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Synthesis and mass spectrometric study of α,ω-bis(heptamethylcyclotetrasiloxanyloxy)oligodimethylsilanes

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α,ω-Bis(heptamethylcyclotetrasiloxanyloxy)oligodimethylsilanes were synthesized by the reaction of dichlorodimethylsilane and 1,3-dichlorohexamethyltrisilane with hydroxyheptamethylcyclotetrasiloxane. The peculiarities of fragmentation of the compounds obtained by electron impact mass spectrometry are discussed.

Key words: α,ω-dichloropermethyloligosilanes, cyclolinear permethyloligosilane-siloxanes, mass spectra, ^{29}Si NMR spectra.

Polysilane-siloxanes with a regular structure combine the properties of two main and most important classes of organosilicon polymers — polysiloxanes and polysilanes. For example, introduction of siloxane units into polysilanes increases their solubility and fusibility.[1,2] Methods for synthesis of linear permethylpolysilane-siloxanes have been developed in recent time.[1—7] We have recently reported[8] the synthesis of the first representatives of cyclolinear permethyloligosilane-siloxanes — α,ω-bis(heptamethylcyclotetrasiloxanyloxy)-oligodimethylsilanes containing an even number of dimethylsilane units $-(SiMe_2)_n-$ (**1b,d,e**: n = 2, 4, and 6, respectively) between two siloxane cycles. In the present work, we obtained compounds with a similar structure, but with an odd number of $-(SiMe_2)_n-$ units (**1a,c**: n = 1 and 3, respectively) between siloxane cycles, and studied the ^{29}Si NMR spectra of oligosilanes **1a—e** and the specific features of their fragmentation under electron impact.

Results and Discussion

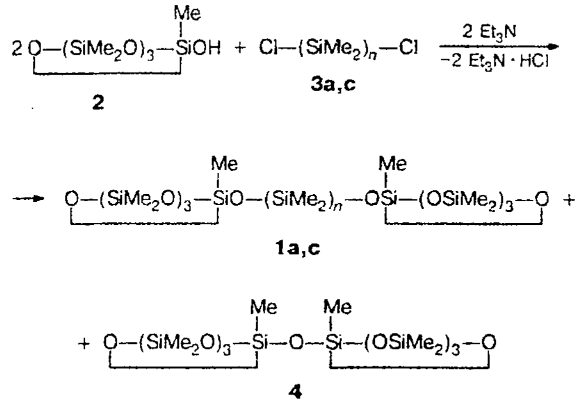
Compounds **1a,c** were synthesized by heterofunctional condensation of hydroxyheptamethylcyclotetrasiloxane (**2**) with dichlorodimethylsilane (**3a**) and 1,3-dichlorohexamethyltrisilane (**3c**), respectively (Scheme 1).

Bis(heptamethylcyclotetrasiloxanyl)oxide (**4**), which is formed in a minor amount as a by-product due to homocondensation of cyclosiloxane **2**, was also obtained in a 73% yield by the counter synthesis: the reaction of hydroxycyclosiloxane **2** with chloroheptamethylcyclotetrasiloxane **5** (Scheme 2).

The oligosilane-siloxanes **1a—e** obtained are of interest as models of cyclolinear polysilane-siloxanes (**6**).

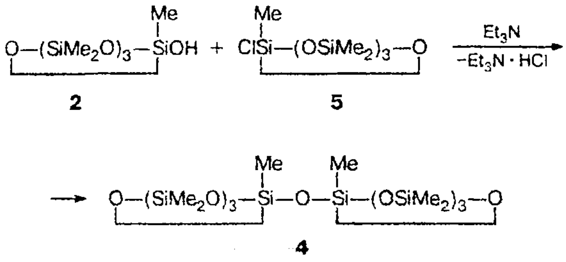
Some parameters of the ^{29}Si NMR spectra of compounds **1a—e** (the full spectra of oligosilanes **1a,c** are

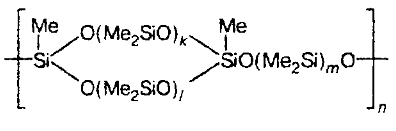
Scheme 1



n = 1 (**a**), 3 (**c**)

Scheme 2





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presented in Experimental, and those of compounds **1b,d,e** have been published earlier[8]) and linear permethylpolysilane-siloxanes[1–3,7] $-[O(SiMe_2)_k-(OSiMe_2)_m]_n-$ (**7**: $k = 2-4, 6$; $m = 0-3$) are presented in Table 1. Chemical shifts of Si atoms of the oligosilane chain in the spectra of compounds of both types are close. For example, for compounds **1b** and **7** ($k = 2$, $m = 0$ or 3) containing two Si atoms in the oligosilane chain, the signals of the Si_a atoms are observed at 0.4—1.4 ppm. When the number of successively connected Si atoms in molecules **1** and **7** increases, the signals of the Si_a atom exhibit a downfield shift, and they lie at ~9 ppm for the compounds with six Si atoms (**1e** and **7** ($k = 6$)). The signals of the Si_b atom also have a downfield shift when the oligosilane chain elongates (from *ca.* −53 ppm for **1c** and **7** ($k = 3$, $m = 0$) to −45.5 ppm for **1e** and **7** ($k = 6$, $m = 0-3$)). The chemical shifts of the Si_c atom for compounds **1e** and **7** ($k = 6$, $m = 0-3$) are almost the same and amount to −40 ppm. Thus, comparative analysis of the ^{29}Si NMR spectra of cyclolinear oligosilane-siloxanes **1** and linear polysilane-siloxanes **7** shows that the presence of bulky substituents (siloxane cycles) at the ends of the oligosilane chain in molecules **1b—e** has no effect on the chemical shifts of signals of Si atoms in the oligosilane chain

The mass spectra of oligosilanes **1a—e** and bisoxide **4** (Table 2) contain no peak of a molecular ion, which is characteristic of siloxanes.[9] This is their distinction from compounds with a similar, but purely silane structure, α,ω-bis[permethylcyclopenta(hexa)silanyl]oligodimethylsilanes,[10–14] whose mass spectra contain rather high-intensity peaks of molecular ions. The main fragmentation pathways of molecules **1a—e** under electron impact occur with elimination of the methyl substituent from the silicon atom and cleavage of the Si—Si and Si—O bonds. The intensity of the peak of the $[M - Me]^+$ ion in the mass spectrum of compound **1a** is 21% and decreases sharply to 0.2—0.3% for compounds **1b—e** as the number of $-SiMe_2-$ units between siloxane cycles increases. This is due to a lower energy of the Si—Si bond as compared to that of the Si—C bond and, hence, to the appearance of alternative routes of decomposition. In addition, compound **1a** is formally the first member of the homological series of oligosilanes **1**, which differ by the $-SiMe_2-$ unit, but contains no Si—Si bond. Therefore, the scheme of its fragmentation under electron impact (Scheme 3) virtually coincides with that for bisoxide **4**, also containing siloxane units only.

The molecular ion of compound **1a** (it is absent in the mass spectrum) loses the methyl radical to form an ion with m/z 637. The two other directions of decomposition occur with the cleavage of the Si—O bond and give ions with m/z 281 and 355, respectively. Further fragmentation of the $[M - Me]^+$ ion proceeds with successive elimination of two $SiMe_4$ molecules and formation of ions with m/z 549 and 461, respectively. The elimination of hexamethyldisiloxane, hexamethylcyclotrisiloxane, octamethyltrisiloxane, and octamethylcyclotetrasiloxane molecules from the $[M - Me]^+$ ion is accompanied by the formation of ions with m/z 475, 415, 401, and 341, respectively. The mass spectrum of compound **1a** also exhibits the peaks of ions with m/z 147, 207, 221, and 281, due to the elimination of siloxane species with seven, six, and five Si atoms, respectively, from the ion with m/z 637. Formally, these ions have the structure of disiloxane, cyclotrisiloxane, trisiloxane, and cyclotetrasiloxane without one methyl group. The peak of the $[Me_3Si]^+$ ion with m/z 73, which is formed from ions with m/z 637 and 549, is the highest-intensity in the mass spectrum of compound **1a**.

Table 1. Some parameters of ^{29}Si NMR spectra of cyclolinear oligosilane-siloxanes **1a—e** and linear permethylpolysilane-siloxanes **7**

Compound[a]	Solvent	δ			Reference
		Si_a	Si_b	Si_c	
$D_4-OSi_aO-D_4$ (**1a**)	CCl_4-CDCl_3 (9 : 1)	−21.15			[b]
$D_4-OSi_aSiO-D_4$ (**1b**)	CCl_4	1.43			8
$D_4-OSi_aSi_bSiO-D_4$ (**1c**)	CCl_4-CDCl_3 (9 : 1)	8.55	−52.71		[b]
$D_4-OSi_aSi_bSiSiO-D_4$ (**1d**)	CCl_4	9.45	−47.53		8
$D_4-OSi_aSi_bSi_cSiSiSiO-D_4$ (**1e**)	CCl_4-CDCl_3 (9 : 1)	9.14	−45.44	−40.22	8
$-(OSi_aSi)_n-$	CCl_4	0.8			1
$-[OSi_aSi-(OSi)_3]_n-$	CCl_4	0.39			7
$-(OSi_aSi_bSi)_n-$	CCl_4	8.3	−53.5		1
$-(OSi_aSi_bSiSi)_n-$	CCl_4	8.92	−48.11		2
$-(OSi_aSi_bSi_cSiSiSi)_n-$	$CDCl_3$	9.03	−45.67	−40.00	3
$-(OSi_aSi_bSi_cSiSiSi-OSi)_n-$	$CDCl_3$	7.90	−45.39	−40.00	3
$-[OSi_aSi_bSi_cSiSiSi-(OSi)_2]_n-$	$CDCl_3$	8.18	−45.41	−39.97	3
$-[OSi_aSi_bSi_cSiSiSi-(OSi)_3]_n-$	CCl_4	9.01	−45.34	−39.78	7

[a] Methyl groups at Si atoms are not shown. Siloxane cycles in molecules **1a—e** are designated as D_4.

[b] Data of this work.

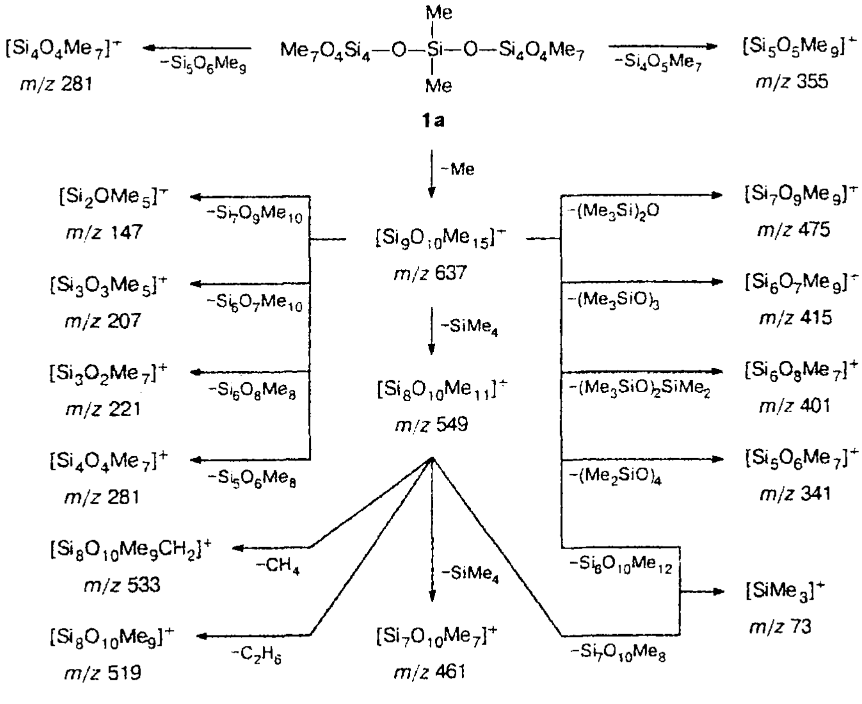
Table 2. Mass spectra of compounds **1a—e** and **4** transformed into the monoisotopic form

m/z	Ion	I_{rel} (%)					
		4	**1a**	**1b**	**1c**	**1d**	**1e**
73	$[SiMe_3]^+$	50.9	100.0	77.3	73.2	100.0	100.0
117	$[Si_2OMe_3]^+$	—	2.4	4.8	16.2	15.6	14.2
131	$[Si_2OMe_3CH_2]^+$	1.4	2.2	18.5	11.4	28.9	26.7
147	$[Si_2OMe_5]^+$	34.1	60.1	18.5	16.8	25.3	26.9
207	$[Si_3O_3Me_5]^+$	6.9	17.6	6.6	31.4	16.8	13.5
221	$[Si_3O_2Me_7]^+$	3.8	35.7	6.1	3.9	5.7	7.2
249	$[Si_4O_2Me_7]^+$	—	—	1.6	6.7	11.1	19.0
267	$[Si_4O_5Me_5]^+$	2.4	9.3	31.2	53.1	44.7	29.2
281	$[Si_4O_4Me_7]^+$	7.3	52.2	12.1	12.8	12.3	20.4
325	$[Si_5O_5Me_7]^+$	—	4.4	8.1	16.2	11.3	8.8
327	$[Si_5O_7Me_5]^+$	8.5	11.1	3.8	8.0	8.7	3.5
339	$[Si_5O_5Me_7CH_2]^+$	—	0	5.5	9.1	4.5	5.3
341	$[Si_5O_6Me_7]^+$	19.1	13.7	5.9	14.7	12.1	7.2
355	$[Si_5O_5Me_9]^+$	—	24.0	100	100	23.7	21.5
383	$[Si_6O_5Me_9]^+$	—	—	—	3.6	4.9	5.0
385	$[Si_6O_7Me_7]^+$	6.7	3.0	1.5	2.2	1.9	1.7
387	$[Si_6O_9Me_5]^+$	6.8	2.8	0.5	0.81	0.7	0
401	$[Si_6O_8Me_7]^+$	43.5	9.9	2.6	4.2	3.1	1.3
413	$[Si_6O_5Me_{11}]^+$	—	0	4.7	17.8	3.2	3.9
415	$[Si_6O_7Me_9]^+$	—	3.7	1.3	7.0	1.8	1.6
445	$[Si_7O_9Me_7]^+$	4.7	0	0.5	0	0.2	0
459	$[Si_7O_9Me_7CH_2]^+$	47.8	6.0	1.8	1.9	0.9	0
461	$[Si_7O_{10}Me_7]^+$	—	45.4	4.1	2.3	1.5	0
471	$[Si_7O_5Me_{13}]^+$	—	0	0	3.4	14.8	40.7
473	$[Si_7O_7Me_{11}]^+$	—	0	2.2	1.4	5.2	11.9
475	$[Si_7O_9Me_9]^+$	100	21.8	1.5	1.0	1.3	1.9
489	$[Si_7O_8Me_{11}]^+$	—	2.9	0.1	0	0.3	0
519	$[Si_8O_{10}Me_9]^+$	—	4.5	1.7	0	0.3	0
529	$[Si_8O_5Me_{15}]^+$	—	—	—	—	0	0.6
533	$[Si_8O_{10}Me_9CH_2]^+$	—	10.0	1.0	0	0	0
549	$[Si_8O_{10}Me_{11}]^+$	—	10.2	0.7	0.4	0	0
563	$[Si_8O_9Me_{13}]^+$	89.0	—	—	—	—	—
587	$[Si_9O_5Me_{17}]^+$	—	—	—	—	—	0.4
637	$[Si_9O_{10}Me_{15}]^+$	—	21.3	—	—	—	—
695	$[Si_{10}O_{10}Me_{17}]^+$	—	—	0.3	—	—	—
753	$[Si_{11}O_{10}Me_{19}]^+$	—	—	—	0.2	—	—
811	$[Si_{12}O_{10}Me_{21}]^+$	—	—	—	—	0.2	—
927	$[Si_{14}O_{10}Me_{25}]^+$	—	—	—	—	—	0.3

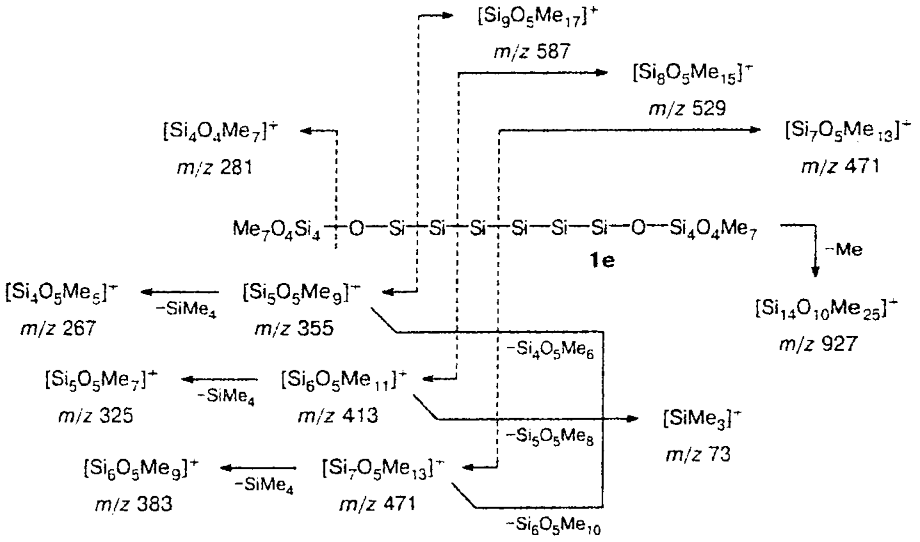
The presence of peaks of ions with m/z 533 and 519 in the mass spectrum is due to the elimination of methane and ethane molecules, respectively, from the ion with m/z 549.

The mass spectra of compounds **1b—e**, whose molecules contain Si—Si bonds, contain, along with the low-intensity peak of the $[M - Me]^+$ ion, peaks of ions formed due to the cleavage of the Si—Si bond (see Table 2). For example, the decomposition of compound **1e** results in the formation of ions with m/z 355, 413, and 471 and with m/z 529 and 587 that differ from one another in mass by the homological $SiMe_2$ unit (Scheme 4). The highest-intensity peaks are attributed to ions with m/z 355 and 471 (21.5 and 40.7%, respectively) and an odd number of Si atoms (1 and 3, respectively) in the oligosilane fragment bound to the

Scheme 3



Scheme 4



siloxane cycle. At the same time, the peaks of ions with *m/z* 413 and 529 that contain an even number of Si atoms (2 and 4) in the oligosilane fragment are much lower-intensity (3.9 and 0.6%, respectively). Therefore, the high intensity of the peak of the ion with *m/z* 471 is not related to the symmetrical decomposition of molecule **1e**. This is confirmed by the fact that for fragmentation of compound **1d** with four successively linked Si atoms in the bridge between siloxane cycles, the intensity of the peak of the ion with *m/z* 413, which is formed during the symmetrical decomposition of the molecule and has two Si atoms in the oligosilane fragment, is only 3.2%, whereas the intensity of peaks of ions with *m/z* 355 and 471, apparently due to nonsymmetrical decomposition and containing one and three Si atoms in the oligosilane fragment, is 23.7 and 14.8%, respectively (see Table 2).

Further decomposition of ions with *m/z* 355, 413, and 471 occurs with elimination of neutral $SiMe_4$ molecules. The mass spectrum of compound **1e** (as in the spectrum of **1a**) also exhibits ions (they are not indicated in Scheme 4) that formally have the structure of disiloxane, cyclotrisiloxane, trisiloxane, and cyclotetrasiloxane, but without one methyl radical at the Si atom. Their formation is related to the decomposition of cyclotetrasiloxane fragments in molecule **1e** under electron impact. The intensity of peaks of these ions does not exceed 20% of the total ion current.

Fragmentation of compounds **1b—d** occurs *via* a similar scheme.

Experimental

The course of reactions was monitored by GLC using an LKhM-8MD chromatograph (a stainless steel column 0.3×100 cm, 5% SE-30 on Chromaton N-AW-DMCS, a thermal conductivity detector, temperature programming from 30 to 300 °C, temperature rise rate 12 deg min^{-1}, helium as a carrier gas). GC-MS analysis was carried out on a Kratos MS-890 instrument (a capillary column 15 m × 0.32 mm, SE-30 as a liquid phase, helium as a carrier gas, ionizing voltage 70 eV, temperature programming from 30 to 270 °C, temperature rise rate 10 deg min^{-1}). ^{29}Si NMR spectra were recorded on a Bruker WP-400 SY spectrometer (79.46 MHz) in CCl_4—$CDCl_3$ (9 : 1) using Me_4Si as the internal standard. IR and UV spectra were recorded in thin films on Specord M-80 and Specord M-40 spectrophotometers, respectively.

Dichlorotrisilane **3c** and cyclosiloxanes **2** and **5** were synthesized by known procedures.[7,15] Synthesis of compounds **1b,d,e** has previously been described.[8] Ether was distilled in an N_2 flow above sodium metal in the presence of benzophenone. All reactions were carried out in a dry nitrogen atmosphere.

Bis(heptamethylcyclotetrasiloxanyloxy)dimethylsilane (1a). A solution of dichlorosilane **3a** (0.85 g, 6.7 mmol) in anhydrous ether (50 mL) was added dropwise at −5 to −10 °C to a solution of cyclosiloxane **2** (4.0 g, 13.4 mmol) and Et_3N (1.36 g, 13.4 mmol) in anhydrous ether (80 mL). The reaction mixture was stirred for 3 h at −5 °C and then for 20 h at 20 °C. The precipitate of $Et_3N \cdot HCl$ was filtered off, and the ether solution was washed three times with water aliquots and dried with Na_2SO_4. Compound **1a** was obtained after the solvent was distilled off and the residue was fractionated, b.p. 133—134 °C (3 Torr), n_D^{23} 1.4045. Found (%): C, 29.15; H, 7.26; Si, 38.37. $C_{16}H_{48}O_{10}Si_9$. Calculated (%): C, 29.42; H, 7.41; Si, 38.69. IR (CsI), ν/cm^{-1}: 2960, 2896 (C—H); 1262, 859, 808, 762 (Si—Me); 1080, 1039 (Si—O—Si). ^{29}Si NMR, δ: −19.05 (OSiOSiOSiO); −19.24 (OSiOSiMe(O—)$_2$); −21.15 (Me(—O)$_2$SiOSiOSi(O—)$_2$Me); −65.03 (MeSi(O—)$_3$).

1,3-Bis(heptamethylcyclotetrasiloxanyloxy)hexamethyltrisilane (1c). Compound **1c** with b.p. 132—133 °C (0.007 Torr) and n_D^{23} 1.4272 was obtained in a 59.7% yield (3.08 g) from cyclosiloxane **2** (4.0 g, 13.4 mmol), Et_3N (1.36 g, 13.4 mmol), and dichlorotrisilane **3c** (1.64 g, 6.7 mmol) according to a procedure similar to that presented above. Found (%): C, 31.47; H, 7.97; Si, 40.38. $C_{20}H_{60}O_{10}Si_{11}$. Calculated (%): C, 31.21; H, 7.86; Si, 40.14. UV, λ_{max}/nm: 221. IR (CsI), ν/cm^{-1}: 2962, 2902 (C—H); 1262, 856, 811, 777 (Si—Me); 1082, 1057 (Si—O—Si). ^{29}Si NMR, δ: 8.55 (O$\underline{\mathrm{Si}}$Si$\underline{\mathrm{Si}}$O); −19.05 (OSiO$\underline{\mathrm{Si}}$OSiO); −19.44 (O$\underline{\mathrm{Si}}$OSiMe(O—)$_2$); −52.71 (OSi$\underline{\mathrm{Si}}$SiO); −64.18 (MeSi(O—)$_3$).

Bis(heptamethylcyclotetrasiloxanyl)oxide (**4**). Bisoxide **4** with b.p. 112 °C (2 Torr) and n_D^{23} 1.4042 was obtained in a 73.0% yield (7.78 g) from hydroxycyclosiloxane **2** (5.70 g, 18.4 mmol), Et_3N (1.87 g, 18.4 mmol), and chlorocyclosiloxane **5** (5.85 g, 18.4 mmol) by a procedure similar to that used for the synthesis of compound **1a**. Found (%): C, 29.35; H, 7.43; Si, 38.79. $C_{14}H_{42}O_9Si_8$. Calculated (%): C, 29.03; H, 7.31; Si, 38.79. IR (CsI), ν/cm^{-1}: 2964, 2900 (C—H); 1261, 854, 809, 770 (Si—Me); 1084, 1048 (Si—O—Si). ^{29}Si NMR, δ: −19.04 (O$\underline{\mathrm{Si}}$OSiMe(O—)$_2$); −65.42 (MeSi(O—)$_3$).

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