Macrocyclization of α-(Alkynyloxy)silyl-α-diazoacetates by Inter-/Intramolecular [3 + 2] Cycloaddition Reaction Sequences

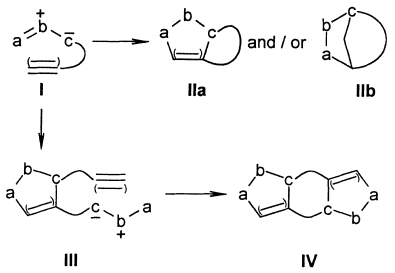
Gerhard Maas,*[a] Volker Gettwert,[a] Fred Krebs,[b] and Günter Schmidtberg[c]

Abstract: Thermally induced intra-/intermolecular [3 + 2] cycloaddition reaction sequences of α-(alkynyloxy)silyl-α-diazoacetates **1** lead to [3.3](1,4)pyrazolophanes $\mathbf{(2)_2}$ and higher cyclooligomers thereof [$\mathbf{(2)_n}$, $n > 2$]. In most cases, the cyclodimer was isolated by crystallization, while a complete separation of the mixture of the higher cyclooligomers was not possible. Solid state structures of cyclodimers $\mathbf{(2b)_2}$ and $\mathbf{(2c)_2}$, cyclotrimer $\mathbf{(2b)_3}$, and cyclotetramer $\mathbf{(2e)_4}$ were determined by X-ray diffraction analysis. Field-desorption mass spectra were used to characterize the cyclooligomer mixtures. The relative amounts of the cyclooligomers depend on the substitution pattern of the diazo compound. The cyclooligomerization reactions reported herein demonstrate, for the first time, the involvement of diazo functions in macrocyclization reactions via 1,3-dipolar cycloaddition.

Keywords: cyclooligomerizations · cyclophanes · diazo compounds · heterocycles · macrocycles

Introduction

Intramolecular 1,3-dipolar cycloaddition reactions represent a valuable and versatile strategy for the synthesis of fused and bridged heterocyclic ring systems (Scheme 1, **I** → **II**).[1–3] Use of this methodology,[4] sometimes incorporated in tandem reactions,[3, 5] allows the rapid construction of polycyclic systems with amazing complexity. Instead of the intramolecular [3 + 2] cycloaddition reaction, a bimolecular version of this process can also be expected, that is cycloaddition of the 1,3-dipole across the dipolarophilic function (usually a C–C double or triple bond) of a second molecule of the same kind. The resulting cyclodimer **III** may undergo further transformation leading to a cyclodimer **IV** or to macrocycles depending on whether or not the subsequent intramolecular 1,3-dipolar cycloaddition is preceded by further intermolecular cycloaddition steps.



Scheme 1. Cycloaddition pathways for 1,3-dipoles linked to a dipolarophile unit.

Bimolecular reaction pathways of dipolarophile-tethered 1,3-dipoles **I** are reported in the literature much less frequently than the intramolecular version **I** → **II**.[6] Formation of cyclodimers according to the transformation **I** → **IV** has been observed for a variety of 1,3-dipoles such as nitriloxides,[7] nitrilimines,[8] O-silyl nitronates,[9] and azomethinylides.[10] To the best of our knowledge, participation of diazo functions in tandem intermolecular–intramolecular cycloaddition reactions has not been reported, although they are among the most common and most easily accessible 1,3-dipoles. Even simple intermolecular cycloadditions of unsaturated diazo ketones appear to be rare.[11]

We report in this paper that α-(alkynyloxy)silyl-α-diazoacetates **1** undergo intermolecular–intramolecular cycloaddition sequences on thermal impact, thereby giving rise not only to cyclodimers but also to higher cyclooligomers some of which could be isolated and structurally characterized.

Results and Discussion

Cyclooligomerization reactions: The synthesis of α-[(2-alkynyl)oxy]silyl-α-diazoacetates **1a–e** has been described.[12, 13]

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They are readily assembled by consecutive reaction of a silyl bis(triflate) with methyl diazoacetate and a propargyl alcohol.

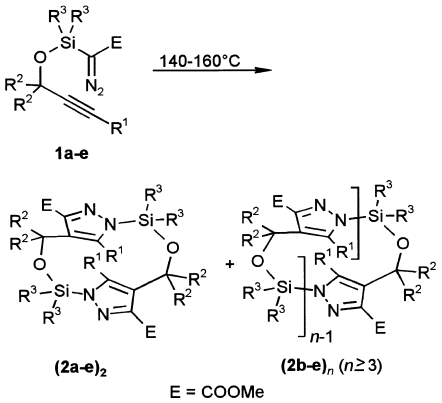
When diazoacetate **1a** was heated in boiling xylene (139 °C) for 1 h, the ^{1}H-NMR spectrum of the reaction mixture showed the presence of one major product, namely [3.3](1,4)pyrazolophane **(2a)$_2$** formed in ca. 70% yield, besides minor amounts of a hydrolysis product thereof (vide infra). The pyrazolophane was isolated in 30% yield after crystallization. Its identity as a cyclodimer of **1a** was revealed by the molecular ion peak in the mass spectrum, while the ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra showed only signals expected for a monomer unit in accordance with the symmetrical nature of this dimer. The close agreement of the relevant NMR data with those of pyrazolophanes **(2b)$_2$** and **(2c)$_2$**, both of which were characterized by crystal structure analysis, leaves no doubt about the structure of **(2a)$_2$**.

In contrast to **1a**, heating of **1b** in boiling xylene afforded both cyclodimer **(2b)$_2$** and higher cyclooligomers **(2b)$_n$** (Scheme 2, Table 1). A chromatographic separation of the reaction mixture was precluded by the easy solvolytic cleavage of the Si–N(pyrazole) bond in all these compounds, and all attempts to obtain individual components had to rely on fractionating crystallization. The cyclodimer proved to be the least soluble component in ether and was isolated in low yield (6%). The solvent of the mother liquor was replaced with pentane from which a mixture of higher cyclooligomers **(2b)$_n$** crystallized slowly in remarkably good yield (50%). While further separation of this mixture could not be achieved, several cycles of careful recrystallization from a CH_2Cl_2/ether provided a small amount of pure cyclotrimer **(2b)$_3$**. Both **(2b)$_2$** (two modifications) and **(2b)$_3$** were characterized structurally by single-crystal X-ray diffraction analysis (vide infra).

Table 1. Thermal cyclooligomerization of diazoacetates **1**.

Diazo-acetate	R^1	R^2,R^2	R^3	T [°C]	Solvent	Product	Yield [%][a] (n ratio)[b]
1a	H	Me,Me	Me	139	xylene	**(2a)$_2$**	30[c]
1b	H	Me,Me	*i*Pr	139	xylene	**(2b)$_2$**	6
						(2b)$_n$ ($n=3-5$)	50
				120–162	neat	**(2b)$_n$** ($n=3-5$)	54 (67:21:12)[d]
1c	H	$(CH_2)_5$	*i*Pr	142	neat	**(2c)$_2$**	4–7
						(2c)$_n$ ($n>2$[e])	29–31
1d	H	H,H	*i*Pr	142	neat	**(2d)$_2$**	18
						(2d)$_n$ ($n=3-5$)	76 (91:6:3)[f]
1e	Me	H,H	*i*Pr	162	mesitylene	**(2e)$_n$** ($n=2-5$)	4 (28:9:61:2)

[a] Yields of isolated compounds are given. [b] Relative ratios of cyclooligomers were determined from the peak profile data of field desorption (FD) mass spectra. [c] A yield of 70% was indicated by ^{1}H NMR of the reaction mixture. [d] Peaks associated with $n=3-5$ account for ca. 37% of the FD spectrum, peaks for the cyclodimer, formed by thermal degradation, for 63%; minor peaks for $n=6,7,8$ were detected under special conditions (see text). [e] The composition of the mixture was not determined. [f] Peaks associated with $n=3-5$ account for ca. 72% of the FD spectrum, peaks for the cyclodimer, formed by thermal degradation, for 28%.



Scheme 2. Cyclooligomerization reactions of diazoacetates **1**; see Table 1 for substituents and yields.

The NMR chemical shifts of **(2b)$_2$**, **(2b)$_3$**, and **(2b)$_n$** are compared in Table 2. In all cases, only the signal set of a monomeric unit was observed pointing to the symmetrical character of all these cyclooligomers in solution. While most differences between the chemical shifts of the cyclodimer and the higher cyclooligomers are only marginal, the ^{1}H-NMR

Abstract in German: *α-(Alkinyloxy)silyl-α-diazoacetate **1** reagieren bei thermischer Belastung in einer Folge von intra-/intermolekularen [3+2]-Cycloadditionen zu [3.3](1,4)Pyrazolophanen **(2)$_2$** und homologen Cyclooligomeren [**(2)$_n$**, $n>2$]. In den meisten Fällen konnte das Cyclodimer durch Kristallisation abgetrennt werden, während eine vollständige Auftrennung der Cyclooligomerengemische nicht möglich war. Die Kristallstrukturen der Cyclodimeren **(2b)$_2$** und **(2c)$_2$**, des Cyclotrimers **(2b)$_3$** und des Cyclotetramers **(2e)$_4$** konnten bestimmt werden. Die Zusammensetzung der Cyclooligomerengemische wurde durch Felddesorptionsmassenspektrometrie ermittelt. Die Mengenverhältnisse der Cyclooligomere hängen vom Substitutionsmuster der Diazoverbindung ab. Die hier berichteten Cyclooligomerisierungsreaktionen sind die ersten Beispiele für den Aufbau von Makrocyclen durch 1,3-dipolare Cycloadditionsreaktionen von ungesättigten Diazoverbindungen.*

Table 2. ^{1}H-, ^{13}C-, ^{29}Si-NMR chemical shifts (δ, $CDCl_3$) of cyclodimer **(2b)$_2$**, cyclotrimer **(2b)$_3$**, and cyclooligomer mixture **(2b)$_n$** ($n>2$).

Entry	**(2b)$_2$**[a]	**(2b)$_3$**[b]	**(2b)$_n$**[b]
$SiCH(CH_3)_2$	1.26, 1.08	1.04, 1.06	1.08, 1.09
$SiCH$	1.55	1.53	1.51
$C(CH_3)_2$	1.68	1.75	1.65
OCH_3	3.90	3.88	3.85
NCH=	6.78	7.86	7.82
$SiCHCH_3$	17.56, 17.74	16.95, 17.18	17.22, 17.32
$SiCH$	14.26	13.78	13.55
$C(CH_3)_2$	30.91	30.87	30.36
OCH_3	52.25	51.87	51.82
$C(CH_3)_2$	71.95	75.70	75.38
CH=C	130.76	134.27	134.06
NCH=	133.19	134.71	134.08
C-C=O	145.03	141.52	142.87
C=O	164.76	163.91	163.88
Si	−7.98		−8.82

[a] In CD_2Cl_2. [b] In $CDCl_3$.

spectrum of **(2b)$_2$** is distinguished by a larger separation of the signals for the diastereotopic methyl groups of Si*i*Pr and an upfield shift of the pyrazole proton signal by 1 ppm. Both observations indicate that magnetic anisotropy effects are substantial in the more rigid pyrazolophane structure (e.g. the pyrazole proton is situated in the shielding region of the opposite heteroaromatic ring, see Figures 1 and 2), whereas they more or less vanish in the larger macrocycles due to rapid conformational changes of the ring skeleton. As a consequence of this dynamic behavior, all cyclooligomers in the mixture have about the same NMR chemical shifts (additional line broadening with some small "spikes" at the base of the methoxy and methyl ^{1}H signals may be caused by the minor cyclooligomers in the mixture). A look at other recently published types of macrocycles with sufficient conformational flexibility [e.g. lactone oligomers ("oligolides"),[14] [1.$_n$](2,5)-thiophenophanes[15]] shows that chemical shift differences between the higher cyclooligomers ($n > 2$) are also very small.

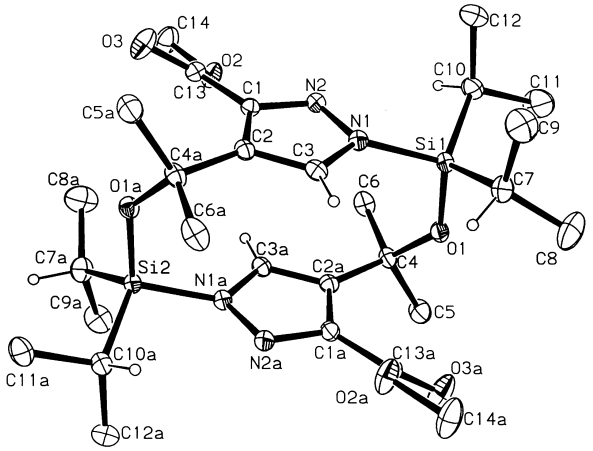


Figure 1. Molecular structure of **(2b)$_2$**, modification 1 (ORTEP plot, ellipsoids of thermal vibration are shown at the 20% probability level); selected bond lengths [Å] and angles [°]: Si1–O1 1.628(2), Si2–O1a 1.629(2), Si1–N1 1.786(2), Si2–N1a 1.792(2), N1–N2 1.363(3), N1a–N2a 1.362(3), N2–C1 1.324(4), N2a–C1a 1.329(4), C1–C13 1.485(4), C1a–C13a 1.481(4), C13–O3 1.189(4), C13a–O3a 1.179(4); C4-O1-Si1 133.7(2), C4a-O1a-Si2 132.3(2); torsion angles: N2-C1-C13-O3 –146.0(3), N2a-C1a-C13a-O3a 144.3(3).

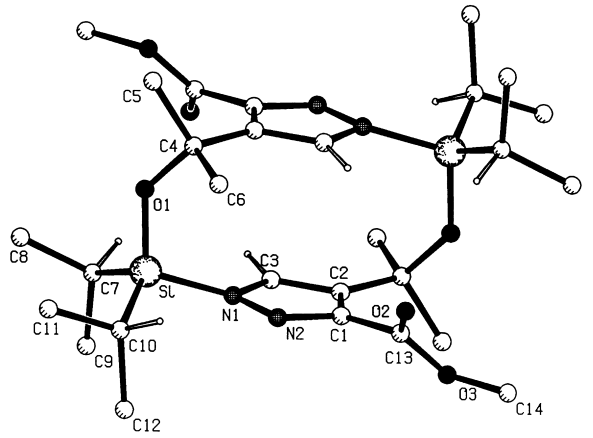


Figure 2. Molecular structure of **(2b)$_2$**, modifcation 2 (PLUTON plot); selected bond lengths [Å] and angles [°]: Si–O1 1.622(2), Si–N1 1.782(2), N1–N2 1.363(3), N2–C1 1.316(3), C1–C13 1.481(4), C13–O2 1.189(3); C4-O1-Si 133.3(2), O1-Si-N1 109.1(1), C3-N1-Si 129.7(2), N2-N1-Si 118.1(2), C3-N1-N2 109.7(2); torsion angle N2-C1-C3-O2 44.0(3).

Due to the similar NMR spectra of **(2b)$_3$** and what was considered to be the cyclooligomer mixture **(2b)$_n$**, it was obvious that NMR spectroscopy conveys no information on the components of this mixture. However, field-desorption mass spectrometry turned out to be an appropriate tool to analyze these mixtures (see below). This method proved the presence of all cyclooligomers **(2b)$_n$** with $n = 3-5$ and showed the cyclotrimer as the major component.

Mixtures of cyclodimers and higher cyclooligomers were obtained also from diazoacetates **1c–e** (Table 1). In all cases, the combined yield of the latter was again much higher than the cyclodimer yield. Pyrazolophanes **(2c)$_2$** and **(2d)$_2$** could be separated from the higher cyclooligomers by crystallization, and the structure of **(2c)$_2$** was established by X-ray structure analysis. The characteristic upfield shift of the pyrazole proton, already discussed above for **(2b)$_2$**, was also observed for these two cyclodimers.

For diazoacetate **1e**, containing an internal acetylenic bond, the thermal cyclooligomerization reaction required a higher temperature than in the other cases and the total yield of all cyclooligomers formed in boiling mesitylene was very low (4%). According to the field-desorption mass spectra, the cyclotetramer dominated in the mixture **(2e)$_{2-5}$**. In fact, fractionating crystallization gave **(2e)$_4$** reproducibly which was identified by a crystal structure analysis. It should not be concealed that in the very first crystallization experiment, some crystals of the pyrazolophane **(2e)$_2$** were obtained but this could not be reproduced.

Since the cyclooligomerization reactions of **1a–e** include one or more bimolecular steps, higher concentrations should improve the yields. This issue was studied examplarily with **1b**. For the reactions in xylene at 139 °C, the highest combined yield of macrocycles (56–60%) was obtained at a concentration of ca. 0.1–0.2 M of **1b** in xylene. When the concentration was lowered to 0.05 M or raised to 0.9 M, the yield dropped to 30–35%. In all cases, the product ratios **(2b)$_2$**:**(2b)$_n$** did not vary much. On the other hand, heating of **1b** without solvent also gave a 54% yield of macrocycles; interestingly, the yields of **(2b)$_2$** and **(2b)$_n$** were 6 and 50% at 139 °C (in xylene) and 0 and 54% at 162 °C (no solvent). Heating of the neat diazoacetate was also used to achieve the cyclooligomerization of **1c**,**d**. With **1e**, however, only undefined product mixtures resulted rather than the expected yield improvement for **(2e)$_n$**.

Crystal structure analyses: Pyrazolophane **(2b)$_2$** was obtained in two crystal modifications both of which were studied by single-crystal X-ray diffraction analysis. The major differences of the two structures (Figures 1 and 2) were found in the crystal system, the orientation of one of the Si*i*Pr groups, and in the orientation of the COOMe groups with respect to the pyrazole rings. Modification 1 is orthorhombic, the two isopropyl groups at each silicon atom have different geometries with respect to the Si–N bond (the C–H bond of one *i*Pr being arranged *anti*, the C–H bond of the other *i*Pr group *gauche*), and the ester groups are strongly tilted out of the respective pyrazole ring plane (torsion angles of 146.0 and 144.3°, see Table 3) with the carbonyl oxygen atoms pointing in the direction opposite to the skeleton of the molecule. In

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Table 3. Some geometrical features of cyclooligomers **(2b)$_2$**, **(2c)$_2$**, **(2b)$_3$**, and **(2e)$_4$**.

Entry	**(2b)$_2$** modification 1	**(2b)$_2$** modification 2[a]	**(2c)$_2$**[b]	**(2b)$_3$**	**(2e)$_4$**[a]
bond angle Si-O-C [°]	133.7(2), 132.3(2)	133.3(2)	137.4(1), 139.4(1)	142.1(2), 139.8(2), 145.3(2)	131.0(2), 131.2(2)
bond angle N-Si-O [°]	109.3(1), 111.1(3)	109.1(1)	110.5(1), 110.3(6)	98.1(1), 111.0(1), 99.7(1)	101.9(1), 102.0(1)
sum of valence angles at N(−Si) [°]	357.8, 357.7	357.5	358.4, 358.4	360.0, 359.5, 359.6	359.9, 359.9
ΔN(−Si)[c] [Å]	0.010(4), 0.016(4)	0.015(3)	−0.005(3), −0.013(3)	−0.008(4), 0.018(4), −0.009(4)	0.009(3), −0.003(3)
ΔSi[d] [Å]	−0.399(4), −0.385(4)	0.413(3)	0.358(3), 0.325(3)	−0.042(4), −0.168(4), 0.167(4)	0.078(6), −0.024(6)
ΔCR_2[d] [Å]	−0.081(5), −0.075(5)	0.105(4)	0.039(3), 0.093(3)	−0.030(5), 0.013(5), 0.013(5)	−0.034(5), 0.076(5)
torsion angle N=C−C=O [°]	−146.0(3), 144.3(3)	44.0(3)	−175.7(2), −152.9(2)	−174.6(4), −153.2(3), −179.9(4)	−168.3(3), −177.8(3)

[a] Centrosymmetric structure in the solid state. [b] Two independent centrosymmetric molecules in the unit cell. [c] Deviation of pyrazole-N1 (bonded to silicon) from least-squares plane defined by the other four ring atoms, which deviate from this plane by 0.000(2)–0.003(2) Å. [d] Deviation of Si (or CR_2) from the least-squares plane defined by all five pyrazole ring atoms.

the monoclinic modification 2, the molecules have crystallographic inversion symmetry, both isopropyl groups at silicon have the same orientation (C−H bond *gauche* to the Si−N bond), and the carbonyl oxygen of the COOMe group points towards the pyrazolophane skeleton while the tilt of the ester group with respect to the pyrazole ring is again substantial (44.0°). Crystal structures could also be determined for pyrazolophane **(2c)$_2$** (two independent centrosymmetric molecules in the unit cell, Figure 3), cyclotrimer **(2b)$_3$** (Figure 4) and cyclotetramer **(2e)$_4$** (Figure 5).

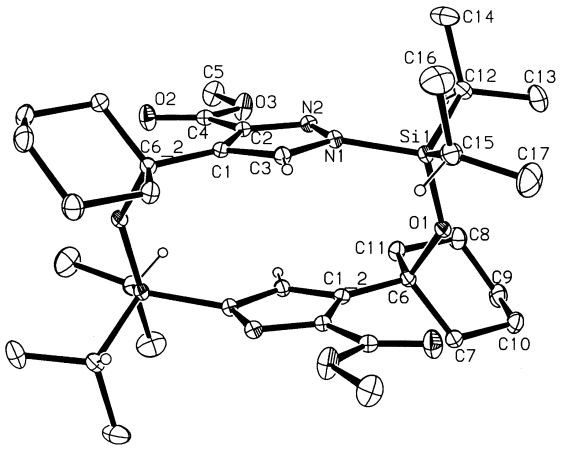

Figure 3. Molecular structure of **(2c)$_2$** (ORTEP plot); selected bond lengths [Å] and angles [°], values for the second independent molecule are given in brackets: Si1−O1 1.616(1) [1.619(1)], Si1−N1 1.795(1) [1.795(1)], N1−N2 1.363(2) [1.365(2)], N2−C2 1.334(2) [1.328(2)], C2−C4 1.484(2) [1.483(2)], C4−O2 1.196(2) [1.173(2)]; C6-O1-Si1 137.4(1) [139.4(1)], O1-Si1-N1 110.5(1) [110.3(6)], C3-N1-Si1 129.6(1) [131.3(1)], N2-N1-Si1 118.8(1) [117.1(1)], C3-N1-N2 110.0(1) [110.0(1)]; torsion angle N2-C2-C4-O2 −175.7(2) [-152.9(2)].

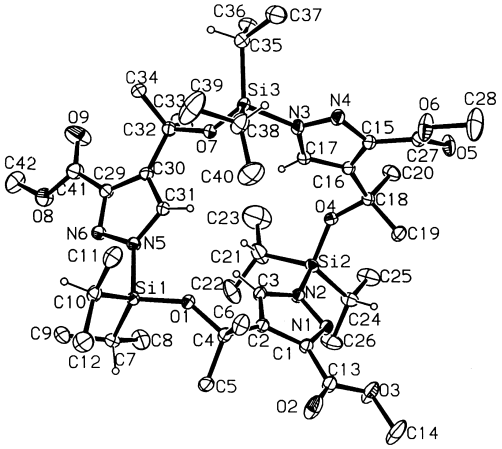

Figure 4. Molecular structure of **(2b)$_3$** (ORTEP plot); selected bond lengths [Å] and angles [°]; Si1−O1 1.619(2) [values for corresponding bonds in the other two moieties of the cyclotrimer, given counterclockwise: 1.611(2), 1.596(2)] , Si1−N5 1.785(2) [1.787(2), 1.790(2)], N5−N6 1.354(3) [1.359(3), 1.352(2)], N6−C29 1.334(3) [1.333(3), 1.337(3)], C29−C41 1.479(4) [1.471(4), 1.486(4)], C41−O9 1.179(4) [1.183(2), 1.185(3)]; Si1-O1-C4 142.1(2) [139.8(2), 145.3(2)], O1-Si1-N5 98.1(1) [111.0(1), 99.7(1)].

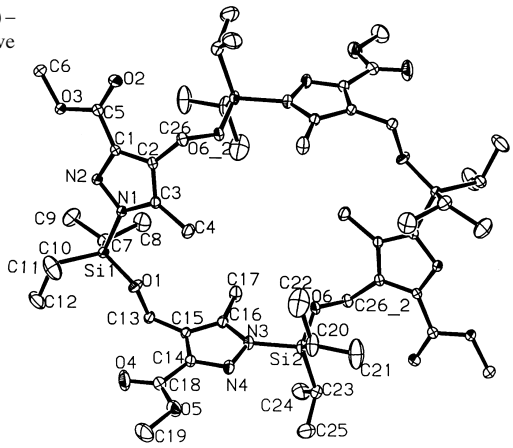

Figure 5. Molecular structure of **(2e)$_4$** (ORTEP plot); selected bond lengths [Å] and angles [°]: Si1−O1 1.617(2) [value for corresponding bond in the other symmetrically non-related moiety of the centrosymmetric cyclotetramer: 1.624(2)], Si1−N1 1.792(2) [1.796(2)], N1−N2 1.368(3) [1.366(3)], N2−C1 1.331(3) [1.329(3)], C1−C5 1.469(3) [1.470(3)], C5−O2 1.201(3) [1.199(3)], Si1-O1-C13 131.0(2) [131.2(2)], O1-Si1-N1 101.9(1) [102.0(1)].

In the three pyrazolophanes, the two pyrazole rings are virtually parallel (e.g. interplanar angle of least-squares planes in the orthorhombic modification of **(2b)$_2$**: 0.56°) with a spacing of 3.12–3.23 Å. Cyclotetramer **(2e)$_4$** can be viewed as an expanded pyrazolophane in which the two opposite rings are parallel and the two adjacent ones nearly perpendicular (interplanar angle: 69.8°). Some geometrical features which are indicative of the ring strain in these cyclooligomers are given in Table 3. In some pyrazole rings of the five structures, the nitrogen atom connected to silicon is slightly displaced from the ideal plane defined by the other four ring atoms [see ΔN(−Si)]. In all cases, however, the substituent atoms which are part of the cyclophane bridges, Si and CR_2 (CMe_2, cyclohexyl, CH_2), are displaced significantly from the plane of

the heteroaromatic ring. While ΔCR_2 shows no systematic change within the series cyclodimer, -trimer, and -tetramer, it is clearly seen that the deviation of the silicon atom is largest in the three cyclodimers, and lowest in the cyclotetramer. The large deviation in the cyclodimers is accompanied by a slight pyramidalization of the adjacent pyrazole nitrogen atom, but not by a significantly higher folding of the pyrazole ring than in the higher cyclooligomers. Not unexpectedly, ring strain also affects the bond angles in the Si-O-C tethers connecting the pyrazole rings. The Si-O-C bond angle range is 131.0–145.3°, and that of N-Si-O 98.1–111.1°. The largest Si-O-C and the smallest N-Si-O angles are found in the cyclotrimer, but at the same time this structure also incorporates a rather large N-Si-O angle [111.0(1)°]. The latter observation suggests that it is not appropriate to propose a general correlation between ring size of the cyclooligomer and bond angles. As far as the deviation of the ester groups from coplanarity with the adjacent pyrazole ring is concerned, relief of steric interaction with the neighboring CR_2 group is certainly the most important factor, and deviations from coplanarity up to 44° indicate that extended π-conjugation between pyrazole ring and COOMe group is not a major structure-determining motif.

Field-desorption (FD) mass spectrometry of cyclooligomers: This technique was used to analyze the cyclooligomer mixtures **(2)**$_n$ and to obtain an estimate of the product ratios by using accumulation of peak profile data (see Experimental Section). This method does not require high temperatures to evaporate the compounds, avoids the application of polar-protic solvents which may solvolyze these cyclooligomers, and under appropriate conditions does not lead to extensive fragmentation.[16] Thus, the FD mass spectra of isolated cyclooligomers **(2b)$_2$** (Figure 6), **(2b)$_3$**, and **(2e)$_4$** showed as the only significant peaks those of the protonated molecular ion $[M\mathrm{H}]^+$ (13–100%), the fragment $[M - i\mathrm{Pr}]^+$ (100–45%) and of $[M+\mathrm{CH_3}]^+$ (0–6%). The occurrence of the last-mentioned peak is probably due to an intermolecular methyl group transfer from an ester function to a nitrogen atom of the pyrazole ring.[17, 18] In the FD spectra of the mixture of the higher cyclooligomers **(2b)**$_n$ and **(2d)**$_n$, we observed a significant portion of signals attributed to the respective cyclodimer, although a proton NMR spectrum clearly showed the absence of **(2)$_2$** from the mixture. Since higher temperatures were applied to desorb the oligomer mixture from the field anode as compared with the conditions for the pure cyclooligomers, it must be assumed that the cyclodimers resulted from thermal degradation of the higher cyclooligomers under the given conditions. For these spectra, the relative amounts of higher cyclooligomers as given in Table 1 do not consider the possibility that the individual cyclooligomer components are degraded thermally to form **(2)$_2$** to different extents. However, the fact that we were able to crystallize exactly those cyclooligomers [**(2b)$_3$** and **(2e)$_4$**] which constitute the major components in the respective mixture of higher cyclooligomers lends some credibility to our semi-quantitative interpretation of the FD mass spectra. In the FD spectrum of **(2e)$_{2-5}$** (Figure 7), the portion of the cyclodimer amounts to only 28%. Taking into account that a major part of it, like in the other cases, results from thermal degradation of the higher cyclooligomers, the true content of **(2e)$_2$** in the mixture should be much lower. This would agree with the absence of a separate signal set for **(2e)$_2$** from the NMR spectra of the mixture **(2e)$_{2-5}$**.

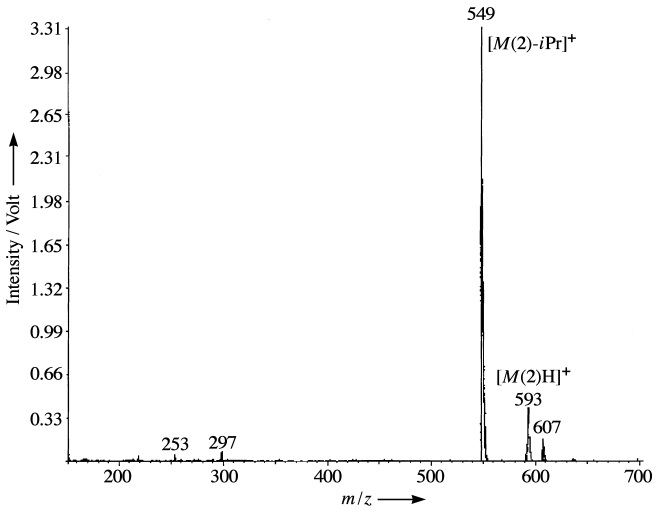

Figure 6. FD mass spectrum of pure **(2b)$_3$** (11 kV, anode current gradient 17 →21 mA during 30 min, peak profile data).

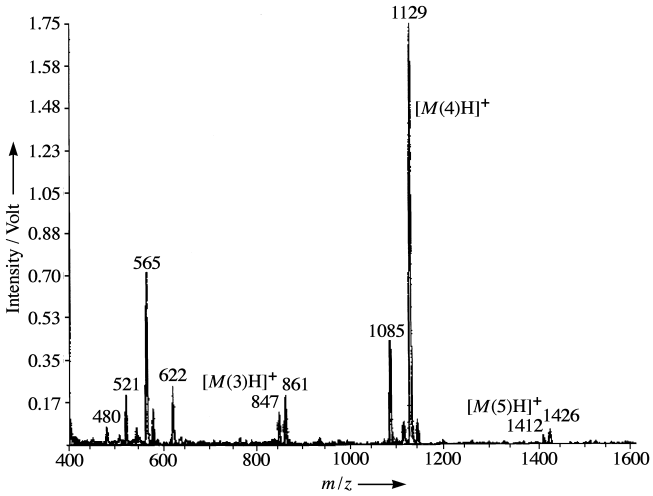

Figure 7. FD mass spectrum of pure cyclooligomer mixture **(2e)$_{2-5}$** (11 kV, anode current gradient 17 →21 mA during 30 min, peak profile data).

It needs to be mentioned that the peak profile data were all collected up to 1600 Da which does not allow to detect cyclooligomers larger than the cyclopentamer. A separate experiment with the **(2b)**$_n$ mixture, in which centroid data were recorded and masses up to 3000 Da were monitored, showed not only the presence of **(2b)$_{3-5}$** but also masses correspondig to molecular ion peaks for $n = 6,7,8$, all of which were lower in intensity than the cyclopentamer peak. The possibility that these peaks represent clusters consisting of the lower cyclooligomers has, however, not been ruled out.

With the product ratios shown in Table 1, the following relationships between the substituent pattern and the yields of cyclooligomers **(2)**$_n$ emerge: In the case of $SiMe_2$-substituted diazoacetate **1a**, only the cyclodimer is formed, whereas with

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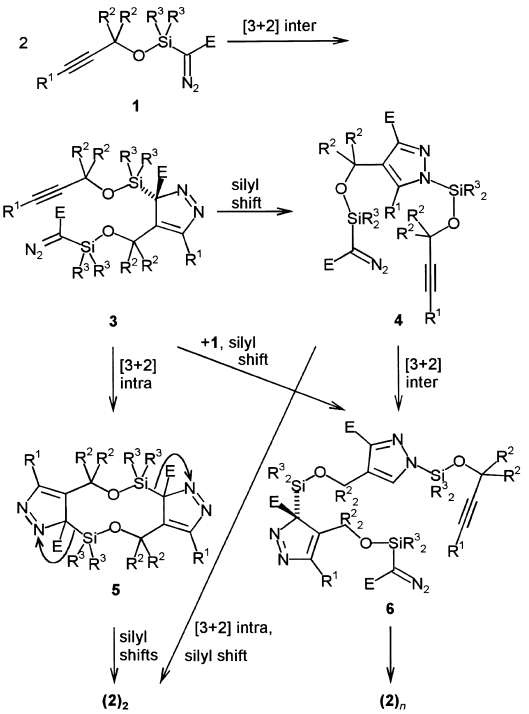
Si*i*Pr$_2$–diazoacetates **1b–e**, the higher cyclooligomers [**(2)**$_n$ ($n > 2$] dominate by large. When R^1 and R^2 are methyl groups rather than hydrogen atoms, the ratio **(2)**$_3$:**(2)**$_4$ changes in favor of the latter.

Mechanistic pathways for cyclooligomerization: The macrocyclization reactions reported here do not only consist in a sequence of inter-/intramolecular [3 + 2] cycloaddition steps, but include also silyl shifts which can occur at the stage of any 3*H*-pyrazole resulting from a 1,3-dipolar cycloaddition reaction (Scheme 3). These rearrangements can occur as a 1,3- or two subsequent 1,5-sigmatropic shifts of the silicon atom.

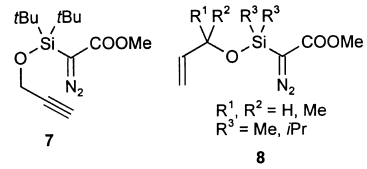


Scheme 3. Mechanistic pathways for cyclooligomerization of **1**.

Thus, the first formed 3*H*-pyrazole **3** may undergo intramolecular 1,3-dipolar cycloaddition to form tricycle **5** which rearranges to pyrazolophane **(2)**$_2$ by silyl shifts at each pyrazole ring. Alternatively, cycloadduct **3** could undergo a silyl shift first to form 1*H*-pyrazole **4**. Intramolecular cycloaddition of **4** would also lead to **(2)**$_2$, and inter-/intramolecular cycloaddition sequences would generate the higher cyclooligomers **(2)**$_n$. Since the sigmatropic silyl migrations at the pyrazole ring are expected to be fast,[19] we consider it unlikely that **3** undergoes an intermolecular 1,3-dipolar cycloaddition with **1** faster than the silyl migration (e.g. **3**→**6**).

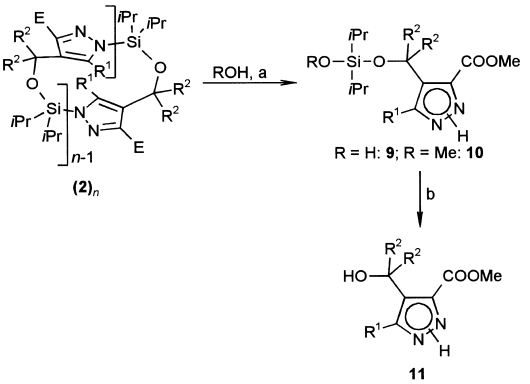
The observation that from the SiMe$_2$-substituted diazoacetate **1a** only cyclodimer **(2a)**$_2$ is formed whereas for all Si*i*Pr$_2$-substituted diazocompounds the higher cyclooligomers dominate, may have two reasons: Firstly, the SiMe$_2$ group may allow each of the two side chains in **3** to align without much steric strain for a facile intramolecular 1,3-dipolar cycloaddition. Secondly, it is conceivable that a silyl shift **3**→**4** occurs faster for the Si*i*Pr$_2$ than for the SiMe$_2$ compounds since more steric strain, caused by the two adjacent quaternary centers, is released. The latter argument implies that **4** reacts preferentially to form the higher oligomers but not cyclodimer **(2)**$_2$. This is not unreasonable, since an intramolecular [3 + 2] cycloaddition occuring in **4** appears to require for both side chains a conformation of higher energy than in the case of **3** reacting to give **4**.

Along these lines, it appears that the migrating ability of the silyl group is a decisive factor for the first-time observation of cyclic oligomers larger than the cyclodimer in macrocyclizations via cycloaddition reactions of unsaturated 1,3-dipoles. Another question arises, namely why the starting dipoles **1a–e** prefer the bimolecular cycloaddition over the monomolecular intramolecular cycloaddition which would afford an oxasilolopyrazole. In fact, the Si*t*Bu$_2$-substituted diazoacetate **7** undergoes an intramolecular [3 + 2] cycloaddition when heated at 160 °C (11 % yield).[20] Perhaps, the two *tert*-butyl substituents at silicon in **7** force the molecule to adopt an *s-cis* or *s-gauche* conformation at the Si–O bond (as compared to *s-trans* in **1**) which is a geometrical prerequisite for the intramolecular reaction. More astonishing is the different reactivity of diazoacetates **1** as compared to their olefinic analogues, α-(alkenyloxy)silyl-α-diazoacetates **8**, which follow intramolecular (carbene and pyrazoline) pathways on heating.[21] By comparing the initial products of an intramolecular cycloaddition reaction of **1** and **8** (both with SiMe$_2$ or Si*i*Pr$_2$ groups), one may argue that the oxasilolopyrazole arising from **1** is more strained (due to the additional double bond in the 3*H*-pyrazole ring) than the oxasilolopyrazoline obtained from **8** and therefore is not formed. In the intermolecular reaction mode, the ring strain argument plays no role since the cycloaddition products are monocyclic.



7 **8**

Solvolyses of cyclooligomers: As mentioned above, the N–Si bond in cyclooligomers **2** is cleaved readily by protic-polar solvents, and partial hydrolysis during workup was hard to avoid. Therefore, solvolyses of some of the cyclooligomers **(2)**$_n$ were investigated on a preparative scale (Scheme 4, Table 4). Thus, heating of **(2b)**$_n$ and **(2d)**$_n$ ($n = 2,3$, etc.) with water afforded the corrresponding 4-[(hydroxysilyl)oxymethyl]pyrazoles **9b,d** in high yield. Surprisingly, pyrazolophane **(2c)**$_2$ resisted hydrolysis under the same conditions, whereas the higher homologues **(2c)**$_n$ ($n > 2$) were hydrolyzed as expected. Analogously, methanolysis afforded the corresponding 4-[(methoxysilyl)oxymethyl]pyrazoles **10**. Fluoride-induced or acid-catalyzed desilylation of **9** or **10** generated the 4-(hydroxymethyl)pyrazoles **11**. The macrocyclization/solvolysis sequence can be carried out as a one-pot procedure to convert diazoacetates **1** into **9** or **10**, respectively (e.g. **1b**→**9b**: 58 % yield). In this context, it is interesting to note that the 1,3-dipolar cycloaddition of ethyl diazoacetate with propargyl alcohol leads exclusively to the 5-hydroxymethylpyrazole-3-carboxylate,[22] and with propargyl acetate, the 5-acetoxymethylpyrazole is formed besides a minor amount of the 4-acetoxymethyl isomer.[23] Thus, the conversion of **1**



Scheme 4. Solvolyses of cyclooligomers **2**; a) H_2O/CH_3CN, reflux (**2** → **9**) or CH_3OH, reflux (**2** → **10**), see Table 3 for yields; b) KF, 18-crown-6 [**9b** → **11b** (90%), **10d** → **11d** (82%)] or HOAc, $CHCl_3$ [**9d** → **11d** (93%)]; E = COOMe.

Table 4. Solvolyses of cyclooligomers $(\mathbf{2})_n$; products and yields (R^1 = H).

Cyclo-oligomer	R^2,R^2	R	Product (yield, %)
$(\mathbf{2b})_2$	Me,Me	H	**9b** (quant.)
$(\mathbf{2b})_{3-5}$	Me,Me	H	**9b** (quant.)
$(\mathbf{2b})_{2-5}$	Me,Me	Me	**10b** (quant.)
$(\mathbf{2c})_2$	$(CH_2)_5$	H	no reaction
$(\mathbf{2c})_n$ ($n > 2$)	$(CH_2)_5$	H	**9c** (91)
$(\mathbf{2d})_2$	H,H	H	**9d** (90)
$(\mathbf{2d})_{3-5}$	H,H	H	**9d** (90)
$(\mathbf{2d})_{2-5}$	H,H	Me	**10d** (86)

into **11** allows the synthesis of the target compounds with a regioselectivity opposite to the intermolecular [3 + 2] cycloaddition of diazoacetic esters with propargyl systems.

Conclusion

The macrocyclization reactions of α-(alkynyloxy)silyl-α-diazoacetates **1** represent the first reported cyclooligomerization reactions in which diazo dipoles are involved in intermolecular/intramolecular [3 + 2] cycloaddition sequences. Furthermore, the isolation and structural characterization of a cyclotrimer and a cyclotetramer seems not to have been reported for any other 1,3-dipole so far. It is likely that the high migrating ability of a silyl group in a 3*H*-pyrazole resulting from the first intermolecular cycloaddition step is responsible for this pecularity, since the transformation of a 1,2- into a 1,3-disubstituted pyrazole renders a subsequent intramolecular reaction between the diazo function in one substituent and the dipolarophile in the other substituent more difficult than an intermolecular cycloaddition. Thus, the oligomer can grow linearly before an intramolecular reaction becomes sterically favorable and terminates the cycloaddition cascade. We envisage that unsaturated dipoles similar to **1**, but with the diazo function replaced by another 1,3-dipole, will give rise to analogous macrocyclization reactions.

Experimental Section

General methods and procedures: NMR were recorded on Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.76 MHz, ^{29}Si: 99.36 MHz) and Bruker AC 200 instruments (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz); $CDCl_3$, CD_2Cl_2 and C_6D_6 were used as solvents. As the internal reference, Me_4Si was used for the ^{1}H- and ^{29}Si-NMR spectra, and the solvent signal for the ^{13}C-NMR spectra [$\delta(CDCl_3) = 77.0$, $\delta(CD_2Cl_2) = 53.73$, $\delta(C_6D_6) = 128.7$]. Assignments of ^{13}C chemical shifts are based on proton-coupled ^{13}C, (C,H) correlation, and DEPT-135 spectra. IR spectra were recorded on Perkin–Elmer IR 883 and IR 1310 instruments. Mass spectra were obtained with spectrometers Finnigan MAT SSQ7000 (EI, CI spectra) and Varian MAT 711 (FD spectra, see below). Microanalyses were performed on Perkin–Elmer EA 240 and EA 2400 instruments in the Sektion für Analytik und Höchstreinigung, Universität Ulm.

Solvents were dried by standard procedures. The petroleum ether (ether) used had a boiling range of 40–60 °C. The cyclooligomerization reactions were carried out in heat gun dried glassware and under an argon atmosphere. **Caution**: Although silyl-substituted diazoacetates are thermally rather stable compounds, all thermal reactions of **1a–e** reported here should be carried out with appropriate precaution (safety shield), since uncontrolled thermal decomposition with elimination of molecular nitrogen cannot be totally excluded.

Cyclooligomerization of 1a. Dimethyl 2,2,4,4,9,9,11,11-octamethyl-3,10-dioxa-1,7,8,14-tetraaza-2,9-disilatricyclo[10.2.1.1^{5,8}]hexadeca-5(16),6,12(15),13-tetraene-6,13-dicarboxylate $(\mathbf{2a})_2$: A solution of diazoacetate **1a**[13] (424 mg, 1.76 mmol) in xylene (3 mL) was heated in an oil bath at 120 °C and then slowly heated (2 °C per min) to 139 °C. After one hour, the solvent was evaporated and ether (5 mL) was added. The white precipitate was separated by centrifugation and washed with ether (3 mL) to give $(\mathbf{2a})_2$ (128 mg, 30%). Colorless crystals were obtained from CH_2Cl_2/ether; m.p.: 159–161 °C; IR (KBr): $\tilde{\nu} = 1728$ (C=O), 1270, 1259, 1192, 1164, 1151, 1107, 1071, 1049 cm^{-1}; ^{1}H NMR (200.14 MHz, $CDCl_3$): $\delta = 0.57$ (s, 12H, $SiMe_2$), 1.68 (s, 12H, CMe_2), 3.69 (s, 6H, OMe), 6.81 (s, 2H, =CH); ^{13}C NMR (50.34 MHz, $CDCl_3$): $\delta = -1.13$ ($SiMe_2$), 30.62 (CMe_2), 52.17 (OMe), 71.74 (s, CMe_2), 130.38 (CH=*C*), 132.00 (NCH=), 144.76 (C=N), 164.42 (C=O); ^{29}Si{^{1}H} NMR ($CDCl_3$): $\delta = -3.89$; MS (CI, CH_4, 120 eV): *m*/*z* (%): 521 (3) [*M*+Allyl]$^+$, 509 (11) [*M*+Et]$^+$, 480 (7) [*M*]$^+$, 465 (24) [*M* − CH_3]$^+$, 315 (100), 299 (11); $C_{20}H_{32}N_4O_6Si_2$ (480.67): calcd C 49.98, H 6.71, N 11.66; found C 49.71, H 6.71, N 11.57.

Cyclooligomerization of 1b. Dimethyl 2,2,9,9-tetraisopropyl-4,4,11,11-tetramethyl-3,10-dioxa-1,7,8,14-tetraaza-2,9-disilatricyclo[10.2.1.1^{5,8}]hexadeca-5(16),6,12(15),13-tetraene-6,13-dicarboxylate $(\mathbf{2b})_2$, trimethyl 2,2,9,9,16,16-hexaisopropyl-4,4,11,11,18,18-hexamethyl-3,10,17-trioxa-1,7,8,14,15,21-hexaaza-2,9,16-trisilatetracyclo[17.2.1.1^{5,8}.1^{12,15}]tetracosa-5(24),6,12(23),13,19(22),20-hexaene-6,13,20-tricarboxylate $(\mathbf{2b})_3$, and higher cyclooligomers $(\mathbf{2b})_n$: A solution of diazoacetate **1b**[12] (297 mg, 1.00 mmol) in xylene (6 mL) was heated at reflux (139 °C) for 1 h. After cooling to rt and evaporation of the solvent, ether (3 mL) was added. A white precipitate formed within 1 h. Separation by centrifugation and washing with ether gave cyclodimer $(\mathbf{2b})_2$ as colorless crystals (18 mg, 6%). Pentane (10 mL) was added to the mother liquor. A white precipitate formed immediately which was separated by centrifugation and washed with cold pentane to afford a mixture of cyclooligomers $(\mathbf{2b})_n$ (149 mg, 50%) ($n = 3-5$ detected by FD-MS).

A mixture of cyclooligomers without the cyclodimer was obtained as follows: In a pressure Schlenk tube, diazoacetate **1b** (297 mg, 1.00 mmol) was heated at 120 °C and then slowly heated (2 °C per min) to 162 °C. [The slow heating beyond 120 °C was important since otherwise a vigorous decomposition occurred (**Caution!**) with gas elimination (N_2) and formation of a black mass.] After one hour, a viscous orange mass had formed which was cooled to rt and dissolved in pentane (5 mL). Upon magnetic stirring, a white solid separated from the mixture within one hour. Separation by centrifugation and washing with pentane afforded colorless $(\mathbf{2b})_{3-5}$ (160 mg, 54%); composition according to FD mass spectra: $(\mathbf{2b})_3$:$(\mathbf{2b})_4$:$(\mathbf{2b})_5$ = 67:21:12.

The mixture of cyclooligomers $(\mathbf{2b})_n$ was dissolved in CH_2Cl_2 and ether was added until the solution became turbid. Upon very slow evaporation of the solvent, colorless crystals appeared which were isolated and subjected to the same recrystallization procedure several times to give a small amount of pure cyclotrimer $(\mathbf{2b})_3$ as transparent colorless crystals which were suitable for X-ray diffraction analysis.

Data for $(\mathbf{2b})_2$: M.p.: 246 °C; IR (KBr): $\tilde{\nu} = 1734$ (C=O), 1270 cm^{-1}; ^{1}H NMR (500.14 MHz, CD_2Cl_2): $\delta = 1.08$ (d, $^3J = 7.6$ Hz, 12H, CH*Me*),

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1.26 (d, $^3J = 7.6$ Hz, 12H, CH*Me*), 1.55 (sept, $^3J = 7.6$ Hz, 4H, SiCH), 1.68 (s, 12H, CMe_2), 3.90 (s, 6H, OMe), 6.78 (s, 1H, =CH); ^{13}C NMR (125.77 MHz, CD_2Cl_2): $\delta = 14.26$ (SiCH), 17.56 (CH*Me*), 17.74 CH*Me*), 30.91 (*CMe*$_2$), 52.25 (OMe), 71.95 (s, *C*Me$_2$), 130.76 (HC=*C*), 133.19 (NCH=), 145.03 (C=N), 164.76 (C=O); ^{29}Si{^{1}H} NMR (CD_2Cl_2): $\delta = -7.98$; MS (EI, 70 eV): *m*/*z* (%): 592 (1) $[M]^+$, 549 (56) $[M - i\mathrm{Pr}]^+$, 426 (9), 383 (100), 253 (31); MS (FD): *m*/*z* (%): 607 (6) $[M+CH_3]^+$, 593 (13) $[M\mathrm{H}]^+$, 549 (100) $[M - i\mathrm{Pr}]^+$, 297 (2) $[M+\mathrm{H}]^{2+}$, 253 (2); $C_{28}H_{48}N_2O_6Si_2$ (592.88): calcd C 56.72, H 8.16, N 9.45; found C 56.68, H 7.98, N 9.37.

Data for **(2b)$_3$**: IR (KBr): $\tilde{\nu} = 2954$, 2868, 1733 (C=O), 1260, 1171, 1099, 1074 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 1.04$ (d, $J = 7.5$ Hz, 18H, CH*Me*), 1.06 (d, $J = 7.5$ Hz, 18H, CH*Me*), 1.53 (sept, $J = 7.5$ Hz, 6H, SiCH), 1.75 (s, 18H, $CHMe_2$), 3.88 (s, 9H, OMe), 7.86 (s, 3H, =CH); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 13.77$ (SiCH), 16.95 (CH*Me*), 17.18 (CH*Me*), 51.87 (OMe), 75.70 (*C*Me$_2$), 134.27 (CH=*C*), 134.71 (NCH=), 141.52 (C=N), 163.33 (C=O); MS (FD): *m*/*z* (%): 911 (4) $[M+\mathrm{Na}]^+$, 903 (4) $[M+CH_3]^+$, 889 (26) $[M\mathrm{H}]^+$, 845 (100) $[M - i\mathrm{Pr}]^+$, 593 (6), 401 (2), 297 (5); $C_{42}H_{72}N_6O_9Si_3$ (889.32): calcd C 56.72, H 8.16, N 9.45; found C 56.67, H 7.93, N 9.46.

Data for **(2b)$_{3\text{–}5}$**: M.p.: 158–160 °C; IR (KBr): $\tilde{\nu} = 2950$, 2869, 1722 (C=O), 1466, 1271, 1172, 1072 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 1.08$ (d, $J = 7.3$ Hz, 6*n*H, CH*Me*), 1.09 (d, $J = 7.4$ Hz, 6*n*H, CH*Me*), 1.51 (sept, $J = 7.5$ Hz, 2*n*H, SiCH), 1.65 (s, 6*n*H, C*Me*$_2$), 3.85 (s, 3*n*H, OMe), 7.82 (s, 1*n*H, =CH); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 13.55$ (SiCH), 17.22 (CH*Me*), 17.32 (CH*Me*), 30.36 (*CMe*$_2$), 51.82 (OMe), 75.38 (*C*Me$_2$), 134.06 (CH=*C*), 134.38 (NCH=), 142.27 (C=N), 163.88 (C=O); ^{29}Si{^{1}H} NMR ($CDCl_3$): $\delta = -8.82$; MS (FD): *m*/*z* (%): 1495 (3), $[M_5+CH_3]^+$, 1481 (3) $[M_5\mathrm{H}]^+$, 1437 (3) $[M - i\mathrm{Pr}]^+$, 1199 (5) $[M_4+CH_3]^+$, 1185 (6) $[M_4\mathrm{H}]^+$, 1141 (3) $[M_4 - i\mathrm{Pr}]^+$, 903 (8) $[M_3+CH_3]^+$, 889 (16) $[M_3\mathrm{H}]^+$, 845 (20) $[M_3 - i\mathrm{Pr}]^+$, 607 (15) $[M_2+CH_3]^+$, 593 (46) $[M_2]^+$, 549 (51) $[M_2 - i\mathrm{Pr}]^+$, 297 (100) $[M\mathrm{H}]^+$; $(C_{14}H_{24}N_2O_3Si)_n$ ($n = 296.44$): calcd C 56.72, H 8.16, N 9.45; C 56.40, H 8.00, N 9.34.

Cyclooligomerization of 1c. Dimethyl 2,2,9,9-tetraisopropyl-4,4′,11,11′-di(spirocyclohexyl)-3,10-dioxa-1,7,8,14-tetraaza-2,9-disilatricyclo[10.2.1.1^{5,8}]-hexadeca-5(16),6,12(15),13-tetraene-6,13-dicarboxylate (2c)$_2$ and higher cyclooligomers (2c)$_n$ ($n > 2$): A pressure Schlenk tube was charged with diazoacetate **1c**[13] (794 mg, 2.36 mmol), immersed in an oil bath, and heated slowly to 120 °C and then slowly heated (2 °C per min) to 142 °C. After one hour, the solution was cooled and ether (20 mL) was added. The white precipitate was separated by centrifugation and washed with ether to give **(2c)$_2$** (33–56 mg, 4–7%). Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from CH_2Cl_2/pentane or CH_2Cl_2/ether.

The solvent of the mother liquor from which **(2c)$_2$** had separated was replaced by pentane. A white precipitate formed which was isolated by centrifugation and washed with cold pentane (3 mL) to afford the cyclooligomer mixture **(2c)$_n$** (231 mg, 31%) ($n > 2$).

Data of **(2c)$_2$**: M.p.: 249–251 °C; IR (KBr): $\tilde{\nu} = 2935$, 1731 (C=O), 1241, 1115, 1053 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 1.07$ (d, $J = 7.8$ Hz, 12H, CH*Me*; sept, 4H, SiCH), 1.32 (d, 12H, $J = 7.5$ Hz, CH*Me*), 1.27 (m, 2H, 4′-CH), 1.42 (m, 4H, 3′-CH), 1.52 (m, 2H, 4′-CH), 1.70 (m, 4H, 3′-CH), 1.82 (m, 4H, 2′-CH), 2.26 (m, 4H, 2′-CH), 6.75 (s, 2H, =CH); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 14.26$ (SiCH), 17.50/17.61 (CH*Me*), 22.73 (3′-CH_2), 25.73 (4′-CH_2), 38.16 (2′-CH_2), 52.09 (OMe), 73.32 (spiro-C), 128.95 (CH=*C*), 133.32 (CH=), 144.43 (C=N), 164.91 (C=O); ^{29}Si{^{1}H} NMR ($CDCl_3$): $\delta = -11.13$; MS (EI, 70 eV): *m*/*z* (%): 672 (0.6) $[M]^+$, 629 (37) $[M - i\mathrm{Pr}]^+$, 466 (14), 423 (100), 409 (7), 319 (4), 293 (15); $C_{34}H_{56}N_4O_6Si_2$ (673.01): calcd C 60.68, H 8.39, N 8.32; found C 59.82, H 8.52, N 7.89.

Data of **(2c)$_n$**: M.p.: 133–134 °C; IR (KBr): $\tilde{\nu} = 2944$, 1728 (C=O), 1237, 1081 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 0.87$ (d, 12*n*H, $J = 6.1$ Hz, CH*Me*), 1.15–2.10 (br m, 10*n*H, SiCH, CH_2), 2.40–2.60 (br m, 2*n*H, CH_2), 3.83 (s, 3*n*H, OMe), 8.21 (s, 1*n*H, =CH); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 13.46$ (SiCH), 16.54/16.72 (CH*Me*), 23.77 (3′-CH_2), 25.80 (4′-CH_2), 39.53 (2′-CH_2), 51.71 (OMe), 74.39 (spiro-C), 127.19 (CH=*C*), 137.28 (NCH=), 144.12 (C=N), 164.39 (C=O); ^{29}Si{^{1}H} NMR (99.37 MHz, $CDCl_3$): $\delta = -5.62$; $(C_{17}H_{28}N_2O_3Si)_n$ ($n = 336.51$): calcd C 60.68, H 8.39, N 8.32; found C 60.21, H 8.31, N 8.01.

Cyclooligomerization of 1d. Dimethyl 2,2,9,9-tetraisopropyl-3,10-dioxa-1,7,8,14-tetraaza-2,9-disilatricyclo[10.2.1.1^{5,8}]hexadeca-5(16),6,12(15),13-tetraene-6,13-dicarboxylate (2d)$_2$ and higher cyclooligomers (2d)$_n$ ($n > 2$): Diazoacetate **1d**[12] (804 mg, 3.00 mmol) was placed in a pressure Schlenk tube and heated in an oil bath at 120 °C and then slowly heated (2 °C per min) to 142 °C. After 1.5 h at this temperature, the red-brown viscous oil was cooled to rt and dissolved in ether (4 mL). Within 1–3 h, a white precipitate formed which was separated by centrifugation and washed with ether and pentane to give **(2d)$_2$** (145 mg, 18%). Crystals could be obtained from CH_2Cl_2 by slow evaporation of the solvent.

The mother liquor from which **(2d)$_2$** was crystallized was concentrated and all volatiles were removed at 140 °C at 0.02 mbar. The foam-like residue was a mixture of cyclooligomers **(2d)$_n$** (610 mg, 76%) with the following composition according to FD-MS: **(2d)$_3$**:**(2d)$_4$**:**(2d)$_5$** = 91:6:3.

Data for **(2d)$_2$**: M.p.: 148–150 °C; IR (KBr): $\tilde{\nu} = 1730$ (C=O), 1277, 1249, 1114, 1067 cm^{-1}; ^{1}H NMR (500.14 MHz, CD_2Cl_2): $\delta = 1.15$ (d, $J = 7.6$ Hz, 12H, CH*Me*), 1.21 (d, $J = 7.6$ Hz, 12H, CH*Me*), 1.55 (sept, $J = 7.6$ Hz, 4H, SiCH), 3.90 (s, 6H, OMe), 4.96 (s, 4H, CH_2), 6.77 (s, 1H, =CH); ^{13}C NMR (125.77 MHz, CD_2Cl_2): $\delta = 12.48$ (SiCH), 17.28 (CH*Me*), 17.41 (CH*Me*), 52.02 (OMe), 57.36 (CH_2), 123.59 (CH_2*C*=), 137.20 (NCH=), 144.75 (C=N), 163.33 (C=O); ^{29}Si{^{1}H} NMR (CD_2Cl_2): $\delta = -4.15$; MS (EI, 70 eV): *m*/*z* (%): 536 (14) $[M]^+$, 493 (46) $[M - i\mathrm{Pr}]^+$, 479 (2), 398 (5), 367 (9), 355 (100), 269 (12), 252 (13), 225 (15); $C_{24}H_{40}N_4O_6Si_2$ (536.77): calcd C 53.71, H 7.52, N 10.45; found C 53.33, H 7.55, N 10.33.

Data for **(2d)$_{3\text{–}5}$**: M.p.: 76–77 °C; IR (KBr): $\tilde{\nu} = 2952$, 2868, 1720 (C=O), 1242, 1091 cm^{-1}; ^{1}H NMR (200.13 MHz, CD_2Cl_2): $\delta = 1.05$ (pseudo-t, $J = 7.3$ Hz, 12*n*H, CH*Me*), 1.50 (sept, $J = 7.3$ Hz, 2*n*H, SiCH), 3.86 (s, 3*n*H, OMe), 5.16 (s, 2*n*H, CH_2), 7.80 (s, 1H, =CH); ^{13}C NMR (50.32 MHz, C_6D_6): $\delta = 12.57$ (SiCH), 16.74 (CH*Me*), 16.93 (CH*Me*), 51.22 (OMe), 59.15 (CH_2), 125.50 (CH_2*C*=), 135.69 (NCH=), 144.42 (C=N), 163.58 (C=O); MS (FD): *m*/*z* (%): 1355 (1) $[M_5+CH_3]^+$, 1341 (3) $[M_5\mathrm{H}]^+$, 1087 (1) $[M_4+CH_3]^+$, 1073 (8) $[M_4\mathrm{H}]^+$, 819 (11) $[M_3+CH_3]^+$, 805 (100) $[M_3\mathrm{H}]^+$, 761 (22) $[M_3 - i\mathrm{Pr}]^+$, 551 (11) $[M_2+CH_3]^+$, 537 (30) $[M_2\mathrm{H}]^+$, 511 (26), 493 (15) $[M_2 - i\mathrm{Pr}]^+$, 381 (6) $[M_3 - i\mathrm{Pr}]^{2+}$, 359 (14) $[M_3 - 2i\mathrm{Pr}]^{2+}$; $(C_{12}H_{20}N_2O_3Si)_n$ ($n = 268.39$): calcd C 53.68, H 7.51, N 10.43; found C 53.74, H 7.62, N 10.09.

Cyclooligomerization of 1e. Dimethyl 2,2,9,9-tetraisopropyl-15,16-dimethyl-3,10-dioxa-1,7,8,14-tetraaza-2,9-disilatricyclo-[10.2.1.1^{5,8}]hexadeca-5(16),6,12(15),13-tetraene-6,13-dicarboxylate (2e)$_2$, cyclotrimer (2e)$_3$, tetramethyl 2,2,9,9,16,16,23,23-octaisopropyl-29,30,31,32-tetramethyl-3,10,17,24-tetraoxa-1,7,8,14,15,21,22,28-octaaza-2,9,16,23-tetra-silapentacyclo-[24.2.1.1^{5,8}.1^{12,15}.1^{19,22}]dotriaconta-5(32),6,12(31),13,19(30),20,26(29),27-octaene-6,13,20,27-tetracarboxylate (2e)$_4$, and cyclopentamer (2e)$_5$: Diazoacetate **1e**[12] (1.70 g, 6.0 mmol) in mesitylene (30 mL) was heated in an oil bath at 162 °C. After 1 h at reflux, the solvent was removed at 80 °C at 20 mbar (final traces removed at 0.01 mbar). Pentane (5 mL) was added to the residual light-brown oil. The white precipitate which formed after some time was separated by centrifugation and washed with cold pentane, yielding a mixture of cyclooligomers **(2e)$_n$** (68 mg, 4%) ($n = 2$–5 detected by FD-MS). Recrystallization of this mixture as described above for the isolation of **(2b)$_3$** gave a few transparent colorless crystals of **(2e)$_4$** suitable for X-ray diffraction analysis.

Data of **(2e)$_4$**: M.p.: 243 °C; IR (KBr): $\tilde{\nu} = 1718$ (C=O), 1089, 1063 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 1.02$ (d, $J = 7.5$ Hz, 24H, CH*Me*), 1.04 (d, $J = 7.5$ Hz, 24H, CH*Me*), 1.56 (sept, $J = 7.5$ Hz, 6H, SiCH), 2.20 (s, 12H, CMe_2), 3.87 (s, 12H, OMe), 5.14 (s, 8H, OCH_2); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 10.66$ (pyrazole-Me), 12.66 (SiCH), 16.33/16.56 (CH*Me*), 51.66 (OMe), 55.94 (CH_2), 119.77 (CH_2*C*=), 143.74 (=*C*Me), 147.94 (C=N), 163.67 (C=O); ^{29}Si{^{1}H} NMR (CD_2Cl_2): $\delta = 3.11$; MS (FD, 11 kV, centroid data): *m*/*z*: 1129.3 (100) $[M\mathrm{H}]^+$, 1085.5 (45) $[M - i\mathrm{Pr}]^+$, 861.3 (29) $[M_3+CH_3]^+$; $C_{52}H_{88}N_8O_{12}Si_4$ (1129.66): calcd C 55.29, H 7.85, N 9.92; found C 55.50, H 7.77, N 9.91.

Data of **(2e)$_n$** ($n = 2$–5): M.p.: 174 °C; IR (KBr): $\tilde{\nu} = 1720$ (C=O), 1254, 1089, 1064 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 1.02$ (d, $J = 7.5$ Hz, 6*n*H, CH*Me*), 1.04 (d, $J = 7.5$ Hz, 6*n*H, CH*Me*), 1.56 (sept, $J = 7.5$ Hz, 2*n*H, SiCH), 2.20 (s, 3*n*H, pyrazole-Me), 3.88 (s, 3*n*H, OMe), 5.14 (s, 2*n*H, OCH_2); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 10.65$ (pyrazole-Me), 12.66 (SiCH), 16.33 (CH*Me*), 16.55 (CH*Me*), 51.65 (OMe), 55.94 (CH_2), 119.76 (CH_2*C*=), 143.74 (=*C*Me), 147.92 (C=N), 163.66 (C=O); MS (FD): *m*/*z* (%): 1426 (3) $[M_5+CH_3]^+$, 1412 (2) $[M_5\mathrm{H}]^+$, 1129 (100) $[M_4\mathrm{H}]^+$, 1085 (24) $[M_4 - i\mathrm{Pr}]^+$, 861 (11) $[M_3+CH_3]^+$, 847 (8) $[M_3\mathrm{H}]^+$, 622 (14), 579 (5) $[M_2+CH_3]^+$, 565 (41) $[M_2\mathrm{H}]^+$, 521 (12) $[M_2 - i\mathrm{Pr}]^+$; $(C_{13}H_{22}N_2O_3Si)_n$ ($n = 282.41$): calcd C 55.29, H 7.85, N 9.92; found C 54.74, H 7.94, N 9.70.

Solvolyses of cyclodimers $(2)_2$ and cycloligomers $(2)_n$

Methyl 4-{1-[(hydroxy-diisopropylsilyl)oxy]-1-methylethyl}-1*H*-3(5)-pyrazolecarboxylate (9b): Water (1 mL) was added to a suspension of cyclodimer **(2b)$_2$** (296 mg, 0.005 mmol) or cyclooligomer mixture **(2b)$_n$** ($n > 2$) (296 mg) in acetonitrile (20 mL). After heating at reflux temperature for 2 h, the colorless solution was cooled at rt, diluted with dichloromethane (10 mL), and Na_2SO_4 was added to remove the water. Filtration and removal of the solvents afforded **9b** as a very viscous white mass (314 mg, 100 %); IR (film): $\tilde{\nu} = 3700-3100$ [3159] (br, OH, NH), 2945 (br), 1765 (C=O), 1462, 1268, 1171, 1065 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta =$ 1.01 (sept, $J = 6.3$ Hz, 2H, SiCH), 1.07 (d, $J = 6.7$ Hz, 12H, CH*Me*), 1.79 (s, 6H, CMe_2), 3.92 (s, 3H, OMe), 7.73 (s, 1H, =CH), 13.47 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$, 58 °C, 125.77 MHz, signal assignment by gradient-selected HMBC and C,H-correlation spectra, spectra recorded at 58, [30, −20] °C): $\delta = 13.58$ [13.81, 13.58] (SiCH), 17.31 [17.48, 17.35] (CH*Me*), 17.48 [17.55, 17.49] (CH*Me*), 30.37 [30.89/30.36] (CMe_2), 51.65 [51.78, 51.74] (OMe), 73.10 [73.16, 73.06] (CMe_2), 132.93 [131.94, 128.30 br] (=CH), 133.95 [134.92, 136.65 br] (C-3(5)), 135.00 [134.92/134.97] (C-4), 161.72 [162.21/162.54 br] (C=O); ^{29}Si{^{1}H} NMR ($CDCl_3$): $\delta = -11.99$; MS (FD): *m*/*z* (%): 629 (20) $[2M + H]^+$, 315 (43) $[MH]^+$, 297 (6) $[MH - H_2O]^+$, 271 (100) $[M - i\mathrm{Pr}]^+$, 167 (14) $[M - \mathrm{OSi}i\mathrm{Pr}_2]^+$, 148 (5) $[i\mathrm{Pr}_2\mathrm{Si(OH)}_2]^+$, 131 (4) $[\mathrm{HOSi}i\mathrm{Pr}_2]^+$; $C_{14}H_{26}N_2O_4Si$ (314.18): calcd C 53.53, H 8.34, N 8.92; found C 52.59, H 8.25, N 8.59 [calcd for hemihydrate: C 52.03, H 8.42, N 8.67].

Methyl 4-{1-[hydroxy-diisopropylsilyl)oxy]cyclohexyl}-1*H*-3(5)-pyrazolecarboxylate (9c): The mixture of cyclooligomers **(2c)$_n$** ($n > 2$) (74 mg) was hydrolyzed in acetonitrile/water (20:0.1 mL) at 82 °C for 1 h. Workup as described for **9b** yielded an oil from which a white sticky solid was obtained after addition of ether or pentane (70 mg, 91 %); m.p.: 103–105 °C; IR (KBr): $\tilde{\nu} = 3422$ (br), 3163 (br), 2939 , 2864, 1721 (C=O) cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 0.80$ (sept, 2H, $J = 7.5$ Hz, SiCH), 0.96 (d, 6H, $J = 7.5$ Hz, CH*Me*), 0.97 (d, 6H, $J = 7.5$ Hz, CH*Me*), 1.33 (m, 1H, 4′-H), 1.45 (m, 2H, 3′-H), 1.55 (m, 1H, 4′-H), 1.79 (m, 2H, 3′-H), 2.01 (m, 2H, 2′-H), 2.18 (m, 2H, 2′-H), 3.92 (s, 3H, OMe), 7.65 (s, 1H, CH=); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 13.60$ (SiCH), 17.32 (CH*Me*), 17.47 (CH*Me*), 22.59 (CH_2-3′), 25.53 (CH_2-4′), 38.89 (CH_2-2′), 52.27 (OMe), 71.55 (ipso-C), 130.66 (C-4), 131.79 (br, =CH), 137.09 (br, C-3(5)), 163.51 (C=O); ^{29}Si{^{1}H} NMR ($CDCl_3$): $\delta = -13.31$; $C_{17}H_{30}N_2O_4Si$ (354.52): calcd C 57.60, H 8.53, N 7.90; found C 57.41, H 8.43, N 7.71.

Methyl 4-{[(hydroxy-diisopropylsilyl)oxy]methyl}-1*H*-3(5)-pyrazolecarboxylate (9d): Cyclodimer **(2d)$_2$** (268 mg, 5 mmol) or the mixture of cycloligomers **(2d)$_{3-5}$** (268 mg) was hydrolyzed as described for **9b**. Workup gave a yellow oil, from which a white precipitate was obtained after addition of pentane (10 mL). Centrifugation and washing of the solid with cold pentane afforded **7c** (258 mg, 90 %) as a white microcrystalline solid; m.p.: 92–94 °C; IR (KBr): $\tilde{\nu} = 3407$ (br), 3269 (br), 1723, 1155, 1085 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 1.06/1.07$ (14H, C*HMe*$_2$), 3.90 (s, 3H, OMe), 5.03 (s, 2H, CH_2), 7.72 (s, 1H, =CH); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 12.41$ (SiCH), 16.99 (CH*Me*), 17.04 (CH*Me*), 51.77 (OMe), 56.56 (CH_2), 125.38 (CH_2C=), 131.08 (=CH), 136.87 (C-3(5)), 162.66 (C=O); ^{29}Si{^{1}H} NMR ($CDCl_3$): $\delta = -5.61$; MS (FD): *m*/*z* (%): 573 (50) $[2M+H]^+$, 287 (100) $[MH]^+$, 269 (13), 243 (89) $[M - i\mathrm{Pr}]^+$, 139 (8); $C_{12}H_{22}N_2O_4Si$ (286.13): calcd C 50.33, H 7.75, N 9.79; found C 50.16, H 7.87, N 9.90.

Methyl 4-{1-[(diisopropyl-methoxysilyl)oxy]-1-methylethyl}-1*H*-3(5)-pyrazolecarboxylate (10b): The mixture of cyclooligomers **(2b)$_{2-5}$** (320 mg) was suspended in methanol (20 mL) and heated at reflux for 1 h. Evaporation of the solvent left **10b** as a colorless oil, which crystallized at 4 °C (354 mg, 100 %); m.p.: 78 °C; IR (film): $\tilde{\nu} = 3147$ (br, NH), 2948 (br), 2866, 1730, 1461, 1264, 1171 cm^{-1}; ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 1.11$ (s, 14H, C*HMe*$_2$), 1.84 (s, 6H, CMe_2), 3.59 (s, 3H, SiOMe), 3.98 (s, 3H, COMe), 7.86 (s, 1H, =CH), 13.96 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$, 50.32 MHz, signal assignment by gradient-selected HMBC and C,H-correlation spectra): $\delta =$ 13.20 (SiCH), 17.52 (CH*Me*), 17.64 (CH*Me*), 30.42 (CMe_2), 50.98 (OMe), 51.72 (COMe), 73.42 (CMe_2), 129.71 (=CH), 134.77 (C-4), 136.14 (C-3(5)), 162.58 (C=O); ^{29}Si{^{1}H} NMR ($CDCl_3$): $\delta = -14.5$; $C_{15}H_{28}N_2O_4Si$ (316.48): calcd C 54.85, H 8.59, N 8.53; C 54.96, H 8.41, N 8.60.

Methyl 4-{[(diisopropyl-methoxysilyl)oxy]methyl}-1*H*-3(5)-pyrazolecarboxylate (10d): Reaction of a mixture of cyclooligomers **(2d)$_{2-5}$** (536 mg) with methanol as described above for **10b** gave **10d** as a white amorphous solid (515 mg, 86 %); m.p.: 67–70 °C; IR (KBr): $\tilde{\nu} = 3151$ (br, NH), 2945, 2866, 1730, 1086 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 1.09$ (s, 14H, C*HMe*$_2$), 3.57 (s, 3H, SiOMe) 3.94 (s, 3H, COMe), 5.08 (s, 2H, CH_2), 7.76 (s, 1H, =CH); ^{13}C NMR (50.33 MHz, $CDCl_3$): $\delta = 11.79$ (SiCH), 17.19 (CH*Me*), 17.73 (CH*Me*), 50.90 (SiOMe), 51.6 (CO*Me*), 57.39 (CH_2), 125.43 (=CCH_2), 129.97 (=CH), 137.18 (C-3(5)), 162.85 (C=O); $C_{13}H_{22}N_2O_4Si$ (300.43): calcd C 51.97, H 8.05, N 9.02; C 52.27, H 8.01, N 8.56.

4-(1-Hydroxy-1-methylethyl)-1*H*-3(5)-pyrazolecarboxylate (11b): The solution of **9b** (385 mg, 1.22 mmol), 18-crown-6 (95 mg, 0.36 mmol), and potassium fluoride (21 mg, 0.36 mmol) in dichloromethane (20 mL) was stirred for 1 h. The white precipitate was isolated by centrifugation and washed with dichloromethane, yielding **11b** as a white solid (202 mg, 90 %); m.p.: 150–152 °C; IR (KBr): $\tilde{\nu} = 3460$, 3200 (br), 1680, 1290 cm^{-1}; ^{1}H NMR (500.14 MHz, $CDCl_3$): $\delta = 1.62$ (s, 6H, CMe_2), 3.99 (s, 3H, OMe), 5.56 (br s, 1H), 7.48 (s, 1H, =CH), 12.98 (br s, 1H, NH); ^{13}C-NMR (50.32 MHz, $CDCl_3$): $\delta = 30.15$ (Me), 52.53 (OMe), 67.33 (CMe_2), 128.37 (CH=), 133.97 (C-4), 136.90 (C-3(5)), 164.45 (C=O); MS (EI, 70 eV): *m*/*z* (%) = 169 (76) $[M - \mathrm{Me}]^+$, 154 (5) $[M - 2\mathrm{Me}]^+$, 139 (15), 137 (100) $[M - \mathrm{Me} - \mathrm{HOMe}]^+$, 135 (6), 119 (7), 95 (10), 86 (16); $C_8H_{12}N_2O_3$ (184.19): calcd C 52.17, H 6.57, N 15.21; C 52.05, H 6.66, N 14.83.

Methyl 4-hydroxymethyl-1*H*-3(5)-pyrazolecarboylate (11d): a) The solution of pyrazole **9d** (400 mg, 1.4 mmol) in chloroform (20 mL) containing acetic acid (0.5 mL) was kept at reflux for 24 h. Column chromatography [silica gel (50 g), elution with ethyl acetate] afforded **11d** as a white microcrystalline solid (203 mg, 93 %). b) Treatment of **10d** (103 mg, 0.66 mmol) with potassium fluoride as described for the synthesis of **11b** yielded **11d** (46 mg, 82 %); m.p.: 106 °C; IR (KBr): $\tilde{\nu} = 3420$ (br, OH), 3215 (br, NH), 2952, 1724, 1703, 1461, 1367, 1248, 1041 cm^{-1}; ^{1}H NMR (200.13 MHz, [D]$_6$acetone): $\delta = 3.84$ (s, 3H, OMe), 4.02 (t, $J = 6.0$ Hz, 1H, OH), 4.73 (d, $J = 5.4$ Hz, 2H, CH_2), 7.72 (s, 1H, =CH), 12.62 (br s, 1H, NH); ^{13}C NMR (125.76 MHz, D_2O): $\delta = 52.33$ (OMe), 54.28 (CH_2), 123.33 (C-4), 131.98 (br, =CH), 138.70 (br, C-3(5)), 164.13 (C=O); MS (EI, 70 eV): *m*/*z* (%): 156 (27) $[M]^+$, 141 (79), 123 (100), 107 (24), 95 (27); $C_6H_8N_2O_3$ (156.14): calcd C 46.16, H 5.16, N 17.94; found C 46.37, H 5.12, N 17.54.

X-ray Crystallographic study: The preparation of single crystals is described above for the individual compounds. Data collection was carried out on a four-circle diffractometer (CAD4, Enraf-Nonius) for **(2b)$_2$** (crystal modification 2) and on an imaging plate diffractometer (IPDS, STOE&-CIE) for **(2b)$_2$** (crystal modification 1), **(2c)$_2$**, **(2b)$_3$**, and **(2e)$_4$**. Graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was used in all cases. The structures were solved by direct methods and refined by full-matrix least-squares methods with the following program packages: MolEn[24] for compound **(2b)$_2$**, modification 2, and SHELXL-93 or SHELXL-97[25] for all others. Molecule plots were obtained with ORTEP-3[26] or PLUTON-93.[27] Relevant crystallographic data and details of the refinement for the five structures are given in Table 5. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134001 **(2b)$_2$**, modification 1, -134060 **(2b)$_2$**, modification 2, -133998 **(2c)$_2$**, -134000 **(2b)$_3$**, -133999 **(2e)$_4$**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Field-desorption mass spectra: The sample was dissolved in dichloromethane, a potential differences of 11 kV between emitter and counter electrode was applied (kinetic electron energy 8 keV), and the source temperature was 50 °C. Peak profile data were obtained by accumulation of ca. 50–100 spectra with a cycle time of 18 s, corresponding to an aquisition time of 15–30 min. During this time, an anode current gradient was applied: 17–21 mA for pure compounds and 15–32 mA for mixtures of cyclooligomers **(2)$_n$**. In order to obtain a semiquantitative estimate of the composition of the mixtures **(2)$_n$**, the sums of the intensities of the peaks associated with each cyclooligomer ($[MH]^+$, $[M+CH_3]^+$, $[M - i\mathrm{Pr}]^+$) were compared.

Centroid data covering masses up to 3000 Da were obtained on a Varian MAT 711 instrument at the Universität Tübingen.

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Table 5. Crystallographic data for compounds **(2b)$_2$**, **(2c)$_2$**, **(2b)$_3$**, and **(2e)$_4$**.

	(2b)$_2$ modification 1[a]	**(2b)$_2$** modification 2[b]	**(2c)$_2$**	**(2b)$_3$**[c]	**(2e)$_4$**
empirical formula	$C_{28}H_{48}N_4O_6Si_2$	$C_{28}H_{48}N_4O_6Si_2$	$C_{34}H_{56}N_4O_6Si_2$	$C_{42}H_{72}N_6O_9Si_3$	$C_{52}H_{88}N_8O_{12}Si_4$
formula weight	592.88	592.88	673.01	889.33	1129.66
temperature [K]	293(2)	293(2)	293(2)	293(2)	293(2)
crystal size [mm]	0.38 × 0.19 × 0.11	0.6 × 0. 6 × 0.45	0.46 × 0.38 × 0.15	0.38 × 0.31 × 0.23	0.38 × 0.27 × 0.15
crystal system	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
space group	*P*bca	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	8.506(1)	9.324(2)	9.909(1)	11.358(2)	7.996(1)
b [Å]	17.940(2)	10.592(3)	13.616(1)	35.214(5)	14.839(1)
c [Å]	42.319(5)	16.142(4)	15.227(2)	13.524(2)	15.424(1)
α [°]	90	90	67.15(1)	90	62.14(1)
β [°]	90	90.01(4)	82.23(1)	111.68(2)	82.28(1)
γ [°]	90	90	84.11(1)	90	81.87(1)
V [Å^3]	6457.6(12)	1594.2(7)	1873.1(3)	5026.6(13)	1596.9(4)
Z	8	2	2	4	1
ρ_{calcd} [g cm^{-3}]	1.220	1.235	1.193	1.175	1.175
$\mu(Mo_{K\alpha})$ [cm^{-1}]	1.54	1.56	1.41	1.49	1.53
θ range [°]	2.27–24.37	2.00–23.00	2.08–26.00	1.72–24.16	2.58–26.08
index ranges	$-9 \le h \le 9$	$-10 \le h \le 10$	$-12 \le h \le 12$	$-12 \le h \le 13$	$-9 \le h \le 9$
	$-20 \le k \le 20$	$0 \le k \le 11$	$-16 \le k \le 16$	$-40 \le k \le 40$	$-18 \le k \le 18$
	$-48 \le l \le 48$	$0 \le l \le 17$	$-18 \le l \le 18$	$-15 \le l \le 15$	$-18 \le l \le 18$
reflections collected	23558	2223	26805	29364	13470
independent reflections (R_{int})	5020 (0.079)	2223 (–)	6848 (0.042)	7559 (0.0523)	5821 (0.058)
completeness of data set [%]	94.9		93.0	94.1	92.1
data/restraints/parameters[d]	5015/0/375	1945/0/259	6848/0/481	7559/0/561	5821/0/355
goodness-of-fit on F^2	0.984		0.902	0.993	0.808
final R indices [$I > 2\sigma(I)$]; $R1$, $wR2$	0.0533, 0.1326	0.045, 0.055	0.0351, 0.0824	0.0495, 0.1268	0.0431, 0.0871
R indices (all data); $R1$, $wR2$	0.0841, 0.1569		0.0567, 0.0875	0.0718, 0.1359	0.0970, 0.0991
largest diff. peak and hole [e Å^{-3}]	0.40, −0.24	0.28, −0.19	0.20, −0.25	0.56, −0.45	0.20, −0.21

[a] Recrystallized from CH_2Cl_2/ether. [b] Recrystallized from ether. [c] Isopropyl groups around C21 and C38 show disorder which could not be resolved, however. [d] Full-matrix least-squares refinement on F^2 values [on F values for **(2b)$_2$**, modification 2].

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