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Silicon-Tethered 1,3-Dipolar Cycloaddition Reactions of Unsaturated α-Silyl-α-diazoacetates and Diazoacetic Acid Silyl Esters

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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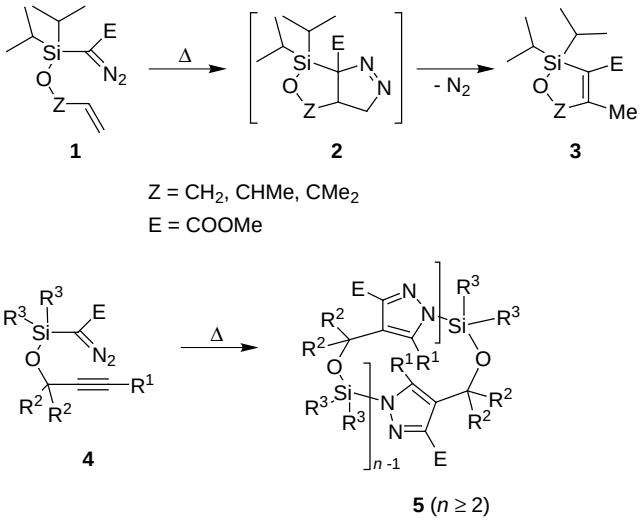
Abstract—Methyl α-[di-*tert*-butyl(propargyloxy)silyl]-α-diazoacetate (**6**) undergoes a thermal intramolecular 1,3-dipolar cycloaddition reaction to form bicyclic pyrazole **8**. Structurally similar, but Si–*i*Pr_2- rather than Si–*t*Bu_2-linked diazoacetates **12a**,**b**, which react thermally to form cyclooligomers by inter-/intramolecular cycloaddition sequences, undergo the intramolecular [3+2] cycloaddition in the presence of silver(I) oxide. Silver pyrazolide **13a** could be isolated and was transformed into NH-pyrazole **14a** under acidic conditions. (Alkenyloxy)silyl and (alkynyloxy)silyl diazoacetates **15a**–**h** were prepared from a silyl bis(triflate), *tert*-butyl diazoacetate, and an unsaturated alcohol. A thermally induced intramolecular [3+2] cycloaddition leading to bicyclic pyrazoles **16** was observed for **15b** and **15c**, while all other diazoacetates **15** underwent unspecific decomposition. Only in the case of **15f**, the tetracyclic 1,5-diazabicyclo[3.3.0]octane derivative **20** could be isolated in 2% yield and was structurally characterized by X-ray diffraction analysis. © 2000 Published by Elsevier Science Ltd.

Introduction

Intramolecular 1,3-dipolar cycloaddition reactions represent an important synthetic strategy for the rapid construction of fused or bridged heterocyclic ring systems.[1–4] Remarkably enough, the involvement of diazo dipoles in reactions of this kind has been reported less frequently than for some other common 1,3-dipoles. The relatively low number of reports dealing with intramolecular dipolar cycloaddition reactions of unsaturated diazoalkanes,[1a,5] unsaturated diazocarbonyl[6] and diazophosphoryl[7] compounds, *N*-allyl carboxamides,[8] and allyl diazophosphinates[9] contrasts with the fact that many unsaturated diazo (especially diazocarbonyl) compounds are known and have been used successfully for transition-metal-catalyzed intramolecular carbenoid reactions, e.g. cyclopropanation[10] and ylide-forming cyclization followed by cycloaddition.[3a,3b,11] We have recently started to investigate the propensity of unsaturated α-silyl-α-diazoacetates to undergo intramolecular [3+2] cycloaddition reactions (Scheme 1). It was found that α-[(alkenyloxy)silyl]-α-diazoacetates **1** are transformed into 2,5-dihydro-1,2-oxasiloles **3** when heated at ca 140°C, most likely via the bicyclic pyrazolines **2** resulting from an initial intramolecular cycloaddition reaction.[12] On the other hand, the related α-[(alkynyloxy)silyl]-α-diazoacetates **4** yield cyclooligomers **5** (n=2–5) by a reaction sequence in which one or more intermolecular [3+2] cycloaddition reactions precede the intramolecular macrocycle-forming step.[13]



1 **2** **3**

4

5 ($n \geq 2$)

Scheme 1. Intramolecular cycloaddition reactions of unsaturated α-silyl-α-diazoacetates **1** and **4**.

Keywords: diazo compounds; cycloadditions; silicon heterocycles; silver and compounds.

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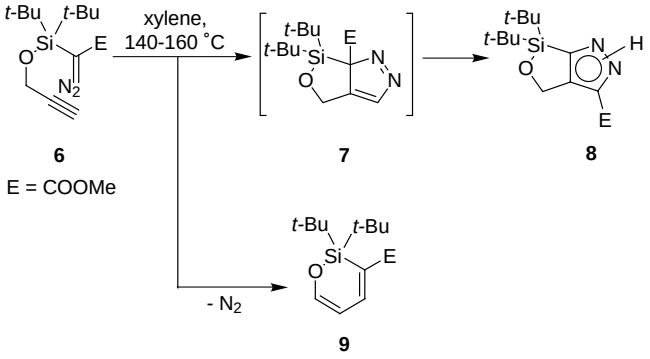


Scheme 2.

In contrast to other intramolecular reactions of two functional groups attached to a silicon atom,[14] silicon-tethered 1,3-dipolar cycloaddition reactions have been reported only very recently.[15] An unequivocal demonstration of a diazo dipole participating in such a reaction is still lacking, however. Since pyrazolines **2** could not be isolated from the thermal reaction of olefinic diazo compounds **1**, and acetylenic diazo compounds **4** underwent an inter- rather than an intramolecular cycloaddition as the initial step, we explored structural variations and reaction conditions which would allow us to observe a silicon-tethered intramolecular [3+2] cycloaddition between a diazo function and an olefinic or acetylenic unit. The results are reported in this study.

Results and Discussion

Intramolecular reactions of α-(alkynyloxy)silyl-α-diazoacetates

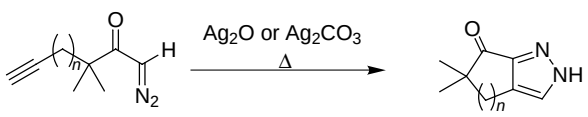
When [di-*tert*-butyl-(propargyloxy)silyl]diazoacetate **6**[16] was heated in xylene at 140–160°C, bicyclic pyrazole **8** was formed in 11% yield (Scheme 2). Under the harsh reaction conditions, most of the diazo compound seemed to decompose unspecifically, and only oxasiline **9**, which is likely to result from an intramolecular carbene reaction,[17] could be isolated additionally in trace amounts (<2%). Evidently, pyrazole **8** results from an intramolecular 1,3-dipolar cycloaddition of diazoacetate **6** followed by a formal 1,3-migration of the silyl or carboxylate group[18] and a C→N proton shift. No efforts were made to determine in which NH-tautomeric form pyrazole **8** exists.

The ^{1}H NMR spectrum of the reaction mixture indicated the absence of cyclodimers and higher cyclooligomers **5** (see Scheme 1). The different behavior of **6** as compared to **4**, i.e. the switch from an intermolecular to an intramolecular 1,3-dipolar cycloaddition pathway upon replacement of the $SiMe_2$ or Si–iPr$_2$ (**4**) by the bulkier Si–tBu$_2$ (**6**) unit, may be rationalized by a reactive conformer effect[19] which implies a conformational change at the Si–O bond. Rotamer *syn*-**6**, from which an intramolecular cycloaddition can occur, appears to be energetically favored over *anti*-**6** due to less steric repulsion towards the *tert*-butyl groups at silicon. With the less bulky Si–iPr$_2$ and $SiMe_2$ group, however, the equilibrium may be shifted to the *anti*-rotamer.

anti - **6** *syn* - **6**

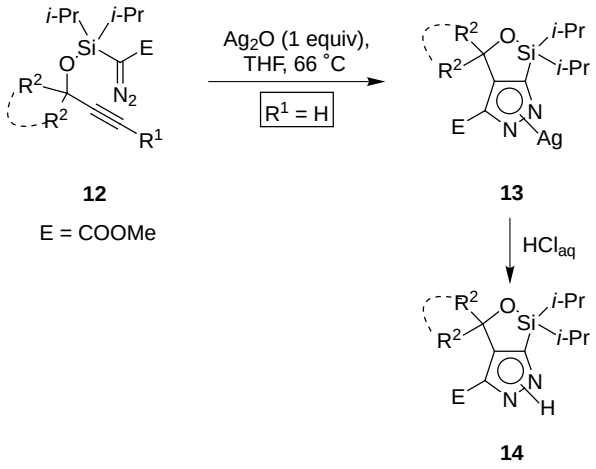
Kende[20] has recently reported that diazoketones such as **10** bearing a terminal alkyne function in the presence of substoichiometric quantities of a silver(I) compound undergo an intramolecular [3+2] cycloaddition (**10→11**) rather than the expected Wolff rearrangement (Scheme 3).

This report led us to submit α-[(alkynyloxy)silyl]-α-diazoacetates to similar reaction conditions. In fact, Si–iPr$_2$-substituted diazo compounds **12a** and **12b**, which under purely thermal conditions react according to Scheme 1, underwent an intramolecular [3+2] cycloaddition when treated with Ag_2O in THF (Scheme 4, Table 1). From **12a**, silver pyrazolide **13a** could be isolated in good yield when an equimolar amount of Ag_2O was applied. Since **13a** could be crystallized only in the form of long and thin needles unsuited for XRD analysis, the coordination mode[21–23] of this pyrazolide remains unknown. Treatment with aqueous acid converted **13a** into bicyclic pyrazole **14a**. In the case of **12b**, silver pyrazolide **13b** could not be isolated in pure form and therefore was converted in situ into **14b**. In complete agreement with Kende's findings,[20] the *gem*-dialkyl substitution present in **12a,b** as well as a terminal ethynyl group are necessary for a successful reaction, since diazoacetates **12c,d** did not react under the same conditions. On the other hand, Si–tBu$_2$-substituted diazoacetate **6** suffered unspecific decomposition.



10 *n* = 1,2 **11**

Scheme 3.



Scheme 4.

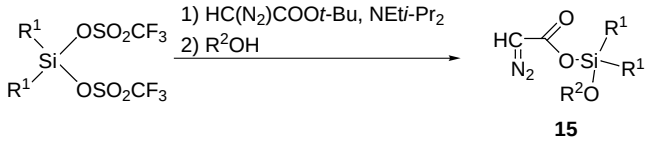
Table 1. Silver(I)-assisted intramolecular 1,3-dipolar cycloaddition of diazoacetates **12**; see Scheme 4

Diazo-acetate	R^1	R^2	Yield of **13** (%)	Yield of **14** (%)
12a	H	Me,Me	76	86 (from **13a**)
12b	H	$(CH_2)_5$	N.I.	49[a] (from **12b**)
12c	H	H,H	No reaction	
12d	Me	H,H	No reaction	

[a] At 84% conversion of **12b**.

The reaction conditions shown in Scheme 4 appear to be the best. A change of solvent (dioxane, xylene, EtOH) or the use of Ag_2CO_3 instead of Ag_2O gave lower or no yields of **14**. The transformation shown in Scheme 3 requires only ca 10–20 mol% of a silver catalyst, which is likely due to the presence of a proton source (EtOH or THF/Celite) which is able to displace the silver ion from the silver pyrazolide intermediate. In contrast, silyl-diazoacetates **12** are not sufficiently stable to protic solvents and Celite, especially not at elevated temperature, and consequently the use of an aprotic solvent allows the isolation of a silver pyrazolide **13**. As expected, the yield of **13a** decreased to 49 and 9% when only 50 or 10 mol% of Ag_2O were applied.

It is not yet clear how the silver reagent promotes the [3+2] cycloaddition of alkynyl-substituted diazoacetates. Kende[20] has postulated an activation of the acetylenic bond by side-on coordination of Ag(I), but in our opinion, an end-on coordination, i.e. formation of a silver acetylide, must be considered as well. The latter possibility is in agreement with the observation that internal alkynes (**12d** and Ref. 20; however, all examples are also without *gem*-dialkyl substitution which is another prerequisite for the intramolecular reaction) do not react and that a basic silver compound rather than simply silver nitrate is required. Furthermore, when we stopped the reaction of **12b** before completion, the alkynyl proton of **12b** was not observed by ^1H NMR, but after addition of HCl, the intact diazo compound could be isolated again in 16% yield besides pyrazole **14b** (see Experimental).



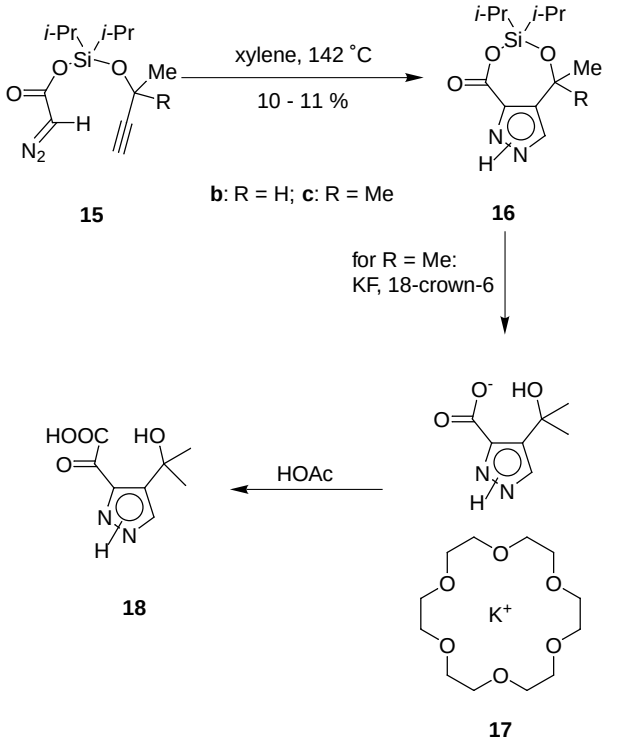
Scheme 5.

Table 2.

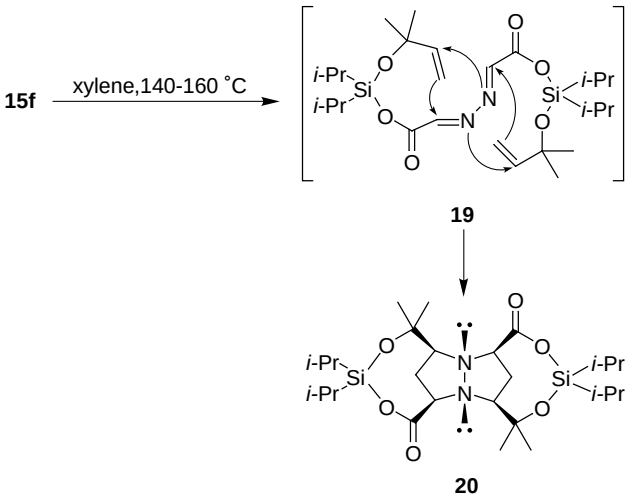
15	R^1	R^2	Yield (%)
a	*i*Pr	HC≡CCH$_2$	45
b	*i*Pr	HC≡CCH(Me)	62
c	*i*Pr	HC≡CCMe$_2$	60
d	*i*Pr	HC≡C(CH$_2$)$_2$	51
e	*i*Pr	H$_2$C=CH–CH(Me)	42
f	*i*Pr	H$_2$C=CH–CMe$_2$	52
g	*i*Pr	MeOOC–CH=CH–CH$_2$	49
h	Me	HC≡CCMe$_2$	30

Intramolecular reactions of (alkenyloxy)silyl and (alkynyloxy)silyl diazoacetates

In diazoacetates **4**, **6**, and **12**, a silicon atom directly attached to the diazo function links the dipole to the potential dipolarophilic unit. An alternative molecular design, namely diazoacetic acid silyl esters **15** with the dipolarophilic unit in the ester moiety, has not been realized so far. Simple trialkylsilyl diazoacetates can be prepared by transesterification of *tert*-butyl diazoacetate with a trialkylsilyl triflate.[24] Analogously, reaction of the same diazoester with diisopropylsilyl or dimethylsilyl bis(triflate) generated a



Scheme 6.



Scheme 7.

trifloxysilyl diazoacetate which after replacement of the remaining OTf group by an unsaturated alcohol gave the desired diazoacetic acid silyl esters **15a–h** (Scheme 5, Table 2). The highest yields were obtained when the transesterification step was conducted in pentane as solvent (from which the formed trialkylammonium triflate precipitates almost quantitatively, in contrary to ether or petroleum ether) and with an excess (2 equiv.) of amine base. Furthermore, immediate purification by column chromatography was necessary to prevent these diazo compounds from rapid decomposition. In the 500 MHz NMR spectrum, the signal of the diazo proton is distinctly broadened; as in simple alkyl diazoacetates and diazoketones,[25] this indicates an *s-cis*/*s-trans* equilibrium at the C(O)(C(N_2) bond.[26]

When silyl diazoacetates **15b,c** were kept in xylene at 142°C for 1 h, bicyclic pyrazoles **16b,c** were obtained in low yield (Scheme 6). An analogous product may have formed from **15a**, as indicated by the ^{1}H NMR spectrum (δ 7.5 for the pyrazole ring proton), but it could not be isolated. On the other hand, thermal impact on **15d,e,g,h** resulted in unspecific decomposition, and even column chromatography did not allow to isolate a defined product. While the overall result of the thermal behavior of this class of unsaturated diazoacetates is disappointing, it should be kept in mind that the chances for high-yielding intramolecular cycloaddition where not very good anyway due to the following reasons. (1) Silyl diazoacetates, like alkyl diazoacetates, are thermally less stable towards elimination of molecular nitrogen than α-silyl-α-diazoacetates. If the activation energy of the projected intramolecular cycloaddition is rather high, N_2 elimination and subsequent carbene chemistry may take over. (2) A successful intramolecular cycloaddition requires the *E* conformation around the C–O bond of the ester moiety which is distinctly higher in energy than the *Z* conformation.[27] Padwa and Kinder[11c] have made a similar observation when they tried to generate carbonyl ylides by intramolecular carbenoid chemistry; reactions of this type were successful with corresponding diazoketones but not with diazoesters bearing a carbonyl group in the ester residue. (3) Some factors specific to the individual diazo compounds may also be important; for example, the tether may be too long in **15d** (homopropargyloxy substituent), and the olefinic bonds in **15e–g** may display too little dipolarophilic character.

Typically, a silicon tether is removed after a successful intramolecular reaction. Therefore, we cleaved examplarily the two Si–O bonds in **16c** with KF/18-crown-6. The resulting salt **17** could be isolated almost quantitatively and was transformed into pyrazole **18** by acid treatment.

An elusive compound was isolated in 2% yield from the thermal reaction of **15f** in xylene. While the overall result was again unspecific decomposition, a minor amount of a colorless solid could be precipitated with ether. X-Ray diffraction analysis revealed the tetracyclic structure **20** (Scheme 7 and Fig. 1). We propose that this compound results from a lateral criss-cross cycloaddition[28,29] of the intermediate azine **19** which is formed from two molecules of **16f** by a diazo+diazo or diazo+carbene reaction. All efforts to increase the yield of **20** (variation of solvent and

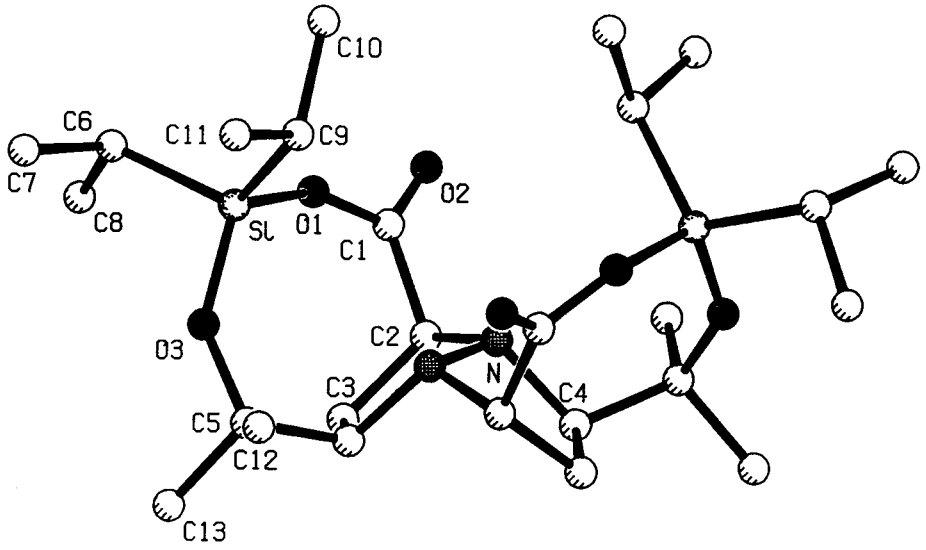


Figure 1. Molecular structure of **20** in the crystal (PLUTON[37] plot); ellipsoids of thermal vibration are shown at the 20% probability level. The molecule has C_2 symmetry.

temperature, reaction without solvent) or to obtain azine **19** selectively (treatment of **15f** with Cu powder or CuCl in benzene, 80°C[30]) remained unsuccessful.

Conclusion

In this study, the first silicon-tethered intramolecular [3+2] cycloaddition reactions of diazo dipoles with acetylenic dipolarophiles are reported. Both α-(propargyloxy)silyl-α-diazoacetates and diazoacetic acid (propargyloxy)silyl esters are able to enter such a reaction, but very specific structural details are required to populate the reactive conformer. Even then, rather high temperatures must be applied which eventually induce thermal dediazoniation as an alternative reaction channel. A remarkable result is the observation that some α-[diisopropyl(propargyloxy)silyl]-α-diazoacetates, with a *gem*-dialkyl substitution in the propargylic position, undergo a silver-assisted intramolecular [3+2] cycloaddition, but under purely thermal conditions yield pyrazolophanes and higher cyclooligomers that result from an initial intermolecular 1,3-dipolar cycloaddition.

Our results suggest that intramolecular 1,3-dipolar cycloaddition reactions will also be possible with some out of the variety of unsaturated (olefinic and acetylenic) diazocarbonyl compounds reported in the literature. Since interest in these compounds has been focused on their transition-metal-catalyzed carbenoid reactivity, we suspect that the thermal cycloaddition potential of the intact diazo function has simply been overlooked so far.

Experimental

General methods

All reactions were carried out in heat gun dried glassware and under an argon atmosphere. Solvents were dried by standard procedures. The petroleum ether used had a boiling range of 40–60°C. NMR: Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.76 MHz, ^{29}Si: 99.36 MHz) and Bruker AC 200 (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz); $CDCl_3$ was used as solvent. As the internal reference, Me_4Si was used for the ^{1}H and ^{29}Si spectra, and the solvent signal for the ^{13}C NMR spectra [$\delta(CDCl_3)$=77.0 ppm]. Assignments of ^{13}C chemical shifts are based on proton-coupled ^{13}C, (C,H) correlation, and DEPT 135 spectra. IR: Perkin–Elmer IR 883 and IR 1310. MS: Finnigan MAT SSQ7000 (EI, CI, FAB) and MAT 711 (FD). Microanalyses were carried out on Perkin–Elmer EA 240 and EA 2400 instruments in the Division of Analytical Chemistry of the University of Ulm. Chromatographic separations were performed on silica gel Si 60 (Macherey–Nagel, 0.063–0.2 mm). The petroleum ether used had a boiling point range of 40–60°C. α-Silyl-α-diazoacetates **6**,[16] **12a**,**c**,**d**[16] and **12b**[17] were prepared as described.

Thermal cylization of 6; methyl 6,6-di(*tert*-butyl)-4(2),6-dihydro-1(4)*H*-[1,2]oxasilolo[3,4-*c*]pyrazole-3-carboxylate (8). A solution of **6** (0.623 g, 2.0 mmol) in *p*-xylene (10 mL) was placed in a Schlenk pressure tube and heated for 1 h at 140°C, then for 1 h at 160°C. A color change from yellow to red-brown was observed. The solvent was evaporated and ether (5 mL) was added to the residue. After some time, a white precipitate had formed which was isolated by centrifugation and washed with ether to give 66 mg (11%) of **8**: mp 242°C; IR (KBr) ν 3247 (s, br, NH), 1724 (s), 1705 (s), 1260 (s), 1033 (vs) cm^{-1}; ^{1}H NMR (500.14 MHz) δ 1.01 (s, 18H, CMe_3), 3.88 (s, 3H, OMe), 5.06 (s, 2H, OCH_2), 11.62 (s, br, 1H, NH); ^{13}C NMR (125.77 MHz) δ 20.79 (*C*Me$_3$), 26.95 (C*Me*$_3$), 51.88 (OMe), 65.53 (OCH_2), 136.18 (SiC=), 141.41 (CH_2C=), 143.85 (C(O)*C*=), 162.77 (C=O); ^{29}Si NMR δ 16.34; MS (EI, 70 eV) *m/z* (rel int%) 296 (M^+, 18), 265 (M^+-OMe, 5), 239 (M^+-tBu, 100), 209 (M^+-2 *t*Bu, 15), 207 (61), 197 (12), 179 (6). Anal. Calcd for $C_{14}H_{24}N_2O_3Si$ (296.44): C, 56.73; H, 8.17; N, 9.46. Found: C, 56.55; H, 8.02; N, 9.33.

1,1-Diisopropyl-3,3-dimethyl-4-(methoxycarbonyl)-3,5(6)-dihydro-1*H*-[1,2]oxasilolo[3,4-*c*]pyrazol-5(6)-yl silver (13a). The mixture of diazoacetate **12a** (0.100 g, 0.36 mmol) and Ag_2O (0.085 g, 0.36 mmol) in THF (10 mL) was heated at reflux during 24 h. After cooling, the unsoluble components were removed by centrifugation to leave a yellow solution. The solvent was evaporated, and the residue was subjected to column chromatography (silica gel, 20 g, ether as eluent) to afford **13a** (0.11 g, 76%) as a colorless powder: mp. 127–130°C; IR (KBr) ν 2941 (s), 2864 (s), 1705 (vs, C=O), 1268 (s) cm^{-1}; ^{1}H NMR (500.14 MHz) δ 1.09/1.10 (each: d, J=7.4 Hz, 6H, CH*Me*), 1.28 (sept, J=7.4 Hz, 2H, SiCH), 1.65 (s, 6H, CMe_2), 3.93 (s, 3H, OMe); ^{13}C NMR (125.77 MHz) δ 12.64 (SiC), 17.39/17.74 (CH*Me*), 30.19 (CMe), 51.54 (OMe), 78.93 (SiOC), 135.65 (SiC=), 146.15 (C-3a), 153.93 (C-4), 163.12 (C=O); ^{29}Si NMR δ 13.2; MS (EI, 70 eV) *m/z* (rel int%) 296 (M^+-Ag, 1), 281 (M^+-Ag–CH_3, 100), 253 (M^+-iPr, 85), 225 (M^+-Ag–COOMe, 29), 221 (52), 193 (26), 119 (16), 91 (33); MS (CI, CH_4, 100 eV) *m/z* (rel int%) 337 ([M+Allyl]$^+-$ Ag, 4), 325 ([MEt]$^+-$ Ag, 14), 297 (MH^+-Ag, 100), 281 (20), 265 (14), 253 (38). Anal. Calcd for $C_{14}H_{23}AgN_2O_3Si$ (403.30): C, 41.69; H, 5.75; N, 6.95. Found: C, 41.87; H, 5.76; N, 6.68.

Methyl 1,1-diisopropyl-3,3-dimethyl-3,5(6)-dihydro-1*H*-[1,2]oxasilolo[3,4-*c*]pyrazole-4-carboxylate (14a). Silver pyrazolide **13a** (0.250 g, 0.62 mmol) was dissolved in CH_2Cl_2 (30 mL) and water (10 mL) and conc. HCl (0.1 mL) were added. The precipitated AgCl was filtered off, and the organic layer was separated, washed with water (2×1 mL), and dried (Na_2SO_4). After evaporation of the solvent, **14a** (0.158 g, 86%) was obtained as a white powder: mp 145–147°C; IR (KBr) ν 3161 (s, br, NH), 2945 (s), 2864 (s), 1726 (s, C=O) cm^{-1}; ^{1}H NMR (500.14 MHz) δ 0.97 (d, J=7.4 Hz, 6H, CH*Me*), 1.05 (d, J=7.5 Hz, 6H, CH*Me*), 1.26 (sept, J=7.5 Hz, 2H, C*H*Me), 1.67 (s, 6H, CMe_2), 3.91 (s, 3H, OMe), 12.77 (s, br, 1H, NH); ^{13}C NMR (125.77 MHz) δ 12.61 (SiC), 17.13 (CH*Me*), 17.45 (CH*Me*), 29.90 (C*Me*$_2$), 51.63 (OMe), 78.62 (SiOC), 135.46 (SiC=), 142.88 (C-4), 148.19 (C-3a), 162.81 (C=O); ^{29}Si NMR δ 14.30; MS (EI, 70 eV) *m/z* (rel int%) 296 (M^+, 3), 281 (M^+-Me, 100), 265 (6), 253 (M^+-iPr, 71), 238 (M^+-Me–*i*Pr, 3), 221 (42), 193 (21), 179 (4), 151 (4), 125 (6), 119 (11), 91 (23). Anal. Calcd for $C_{14}H_{24}N_2O_3Si$ (296.44): C, 56.72; H, 8.16; N, 9.45. Found C, 56.90; H, 8.11; N, 9.46.

Methyl 1,1-diisopropyl-spiro{cyclohexane-3,5(6)-dihydro-1*H*-[1,2]oxasilolo[3,4-*c*]pyrazole-4-carboxylate} (14b). To a solution of **12b** (0.425 g, 1.26 mmol) in THF (15 mL) was added Ag_2O (0.292 g, 1.26 mmol), and the suspension was heated at 66°C during 24 h. The unsoluble components were removed by centrifugation, the solvent was evaporated and CH_2Cl_2 (20 mL) and aq HCl (ca 10%, 10 mL) were added to the residue. The precipitated AgCl was removed by centrifugation, and the organic phase was separated, washed with water (2×5 mL), and dried (Na_2SO_4). Chromatographic work-up (silica gel, 25 g, petroleum ether–ether (9:1) as eluent) gave first unchanged **12b** (66 mg, 16 %), then pyrazole **14b** (0.210 g, 49%). Data for **14b**: mp 50–52°C; IR (KBr) (3250/3160 (m, vb, NH), 2930 (s), 2863 (s), 1726 (vs, C═O) cm^{-1}; ^1H NMR (200.13 MHz) δ 1.00 (d, J=7.5 Hz, 6H, CH*Me*), 1.02 (d, J=7.5 Hz, 6H, CH*Me*), 1.17 (sept, J=7.5 Hz, 2H, C*H*Me), 1.32–1.40 (m, 1H, CH_2), 1.57 (t, 4H, J=14.0 Hz, CH_2), 1.71–1.81 (m, 3H, CH_2), 2.30 (dt, J=12.8, 4.4 Hz, 2H, CH_2), 3.92 (s, 3H, OMe); ^{13}C NMR (50.32 MHz) δ 12.66 (SiC), 17.21 (CH*Me*), 17.47 (CH*Me*), 21.85 (CH_2), 25.21 (CH_2), 37.10 (CH_2), 51.78 (OMe), 79.93 (C-3), 135.69 (SiC═), 143.49 (C(O)*C*═), 149.56 (C-3a), 162.53 (C═O). Anal. Calcd for $C_{17}H_{28}N_2O_3Si$ (336.51): C, 60.68; H, 8.39; N, 8.32. Found: C, 60.65; H, 8.32; N, 7.99.

Diazoacetic acid silyl esters 15.

General procedure. To a solution of diisopropylsilyl bis(trifluoromethanesulfonate)[31,32] (8.25 g, 5.8 mL, 20.0 mmol) and ethyldiisopropylamine (5.16 g, 7.0 mL, 40.0 mmol) in pentane (150 mL) was added slowly the solution of *tert*-butyl diazoacetate[33] (2.80 g, 20.0 mmol) in pentane (20 mL). After stirring for 8 h, an alcohol (ROH) (20.0 mmol) dissolved in ether (20 mL) was added and stirring was continued for 12 h. After evaporation of the solvent, the residue was purified by column chromatography (50 g of silica gel which had been kept at 100°C/0.01 mbar for 12 h, column cooled at −30 to −40°C, dry petroleum ether–ether (9:1) as eluent).

[Diisopropyl-(2-propynyl)oxy]silyl diazoacetate (15a). ROH=prop-2-yn-1-ol (1.10 g, 1.20 mL, 20.0 mmol); yield: 2.30 g (45%), yellow oil. Bp 140°C/0.01 mbar; IR (film) ν 3308 (m, ≡CH), 3122 (m), 2948 (s), 2869 (s), 2110 (s, CN_2), 1679 (s, C═O) cm^{-1}; ^1H NMR (500.14 MHz) δ=1.08/1.09 (each: d, J=7.5 Hz, 6H, CH*Me*), 1.26 (sept, J=7.5 Hz, 2H, SiCH), 2.46 (t, ^4J= 2.4 Hz, 1H, HC≡), 4.51 (d, ^4J=2.4 Hz, 1H, CH_2), 4.80 (s, br, 1H, CHN_2); ^{13}C NMR (125.77 MHz) δ 11.85 (SiC), 16.31/16.33 (CH*Me*), 46.98 (CN_2), 51.82 (CH_2), 72.86 (HC≡), 81.24 (C≡), 164.18 (C═O); ^{29}Si NMR δ −4.01. Anal. Calcd for $C_{11}H_{18}N_2O_3Si$ (254.36): C, 51.94; H, 7.13; N, 11.01. Found C, 51.49; H, 7.26; N, 10.08.

[Diisopropyl-(1-methylprop-2-yn-1-yl)oxy]silyl diazoacetate (15b). ROH=but-1-yn-3-ol (1.40 g, 1.50 mL, 20.0 mmol); yield: 3.30 g (62%), yellow oil. IR (film) ν 3308 (m, ≡CH), 3122 (w), 2948 (s), 2869 (s), 2112 (s, CN_2), 1679 (s, C═O) cm^{-1}; ^1H NMR (500.14 MHz) δ 1.05/1.07 (each: d, J=7.8 Hz, 6H, SiCH*Me*), 1.09/1.11 (each: d, J=7.5 Hz, 6H, SiCH*Me*), 1.21/1.31 (each: sept, J=7.5 Hz, 1H, SiCH) 1.46 (d, J=6.5 Hz, 3H, OCMe), 2.39 (d, ^4J=2.0 Hz, 1H, HC≡), 4.71 (br s, 1H, CHN_2), 4.85 (dq, ^3J=6.5, ^4J=2.1 Hz, 1H, OCH); ^{13}C NMR (50.32 MHz) δ 12.17 (SiCH), 16.67 (SiCH*Me*$_2$), 24.86 (OC*Me*), 47.37 (CHN_2), 59.43 (OCH), 71.32 (HC≡), 85.48 (C≡), 164.54 (C═O); ^{29}Si NMR δ −5.04. Anal. Calcd for $C_{12}H_{20}N_2O_3Si$ (268.39): C, 53.70; H, 7.51; N, 10.43. Found: C, 53.31; H, 7.79; N, 10.29.

[Diisopropyl-(1,1-dimethylprop-2-yn-1-yl)oxy]silyl diazoacetate (15c). ROH=2-methylbut-3-yn-2-ol (1.68 g, 1.94 mL, 20.0 mmol); yield: 3.39 g (60%), yellow oil. Bp 120°C/0.02 mbar; IR (film) ν 3307 (m, br, ≡CH), 3125 (w, br), 2947 (s), 2869 (s), 2110 (s, CN_2), 1687 (s, C═O) cm^{-1}; ^1H NMR (500.14 MHz) δ 1.07 (d, J=7.4 Hz, 12H, CH*Me*$_2$), 1.25 (sept, J=7.4 Hz, 2H, C*H*Me$_2$), 1.56 (s, 6H, CMe$_2$), 2.41 (s, 1H, HC(), 4.69 (br s, 1H, NCH); ^{13}C NMR (50.32 MHz) δ 13.17 (SiCH), 16.92 (CH*Me*$_2$), 32.40 (C*Me*$_2$), 47.39 (CN_2), 67.34 (*C*Me$_2$), 70.43 (HC≡), 88.15 (≡C), 163.90 (br, C═O); ^{29}Si NMR δ −9.2. Anal. Calcd for $C_{13}H_{22}N_3O_3Si$ (282.39): C, 55.29; H, 7.85; N, 9.92. Found: C, 55.30; H, 7.94; N, 10.05.

[Diisopropyl-(3-butynyl)oxy]silyl diazoacetate (15d). ROH=3-butyn-1-ol (1.40 g, 1.51 mL, 20.0 mmol); yield: 2.70 g (51%), yellow oil. IR (film) ν 3310 (w, (CH), 3122 (w), 2949 (s), 2868 (s), 2111 (s, CN_2), 1679 (s, C═O) cm^{-1}; ^1H NMR (500.14 MHz) δ 1.07 (d, J=7.4 Hz, 12H, CH*Me*$_2$), 1.23 (sept, J=7.4 Hz, 2H, SiCH), 1.96 (t, ^4J=2.7 Hz, 1H, HC≡), 2.45 (dt, ^3J=7.1 Hz, ^4J=2.7 Hz, 2H, CH_2C≡), 3.96 (t, J=7.1 Hz, 2H, OCH_2), 4.77 (br s, 1H, CHN_2); ^{13}C NMR (50.32 MHz) δ 11.97 (SiC), 16.64 (CH*Me*$_2$), 22.32 (*C*H_2C≡), 47.24 (CN_2), 62.11 (OCH_2), 69.26 (HC≡), 80.97 (C≡), 164.56 (C═O); ^{29}Si NMR δ −6.0. Anal. Calcd for $C_{12}H_{20}N_2O_3Si$ (268.39): C, 53.70; H, 7.51; N, 10.44. Found: C, 53.76; H, 7.49; N, 10.44.

[Diisopropyl-(1-methylallyl)oxy]silyl diazoacetate (15e). ROH=but-3-en-2-ol (1.44 g, 1.20 mL, 20.0 mmol); yield: 2.27 g (42%), yellow oil. Bp 100°C/0.028 mbar; IR (film) ν 3124 (w), 3095 (w), 2947 (s), 2868 (m), 2110 (s, CN_2), 1686 (s, C═O) cm^{-1}; ^1H NMR (500.14 MHz) δ 1.052/ 1.061/1.071/1.074 (each: d, J=7.4 Hz, 3H, CH*Me*), 1.24 (sept, J=7.4 Hz, 2H, SiCH), 1.26 (d, J=6.4 Hz, 3H, OCH*Me*), 4.62 (mc, 1H, OCH), 4.68 (s, br, 1H, CHN_2), 5.00 (dt, J=17.2, 1.6 Hz, 1H, ═CH_2), 5.18 (dt, J=10.4, 1.6 Hz, 1H, ═CH_2), 5.86 (ddd, J=17.2, 10.4, 5.4 Hz, 1H, ═CH); ^{13}C NMR (125.76 MHz) δ 12.40 (SiC), 16.87 (CH*Me*$_2$), 23.93 (OC*Me*), 47.31 (CN_2), 70.32 (O*C*H), 112.68 (═CH_2), 141.98 (═CH), 164.57 (C═O); ^{29}Si NMR δ −7.03. Anal. Calcd for $C_{12}H_{22}N_2O_3Si$ (270.40): C, 53.31; H, 8.21; N, 10.37. Found: C, 53.21; H, 8.20; N, 10.32.

[Diisopropyl-(1,1-dimethylallyl)oxy]silyl diazoacetate (15f). ROH=2-methyl-3-buten-2-ol (1.72 g, 2.09 mL, 20.0 mmol); yield: 2.90 g (52%), yellow oil. Bp 164°C/ 0.02 mbar; IR (KBr) ν 3126 (w), 3092 (w), 2946 (s), 2868 (s), 2111 (s, CN_2), 1686 (s, C═O) cm^{-1}; ^1H NMR (500.14 MHz) δ 1.05/1.06 (each: d, J=7.5 Hz, 6H, CH*Me*), 1.20 (sept, J=7.5 Hz, 2H, SiCH), 1.37 (s, 6H, CMe_2), 4.69 (br s, 1H, CHN_2), 4.94 (mc, ^3J=17.3 Hz, 1H, ═CH_2), 5.16 (mc, ^3J=10.7 Hz, 1H, ═CH_2), 5.97 (dd, ^3J=17.3, 10.7 Hz, 1H, ═CH); ^{13}C NMR (125.76 MHz) δ

13.42 (SiC), 17.02 (CH*Me*$_2$), 29.63 (C*Me*$_2$), 47.23 (CN_2), 69.22 (*C*Me$_2$), 110.57 (=CH_2), 145.76 (=CH), 164.36 (C=O); ^{29}Si NMR δ −11.15. Anal. Calcd for $C_{13}H_{24}N_2O_3Si$ (284.43): C, 54.90; H, 8.51; N, 9.85. Found: C, 54.40; H, 8.06; N, 9.73.

Methyl (*E*)-4-([[(2-diazoacetyl)oxy]diisopropylsilyl]oxy)-2-butenoate (15g). ROH=methyl 4-hydroxy-2-butenoate[34] (2.32 g, 20 mmol); yield: 3.10 g (49%), yellow oil. IR (film) ν 3121 (w), 2949 (s), 2868 (m), 2110 (s, CN_2), 1726 (s; C=O), 1678 (s, C=O), 1269 (s) cm^{-1}; ^{1}H NMR (200.13 MHz): δ=1.07/1.09 (each: d, 6H, CH*Me*), 1.27 (sept, 2H, SiCH), 3.74 (s, 3H, OMe), 4.59 (dd, ^3J=3.4 Hz, ^4J=2.5 Hz, 2H, OCH_2), 4.73 (br s, 1H, CHN_2), 6.11 (dt, ^3J=15.6 Hz, ^4J=2.5 Hz, 1H, C(O)CH), 7.00 (dt, J=15.6, 3.4 Hz, 1H, CH_2CH); ^{13}C NMR (50.32 MHz) δ 13.02 (Si*C*H), 17.07 (CH*Me*$_2$), 47.76 (CN_2), 51.74 (OMe), 63.84 (OCH_2), 120.23 (CO–*C*H), 147.56 (CH_2*C*H), 162.31 (C=O), 167.18 (C=O); ^{29}Si NMR (C_6D_6) δ 5.50. Anal. Calcd for $C_{13}H_{22}N_2O_5Si$ (314.41): C, 49.66; H, 7.05; N, 8.91. Found: C, 49.43; H, 7.33; N, 8.82.

[Dimethyl-(1,1-dimethyl-2-propynyl)oxy]silyl diazoacetate (15h). Prepared from dimethylsilyl bis(trifluoromethanesulfonate) (7.13 g, 4.51 mL, 20.1 mmol), *tert*-butyl diazoacetate (2.84 g, 20.0 mmol), and 2-methyl-3-butyn-1-ol (1.70 g, 1.97 mL, 20.0 mmol); yield: 1.36 g (30%), yellow oil. IR (KBr) ν 3304 (m, ≡CH), 3122 (w), 2987 (m), 2111 (s, CN_2), 1678 (s, C=O) cm^{-1}; ^{1}H NMR (200.13 MHz) δ 0.42 (s, 6H, $SiMe_2$), 1.55 (s, 6H, CMe_2), 2.47 (s, 1H, ≡CH), 4.72 (br s, 1H, CHN_2); ^{13}C NMR (50.32 MHz) δ −0.05 ($SiMe_2$), 32.35 (C*Me*$_2$), 47.47 (CN_2), 67.31 (O*C*Me$_2$), 71.26 (≡CH), 87.74 (≡C), 165.24 (C=O); ^{29}Si NMR δ −3.38. Anal. Calcd for $C_9H_{14}N_2O_3Si$ (226.31): C, 47.77; H, 6.24; N, 12.38. Found: C, 47.98; H, 5.95; N, 12.63.

Thermal reaction of 15b; 6,6-diisopropyl-4-methyl-2,8-dihydro-4*H*-[1,3,2]dioxasilepino[6,5-*c*]pyrazol-8-one or tautomer (16b). A solution of **15b** (0.611 g, 2.28 mmol) in xylenes (5 mL) was placed in a Schlenk pressure tube and heated at 142°C for 1 h. The solvent was removed at 0.01 mbar and pentane (4 mL) was added to the residue. A white precipitate formed which was isolated by centrifugation and washed with pentane; yield: 67 mg (11%). Mp 163–165°C; IR (KBr) ν=3215 (vs, br, NH), 2946 (s), 2868 (m), 1688 (s, C=O) cm^{-1}; ^{1}H NMR (500.14 MHz) δ 1.00 (s, J=7.2 Hz, 3H, CH*Me*), 1.03 (s, J=7.1 Hz, 3H, CH*Me*), 1.09 (sept, 1H, SiCH), 1.13 (s, J=7.3 Hz, 3H, CH*Me*), 1.13 (s, J=7.0 Hz, 3H, CH*Me*), 1.22 (sept, 1H, SiCH), 1.65 (d, J=6.4 Hz, 3H, OCMe), 5.30 (q, J=6.4 Hz, 1H, OCH), 7.67 (s, 1H, NCH); ^{13}C NMR (50.32 MHz) δ 12.21/12.52 (SiCH), 16.42/16.46/16.62/16.88 (CH*Me*), 22.80 (OC*Me*), 64.10 (OCH), 127.82 (C=), 130.37 (NCH), 139.37 (*C*C=O), 160.05 (C=O); ^{29}Si NMR δ −5.2. Anal. Calcd for $C_{12}H_{20}N_2O_3Si$ (268.39): C, 53.70; H, 7.51; N, 10.44. Found: C, 53.97; H, 7.65; N, 10.14.

Thermal reaction of 15c; 6,6-diisopropyl-4,4-dimethyl-2,8-dihydro-4*H*-[1,3,2]dioxasilepino[6,5-*c*]pyrazol-8-one or tautomer (16c). A solution of **15c** (0.970 g, 3.43 mmol) in xylenes (30 mL) was heated at reflux for 1 h. After evaporation of the solvent, ether (2 mL) was added, and the white precipitate formed was separated by centrifugation and washed with ether; yield: 94 mg (10%). Mp 170–172°C; IR (KBr) (3212 (s, br, NH), 2946 (s), 2868 (s), 1687 (vs, C=O) cm^{-1}; ^{1}H NMR (200.13 MHz): δ=1.00–1.16 (d+sept, 14H, C*HMe*$_2$), 1.70 (s, 6H, CMe_2), 7.82 (s, 1H, NCH), ca 13.2–14.7 (br, 1H, NH); ^{13}C NMR (50.32 MHz) δ 13.31 (SiC), 16.78/16.92 (CH*Me*), 32.88 (C*Me*$_2$), 72.18 (*C*Me$_2$), 130.03 (NCH), 131.59 (C-3a), 140.21 (*C*C=O), 160.96 (C=O); ^{29}Si NMR δ −7.34; MS (EI, 70 eV) *m/z* (rel int%) 282 (M^+, 1), 267 (M^+−Me, 100), 239 (M^+−*i*Pr, 39); MS (FD) *m/z* (rel int%) 565 ([2M+H]$^+$, 33), 283 (MH^+, 100), 267 (M^+−Me, 8), 239 (M^+−*i*Pr, 4). Anal. Calcd for $C_{13}H_{22}N_2O_3Si$ (282.41): C, 55.29; H, 7.85; N, 9.92. Found: C, 55.34; H, 7.98; N, 9.78.

18-Crown-6-potassium 4-(1-hydroxy-1-methylethyl)-1*H*-3(5)-pyrazolecarboxylate (17). A mixture of **16c** (67 mg, 0.24 mmol), 18-crown-6 (0.623 g, 0.24 mmol) and KF (0.500 g) in CH_2Cl_2 (6 mL) was stirred for 12 h. Excess KF was filtered off, and the solvent was replaced by ether (10 mL). After stirring for 2 h, the precipitate was separated by centrifugation and washed with ether; yield: 0.110 g (97%) of a white solid. Mp 187°C; IR (KBR) ν 3517 (m, br), 3200 (s, br), 2903 (s), 1688 (m), 1594 (s), 1352 (s) cm^{-1}; ^{1}H NMR (500.14 MHz) δ 1.57 (s, 6H, CMe_2), 3.61 (s, 24H, CH_2), 7.34 (s, 1H, =CH), 9.00 (s, 1H, OH), 11.35 (br s, 1H, NH); ^{13}C NMR (125.76 MHz) δ 31.34 (C*Me*$_2$), 66.72 (*C*Me$_2$), 69.89 (CH_2), 130.57 (C-4), 136.70 (=CH), 137.44 (*C*C=O), 165.08 (C=O); MS (FAB+) *m/z* 303 (K^++18-crown-6); MS (FAB-) *m/z* (rel int%) 377 ([anion$_2$K]$^-$, 6), 169 (anion, 100), 151 (anion-H_2O, 9), 125 (anion-CO_2, 6). Anal. Calcd for $C_{19}H_{33}KN_2O_9$ (472.58): C, 48.29; H, 7.04; N, 5.93. Found: C, 48.17; H, 7.15; N, 5.91.

4-(1-Hydroxy-1-methylethyl)-1*H*-3(5)-pyrazolecarboxylic acid (18). To a solution of **17** (29 mg, 0.06 mmol) in CH_2Cl_2 (20 mL) was added acetic acid (2 mL). After stirring for 2 h, the white voluminous precipitate was isolated by centrifugation and washed with CH_2Cl_2; yield: 10 mg (96%). Mp 204°C (dec); IR (KBr) ν 3600–2100 (s, OH), 1723 (s, br, C=O), 1454 (s, br) cm^{-1}; ^{1}H NMR (DMSO, 500.14 MHz) δ 1.35 (s, 6H, CMe_2), 7.15 (s, 1H, =CH), 8.98 (s, 1H, OH), 12.45 (br s, 1H, NH); ^{13}C NMR (DMSO, 50.32 MHz) δ 31.94 (C*Me*$_2$), 66.22 (*C*Me$_2$), 130.12 (=*C*CMe), 135.49 (=CH), 137.69 (*C*C=O), 163.68 (C=O); MS (FD) *m/z* (rel int%) 341 ([2M+H]$^+$, 2), 171 (MH^+, 30), 155 (M^+−Me, 100), 152 (M^+−H_2O, 87).

6,6,14,14-Tetraisopropyl-8,8,16,16-tetramethyl-5,7,13,15-tetraoxa-2,10-diaza-6,14-disilatetracyclo[9.5.1.1^{3,9}.0^{2,10}]-octadecane-4,12-dione (20). A solution of **15f** (0.756 g, 2.66 mmol) in xylenes (3 mL) was placed in a Schlenk pressure tube and heated at 142°C for 10 min, then at 162°C for 1 h. After evaporation of the solvent, ether (2 mL) was added, and the white precipitate formed was separated by centrifugation and washed with ether; yield: (12 mg, 1.7%). Crystals suitable for XRD analysis were obtained from $CHCl_3$. Mp 249–250°C; ^{1}H NMR (500.14 MHz) δ 1.02 (br s, 14H, C*HMe*$_2$), 1.05/1.06 (each: d, J=7.4 Hz, 6H, CH*Me*), 1.20 (s, 6H, 8,16-Me), 1.28 (sept, J=7.4 Hz, 2H, C*H*Me$_2$), 1.47 (s, 6H, 8,16-Me), 2.17–2.21 and 2.44–2.52 (each: m, 2H, CH_2), 2.76 (dd, J=10.9, 4.7 Hz, 2H, NCH),

4.05 (d, J=9.1 Hz, 2H, CHCO); ^{13}C NMR (125.76 MHz) δ 12.86/13.90 (*C*HMe), 17.02/17.39/17.53/17.84 (CH*Me*), 27.39, 28.04, 30.16, 69.02, 71.98, 75.33, 168.24 (C=O).

X-Ray crystal structure determination of 20.[35] *Crystal data:* $C_{26}H_{48}N_2O_6Si_2$, *f. w.* 540.84, monoclinic, space group $C2/c$; a=13.196(2), b=9.460(1), c=25.001(4) Å; α=90, β=104.94(2), γ=90°; V=3015.5(8) Å^3, Z=4, D_x=1.191 g cm^{-3}, ((Mo-K$_\alpha$)=1.57 cm^{-1}, crystal size 0.69×0.38×0.23 mm^3. *Data collection*: T=293 K, imaging-plate diffractometer (IPDS, Stoe), monochromatized Mo-K$_\alpha$ radiation, 9272 reflections measured in the range $2.68 \leq \theta \leq 24.04°$, 2340 unique reflections (R_{int}=0.076). *Structure solution and refinement:* the structure was solved by direct methods (program SHELXS-86[36]) and refined by a full-matrix least-squares method based on F^2 values (SHELXL-93[36]). All hydrogen atom positions were calculated geometrically and treated by a riding model. Refinement converged at R=0.0642, R_w=0.1419 for all reflections and at R=0.0547, R_w=0.1368 for reflections with $I>2\sigma(I)$. The residual electron density was between 0.27 and −0.31e Å^{-3}.

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deposited with the Cambridge Crystallographic Data Centre (CCDC 136742). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223) 336-033, e-mail: deposit@ccdc.cam.ac.uk).
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