symmetry-independent, C_2-symmetrical $[PhSi(\beta\text{-D-Ara}f1,2H_{-2})_2]^-$ ions in crystals of **2** (40% probability ellipsoids). Distances [Å] and angles [°] (with standard deviations in parentheses, arabinose atoms C*n*1, O*n*1, and C*n*2, O*n*2 refer to molecules 1 and 2 (the depicted one), respectively): from Si1 to: O21 1.680(2), O11 1.772(2), C13 1.890(4); C11–O11 1.394(3), C11–O41 1.431(3), C21–O21 1.414(3), C31–O31 1.428(3), C41–O41 1.436(3), C51–O51 1.424(4); from Si2 to: O22 1.682(2), O12 1.776(2), C14 1.887(4); C12–O12 1.393(3), C12–O42 1.429(3), C22–O22 1.414(3), C32–O32 1.429(3), C42–O42 1.443(3), C52–O52 1.432(4); arabinose bond angles with largest deviation from the tetrahedral angle: C21-C31-C41 103.5(2), C22-C32-C42 103.8(2); torsion angles in the coordinating diol groups: O11-C11-C21-O21 4.8(3), O12-C12-C22-O22 1.3(3); puckering parameters[10] of the furanose rings: O4–C1: $Q_2=0.288(3)$ Å, $\varphi_2=135.2(5)°$ (molecule 1); $Q_2=0.283(3)$ Å, $\varphi_2=142.0(6)°$ (molecule 2); the conformations are thus between $^{C4}T_{C3}$ and ^{C4}E (ideal φ_2 values: 126 and 144°, respectively) and close to ^{C4}E.



Scheme 3. The monosaccharides of the α-furanose series, in order of furanose abundance (Table 1), and their bonding sites for silicon. From top to bottom: D-ribose, D-galactose, D-xylose, and D-glucose.

higher homologue of D-lyxose. Although it is the last member of the β series of *cis*-furanoses, with only 0.3% of the required form at equilibrium, the reaction mixture shows a marked enrichment of β-1,2-Man*f*.

The α-D-furanose series: ribose, galactose, xylose, glucose: The most abundant sugar with a *cis*-furanose diol function in an α-configuration is D-ribose (D-Rib, Table 1, Scheme 3). Although ribose is not an exception to the rule that numerous monosaccharide-containing species are detected in aqueous alkaline silicate solutions,[3] a single main species is observed in both the ^{29}Si and ^{13}C NMR spectra in phenylsilicate reaction mixtures that have been prepared in the same way as those described above. As expected, ^{13}C NMR spectra reveal the α-ribofuranose form, and structural analysis on solvent-free crystals of [K([18]crown-6)][PhSi(α-D-Rib*f*1,2H_{-2})$_2$] (**3**) confirms this finding (Figure 3). The coordination pattern of the silicon atom is closer to sp than that of **1** and **2** (Table 2).

A special problem arises with D-galactose (D-Gal, Table 1, Scheme 3), which appears as the second most abundant aldohexose of the α-furanose series and which may be viewed as a homologue of L-arabinose (Scheme 2). In this case, the solubility of the free monosaccharide in methanol is particularly low and even in the course of the attempted reaction no clear solution was obtained.

According to Table 1, D-xylose (D-Xyl, Scheme 3) offers only about an order of magnitude less of the *cis*-furanose form than D-ribose. Solution NMR spectra show the presence of two minor species together with a major species that is isolated upon crystallization. Crystals of [K([18]crown-6)][PhSi(α-D-Xyl*f*1,2H_{-2})$_2$]·acetone (**4**) have thus been isolated and show the expected phenylsilicate ion (Figure 4). One of two symmetrically independent anions (the one with Si2) adopts an almost undistorted sp geometry of the central atom (Table 2).

The most important hexose is D-glucose (D-Glc, Scheme 3), the homologue of xylose. In Table 1, it appears as the least promising silicon chelator due to a minimal proportion of *cis*-furanose. However, ^{29}Si and ^{13}C NMR spectra of reaction mixtures prepared under standard conditions reveal a mixture of five-coordinate silicate species, which have been neither fully analyzed nor crystallized yet. Al-

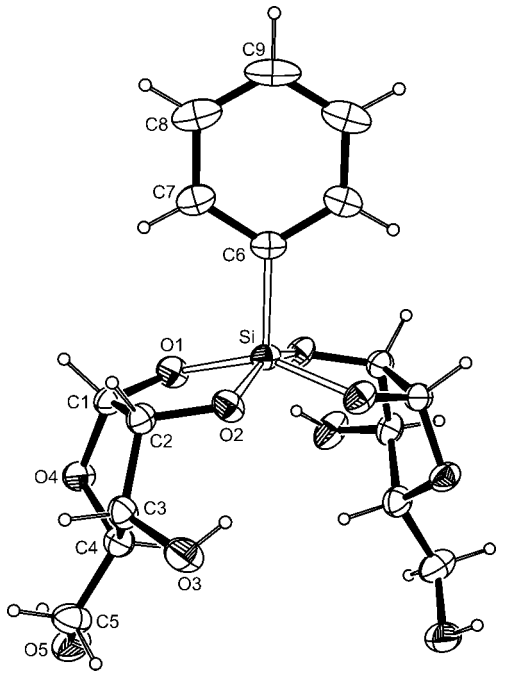


Figure 3. The structure of the C_2-symmetrical $[PhSi(\alpha\text{-D-Rib}f1,2H_{-2})_2]^-$ ions in crystals of **3** (40% probability ellipsoids). Distances [Å] and angles [°] (with standard deviations in parentheses): from Si to: O1 1.722(1), O2 1.733(1), C6 1.885(3); C1–O1 1.372(3), C1–O4 1.442(3), C2–O2 1.393(2), C3–O3 1.406(3), C4–O4 1.435(3), C5–O5 1.413(3); ribose bond angle with largest deviation from the tetrahedral angle: C2-C3-C4 102.5(2); torsion angle in the coordinating diol group: O1-C1-C2-O2 −5.4(2); intramolecular hydrogen bond: O3–H 0.83(1), H···O2 2.02(3), O3···O2 2.634(2), O3–H···O2 130(3); puckering parameters[10] of the furanose ring: O4–C1: $Q_2=0.377(2)$ Å, $\varphi_2=321.3(4)°$; the conformation is thus close to E_{C4} (ideal φ_2 value: 324°).

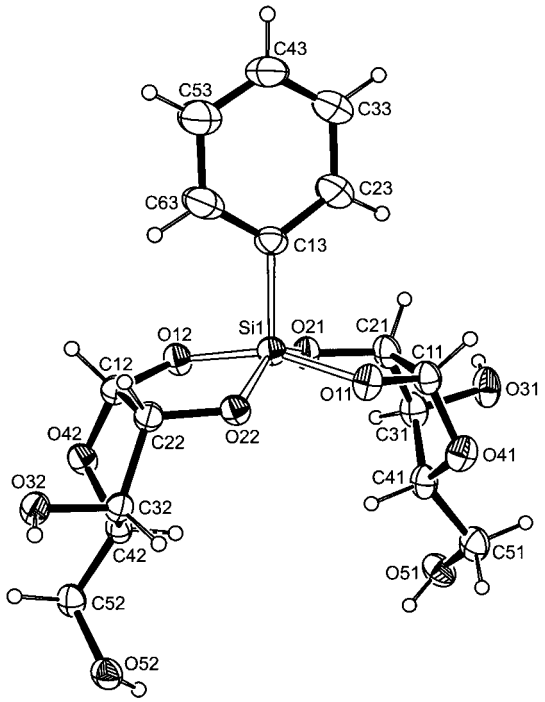
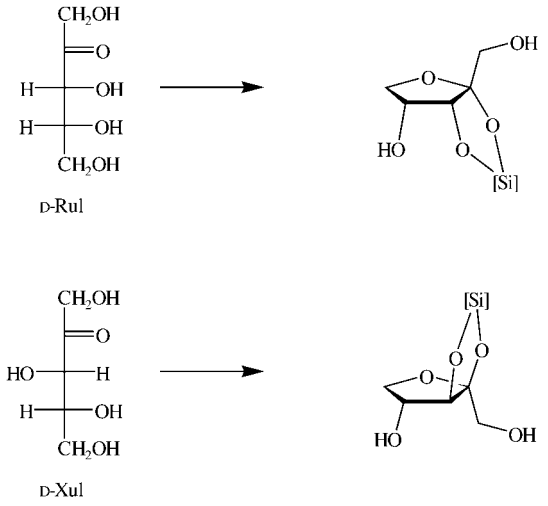


Figure 4. The structure of one of two symmetry-independent, crystallographically C_1-symmetrical $[PhSi(\alpha\text{-D-Xyl}f1,2H_{-2})_2]^-$ ions in crystals of **4** (30% probability ellipsoids). Distances [Å] and angles [°] for the depicted molecule (with standard deviations in parentheses): from Si1 to: O21 1.722(3), O22 1.731(3), O11 1.734(3), O12 1.740(3), C13 1.896(4); C11–O11 1.383(5), C11–O41 1.439(6), C21–O21 1.397(5), C31–O31 1.433(6), C41–O41 1.444(6), C51–O51 1.417(6), C12–O12 1.373(5), C12–O42 1.427(5), C22–O22 1.405(5), C32–O32 1.426(5), C42–O42 1.437(5), C52–O52 1.434(5); xylose bond angles with largest deviation from the tetrahedral angle: C21-C31-C41 101.9(4), C22-C32-C42 101.2(3); torsion angles in the coordinating diol group: O11-C11-C21-O21 −8.5(5), O12-C12-C22-O22 −8.6(5); puckering parameters[10] of the furanose rings: O4–C1: $Q_2=0.399(5)$ Å, $\varphi_2=310.2(7)°$ (xylose 1 atoms); $Q_2=0.420(4)$ Å, $\varphi_2=314.4(6)°$ (xylose 2 atoms); the conformations are thus between $^{C3}T_{C4}$ and E_{C4} (ideal φ_2 values: 306 and 324°, respectively). There is a second anion in the asymmetric unit; xylose atoms are encoded as *Xn*4 and *Xn*5. Distances [Å] and angles [°]: from Si2 to: O15 1.722(3), O24 1.722(3), O14 1.724(3), O25 1.730(3), C16 1.892(5); C14–O14 1.372(5), C14–O44 1.412(6), C24–O24 1.404(5), C34–O34 1.429(5), C44–O44 1.448(5), C54–O54 1.426(6), C15–O15 1.374(6), C15–O45 1.427(6), C25–O25 1.412(5), C35–O35 1.418(5), C45–O45 1.435(5), C55–O55 1.427(6); xylose bond angles with largest deviation from the tetrahedral angle: C24-C34-C44 101.0(3), C25-C35-C45 100.8(3); torsion angles in the coordinating diol group: O14-C14-C24-O24 −11.0(5), O15-C15-C25-O25 −9.2(5); puckering parameters[10] of the furanose rings: O4–C1: $Q_2=0.396(5)$ Å, $\varphi_2=309.4(7)°$ (xylose 4 atoms); $Q_2=0.407(5)$ Å, $\varphi_2=311.6(7)°$ (xylose 5 atoms); both conformations are thus close to $^{C3}T_{C4}$ (ideal φ_2 value: 306°).

though indicating a mixture of species, the ^{29}Si NMR spectra show that no trimethoxy(phenyl)silane starting material is left. It should therefore be noted that an unpromising position in Table 1 is not correlated with diminished reactivity but with a decreasing amount of the expected *cis*-furanose-derived species.

The question of isomerism: preliminary results on anhydroerythritol and the rare D-ketoses ribulose and xylulose: Fortunately, the common monosaccharides that show the suitable isomer for silicon chelation in a high amount seem not to be affected by the *syn*/*anti* isomerism of the bis-diolato-silicate, and they thus yield simple ^{13}C NMR spectra. C_2 symmetry of the solution species appears to be the rule, and, as demonstrated by structural work, this always means the *anti*/*anti* case. The reasons for this are not clear. At first glance, the unsuitable bonding situation of a polar group close to the hydrophobic phenyl substituent appears to be a good reason. However, two of the monosaccharides dealt with so far—xylose and glucose—show a substituent pattern that does not contradict *syn* bonding because they lack further substituents on the diolate face of the oxolane ring (Scheme 3). However, in accordance with their unsuitable position in Table 1, xylose and glucose do not appear to be good tools to further clarify this point. To gain deeper insight into the questions dealing with isomerism at the silicon center, two rare sugars have been investigated, whose number of isomers is restricted due to the lack of any pyranose forms; these sugars, the ketoses D-ribulose and D-xylulose, are the two leading entries in Table 1. Of these, D-xylulose (D-Xul, Scheme 4) shares the lack of further substituents on the diol face of the furanose ring with xylose and glucose, as well, of course, as with anhydroerythritol, which lacks substituents on any oxolane-ring face. In fact, both anhydroerythritol and D-xylulose form five-coordinate phenylsilicate species as the only products in the standard experimental setup. For anhydroerythritol, ^{29}Si and ^{13}C NMR spectra, as well as two preliminary structure analyses of low



Scheme 4. The two ketopentoses and their bonding sites for silicon. Top: D-ribulose (D-*erythro*-2-pentulose); bottom: D-xylulose (D-*threo*-2-pentulose).

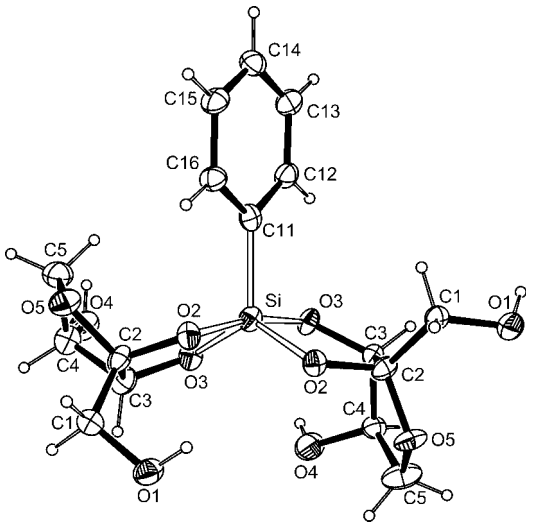


Figure 5. The structure of the C_1-symmetrical $[PhSi(\alpha\text{-D-Rul}f2,3H_{-2})_2]^-$ ions in crystals of **5** (20% probability ellipsoids). Distances [Å] (with standard deviations in parentheses; atoms labeled *Xn* in the right and left ribulose units of the figure are labeled *Xn*1 and *Xn*2, respectively, here): from Si to: O21 1.707(5), O32 1.711(6), O22 1.742(5), O31 1.760(5), C11 1.886(8).

quality, show that both *anti*/*anti* and *syn*/*anti* isomers are formed.[5] Note that the phenylsilicates of anhydroerythritol resemble the hydroxosilicates shown in Scheme 1 in this respect. NMR spectra of the phenylsilicates of D-xylulose also show a signal pattern that is consistent with an almost C_2-symmetrical minor species—probably the *anti*/*anti* isomer—and a *syn*/*anti* major species. For the latter species, the ^{13}C signals are more split, the closer the respective carbon atom comes to the silicon center (C2 ≈ C3 > C4, no split for C1 and C5; see Scheme 4). More details will be reported when we have succeeded with structural analyses of satisfactory quality both for the simple diol and the ketose.

The other top entry of Table 1, D-ribulose (D-Rul, Scheme 4), forms a phenylsilicate with the same ease as its C_4 isomer D-xylulose. In this case, crystallization with the $[K([18]crown\text{-}6)]^+$ counterion results in the formation of very small, weakly diffracting, solvent-free crystals of the formula $[K([18]crown\text{-}6)][PhSi(\alpha\text{-D-Rul}f2,3H_{-2})_2]$ (**5**). Structure analysis succeeded, although it is of somewhat lower quality than for **1**–**4** due to the weak diffracting power of the small crystals available. The result of the analysis is shown in Figure 5. Silicon coordination is closest to tbp for all the compounds described in this work (Table 2). Most importantly, the structure of **5** demonstrates that the expectation that *syn*/*anti* isomerism might be of significance in the class of bis(diolato)(phenyl)silicates was a substantiated one. Interestingly, the diol face of the furanose ring is not free of further substituents but the hydroxy group at C4 points to the same hemisphere as the diol function. It should be noted that both substituents that may interact with the phenyl group—the 4-hydroxy group mentioned and the 1-hydroxymethyl substituent of the ribulose opposite—are close to those alkoxo groups that are in an equatorial position at the silicon center and hence are tilted away from the phenyl residue. However, based on the data now available, it must be said that many aspects of *syn*/*anti* isomerism remain unclear and are the subject of current investigations.

Discussion

Monosaccharide ligands and the problem of binding-site isomerism: The statement made in the introduction, that there is a remarkable lack of knowledge in the structural chemistry of monosaccharide complexes of metals and semimetals, is best illustrated by the structure of **1**. To the best of our knowledge, **1** is the first stable complex of any ketose with any metal or semimetal that has been characterized by single-crystal X-ray work. No structurally characterized, stable metal complexes are known for the other rare ketose in this work, D-ribulose. The same holds true for D-xylose, although this monosaccharide is the natural substrate of the well-investigated metalloenzyme xylose isomerase. For the remaining monosaccharides dealt with in this work, D-arabinose and D-ribose, structural data are available for palladium(II) complexes of their pyranose forms.[6] Comparison of **2** and **3** with these latter structures illustrates the working hypothesis of this investigation. Both monosaccharides act as pyranose ligands with a larger bite towards the larger palladium(II) and as furanose ligands with a flat chelate ring with the smaller silicon. It should however be noted that such rules of thumb lack a sufficiently broad base of structural data. Thus, there is NMR evidence that tetrahedral centers like the even smaller boron and phosphorous atoms may be chelated by *cis*-1,2-pyranose ligands, although they are unable to adopt a diol torsion angle close to 0°.[7,8] Although it contradicts the working hypothesis of this investigation, these forms have not been excluded in the case of silicon on a sound experimental basis yet and have to be taken into account in addition to the furanose forms. More isomers may be formed and may be a reason for the failure to crystallize phenylsilicates with aldohexoses. The possibility should be considered that aldohexopyranoses may provide flat *cis*-1,3 diol chelation by O^4,O^6 bonding.

Conclusion

The new compounds, which are the first structurally characterized silicon chelates of the monosaccharides, deserve interest due to a number of features. They are formed not just by special saccharides, but each of the monosaccharides may adopt a suitable configuration at its anomeric center for silicon chelation. However, the decrease in species count by using a phenyl derivative is most pronounced for those monosaccharides that show the *cis*-furanose form in a larger quantity in the aqueous solution equilibrium. Hence, fructose and ribose produced a single five-coordinate species in methanol in terms of ^{29}Si NMR spectra and, correspondingly, a single silicon-chelating form was detected in the ^{13}C NMR spectra. Thus, the bis(diolato)(phenyl)silicate structures appear to be reasonable models for pentacoordinate oxosilicate species containing monosaccharides in aqueous solution and methanol. Reduction of the functionality of a tetra(alkoxo)silane by means of an inert phenyl substituent effectively reduces the number of equilibrium species in monosaccharide/silicate solutions mainly at the expense of six-coordinate species, which obviously are not formed with the phenylsilicon residue. At the same time, the ability of the silicon center to raise its coordination number from four to five is preserved. The ability of the phenylsilicates to form crystals with the $[K([18]crown-6)]^+$ counterion led to a series of structures including three of the four aldopentoses. Until now, however, crystallization has failed for the aldohexoses, which remain to be studied in the solid state.

For the future, the new compounds deserve further interest in their own right for showing avenues toward a carbohydrate-based siloxane chemistry and new strategies for selective transformations of monosaccharides.

Experimental Section

General: Reagent-grade chemicals were purchased from Fluka and used as supplied. The sugars were dried in vacuo. All syntheses were carried out under dry nitrogen and using standard Schlenk techniques. Organic solvents were dried and purified according to standard procedures and stored under nitrogen. ^{1}H, ^{13}C{^{1}H}, and ^{29}Si NMR spectra were recorded at room temperature on Jeol EX 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{29}Si, 79.4 MHz) and Eclipse 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) NMR spectrometers. The spectra were referenced to external $SiMe_4$. The ^{1}H and ^{13}C signals were assigned by means of ^{1}H/^{1}H COSY and ^{1}H/^{13}C HMQC experiments. Generally, signal positions are given for the reaction mixtures. Identity with the spectra of redissolved crystals has been proven for the ribose and arabinose derivatives.

Compound 1: A solution of [K([18]crown-6)]OMe in methanol (9.709 mL of a 0.206 M solution, 2.00 mmol) was added to a suspension of D-fructose (0.721 g, 4.0 mmol) in methanol (10 mL). Trimethoxy(phenyl)-silane (0.41 mL, 2.0 mmol) was slowly dropped into the stirred mixture. The resulting clear and colorless solution was kept at room temperature for 2 days, then the volume was reduced to approximately 4 mL. Prismatic, colorless crystals formed within a few weeks at 4 °C. ^{13}C{^{1}H} NMR (100 MHz, [D$_4$]methanol, 25 °C): $\delta = 63.6$ (C6), 64.1 (C1), 70.4 ([18]crown-6), 76.2 (C4), 77.1 (C3), 82.6 (C5), 102.6 (C2), 126.6 (C3^{Ph}, C5^{Ph}), 127.2 (C4^{Ph}), 134.7 (C2^{Ph}, C6^{Ph}), 144.4 ppm (C1^{Ph}); ^{29}Si NMR (79.4 MHz, [D$_4$]methanol, 25 °C): $\delta = -89.6$ ppm.

Compound 2: [18]crown-6 (0.528 g, 2.00 mmol) and potassium *tert*-butoxide (0.224 g, 2.00 mmol) were added slowly to a suspension of D-arabi-

Table 3. Crystallographic data for structures **1**–**5**.

	1	**2**	**3**	**4**	**5**
net formula	$C_{31}H_{53}KO_{19}Si$	$C_{30}H_{53}KO_{18}Si$	$C_{28}H_{45}KO_{16}Si$	$C_{31}H_{51}KO_{17}Si$	$C_{28}H_{45}KO_{16}Si$
M_r [g mol^{-1}]	796.925	768.915	704.831	762.910	704.831
crystal size [mm^{-1}]	0.26 × 0.13 × 0.12	0.25 × 0.13 × 0.12	0.20 × 0.12 × 0.10	0.30 × 0.22 × 0.09	0.12 × 0.09 × 0.03
T [K]	200(2)	200(2)	200(2)	200(2)	200(2)
crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$C2$	$C2$	$P2_12_12_1$	$P2_1$
a [Å]	8.76950(10)	22.3252(4)	17.2441(3)	9.40390(10)	9.08010(29)
b [Å]	15.66130(10)	14.5353(2)	11.7861(2)	25.6896(2)	20.81650(59)
c [Å]	27.0259(2)	12.1113(2)	9.7539(2)	30.8247(2)	9.55470(29)
β [°]	90	105.6949(8)	123.9622(8)	90	116.0512(11)
V [Å^{-3}]	3711.79(6)	3783.63(11)	1644.21(5)	7446.71(11)	1622.505(88)
Z	4	4	2	8	2
calcd density [g cm^{-3}]	1.42610(2)	1.34985(4)	1.42368(4)	1.36099(2)	1.44273(8)
μ [mm^{-1}]	0.255	0.246	0.271	0.247	0.275
absorption correction	numerical	numerical	numerical	numerical	none
transmission factor range	0.9504–0.9807	0.9436–0.9752	0.9662–0.9751	0.9359–0.9805	–
reflections measured	47255	41226	16969	72821	18101
R_{int}	0.046	0.060	0.042	0.046	0.144
mean $\sigma(I)/I$	0.027	0.056	0.044	0.028	0.103
θ range	3.2–24.0	3.3–27.5	3.5–27.5	3.2–23.0	3.2–23.0
observed reflections	5371	6547	3189	9367	3003
x, y (weighting scheme)	0.0342, 0.4438	0.0702, 0	0.0529, 0.0225	0.0994, 5.8423	0.0729, 0.7727
Flack parameter	−0.01(3)	−0.04(4)	−0.05(4)	0.00(6)	0.14(10)
reflections in refinement	5789	8647	3763	10326	4486
parameters	498	475	219	874	420
restraints	0	1	3	19	1
$R(F_{obsd})$	0.027	0.046	0.039	0.058	0.068
$R_w(F^2)$	0.064	0.120	0.096	0.161	0.166
S	1.045	1.022	1.087	1.037	1.045
shift/error$_{max}$	0.001	0.001	0.001	0.001	0.001
max. electron density [e Å^{-3}]	0.142	0.528	0.304	0.474	0.386
min. electron density [e Å^{-3}]	−0.182	−0.418	−0.217	−0.402	−0.267

nose (0.601 g, 4.00 mmol) in dry methanol (20 mL). Trimethoxy(phenyl)-silane (0.41 mL, 2.0 mmol) was dropped into the stirred mixture. The clear and colorless solution was stirred at 25 °C for 16 h, then the volume was reduced to approximately 4 mL. Prismatic, colorless crystals formed during the course of a few days at 4 °C. $^{13}C\{^1H\}$ NMR (100 MHz, [D_4]methanol, 25 °C): $\delta = 63.6$ (C5), 70.4 ([18]crown-6), 78.6 (C3), 79.9 (C2), 86.6 (C4), 100.5 (C1), 127.1 ($C3^{Ph}$, $C5^{Ph}$), 127.4 ($C4^{Ph}$), 134.7 ($C2^{Ph}$, $C6^{Ph}$), 143.8 ppm ($C1^{Ph}$); ^{29}Si NMR (79.4 MHz, [D_4]methanol, 25 °C): $\delta = -88.7$ ppm.

Compound 3: D-Ribose (0.603 g, 4.0 mmol) was dissolved in dry methanol (10 mL). A solution of [18]crown-6 (0.528 g, 2.00 mmol) and potassium *tert*-butoxide (0.224 g, 2.00 mmol) in dry methanol (10 mL) was added slowly. Subsequently trimethoxy(phenyl)silane (0.41 mL, 2.0 mmol) was dropped into the solution. The clear and colorless solution was stirred at 25 °C for 2 h, then the volume was reduced to approximately 4 mL. Prismatic, colorless crystals of **3** formed overnight at 25 °C in the resulting syrup: $^{13}C\{^1H\}$ NMR (100 MHz, [D_4]methanol, 25 °C): $\delta =$ 61.9 (C5), 70.4 ([18]crown-6), 72.2 (C3), 72.6 (C2), 79.6 (C4), 98.3 (C1), 127.1 ($C4^{Ph}$), 127.2 ($C3^{Ph}$, $C5^{Ph}$), 134.5 ($C2^{Ph}$, $C6^{Ph}$), 143.9 ppm ($C1^{Ph}$); ^{29}Si NMR (79.4 MHz, [D_4]methanol, 25 °C): $\delta = -87.9$ ppm.

Compound 4: [18]crown-6 (0.528 g, 2.00 mmol) and potassium *tert*-butoxide (0.224 g, 2.00 mmol) were added slowly to a suspension of D-xylose (0.601 g, 4.00 mmol) in methanol (20 mL). Trimethoxy(phenyl)silane (0.41 mL, 2.0 mmol) was dropped into the stirred mixture. After the turbid solution was stirred at 25 °C for 16 h, it became clear. The solvent was distilled off to leave a syrup, which was redissolved in a mixture of dry acetone and dry methanol (1:1; 5 mL). Prismatic, colorless crystals formed during the course of two months at 4 °C. ^{13}C NMR data of the main species out of three: $^{13}C\{^1H\}$ NMR (100 MHz, [D_4]methanol, 25 °C): $\delta = 60.3$ (C5), 70.4 ([18]crown-6), 77.2 (C3), 78.4 (C2), 79.1 (C4), 98.8 (C1), 126.8 ($C3^{Ph}$, $C5^{Ph}$), 127.3 ($C4^{Ph}$), 134.5 ($C2^{Ph}$, $C6^{Ph}$), 144.3 ppm ($C1^{Ph}$); ^{29}Si NMR of all three species (79.4 MHz, [D_4]methanol, 25 °C): $\delta = -89.0$, -89.9 (main species), -90.3 ppm.

Compound 5: A solution of D-ribulose (0.120 g, 0.8 mmol) in methanol (4 mL), trimethoxy(phenyl)silane (0.075 mL, 0.4 mmol), and a 0.8 M solution of [K([18]crown-6)]OMe in methanol (0.5 mL, 0.4 mmol) were stirred for 2 h at a temperature of 4 °C. After the solution was concentrated, colorless crystals of **5** formed within a few days: $^{13}C\{^1H\}$ NMR (100 MHz, [D_4]methanol, 25 °C): $\delta = 65.3$ (C1), 68.2 (C5), 70.0 ([18]crown-6), 72.1 (C3), 72.3 (C4), 105.8 (C2), 126.7 ($C3^{Ph}$, $C5^{Ph}$), 127.2 ($C4^{Ph}$), 134.5 ($C2^{Ph}$, $C6^{Ph}$), 143.0 ppm ($C1^{Ph}$); ^{29}Si NMR (79.4 MHz, [D_4]methanol, 25 °C): $\delta = -89.1$ ppm.

Crystal-structure determination and refinement: Crystallographic data and details of the structure determinations are summarized in Table 3. Crystals suitable for X-ray crystallography were selected by means of a polarization microscope, mounted on the tip of a glass fibre, and investigated on a Nonius KappaCCD diffractometer by using graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SIR 97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97). Anisotropic displacement parameters were refined for all non-hydrogen atoms. CCDC-227301 (**1**), -227300 (**2**), -227302 (**3**), -227304 (**4**), and -227303 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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