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Synthesis of silicon heterocycles via gas phase cycloaddition of aminomethylsilylenes

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Abstract

Co-thermolytical reactions of 1,1,2,2-tetrakis(dimethylamino)- or tetrakis(isopropylamino)dimethyldisilane **1** or **2** with 2,3-dimethylbuta-1,3-diene, 1,4-diheterodienes, 1-oxa- or 1-azadienes gave Si-functionalized unsaturated silicon heterocycles **3**–**15**. The disilanes act as precursors for intermediate aminosilylenes that undergo regioselective [1 + 4]-cycloadditions with 2,3-dimethylbutadiene and 1,4-diheterodienes, affording silacyclopent-3-enes and diheterosilacyclopent-4-enes, respectively. Reactions with unsaturated ketones and imines gave isomer mixtures of 1-oxa- and 1-aza-2-silacyclopent-4-enes (major) and -3-enes (minor), indicating a stepwise mechanism. Co-thermolysis of **2** with 2,3-dimethylbutadiene, a diimine or iminoketone led to cycloaddition products of the NH functional Me(*i*PrNH)Si, but yields were markedly lower than with **1**.

Keywords: Silicon; Aminomethylsilylene; Gas phase cycloaddition

1. Introduction

Silylenes are highly reactive species, detected by spectroscopic methods and a variety of trapping reactions [1]. They possess a considerable potential in the synthesis of silicon compounds. We are interested in exploring the use of functionally substituted silylenes for an easy access to Si-functionally substituted unsaturated silicon heterocyles. Chloromethylsilylene formed by thermolysis of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane was detected by thermolysis-MS [2] and furnished good yields of chlorosilacyclopentenes by thermolysis in the presence of 1,3-dienes. However, attempts to extend the scope of such gas phase cycloadditions to azadienes and iminoketones failed due to the elimination of ammonium salts and ill-defined consecutive reactions. These problems were not observed in cycloadditions of thermal-generated methoxymethylsilylene with N- or O-containing heterodienes [3,4] and oxatrienes [5]. Also aminosilylenes should be useful and generally applicable synthons, and furnish unsaturated amino-substituted silicon heterocycles. Formation of $HSiNH_2$ by photolysis of H_3SiN_3 at 254 nm was detected by matrix IR and UV studies [6], but the reactivity of monoaminosilylenes was sparingly investigated [4,7] and may differ from alkoxysilylenes by higher π-stabilization and nucleophilicity. According to isodesmic calculations the gain in energy is 15.0 and 22.3 kcal mol^{-1} for hydroxy- and aminosilylene, respectively [8,9]. The largest stabilization was determined for diaminosilylene (37.8 kcal mol^{-1}) [10]. The only known trapping reactions of acyclic diaminosilylenes, produced by reduction of diaminodichlorosilanes with potassium, are insertion reactions into the C–H bond of toluene and benzene [11,12]. Some recently isolated cyclic unsaturated diaminosilylenes obeying the Hückel rule exhibit a distinguished reactivity [13–15]. In this paper we report on co-thermolyses of amino-substituted disilanes with 2,3-dimethylbutadiene, heterodienes or diheterodienes.

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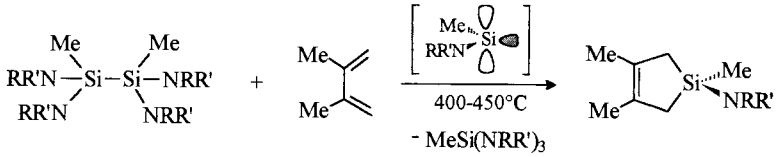
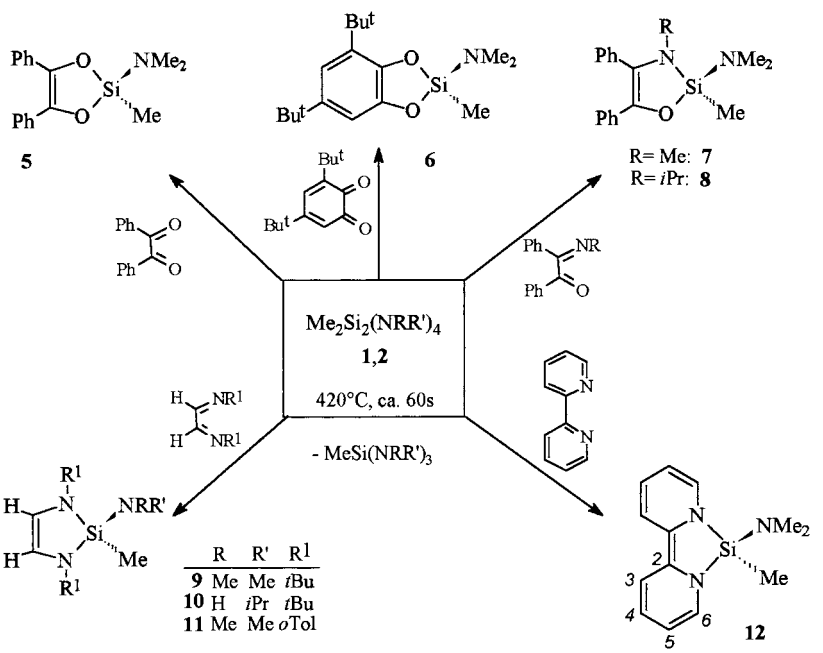
2. Results and discussion

1,2-Dimethyl-1,1,2,2-tetrakis(dimethylamino)disilane **1** and 1,2-dimethyl-1,1,2,2-tetrakis(isopropylamino)disilane **2**, in contrast to more bulky amino-substituted derivatives [16], were conveniently available from $Me_2Si_2Cl_4$ and the respective amine. Co-thermolysis of **1** or **2** with 2,3-dimethylbutadiene at 420–450°C for ca. 50–60 s provided the aminosilacyclopent-3-enes **3** or **4** and $MeSi(NRR')_3$ (see below). The yield of **3** was fairly high, while **4** was formed in a lower amount due probably by competing reactions of the intermediate NH functional silylene.



1 (R = R' = Me)
2 (R = H, R' = *i*Pr)

3 (R = R' = Me)
4 (R = H, R' = *i*Pr)



The scope of this reaction is not limited to dienes. It was found that co-thermolyses of **1** or **2** with some α-diketones, with α-iminoketones or α-diimines furnished in a formally analogous way 1,3-dioxa-, 1,3-oxaza- or 1,3-diazasilacyclopent-4-enes **5**–**12** (eq. 2 below). The co-thermolyses of **1** or **2** and α,β-unsaturated ketones or imines proceeded less selectively and produced isomer mixtures of 1-oxa- or 1-aza-2-silacyclopent-4- and -3-enes **13**–**15** (eq. 3 below). However, in all these reactions and despite of the different functional groups (C=C, C=O, C=N) in the trapping reagents, we observed addition of aminomethylsilylenes. This gives evidence of unsymmetrical cleavage of the disilanes by migration of an amino group and [1 + 4]-cycloaddition reactions of the resulting short-lived aminosilylenes to the diene, diheterodiene or heterodiene. Direct reactions between disilanes and the trapping agents should cause stronger differences. The lower selectivity in conversions with unsaturated ketones or imines is in accordance with a nonconcerted, stepwise cycloaddition. In the following, the results shall be discussed in more detail.

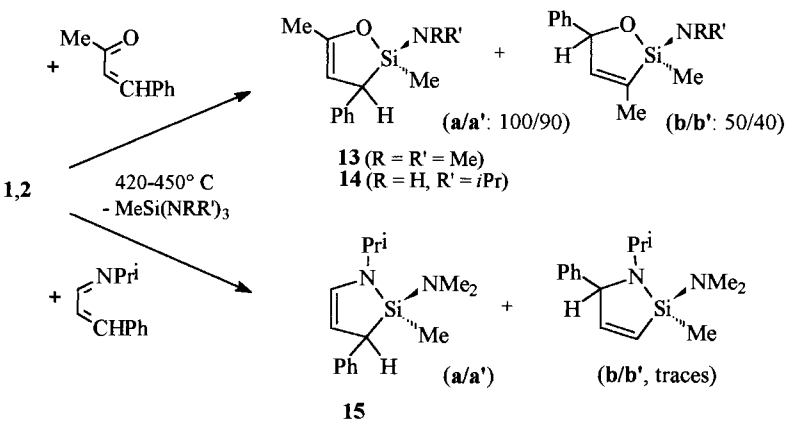
The use of diketones is restricted to less reactive moieties like benzil or 3,5-di-*tert*-butyl-*o*-benzoquinone, but even in these cases yields of **5** and **6** are low. Attempts to react **1** with glyoxal or diacetyl failed to give defined products. However, the reaction of the silicon(II) species with α-iminoketones possessing only one C=O group took place in a more selective manner and allowed the isolation of **7** and **8** in moderate to good yields. Similarly, co-thermolyses of **1** with α-diimines and α,α'-dipyridyl provided with high selectivity the silylene cycloaddition products **9**–**12** and thus offer a convenient access to functionally substituted deriva-

Table 1
Characteristic ^{1}H-NMR chemical shifts of oxa- and azasilacyclopentenes **13**–**15**[a], $\delta(C_6D_6$, TMS), (J_{HH} [Hz])

No.	H(3) or R^1(3)[b]	H(4) or R^1(4)[c]	H(5) or R^1(5)	SiMe	NMe_2
13aa′	2.99 (m), 3.16 (m)	4.90 (m), 4.98 (m)	1.96 (d), 1.95 (d)	−0.15	2.45
	($J_{34} \sim J_{3Me}$ 2–3)	(ca. 3/1.2, ca. 3/1.2)	(2.1, 1.8)	0.44	2.13
14aa′	3.15 (m), 3.01 (m)	4.90 (m)	1.94 (d), 1.95 (d)	0.38	[d]
	($J_{34} \sim J_{3Me}$ 2–3)		(0.9, 0.9)	−0.15	
13bb′	1.83 (d), 1.85 (d)	6.55 (m), 6.59 (m)	5.45 (m), 5.58 (m)	0.33	2.60
	(1.5, 1.7)	(ca. 1.9, 1.9)	(ca. 1.6, 1.6)	0.39	2.56
14bb′	1.87 (d), 1.88 (d)	6.40 (m), 6.53 (m)	5.46 (m), 5.57 (m)	0.24	[d]
	(1.8, 1.8)	(ca. 1.6, 1.6)	(ca. 1.9, 1.9)	0.30	
15aa′[e]	2.97 (dd), 3.10 (dd)	4.82 (dd), 4.75 (dd)	6.44 (dd), 6.41 (dd)	0.43	2.53
	(2.5/2.4, 2.8/1.8)	(5.5/2.5, ca. 5.4/3)	(5.5/2.4, 5.4/1.7)	−0.16	2.09

[a] Values are first-order approximations; phenyl protons $\delta = 7.0$–7.4.
[b] $J_{H_3H_4}$ and $J_{H_3H_5}$ or $J_{H_3Me_5}$.
[c] $J_{H_3H_4}$ and $J_{H_4H_5}$ or $J_{H_4Me_5}$.
[d] **14aa′**: δ 0.5 (br, NH), 3.20 (m, CH), 0.66 (d)/1.17 (d), 0.81 (d)/1.14 (d) (CH*Me*$_{AB}$, $J_{HH} = 6.3$ Hz). **14bb′**: δ 0.5 (br, NH), 2.80 (m, CH), ca. 1.10 (superimposed).
[e] **15aa′**: δ 3.35, 3.32 (m, CH), 1.18, 1.14 (CH*Me*$_{AB}$, $J_{HH} = 6.6$ Hz).

tives of 1,3-diazasiloles [17] or dipyrido[a]-1,3-diazasiloles [18,19]. Formally, the reaction may be considered to be a reduction of diketo compounds by silicon(II), the products being silyl-protected reductone-like compounds. Accordingly, they possess reducing properties. This holds especially for the deep-violet dipyrido[a]-diazasilole **12**, which, as a dihydrodipyridyl derivative, is extremely air-sensitive and oxidized instantaneously with color change to yellow. Structure elucidation based on NMR spectra is unequivocal. An alternative silylene–dipyridyl complex is apparently less stable.



Co-thermolyses of **1** or **2** with 4-phenylbut-3-ene-2-on furnished mixtures of double bond isomers, 1-oxa-2-sila-cyclopent-4-enes and 1-oxa-2-silacyclopent-3-enes, which due to two centers of asymmetry at silicon and C(5) or C(3) each consist of two pairs of diastereoisomers. **13aa′** and **14aa′** are preferred to the respective **bb′** isomers. Reaction of **1** and *N*-isopropyl cinnamaldimine gave rise to two pairs of diastereoisomers of 1-aza-2-sila-cyclopent-4-enes **15aa′**. The content of isomeric 1-aza-2-sila-cyclopent-3-enes **15bb′** was very low, only traces were detected by characteristic NMR signals. The isomer mixtures distilled in a narrow temperature range and could not be separated. Structure elucidation was based on ^{1}H- and ^{13}C-NMR studies (Tables 1 and 2), 2D and DEPT experiments ascertain the assignment of ring CH signals. Chemical shifts of SiMe and NMe_2 groups of the isomers in ^{1}H- and ^{13}C-NMR as well as the $\delta(^{29}Si)$-values are assigned according to the relative intensities.

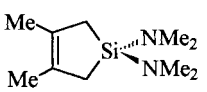
A comparison with respect to the influence of substituents at silicon showed no marked difference between reactions of **1a** and of the analogous 1,2-dimethyl-1,1,2,2-tetramethoxydisilane [3,20], which may be attributed to a general high reactivity of unsymmetrical silylenes MeSiX. In both cases (X = NMe_2, OMe), the cycloaddition of the intermediate heterosubstituted silylene was faster than alternative reactions, such as insertion into Si–N or Si–O bonds [21,22], leading to tri- or oligosilanes. The latter occurred as side reactions

Table 2
^{13}C-NMR chemical shifts of the oxa- and azasilacyclopentenes **13**–**15**[a], δ(C_6D_6, TMS)

No.	C(3)	C(4)	C(5)	CMe	SiMe	NRR′	Ph(*i*)	*o*	*m*	*p*
13aa′	33.7	102.0	*155.7*	18.1	−7.0	36.9	*142.5*	126.3	128.3	124.3
	34.9	102.3	*155.6*	18.0	−3.4	37.4	*143.2*	126.4	127.9	124.1
14aa′	34.7	102.3	156.3	18.2	−6.2	42.8;27.6	*142.5*	126.5	128.1	124.3
	34.3	102.0	155.8	18.2	−3.3	43.2;27.5	*143.2*	126.4	128.4	124.3
13bb′	*134.0*	147.9	79.9	15.5	−4.5	37.2	*142.8*	126.3	128.2	127.1
	133.6	147.7	81.1	15.4	−4.0	37.0		125.7	128.2	127.0
14bb′	*134.5*	147.7	79.8	15.6	−3.9	42.6;26.6	*143.0*	125.71	128.2	127.0
	133.9	147.8	80.8	15.5	−3.3	42.0;27.8	*142.9*	125.66	128.3	
15aa′[b]	36.2	99.5	140.3	—	−4.9	37.4	*144.5*	126.5	127.6	123.6
	35.2	100.3	141.4		−1.2	38.1	*143.6*	126.65	127.7	123.7

[a] Chemical shifts of quarternary carbon atoms in italics.
[b] **15aa′**: δ 47.2, 23.5/23.6 [NCH(CH_3)$_2$].

as seen by the higher yield of $MeSi(NMe_2)_3$ and MeSi(OMe), respectively, compared with the yield of the silylene cycloaddition products [23] and by increasing impurities with oligosilanes if a larger excess of disilane was used to achieve complete conversion of hetero- or diheterodienes. In case of the NH functional **1b**, the side reactions became more significant, caused low yields of cycloaddition products of $MeSiNHPr^i$ and purification problems. Preliminary attempts to use the above reaction type for the synthesis of 1,1-diaminosilacyclopentenes failed. Thus, co-thermolysis of $Si_2(NMe_2)_6$ [24] with 2,3-dimethylbutadiene at 400°C or at 450°C (ca. 60 s) provided a mixture that exhibited ^{29}Si-NMR signals at 2.7, −16.5 and −33.7 (br, st) besides those of unreacted $Si_2(NMe_2)_6$ (δ^{29}Si −25.1) but none for 1,1-bis(dimethylamino)-3,4-dimethylsilacyclopent-3-ene **16** (δ^{29}Si 9.5). Also co-thermolysis of the sterically less hindered Me_3Si–Si(pip)$_3$ (pip = piperidyl) [7] with 2,3-dimethylbutadiene at 480°C (ca. 60 s) did not proceed in the above fashion. The crude reaction mixture revealed ^{29}Si-NMR signals at δ −33.4, 4.1, 10.9, −1.2 (piperidyltrimethylsilane [25]) and signals of unreacted disilane. The formation of silacyclopentene **17** could not unambiguously be detected. Further studies are necessary to establish whether these results are due to the different reactivity of the strongly π-stabilized and symmetrical $Si(NMe_2)_2$ or alternative decomposition routes of the disilanes. Reference samples of **16** (δ^{29}Si 9.5) and **17** (δ^{29}Si 3.1) were prepared by aminolysis of the respective chlorosilanes.



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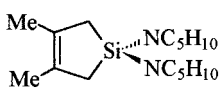

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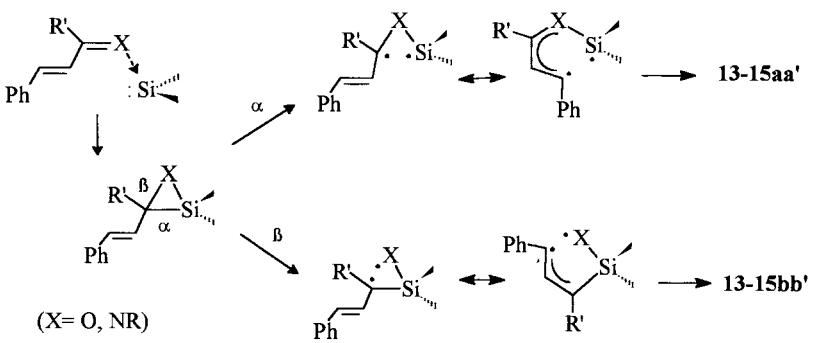
3. Competition experiments

A stepwise mechanism was proposed for cycloadditions of dimethylsilylene to substituted dienes to account for the formation of silacyclopentene isomers [26]. In contrast, the stable diaminosilylene 1,3-di-*t*-butyl-1,3,2λ^2-diazasilole was found to add stereoselectively to *trans*-1,4-diphenylbuta-1,3-diene and seems to react in a concerted way [27]. As for the above reactions of monoaminosilylenes with unsaturated ketones or imines, the occurrence of two double bond isomers, 1-oxa- or 1-aza-2-silacyclopent-4-enes and -3-enes, indicates a stepwise cycloaddition. Competition experiments were carried out to get hints for the primary reaction sites. Co-pyrolysis of **1** with equimolar amounts of 2,3-dimethylbutadiene and PhCH=CH–C(Me)=O at 420°C (ca. 60 s) gave mainly **13aa′** and some **13bb′** besides $MeSi(NMe_2)_3$ and little **3**. The analogous reaction with 2,3-dimethylbutadiene and PhCH=CH–CH=N−*i*Pr revealed also a preferred cycloaddition to the heterodiene, but the content of **3** relative to **15aa′** was markedly higher, indicating a slower relative reaction rate of the unsaturated imine compared with the unsaturated ketone (Table 3).

The results point out that the reactivity is increased in electron-poor (hetero)dienes and that a priority order C=O > C=N > C=C for the primary attack of the silylene is probable. Like for silacyclopentenes [26], the occurrence of two isomers of 1-oxa- and 1-azasilacyclopentenes may be explained by the intermediacy of three-membered rings that undergo a ring-opening/ring-closure isomerization with rupture of the Si–C or C–X bond (X = O, N) (eq. 4 below). Experimental evidence for [1 + 2]-cycloadditions of silylenes to carbonyl compounds succeeded by isolation and solid-state structural analysis of a sterically protected oxasilirane that was formed by initial attack of dimesitylsilylene to the carbonyl oxygen of 1,1,3,3-tetramethyl-2-indanone [28].

Table 3
^{29}Si chemical shifts and relative intensities of ^{1}H(SiMe) signals of crude products in competing co-thermolyses

1 + DMBD + PhCH=CHC(Me)=O			1 + DMBD + PhCH=CHCH=N*i*Pr		
δ(^{29}Si)	Assignment	Rel. int. (%) ^{1}H(SiMe)	δ(^{29}Si)	Assignment	Rel. int. (%) ^{1}H(SiMe)
−16.0	$MeSi(NMe_2)_3$	51	−15.9	$MeSi(NMe_2)_3$	45
−7.2	**1**	6	−7.2	**1**	12
5.8	**13b**	8	2.2	**15a**	17
6.5	**13b′**	3	6.4	**15a′**	7
11.5	**13a**	17	17.0	**3**	9
15.8	**13a′**	11	−0.9	unknown	10
17.0	**3**	4			



4. Experimental

4.1. General considerations

Solvents were dried and freshly distilled before use, **1** [4], unsaturated ketones and imines, imino ketones or diimines were prepared according to literature procedures (PhCH=CHC(Me)=O [29]; PhCH=CHCH=NPr^{i} [30]; R^1N=CH–CH=NR^1 (R^1 = *t*Bu, *o*Tol) [31]; *i*PrN=C(Ph)–C(Ph)=O [32]). For **3** see [4]. Pyrolysis and handling of air-sensitive substances were carried out under an argon atmosphere (Schlenk technique) as described earlier [4]. NMR data were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C) and 59.6 MHz (^{29}Si) with tetramethylsilane as reference. $CDCl_3$ was used as solvent unless indicated otherwise. Assigment numbers of atoms follow the nomenclature except for **12**, where they are given in eq. 2 above. MS spectra (EI, 70 eV) were recorded on a mass spectrometer AMD40 (Intectra).

4.2. 1,2-Dimethyl-1,1,2,2 tetrakis(isopropylamino)-disilane **2**

A solution of 39.2 g of $Me_2Si_2Cl_4/Me_3Si_2Cl_3$ (0.175 mol) in ether (100 ml) was added slowly to a solution of excess isopropylamine (91.6 g, 1.55 mol) in ether (500 ml) at −40°C. After stirring overnight at r.t. the precipitate was removed and the filtrate distilled to yield 27.7 g (51%) of colorless liquid **2**, b.p. 107–110°C/1.5 torr. ^{1}H-NMR: δ 0.07 (s, sb, $^{2}J_{SiH}$ = 6 Hz, SiMe), 0.57 (d, $^{3}J_{HH}$ = 10.1 Hz, NH), 1.06 and 1.08 (2d, $^{3}J_{HH}$ = 6.3 and 6.4 Hz, CH_3), 3.14 (m, CH). ^{13}C-NMR: δ −0.5 (SiMe), 28.1, 28.2 (C*Me*$_2$), 42.7 (*C*Me$_2$). ^{29}Si-NMR: δ −22.2. MS (FAB in sulfolane): *m*/*z* (%) = 319.7 (37) [M + H$^+$], 304 (25) [M$^+$-Me], 277 (22), 260.2 (33) [M$^+$-C_3H_7NH], 216.6 (24), 201.7 (29) [M$^+$-2C_3H_7NH], 159.9 (65), 102.5 (67), 100.5 (100) [MeSiNPr$^+$], 86.4 (31), 59 (24), 43.3 (26). Anal. calc. for $C_{14}H_{38}N_4Si_2$ (318.66): C 52.77, H 12.02, N 17.58; found C 52.66, H 12.12, N 17.05.

4.3. General procedure of co-pyrolysis

The corresponding disilanes and dienes, heterodienes or diheterodienes were dissolved in benzene. The solution was slowly dropped (ca. 1 drop/5–7 s) onto the upper wall of a nearly vertical arranged pyrolysis tube (length 40 cm, diameter 2.5 cm) which was heated to 420–450°C. The product mixture was collected in a Schlenk tube at the bottom cooled to −20 to −40°C, benzene was removed at reduced pressure and the remainder distilled in vacuo.

4.4. 1-Dimethylamino-1,3,4-trimethylsilacyclopent-3-ene (3)

A solution of 3.8 g (14.5 mmol) of $Me_2Si_2(NMe_2)_4$ and 1.3 g (15.8 mmol) of 2,3-dimethylbutadiene in benzene (5 ml) was co-pyrolyzed at 400°C. Distillation

of the condensate gave 1.0 g (59%) of **3** with b.p. 80–83°C/28 torr. ^{1}H-NMR: δ 0.20 (s, SiMe), 1.14/1.38 (m, $^2J_{AB} = 17$ Hz, CH_2), 1.68 (br, s, C_qMe), 2.44 (s, NMe_2). ^{13}C-NMR: δ −3.1 (SiMe), 19.8 (CH_2), 23.9 (C_q*Me*), 38.5 (NMe_2), 131.1 (C_q). ^{29}Si-NMR: δ 17.1. Anal. calc. for $C_9H_{19}NSi$ (169.38): C 63.82, H 11.33, N 8.27; found (C, incomplete combustion), H 11.17, N 8.45.

4.5. 1-Isopropylamino-1,3,4-trimethylsilacyclopent-3-ene (4)

A solution of 6.8 g (21.3 mmol) of $Me_2Si_2(NHPr^i)_4$ and 1.8 g (21.3 mmol) of 2,3-dimethylbutadiene in benzene (5 ml) was pyrolyzed at 400°C and the condensate distilled to give 1.4 g of a colorless oil, b.p. 67–68°C/12 torr, consisting of 75% **4** and 25% **2**. Separation was achieved by GC. ^{1}H-NMR: δ 0.16 (s, SiMe), 0.45 (br, NH), 1.05 (d, $J = 6.4$ Hz, CH*Me*$_2$), 1.37/1.31 (m, $^2J_{AB} = 18.6$ Hz, CH_2), 1.69 (br, s, C_qMe), 3.08–3.14 (m, C*H*Me$_2$). ^{13}C-NMR: δ −2.3 (SiMe), 19.2 (CH_2), 25.4 (C_q*Me*), 28.0, 42.2 (Me_2CH), 130.8 (C_q). ^{29}Si-NMR: δ 10.2. $C_{10}H_{21}NSi$ (183.37): MS (70 eV): m/z (%) = 183 (27) [M$^+$], 168 (73), 159 (48), 145 (24), 125 (100) [M$^+$-NHPr], 100 (89) [SiMeNHPr$^+$], 85 (24) [SiNHPr$^+$], 59 (42), 44 (36).

4.6. 2-Dimethylamino-4,5-diphenyl-2-methyl-1,3-dioxa-2-silacyclopent-4-ene (5)

Compound **1** (6.5 g, 24.7 mmol) and 3.5 g (16.7 mmol) of benzil, dissolved in benzene (20 ml), were thermolyzed at 420°C, $t_{res.}$ ca. 60 s. Distillation at 131–132°C/0.12 torr gave 1.4 g (28%) **5**. ^{1}H-NMR: δ 0.57 (s, SiMe), 2.63 (s, NMe_2), 7.2–7.5 (m, Ph). ^{13}C-NMR (DEPT): δ −6.2 (SiMe), 36.4 (NMe_2), 127.0, 128.1 (4C-*o*, 4C-*m*), 127.4 (2C-*p*), 133.2 (2C_q-*i*), 137.3 (C_q-4, C_q-5). ^{29}Si-NMR: δ −9.5. MS (35 eV): m/z (%) 297 (100) [M$^+$], 239 (26) [M$^+$-NMe_3], 220 (66) [M$^+$-Ph], 178 (50), 105 (20) [PhCO$^+$]. Anal. calc. for $C_{17}H_{19}NO_2Si$ (297.43): C 68.65, H 6.45, N 4.71; found C 68.23, H 6.73, N 4.86.

4.7. 4,6-Di-t-butyl-2-dimethylamino-2-methylbenzo-1,3-dioxa-2-silacyclopentene (6)

A solution of 5.4 g (20.5 mmol) of **1** and 3.0 g (13.6 mmol) of 3,5-di-*t*-butyl-*o*-benzoquinone in benzene (30 ml) was pyrolyzed at 420°C ($t_{res.}$ ca. 65 s) and the product distilled at 132–136°C/0.3 torr to yield 1.1 g (26%) of **6**, contaminated by a small amount of **1b**. ^{1}H-NMR: δ 0.51 (s, SiMe), 2.45, 2.57 (2s, NMe_{AB}), 1.30, 1.41 (2s, *t*Bu), 6.81, 6.88 (2d, $J = 2.2$ Hz, aryl-H). ^{13}C-NMR: δ −6.4 (SiMe), 37.5, 38.2 (NMe_{AB}), 108.3 (CH-7), 114.4 (CH-5), 134.2 (C_q-3a), 142.8, 143.8 (C_q-4, C_q-6), 148.3 (C_q-7a). ^{29}Si-NMR: δ −7.8. $C_{17}H_{29}NO_2Si$ (307.5): MS (70 eV): m/z (%) = 307 (6) [M$^+$], 306 (24) [M$^+$-1], 305 (100) [M$^+$-2], 263 (11) [M$^+$-NMe_2], 249 (16) [M$^+$-NMe_3].

4.8. 2-Dimethylamino-2,3-dimethyl-4,5-diphenyl-1-oxa-3-aza-2-silacyclopent-4-ene (7)

Compound **1** (4.1 g, 15.6 mmol) and 2.3 g (10.3 mmol) of benzil-*N*-methylimine, dissolved in benzene (20 ml), were pyrolyzed at 420°C ($t_{res.}$ ca. 65 s). Distillation gave 1.4 g (44%) of **7**, b.p. 131–134°C/0.15 torr. ^{1}H-NMR: δ 0.50 (s, SiMe), 2.61 (s, NMe_2), 2.50 (s, NMe), 7.10–7.40 (m, Ph). ^{13}C-NMR (DEPT): δ −5.7 (SiMe), 29.1 (NMe), 36.7 (NMe_2), 123.9, 127.6, 128.7, 130.6 (each 2C-*o*, 2C-*m*), 124.0, 128.1 (C-*p*), 131.5, 132.6, 133.7, 134.8 (C_q-4, 2C_q-*i*, C_q-5). ^{29}Si-NMR: δ −10.4. MS (70 eV): m/z (%) 310 (20) [M$^+$], 266 (5) [M$^+$-NMe_2], 252 (7) [M$^+$-NMe_3], 234 (25), 233 (33) [M$^+$-Ph], 221 (42), 205 (20), 193 (26), 120 (35), 118 (100), 77 (49). Anal. calc. for $C_{18}H_{22}N_2OSi$ (310.5): C 69.64, H 7.14, N 9.02; found C 68.48 (incomplete combustion), H 7.16, N 9.23.

4.9. 2-Dimethylamino-4,5-diphenyl-3-isopropyl-2-methyl-1-oxa-3-aza-2-silacyclopent-4-ene (8)

Compound **1** (9.7 g, 37 mmol) and 6.3 g (25.1 mmol) of benzil-*N*-isopropylimine were dissolved in benzene (20 ml) and pyrolyzed at 420°C ($t_{res.}$ ca. 65 s). 4.7 g (58%) of **8** were obtained at 161–164°C/0.15 torr. ^{1}H-NMR: δ 0.58 (s, SiMe), 1.07 (d, $J = 6.6$ Hz, CH*Me*$_2$), 2.59 (s, NMe_2), 3.28 (h, $J = 6.6$ Hz, C*H*Me$_2$), 7.1–7.4 (m, Ph). ^{13}C-NMR (DEPT): δ −2.4 (SiMe), 23.4, 24.4 (CH*Me*$_2$), 36.5 (NMe_2), 43.9 (*C*HMe$_2$), 123.6, 127.3, 128.5, 130.8 (each 2C-*o*, 2C-*m*), 125.8, 129.4 (C-*p*), 127.6, 131.6, 134.1, 134.7 (C_q-4, 2C_q-*i*, C_q-5). ^{29}Si-NMR: δ −12.9. Anal. calc. for $C_{20}H_{26}N_2OSi$ (338.5): C 70.96, H 7.74; found C 70.32, H 7.46.

4.10. 1,3-Di-t-butyl-2-dimethylamino-2-methyl-1,3-diaza-2-silacyclopentene (9)

A solution of 6.2 g (23.6 mmol) of **1** and 2.7 g (16.1 mmol) of *N*,*N*′-di-*t*-butyl-glyoxaldiimine in benzene (20 ml) was co-pyrolyzed at 420°C ($t_{res.}$ ca. 60 s) and the condensate distilled at 83–84°C/4 torr. Yield 2.8 g (68%) **7b**. ^{1}H-NMR: δ 0.41 (s, SiMe), 1.23 (s, 2CMe_3), 2.41 (s, NMe_2), 5.71 (s, H-4, H-5). ^{13}C-NMR: δ 2.3 (SiMe), 30.5 (C*Me*$_3$), 37.0 (NMe_2), 50.6 (*C*Me$_3$), 111.0 (C-4, C-5). ^{29}Si-NMR: δ −21.2. MS (60 eV): m/z (%) = 256 (100) [M$^+$]. Anal. calc. for $C_{13}H_{29}N_3Si$ (255.5): C 61.12, H 11.44, N 16.45; found (C, incomplete combustion), H 11.15, N 16.17.

4.11. 1,3-Di-t-butyl-2-isopropylamino-2-methyl-1,3-diaza-2-silacyclopentene (10)

A solution of 4.4 g (13.7 mmol) **2** and 1.6 g (9.5 mmol) of *N*,*N*′-di-*t*-butyl-glyoxaldiimine in benzene (20 ml) was pyrolyzed at 420°C and distilled at 101–103°C/5 torr yielding 0.95 g of a mixture of **10** and an oligomeric material with SiMe and $NCHMe_2$ signals. **10**: ^{1}H-NMR: δ 0.32 (s, SiMe), 1.29 (s, CMe_3), ca. 1.06, 3.10 (d, m, $CHMe_2$), 5.68 (s, 4,5-H). ^{13}C-NMR: δ 3.4 (SiMe), 27.0 (CMe_2), 30.7 (CMe_3), 42.6 (C_qMe_3), 51.0 (CMe_2), 110.9 (C-4, C-5). ^{29}Si-NMR: δ −25.7. $C_{14}H_{31}N_3Si$ (269.5): GC-MS (70e V): *m*/*z* (%) 269 (1) [M^+], 255 (100) [M^+-Me], 198 (23), 196 (18) [M^+-NHPrMe], 184 (15), 142 (32), 99 (45), 57 (14).

4.12. 2-Dimethylamino-1,3-di-o-tolyl-2-methyl-1,3-diaza-2-silacyclopentene (11)

Compound **1** (4.3 g, 16.5 mmol) and 2.6 g (11 mmol) of *N*,*N*′-di-*o*-tolyl-glyoxaldiimine, dissolved in benzene (40 ml), were co-pyrolyzed at 420°C ($t_{res.}$ ca. 60 s). Distillation furnished 1.9 g (53%) of **11**, b.p. 164–167°C/3.5 torr. ^{1}H-NMR: δ 0.32 (s, SiMe), 2.37 (s, *o*-Me), 2.55 (s, NMe_2), 5.91 (s, 4-H, 5-H), 6.95 (ddd, *J* ca. 7, 7, 2 Hz, 4′-H), 7.1–7.2 (m, 3H, aryl-H). ^{13}C-NMR (C_6D_6, CH-COSY): δ −3.5 (SiMe), 19.8 (*o*-Me), 38.1 (NMe_2), 118.8 (C-4, C-5), 124.4 (C-4′), 125.8, 127.6 (C-6′, C-5′), 131.2 (C-3′), 133.4 (C_q-2′), 145.5 (C_q-1′). ^{29}Si-NMR: δ −18.6. MS (70 eV): *m*/*z* (%) 323 (100) [M^+], 278 (21) [M^+-NMe_2], 221 (16), 192 (15), 162 (51), 148 (22), 131 (26), 118 (26), 91 (24). Anal. calc. for $C_{19}H_{25}N_3Si$ (323.5): C 70.54, H 7.79, N 12.99; found (C 67.26 incomplete combustion), H 7.87, N 12.84.

4.13. 9-Dimethylamino-9-methyl-9H-pyrido[1′,2′:1,5]-1,3,2-diazasilolo[3,4-a]pyridine (12)

Compound **1** (12.1 g, 46.1 mmol) and 4.8 g (30.8 mmol) of α,α′-dipyridyl were dissolved in benzene (30 ml) and co-pyrolyzed at 420°C. Distillation of the crude material at 87–90°C/0.08 torr gave 3.7 g of **12** contaminated with α,α′-dipyridyl, sublimation at 55–60°C/10^{-5} torr afforded 2.8 g (37%) of dark-violet, extremely air-sensitive solid, m.p. 69–71°C. ^{1}H-NMR (^{1}H^{13}C COSY, C_6D_6): δ 0.11 (s, 3H, SiMe), 2.18 (s, 6H, NMe_2), 5.18 (ddd, 2H, H-5), 5.53 (ddd, 2H, H-4), 6.09 (dt, 2H, H-6), 6.33 (dt, 2H, H-3). ^3J(H-3,H-4) = 9.6 Hz, ^3J(H-4,H-5) = 5.7 Hz, ^3J(H-5,H-6) = 7.2 Hz, ^4J(H-3,H-5) ~ ^5J(H-3,H-6) ca. 1.2 Hz, ^4J(H-4,H-6) ca. 1.1 Hz. ^{13}C-NMR (C_6D_6): δ −5.7 (SiMe), 36.8 (NMe_2), 105.2 (C-5), 114.1 (C-4), 117.4 (C_q-2), 119.6 (C-3), 129.75 (C-6). ^{29}Si-INEPT-NMR (C_6D_6): δ −17.25. MS (EI, 70 eV): *m*/*z* (%) 244.6 (22), 243.5 (100) [M^+], 228.5 (9), 199 (22), 185.3 (46) [dipySiH$^+$], 184.3 (35) [dipySi$^+$], 156.5 (18), 92 (7), 72 (27), 56 (25), 55 (27), 43 (25), 41 (46). Anal. calc. for $C_{13}H_{17}N_3Si$ (243.4): C 64.16, H 7.04, N 17.27; found C 63.38, H 7.02, N 16.97.

4.14. 2,5-Dimethyl-2-dimethylamino-3-phenyl-1-oxa-2-silacyclopent-4-ene (13aa′) and 2,3-dimethyl-2-dimethylamino-5-phenyl-1-oxa-2-silacyclopent-3-ene (13bb′)

Compound **1** (6.9 g, 26.9 mmol) and 2.6 g (17.5 mmol) of PhCH=CHC(Me)=O were dissolved in benzene (20 ml) and co-pyrolyzed at 420°C. Distillative work-up at b.p. 141–144°C/15 torr furnished 2.5 g (61%) of a pale-yellow liquid mixture of two pairs of diastereoisomers **13aa**′ and **13bb**′ with a ratio of ca. 100:90:50:40 (based on int. of ^{1}H signals), slightly contaminated by aminooligosilanes. ^{1}H- and ^{13}C-NMR data in Tables 1 and 2. ^{29}Si-NMR: **13aa**′ δ 15.7, 11.5; **13bb**′ δ 6.4, 5.8. MS (EI, 70 eV): *m*/*z* (%) 233.7 (20) [M^+], 218.6 (6) [M-Me^+], 205.6 (8), 189.4 (15), 188.4 (29) [M-Me_2NH^+], 145.4 (16), 128.3 (21), 91.2 (38), 57 (42), 55 (46), 43 (100), 41(94). Anal. calc. for $C_{13}H_{19}NOSi$ (233.4): C 66.90, H 8.21, N 6.00; found C 67.20, H 8.46, N 6.35.

4.15. 2,5-Dimethyl-2-isopropylamino-3-phenyl-1-oxa-2-silacyclopent-4-ene (14aa′) and 2,3-dimethyl-2-isopropylamino-5-phenyl-1-oxa-2-silacyclopent-3-ene (14bb′)

Compound **2** (4.95g, 15.5 mmol) and 1.5 g (10.5 mmol) of PhCH=CHC(Me)=O were dissolved in benzene (10 ml) and co-pyrolyzed at 450°C. Distillation at 126–139°C/5 torr yielded 1.45 g (55%) of a mixture of two pairs of diastereoisomers **14aa**′ and **14bb**′ (100:75:50:25, based on int. of ^{1}H signals), contaminated by oligosilanes with SiMe and $NCHMe_2$ signals. ^{1}H- and ^{13}C-NMR data in Tables 1 and 2. ^{29}Si-NMR: **14aa**′ δ 8.7, 12.3; **14bb**′ δ 1.5, 2.3.

4.16. 2-Dimethylamino-1-isopropyl-2-methyl-3-phenyl-1-aza-2-silacyclopent-4-ene (15aa′)

A solution of 7.0 g (27.3 mmol) of **1** and 3.1 g (17.8 mmol) of PhCH=CHCH=N*i*Pr in 20 ml of benzene was pyrolyzed at 420°C. Distillative work-up gave at 133–136°C/5 torr 2.9 g (63%) of a diastereoisomer mixture of **15aa**′, slightly contaminated by aminooligosilanes. ^{1}H- and ^{13}C-NMR data in Tables 1 and 2. ^{29}Si-NMR: **15aa**′ δ 2.1, 6.3. MS (FAB in sulfolane): *m*/*z* (%) 262.3 (49), 260.9 (100) [M^+], 245.9 (23), 216.9 (23), 202.9 (43) [M-$Me_2NCH_2^+$], 174.6 (15), 145.6 (19), 131.5 (21), 88.4 (39), 72.3 (42), 43.3 (60). Anal. calc. for $C_{15}H_{24}N_2Si$ (260.5): C 69.17, H 9.29, N 10.76; found (C 64.68, incomplete combustion), H 8.83, N 10.62.

4.17. 1,1-Bis(dimethylamino)-3,4-dimethylsilacyclopent-3-ene (**16**)

Dimethylamine (2.5 g, 55 mmol) dissolved in 15 ml of ether was dropped into a cooled (0°C) solution of 1.5 g (8.3 mmol) of 1,1-dichloro-3,4-dimethylsilacyclopent-3-ene [33] in ether (5 ml) and stirred for 2 h at r.t. Filtration and distillation gave 0.7 g (44%) **16** of b.p. 87–101°C/125 torr. ^{1}H-NMR: δ 1.28/1.29 (m, $J = 1$ Hz, $SiCH_2$), 1.70 (br, s, C_qMe), 2.49 (s, NMe_2). ^{13}C-NMR: δ 19.3 (CH_3), 20.8 (CH_2), 38.0 (NMe_2), 130.3 (C_q). ^{29}Si-NMR: δ 9.3. $C_{10}H_{22}N_2Si$ (198.4).

4.18. 1,1-Dipiperidyl-3,4-dimethylsilacyclopent-3-ene (**17**)

A solution of 5.6 g (65.9 mmol) of dry piperidine in 20 ml of ether was added dropwise to a cooled (0°C) solution of 3.0 g (16.6 mmol) of 1,1-dichloro-3,4-dimethylsilacyclopent-3-ene [33] in ether (5 ml) and stirred for 2 h at r.t. Filtration and distillation furnished 2.7 g (59%) **17** of b.p. 120°C/1 torr. ^{1}H-NMR: δ 1.25 (br, q, $J = 1.2$ Hz, 4H, $SiCH_2$), 1.70 (br, t, $J = 1.2$ Hz, 6H, Me), 1.34–1.41 (m, 8H, β-CH_2), 1.52–1.60 (m, 4H, γ-CH_2), 2.84 (m, ^3J ca. 5.3 Hz, 8H, α-CH_2). ^{13}C-NMR (DEPT 135): δ 19.3 (CH_3), 21.9 ($SiCH_2$), 25.7, 27.7, 46.5 (piperidyl-CH_2), 130.1 (C_q). ^{29}Si-NMR: δ 3.1. $C_{16}H_{30}N_2Si$ (278.5): MS (FAB in sulfolane): m/z (%) 279 (40) [$M + H^+$], 196 (25), 195 (100) [$M-C_5H_{10}NH^+$], 194 (56), 181 (11), 179 (11), 112.6 (56), 111.6 (48) [$M-2C_5H_{10}NH^+$], 84.5 (57), 56.3 (58), 43 (23), 41 (22).

4.19. Competition experiments

A: 43.8 mmol of **1** (11.5 g), 2,3-dimethylbutadiene (3.6 g) and PhCH=CHC(Me)=O (6.4 g) were dissolved in benzene (30 ml) and co-pyrolyzed at 420°C. Benzene was removed and the residue distilled in vacuo to give fractions consisting of $MeSi(NMe_2)_3$ (41–53°C/7 torr, 4.8 g), $MeSi(NMe_2)_3$ and **2** (54–66°C/7 torr, 0.4 g), **1** and **13** (67–124°C/7 torr, 3.15 g), **13** (124–127°C/7 torr, 3.35 g).

B: Each 40 mmol of **1** (10.5 g), 2,3-dimethylbutadiene (3.3 g) and PhCH=CHCH=N*i*Pr (7.0 g) were dissolved in benzene (30 ml) and co-pyrolyzed at 420°C. The condensate was distilled to give fractions containing $MeSi(NMe_2)_3$ (47–48°C/11 torr, 3.3 g), $MeSi(NMe_2)_3$ and **3** (49–60°C/11 torr, 1.5 g), **1** (61–116°C/11 torr, 1.0 g), **1** and **15aa**′ (117–119°C/5 torr, 2.0 g), **15aa**′ (151–154°C/12 torr, 4.5 g). Relative intensities of SiMe(^{1}H)- and ^{29}Si-NMR {[$Cr(acac)_3$], C_6D_6} signals in the crude mixtures of *A* and *B* are in Table 3.

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