Intramolecular Copper- and Rhodium-Mediated Carbenoid Reactions of α-(Propargyloxy)silyl-α-diazoacetates

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

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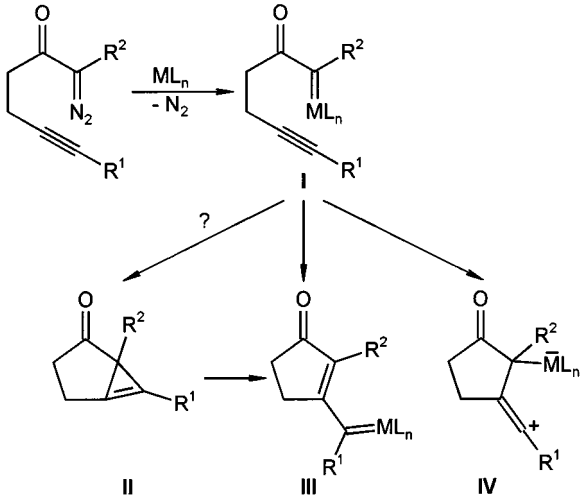
Copper(I) triflate catalyzes the transformation of α-[(2-alkynyl)oxy]silyl-α-diazoacetates **1a–g** into 1,2-bis(2,5-dihydro-1,2-oxasilol-4-yl)ethenes **2** and/or 2*H*-1,2-oxasilines **3**. With rhodium(II) perfluorobutyrate as catalyst, **1a–e** furnish only **3** but no **2**. Bicyclic 2-methoxyfurans **6** are formed when **1a**,**c**,**e** (containing terminal alkyne functions) are treated with catalytic amounts of copper(I) chloride. The experimental observations are explained in terms of metal-mediated intramolecular cyclopropenation and subsequent metal-assisted ring-opening of the strained bicyclic cyclopropene leading to vinylcarbene-metal complexes. An unusual autoxidation of 2*H*-1,2-oxasilines **3a**,**c**,**e** is also described.

Introduction

Diazocarbonyl compounds are involved in a continuously increasing number of chemical syntheses[1]. Recent progress in metal-catalyzed carbenoid transformations has the major share in this development[2−10]. Among the intramolecular carbene reactions, cyclizations resulting from C−H or X−H insertion, cyclopropanation, and ylide formation have found much attention, since they provided an elegant approach to cyclic systems with varying degrees of structural and functional complexity. On the other hand, the intramolecular chemistry of a metal−carbene intermediate derived from a diazocarbonyl compound containing a suitably positioned alkynyl group (Scheme 1) represents one of the less familiar but mechanistically most intriguing reaction pathways.

A simplified mechanistic picture is given in Scheme 1; as Padwa[4][11] and Hoye[12] have pointed out, the true scenario may be much more complicated. According to a common view, the electrophilic metal−carbene intermediate **I** formed from the diazo compound transfers carbenoid reactivity to one of the carbon atoms of the acetylenic π bond to form vinyl carbenoid **III** or its endocyclic, six-membered regioisomer, both of which are transformed further into the final products by various intra- and intermolecular reactions[11−21]. While the majority of these reactions was catalyzed with $Rh_2(OAc)_4$, the influence of rhodium ligands[4] or of the catalyst metal itself[12] (rhodium, palladium, copper) on the reaction outcome indicated the presence of the catalyst in the product-forming step. Whether a bicyclic cyclopropene **II** is involved in the formation of vinyl carbenoid **III** or of its regioisomer is an open question. Experimental evidence for the intermediacy of **II** is rare[11][13] and



Scheme 1

if it is formed indeed, one would expect rapid cyclopropene-to-vinylcarbene isomerization[22] of this very strained bicyclic species anyway.

Based on product analyses, Hoye and Dinsmore[12b] have questioned the transposition of the metal−carbene functionality from **I** to **III**. Rather, they propose electrophilic attack of the carbenoid carbon atom in **I** at the acetylenic bond to form a vinyl cation, either in a 5-*exo*-cyclization mode leading to **IV** or by 6-*endo* cyclization. They argue that these vinyl cations should have a reactivity similar to the metal-complexed vinyl carbenes due to the electrophilic character of both types of reactive intermediates.

In all cases investigated so far, the alkynyl function was connected with the carbenoid center through a carbonyl or carboxy group. In this communication, we describe for the first time intramolecular carbenoid reactions in which an acetylenic π bond and the metal−carbene function are tethered by a Si−O unit. In a forthcoming publication[23a], we will show that intramolecular carbene reactions of silicon-

[a] Abteilung Organische Chemie I, Universität Ulm,
Albert-Einstein-Allee 11, D-89081 Ulm, Germany
Fax: (internat.) + 49(0)731/502-2803
E-mail: gerhard.maas@chemie.uni-ulm.de
[b] Fachbereich Chemie, Universität Kaiserslautern,
Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany

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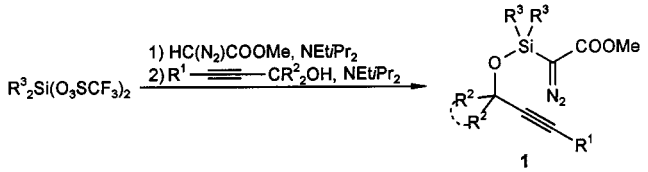
functionalized α-silyl-α-diazoacetates, such as C−H insertion and C=C cyclopropanation, also represent useful methods for the construction of silicon-oxygen heterocycles.

Results and Discussion

The prerequisite α-[(2-alkynyl)oxy]silyl-α-diazoacetates **1a−g** can be assembled by consecutive reaction of a silyl bis(triflate) with methyl diazoacetate and a propargylic alcohol (Scheme 2). We have described the synthesis of **1b**,**c**,**d**,**f** by this method already[24].



1	a	b	c	d	e	f	g
R^1	H	H	H	Me	H	H	Me
R^2, R^2	Me, Me	H, H	Me, Me	H, H	-$(CH_2)_5$-	H, H	H, H
R^3	Me	*i*Pr	*i*Pr	*i*Pr	*i*Pr	*t*Bu	*t*Bu

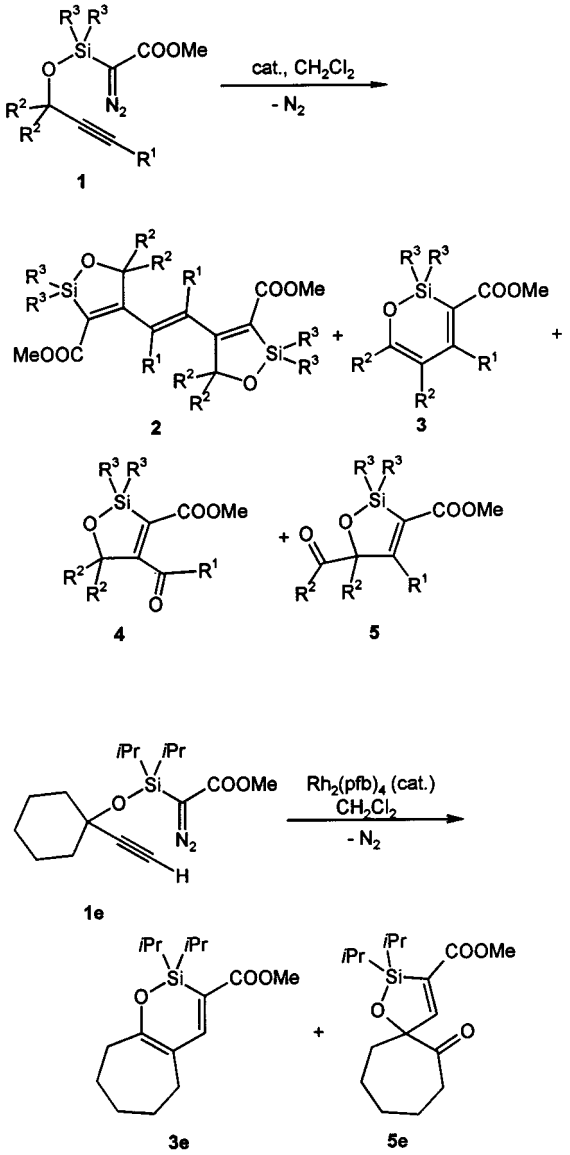
Scheme 2

Treatment of **1a−g** with catalytic amounts of copper(I) triflate in dichloromethane led to product mixtures from which the nitrogen-free oxasilaheterocycles **2** and/or **3** could be isolated in moderate yields (Scheme 3 and Table 1). Higher amounts than usual of the catalyst (10 mol%) were required to achieve complete disappearance of the diazo compounds. Product formation seems to depend on all substituents present in **1**: While 2*H*-1,2-oxasilines **3** were found in all cases except for R^2 = Me, 1,2-bis(2,5-dihydro-1,2-oxasilol-4-yl)ethenes **2** were obtained from terminal alkynes **1a**,**b**,**c**,**e** (i.e. R^1 = H), but not from **1f** where the diisopropylsilyl unit was replaced with di(*tert*-butyl)silyl.

Occasionally, traces of 4-acetyl-2,5-dihydro-1,2-oxasiloles **4** were observed; in line with a related report[17], it was assumed that they originate from air oxidation of an intermediate vinylcarbene-metal complex. In fact, we could demonstrate for **1g** that **4g** was formed in low yield if air was bubbled through the reaction mixture, but not when air was excluded rigorously.

Rhodium(II) carboxylates were also tested as catalysts. As in the case of α-(alkoxy or alkenyloxy)silyl-α-diazoacetates[23], $Rh_2(OAc)_4$ was largely unefficient; while **1c** and **1g** were not decomposed at all even at 140 °C, only low yields of **3d** and **4d** were obtained from **1d**. However, the more electrophilic rhodium(II) perfluorobutyrate [$Rh_2(pfb)_4$], showed the expected catalytic activity. Starting from **1a−e**, 2*H*-1,2-oxasilines **3** were isolated; in contrast to the CuOTf-catalyzed reaction, formal vinyl carbene dimers **2a−c**,**e** were not found at all!

The constitution of **2a−c**,**e**, which formally represent carbene dimers, was firmly established by a single-crystal X-ray diffraction of **2c** (Figure 1). The molecule was found to be a *trans*-1,2-disubstituted, centrosymmetrical ethene derivative with a completely planar skeleton.



Scheme 3. For catalysts and yields, see Table 1

The identification of oxasilines **3** was based mainly on their ^{13}C-NMR spectra showing four signals for olefinic carbon atoms, the chemical shifts of which are in the ranges expected for a donor- and an acceptor-substituted C=C bond, respectively. 2*H*-1,2-oxasilines have been mentioned in the literature only occasionally[25−27]. They were usually obtained from copyrolysis of furans and a silylene precursor[25] or from gas-phase pyrolysis of (4-methoxy-1,3-butadien-1-yl)disilanes[26]. No carboxylate-substituted derivatives have been reported so far. Oxasilines **3** were generally found to be of limited stability. By passing through a silica gel column or in $CDCl_3$ solution, **3c** was converted partially or quantitatively, by ring contraction and incorporation of an oxygen atom, into 5-acetyl-2,5-dihydro-1,2-oxasilole **5c** (Scheme 4). This compound was identified by its mass spectrum and by comparison of NMR chemical shifts with

Table 1. Decomposition of diazoacetates **1a–g** by CuOTf or rhodium(II) carboxylates (see Scheme 3)

1	R^1	R^2	R^3	Catalyst[a]	Yield [%] **2**	**3**	**4**	**5**
a	H	Me	Me	CuOTf	6			
				$Rh_2(pfb)_4$		45		10
b	H	H	*i*Pr	CuOTf	26	25		
				$Rh_2(pfb)_4$		32		
c	H	Me	*i*Pr	CuOTf	25			
				$Rh_2(pfb)_4$		50		
d	Me	H	*i*Pr	CuOTf		39		
				CuCl		18		
				$Rh_2(pfb)_4$		52		
				$Rh_2(OAc)_4$, air		6	11	
e	H	R^2,R^2 = $(CH_2)_5$	*i*Pr	CuOTf	≈ 19[b]			
				$Rh_2(pfb)_4$		38		8
f	H	H	*t*Bu	CuOTf		26		
g	Me	H	*t*Bu	CuOTf		30		
				CuOTf, air		20	6	

[a] Copper triflate: 10 mol%; $Rh_2(OAc)_4$: 5 mol%; $Rh_2(pfb)_4$ [= $Rh_2(OOCC_3F_7)_4$]: 3 mol% (5 mol% for **1d**). All reactions were run at room temp. in CH_2Cl_2 except for $Rh_2(OAc)_4$ (xylene, 137°C). – [b] Not obtained in analytically pure form.

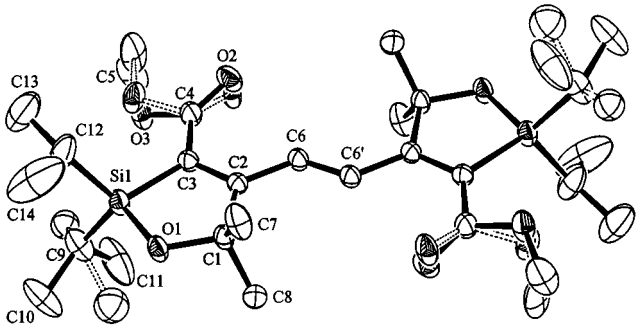
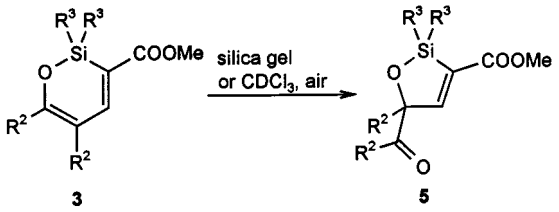


Figure 1. Structure of compound **2c** in the crystal; the structure shows disorder of the ester group and the two isopropyl groups in each half of the centrosymmetric molecule. For COOMe and one *i*Pr group, two sets of positions were refined. Ellipsoids of thermal vibration are shown at the 20% probability level. Selected bond lengths [Å]: O1–C1 1.449(3); C1–C2 1.533(4); C2–C3 1.369(4); C2–C6 1.460(4); C6–C6′ 1.326(6). Bond angles [°]: O1–Si1–C3 92.6(1). Torsion angles [°]: C6–C2–C3–Si1 –178.7(2); C3–C2–C6–C6′ 178.2(4).

The other five-membered rings (**2** and **4**) also had values in the 29–38 range (see Experimental Section).



3,5	a	c	e
R^2	Me	Me	$R^2,R^2 = (CH_2)_5$
R^3	Me	*i*Pr	*i*Pr

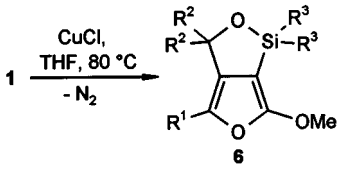
Scheme 4

those of similarly substituted derivatives of this ring system [for example, the only significant change in ^{13}C-chemical shifts in going from 5-H[23b] to 5-Ac is an increase of δ(C-5) by 13.3 ppm]. In an analogous manner, **3a** and **3e** underwent autoxidation to form **5a** and **5e**, respectively, in $CDCl_3$ solution. Thus, it is clear that the isolation of **5a**,**e** from the carbenoid decomposition reactions (Table 1) is due to a secondary reaction of 2*H*-1,2-oxasilines **3**. Although the mechanism of the transformation **3**→**5** is not clear, it seems that both proton catalysis and the presence of oxygen or water are necessary: Monitoring by ^{1}H NMR showed that the transformation of **3c** occurred in $CDCl_3$ solution but not in C_6D_6 and that it was finished more rapidly when the solution was saturated with air.

1-Oxa-2-silaheterocycles **3** and **5** can be distinguished not only by their ^{13}C-NMR spectra but also by their ^{29}Si-chemical shifts which were found at δ = 11.5–13.3 for oxasilines **3a**,**c**,**e** and at 30.9–38.0 for dihydrooxasiloles **5a**,**c**,**e**.

In further experiments, we found that the result of the catalytic decomposition of diazoacetates **1** can vary not only with the catalyst metal (copper vs. rhodium) but also with the nature of the copper catalyst. Decomposition of diazoacetates **1** with copper(I) chloride instead of the triflate required a higher temperature and was performed as a heterogeneous reaction in THF at 80 °C. From **1c**,**e**, the bicyclic 2-methoxyfurans **6c**,**e** were obtained in acceptable yields (Scheme 5), while the reaction of **1a** provided **6a** only in low yield besides some other unidentified products and unspecific decomposition occurred with **1b**,**f**. On the other hand, treatment of **1d**, containing an internal alkyne function, with CuCl or CuOTf led to oxasiline **3d** in both cases; however, the CuCl-catalyzed reaction is inferior since **3d** could be isolated only in low yield (18%) from a complex and unidentified product mixture. Formation of furans analogous to **6** has been reported for $Rh_2(OAc)_4$-mediated reactions of (1-oxopent-4-yn-1-yl)diazoacetates[12] and -di-

azoketones[11] as well as for a (*N*-propargylcarbamoyl)diazoacetate[28].



1, 6	R^1	R^2	R^3	Yield [%]
a	H	Me	Me	17
c	H	Me	*i*Pr	58
e	H	-$(CH_2)_5$-	*i*Pr	61

Scheme 5

As we have briefly mentioned in the Introduction, the discussion about mechanistic details of the transition metal-mediated carbenoid reactions of alkynyl-tethered diazocompounds is not settled and several different mechanistic pathways seem to exist. In the case of silyl-diazoacetates **1**, the initially formed metal−carbene complex **7** could yield the bicyclic cyclopropene **9**, either directly by a coordinative mechanism or via metallacyclobutene **8**. Cyclopropene **9** is presumably too strained to be isolated at room temperature; in the all-carbon bicyclo[*n*.1.0]alkene case, at least four atoms in the larger bridge would be necessary[29]. For bicyclic cyclopropenes which are structurally related to **9**, such as bicyclo[3.1.0]hex-1(6)-enes[29,30] and bicyclo[3.1.0]hexa-3,5-dien-2-ones[31], the cyclopropene-to-vinylcarbene isomerization[22] leading to the six-membered, endocyclic carbene takes place very easily[32]. However, the occurrence of free vinylcarbenes resulting from **9** would not explain the role of the catalyst in the product formation.

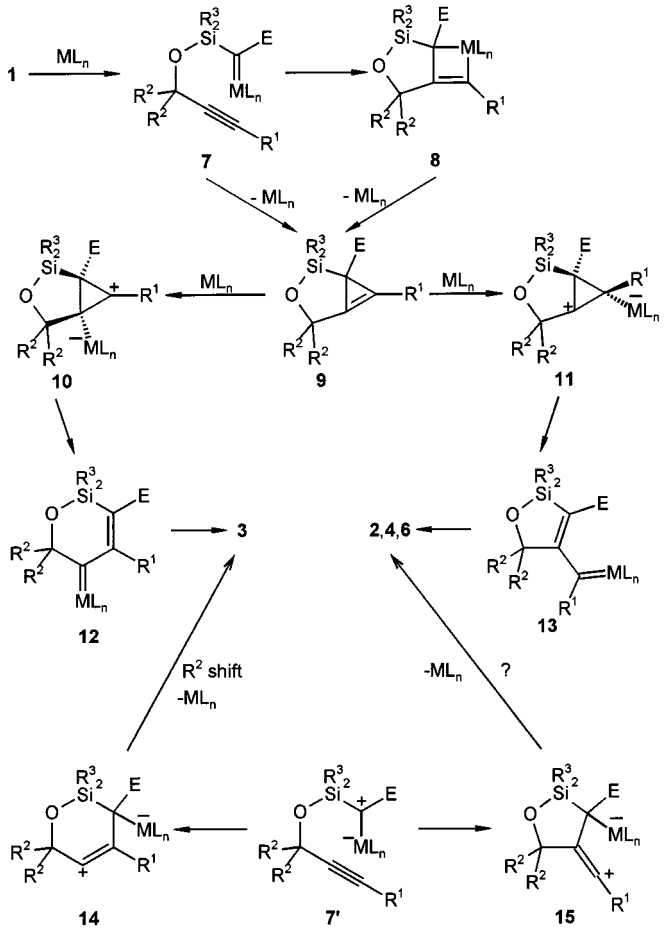
Metal-catalyzed ring-opening of cyclopropene **9** is another possibility. Depending on which of the two C,C single bonds is cleaved, either the endocyclic vinylcarbenoid **12** or the exocyclic isomer **13** would be formed. Thus, **12** would represent the precursor of oxasilines **3**, and **13** would account for the formation of products **2**, **4,** and **6**. Copper-[33−36] and rhodium-catalyzed[20,36,37] ring-opening reactions of cyclopropenes are amply documented. Interestingly, the same catalysts can be used as in the syntheses of these cyclopropenes by carbene transfer to alkynes, but higher reaction temperatures are required. In all cases studied so far, the less-substituted cyclopropene single bond was cleaved, but the final product pattern was found to be sensitive to the catalyst. Both the copper-[34,36] and the rhodium-catalyzed[36] isomerization of cyclopropene-3-carboxylates (a substructure also present in **9**) to form 2-alkoxyfurans have been reported.

Although the details of the metal-mediated ring-opening of cyclopropenes are not established, it is commonly assumed that electrophilic attack at the olefinic bond followed by disrotatory electrocyclic ring-opening of the resulting cyclopropyl cation gives rise to metal-complexed vinyl carbenes[33−37]. The regioselectivity, stereochemistry, and eventually the reversibility of the individual steps of this process could explain why different catalysts can lead to different products. Thus, the catalyst is expected to attack the C=C bond of **9** from the less hindered face, i.e. opposite to the silyl group. Whether **10** or **11** are formed depends on the ability of R^1 to stabilize an adjacent cationic center and on the extent of steric repulsion between ML_n and the CR^2_2 group. All results obtained with diazoacetates **1a−e** and the two copper catalysts, namely preference for **9**→**11** when R^1 = H but regioselective formation of **10** from **1d** (R^1 = Me), are compatible with these arguments. Why **13** undergoes 1,5-cyclization to form furans **6** in the CuCl case, but leads to the formal carbene dimers **2** with CuOTf, is not clear.

An explanation for the exclusive formation of the six-membered heterocycles **3** in the $Rh_2(pfb)_4$-catalyzed reactions of **1a−e** is less obvious. It would require the regioselective formation of cyclopropyl cation **10** from cyclopropene **9**, but with regard of the bulky shape of the dirhodium tetracarboxylate core, this orientation appears as the sterically less favored one. On the other hand, the same argument, i.e. steric repulsion between Rh_2L_4 and the ester group, could suppress the disrotatory ring-opening **11**→**13** while the analogous reaction **10**→**12** profits from relief of steric strain.

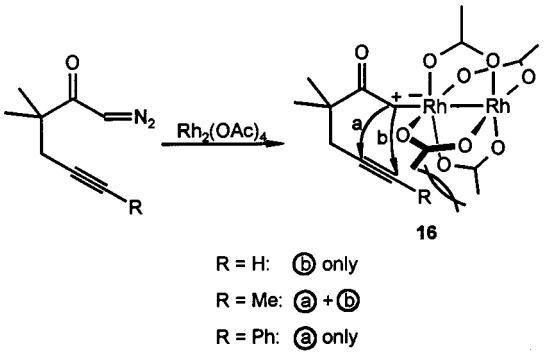
Table 1 also suggests that the size of the alkyl groups attached to silicon has an effect on the product pattern. We had assumed originally that the change from $SiMe_2$ (**1a**) to $Si{i}Pr_2$ (**1b−e**) and $Si{t}Bu_2$ (**1f,g**) in general would increase the efficiency of the intramolecular carbenoid reaction and in particular would favor the formation of five- rather than six-membered rings by the action of the Thorpe−Ingold effect. Neither assumption is confirmed by Table 1. It rather appears that increasing the bulk of the SiR_2 groups, with all other parameters being equal, tends to suppress the formation of five-membered rings **2** and **4**. Within the mechanistic model discussed above, this implies that the bicyclic cation **11** is formed from cyclopropene **9** less readily than **10**. In fact, inspection of a molecular model suggests that **11** does not only have a higher ring strain due to the presence of a carbenium center at the ring fusion but also adopts a conformation in which the *endo*-R^3 substituent at silicon is situated over the concave face of the bicyclic framework. This geometry unavoidably leads to steric strain in the case of a bulky substituent, e.g. R^3 = *t*Bu.

If one follows the mechanistic proposal of Hoye and Dinsmore[12b] (see Introduction), metal−carbene complexes **7** do not rearrange to vinylcarbene complexes **12** and **13** (which also implies that **7** and **13** are not connected by metallacyclobutene **8**) With regard to the electrophilic nature of **7** (cf. resonance structure **7′**), cationic attack at the acetylenic bond would give rise to vinyl cations **14** and **15**. However, while the endocyclic vinyl cation **14** could rearrange to **3** by a 1,2 hydride or alkyl shift and elimination of the metal fragment, it is hard to see how a cationic process should furnish compounds **2** and **4** directly from **15**. Furthermore, it would be expected that a combination of steric and electronic effects favors the cationic 5-*exo*-cyclization mode leading to **15** when R^1 is Me rather than H. This was indeed the case for the presumed rhodium-complexed



Scheme 6. E = COOMe

carbenes **16**[21], but the opposite is observed when the Cu-OTf-catalyzed reactions of **1b** and **1d** are compared.



Conclusion

Intramolecular carbenoid reactions of diazoacetates in which an alkynyl function is tethered to the diazo group by an Si−O link succeed with copper(I) and rhodium(II) catalysts. The interaction between the diazo-derived metal-carbene function with the acetylenic bond can lead to 5-*exo*- or 6-*endo* cyclization, and the regioselectivity depends on both the substituent pattern and on the catalyst. We have discussed two distinct mechanistic alternatives for these processes. It appears that most, if not all, experimental results can be accommodated with the intermediacy of strained bicyclic cyclopropenes, which then react with the catalyst to form vinyl carbene complexes such as **12** and **13**. This proposal of transposition of the metal carbene from the former diazo carbon atom to the triple bond contrasts with the conclusion from a mechanistic study carried out with other α-diazo ketones bearing tethered alkyne units[12b]. Alternatively, the cationic cyclization route, which proposes vinyl cations **14** and **15** rather than metal-complexed vinylcarbenes **12** and **13** as the immediate product precursors, predicts an electronic and steric influence of substituent R^1 at the triple bond on the regioselectivity of the cyclization. While expectations based on the latter mechanism are in line with experimental facts for the $Rh_2(pfb)_4$-catalyzed reactions, there is certainly a divergence in the copper-catalyzed cases; furthermore, vinyl cation **15** does not appear to be a logical precursor for products **2** and **4**.

Experimental Section

General Remarks: 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. Column chromatography was performed under hydrostatic conditions (silica gel Si 60, 0.063−0.2 mm, Macherey-Nagel; silica gel Si 60 silanized, 0.063−0.2 mm, Merck; neutral aluminum oxide 90, activity I, Merck). − 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-NMR spectra, and the solvent signal for the ^{13}C-NMR spectra [$\delta(CDCl_3)$ = 77.0]. Assignments of ^{13}C-chemical shifts are based on proton-coupled ^{13}C, (C,H) correlation, and HMBC spectra. − IR: Perkin−Elmer IR 883 and IR 1310. − MS: Finnigan MAT SSQ7000. − Microanalyses: Perkin−Elmer EA 240 and EA 2400. − α-Silyl-α-diazoacetates **1b**,**c**,**d**,**f**[24], the copper(I) triflate benzene complex [$Cu(O_3SCF_3) \cdot 0.5\ C_6H_6$][38], and dirhodium tetrakis(tetrafluorobutyrate)[39] were prepared as described.

Methyl α-Diazo-α-{[(1,1-dimethyl-2-propynyl)oxy]dimethylsilyl}-acetate (1a): The compound was prepared by analogy to a literature procedure[24] from dimethylsilyl bis(trifluoromethanesulfonate) (7.13 g, 4.51 mL, 20.1 mmol), methyl diazoacetate (2.00 g, 20.0 mmol), and 2-methyl-3-butyn-2-ol (1.70 g, 20.0 mmol); yield: 3.10 g (64%); yellow oil; b.p. 70°C/0.026 mbar. − IR (film): $\tilde{\nu}$ = 3300 (≡CH), 2140 (sh, C≡C), 2100 (CN_2), 1697 (C=O) cm^{-1}. − ^{1}H NMR (200.13 MHz): δ = 0.24 (s, 6 H, $SiMe_2$), 1.32 (s, 6 H, CMe_2), 2.40 (s, 1 H, ≡CH), 3.54 (s, 3 H, OMe). − ^{13}C NMR (50.32 MHz): δ = −0.10 ($SiMe_2$), 32.34 (CMe_2), 46.55 (CN_2), 51.41 (OMe), 66.90 (CMe_2), 71.48 (≡CH), 87.87 (s, *C*≡CH). − $C_{10}H_{16}N_2O_3Si$ (240.3): calcd. C 49.98, H 6.71, N 11.66; found C 49.73, H 6.62, N 11.93.

Methyl α-Diazo-α-[{[1-(ethynyl)cyclohexyl]oxy}diisopropylsilyl]-acetate (1e): The compound was prepared by analogy to a literature procedure[24] from diisopropylsilyl bis(trifluoromethanesulfonate) (4.10 g, 2.90 mL, 10.0 mmol), methyl diazoacetate (1.00 g, 10.0 mmol), and 1-ethynyl-1-cyclohexanol (1.24 g, 10.0 mmol); yield: 2.35 g (76%); yellow oil. − IR (film): $\tilde{\nu}$ = 3305 (≡CH), 2135

(sh, C≡C), 2096 (CN_2), 1694 (C=O) cm^{-1}. – ^1H NMR (200.13 MHz): δ = 1.09 (d, 6 H, CH*Me*), 1.10 (d, 6 H, CH*Me*), 1.12–1.88 (m, 12 H, SiCH, $[CH_2]_5$), 2.56 (s, 1 H, ≡CH), 3.72 (s, 3 H, OMe). – ^{13}C NMR (50.32 MHz): δ = 13.52 (SiCH), 17.31/17.39 (CH*Me*$_2$), 22.59 (CH_2), 25.02 (CH_2), 40.65 (CH_2), 51.49 (OMe), 69.97 (OC), 72.90 (≡CH), 87.38 (s, ≡C). – $^{29}Si\{^1H\}$ NMR: δ = 0.68. – $C_{17}H_{28}N_2O_3Si$ (336.5): calcd. C 60.68, H 8.39, N 8.32; found C 60.73, H 8.62, N 8.59.

Methyl α-Diazo-α-{[(2-butynyl)oxy]di-*tert*-butylsilyl}acetate (1g): The compound was prepared by analogy to a literature procedure[24] from di(*tert*-butyl)silyl bis(trifluoromethanesulfonate) (8.80 g, 6.5 mL, 20 mmol), methyl diazoacetate (2.0 g, 20 mmol), and but-2-yn-1-ol (1.40 g, 20 mmol); yield: 4.00 g (64%); yellow oil; b.p. 130°C/0.008 mbar. – IR (film): ṽ = 2090 (C=N_2), 1694 (C=O) cm^{-1}. – ^1H NMR (200.13 MHz) δ = 1.11 (s, 18 H, CMe_3), 1.83 (t, ^5J = 2.3 Hz, 3 H, CH_3C≡), 3.73 (s, 3 H, OCH_3), 4.47 (q, ^5J = 2.3 Hz, 2 H, OCH_2). – ^{13}C NMR (50.32 MHz): δ = 3.36 (*C*H_3-C≡), 22.57 (*C*Me_3), 27.60 (C*Me*$_3$), 43.48 (CN_2), 51.50 (OMe), 53.50 (OCH_2), 76.71 (H_3CC≡), 81.25 (≡*C*CH_2), 169.35 (C=O). – $^{29}Si\{^1H\}$ NMR: δ = 6.95. – $C_{15}H_{26}N_2O_3Si$ (310.5): calcd. C 58.03, H 8.44, N 9.02; found C 57.83, H 8.63, N 9.12.

Catalytic Decomposition of Diazoacetates 1a,b,c,d,f,g with Copper(I) Triflate. – General Procedure: Under an argon atmosphere, a solution of **1a**,**b**,**c**,**d**,**f**,**g** (1.8–4.5 mmol) in dichloromethane (10 mL) was added gradually during 1 h to a suspension of copper(I) triflate benzene complex (10 mol%) in the same solvent (10–20 mL). The mixture became homogeneous after addition of a few drops of the diazo solution. After stirring for 14 h, the solution was filtered over aluminum oxide [8–14 g, further elution with 100 mL of petroleum ether/ether (9:1)]. The residue obtained after evaporation of the solvent was processed individually as described below.

Methyl 4-[(*E*)-2-(3-Methoxycarbonyl-2,2-dimethyl-2,5-dihydro-1,2-oxasilol-4-yl)-1-ethenyl]-2,2-dimethyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (2a): Trituration of the product mixture obtained from **1a** (200 mg, 0.83 mmol) with pentane (5 mL) gave **2a** as a white solid, which was isolated by centrifugation and washed with more pentane; yield: 11 mg (6%); m.p. 220°C. – IR (KBr): ṽ = 1705 (C=O), 1553, 1137, 1057 cm^{-1}. – ^1H NMR (500.14 MHz): δ = 0.33 (s, 12 H, $SiMe_2$), 1.62 (s, 12 H, CMe_2), 3.76 (s, 6 H, OMe), 7.82 (s, 2 H, C*H*=C*H*). – ^{13}C NMR (125.77 MHz): δ = 0.71 ($SiMe_2$), 30.52 (C*Me*$_2$), 51.60 (OMe), 85.34 (*C*Me_2), 128.32 (=CH), 131.42 (SiC=), 168.01 (CO), 171.59 (SiC=*C*). – MS (EI, 70 eV): *m*/*z* (%) = 424 (71) [M^+], 393 (15), 377 (14), 351 (100), 335 (77), 320 (59), 308 (59), 292 (21), 260 (17). – $C_{20}H_{32}O_6Si_2$ (424.6): calcd. C 56.57, H 7.60; found C 56.80, H 7.30.

Methyl 4-[(*E*)-2-(2,2-Diisopropyl-3-methoxycarbonyl-2,5-dihydro-1,2-oxasilol-4-yl)-1-ethenyl]-2,2-diisopropyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (2b) and Methyl 2,2-Diisopropyl-2*H*-1,2-oxasiline-3-carboxylate (3b): The product mixture obtained from **1b** (991 mg, 3.7 mmol) was fractionated by bulb-to-bulb distillation to give **3b** (218 mg, 25%) at 130 °C/0.006 mbar and **2b** (232 mg, 26%) at 210–230 °C/0.003 mbar; the colorless oil obtained in the latter case solidified on standing at room temp.

Data for **2b**: M.p. 135–136 °C (CH_2Cl_2). – IR (film): ṽ = 1710 (C=O), 1582, 1263, 1194, 1073, 1060 cm^{-1}. – ^1H NMR (500.14 MHz): δ = 0.99 (d, 12 H, CH*Me*$_2$), 1.03 (d, 12 H, CH*Me*$_2$), 1.20 (sept, 4 H, C*H*Me_2), 3.76 (s, 6 H, OMe), 5.01 (s, 4 H, OCH_2), 7.55 (s, 2 H, =CH). – ^{13}C NMR (125.77 MHz): δ = 13.18 (SiCH), 16.82 (CH*Me*), 16.99 (CH*Me*), 51.30 (OMe), 72.58 (OCH_2), 126.58 (=CH), 129.06 (SiC=), 164.58 (SiC=*C*), 167.51 (C=O). – $^{29}Si\{^1H\}$ NMR: δ = 37.97. – MS (EI, 70 eV): *m*/*z* = 480 (35) [M^+], 448 (27), 437 (100), 405 (20), 337 (9), 349 (12). – $C_{24}H_{40}O_6Si_2$ (480.7): calcd. C 59.97, H 8.39; found C 59.50, H 8.10.

Data for **3b**: IR (film): ṽ = 1717, 1687, 1611, 1532, 1276, 1260, 1225, 1115 cm^{-1}. – ^1H NMR (500.14 MHz): δ = 1.02 (d, 6 H, CH*Me*), 1.05 (d, 6 H, CH*Me*), 1.20 (sept, 2 H, C*H*Me_2), 3.73 (s, 3 H, OMe), 5.24 (dd, ^3J = 6.9, 5.4 Hz, 1 H, 5-H), 6.88 (dd, ^3J = 5.4 Hz, ^4J = 1.4 Hz, 1 H, 6-H), 7.72 (dd, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1 H, 4-H). – ^{13}C NMR (125.77 MHz): δ = 13.83 (*C*HMe), 16.20 (CH*Me*), 16.73 (CH*Me*), 50.87 (OMe), 103.52 (C-5), 117.36 (C-3) 150.88 (C-4), 152.83 (C-6), 169.47 (C=O). – $^{29}Si\{^1H\}$ NMR: δ = 13.25. – MS (EI, 70 eV): *m*/*z* (%) = 240 (23) [M^+], 209 (6) [M^+ – OMe], 197 (100) [M^+ – *i*Pr]. – $C_{12}H_{30}O_3Si$ (240.4): calcd. C 59.96, H 8.39; found C 58.38, H 8.34.

Methyl 4-[(*E*)-2-(2,2-Diisopropyl-5,5-dimethyl-3-methoxycarbonyl-2,5-dihydro-1,2-oxasilol-4-yl)-1-ethenyl]-2,2-diisopropyl-5,5-dimethyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (2c): To the crude product mixture obtained from **1c** (0.53 g, 1.8 mmol) was added pentane (10 mL), whereupon colorless crystals of **2c** (0.12 g, 25%) separated, m.p. 194 °C. – IR (KBr): ṽ = 1708 (C=O), 1551, 1275, 1217, 1194, 1164, 1133 cm^{-1}. – ^1H NMR (500.14 MHz): δ = 1.01 (d, 12 H, CH*Me*), 1.06 (d, 12 H, CH*Me*), 1.16 (sept, 4 H, C*H*Me), 1.62 (s, 12 H, CMe_2), 3.74 (s, 6 H, OMe), 7.59 (s, 2 H, C*H*=C*H*). – ^{13}C NMR (125.77 MHz): δ = 13.01 (*C*HMe), 17.28 (CH*Me*), 17.55 (CH*Me*), 30.28 (C*Me*$_2$), 51.35 (OMe), 84.91 (*C*Me_2), 128.14 (=CH), 128.97 (SiC=), 168.45 (C=O), 171.34 (SiC=*C*). – $^{29}Si\{^1H\}$ NMR: δ = 29.32. – MS (EI, 70 eV): *m*/*z* (%) = 536 (100) [M^+], 505 (11), 493 (63), 461 (28), 435 (10), 407 (38), 377 (16), 225 (55), 210 (30). – $C_{28}H_{48}O_6Si_2$ (536.9): calcd. C 62.64, H 9.01; found C 62.77, H 9.09.

Methyl 2,2-Diisopropyl-4-methyl-2*H*-1,2-oxasiline-3-carboxylate (3d): The crude product mixture obtained from **1d** (1.12 g, 4.5 mmol) yielded **3d** (0.45 g, 39%) after bulb-to-bulb distillation at 130 °C/0.004 mbar as a colorless oil. – IR (film): ṽ = 1714 (C=O), 1615, 1528, 1286, 1267, 1205 cm^{-1}. – ^1H NMR (500.14 MHz): δ = 0.99 (d, 6 H, CH*Me*), 1.03 (d, 6 H, CH*Me*), 1.17 (sept, 2 H, C*H*Me), 2.30 (s, 3 H, 4-Me), 3.68 (s, 3 H, OMe), 5.05 (d, *J* = 5.7 Hz, 1 H, 5-H), 6.71 (d, 1 H, *J* = 5.7 Hz, 6-H). – ^{13}C NMR (50.32 MHz): δ = 14.06 (*C*HMe), 16.48 (CH*Me*), 17.12 (CH*Me*), 22.90 (4-Me), 50.25 (OMe), 109.81 (C-5), 111.63 (C-3) 150.49 (C-6), 162.73 (C-4), 169.22 (C=O). – $^{29}Si\{^1H\}$ NMR: δ = 11.18. – MS (EI, 70 eV): *m*/*z* (%) = 254 (17) [M^+], 223 (7) [M^+ – OMe], 211 (100) [M^+ – *i*Pr], 181 (4), 169 (6), 153 (3), 141 (24). – $C_{13}H_{22}O_3Si$ (254.4): calcd. C 61.38, H 8.72; found C 60.80, H 8.60.

Methyl 4-{(*E*)-2-[3,3-Diisopropyl-2-(methoxycarbonyl)-4-oxa-3-silaspiro[4,5]dec-1-en-1-yl]-1-ethenyl}-2,2-diisopropyl-1-oxa-2-silaspiro[4,5]dec-3-ene-3-carboxylate (2e): The crude product mixture obtained from **1e** (0.90 g, 2.67 mmol) was submitted to colum chromatography [silica gel (30 g), petroleum ether/ether (8:2)]. The first fraction furnished **2e** with a little impurity (^1H NMR: trace impurities at δ = 1.2–1.5 and 3.50–3.85) as a yellow solid (yield: 160 mg, 19%; m.p. 114–117 °C); the following fractions also contained **2e** but with more impurities. – IR (film): ṽ = 1707 (C=O) cm^{-1}. – ^1H NMR (500.14 MHz): δ = 1.00 (d, ^3J = 7.5 Hz, 14 H, CH*Me*), 1.05 (d, ^3J = 7.2 Hz, 14 H, CH*Me*), 1.10 (sept, 4 H, C*H*Me_2), 1.50–1.90 [m, 20 H, $(CH_2)_5$], 3.73 (s, 6 H, OMe), 7.11 (s, 2 H, =CH). – ^{13}C NMR (125.77 MHz): δ = 13.15 (SiCH), 17.31/17.54 (CH*Me*$_2$), 21.75 (CH_2), 25.30 (CH_2), 37.04 (CH_2), 51.31 (OMe), 86.36 (spiro-C), 128.34 (SiC=), 128.71 (=CH), 169.22 (COO), 169.91 (SiC=*C*). – $^{29}Si\{^1H\}$ NMR: δ = 28.86. – MS (CI, CH_4, 100 eV): *m*/*z* (%) = 657 (2) [MAllyl$^+$], 645 (14) [MEt$^+$], 616 (58) [M^+], 585 (100), 573 (76), 545 (3), 327 (6), 295 (6), 265 (5).

− $C_{34}H_{56}O_6Si_2$ (616.99): calcd. C 66.19, H 9.14; found C 64.44, H 8.98.

Methyl 2,2-Di-*tert*-butyl-2*H*-1,2-oxasiline-3-carboxylate (3f): Bulb-to-bulb distillation of the product mixture at 109 °C/0.024 mbar gave a fraction which contained both **3f** and di-*tert*-butyldi(2-propynyl)oxy]silane in a 69:32 ratio (GC-MS analysis; calculated yield of **3f**: 26%). The silane was a by-product in the synthesis of **1f** from which it could not be separated. − ^{1}H NMR (200.13 MHz): δ = 1.04 (s, 18 H, CMe_3), 3.75 (s, 3 H, OMe), 5.25 (dd, ^3J = 7.0, 5.3 Hz, 1 H, 5-H), 6.90 (dd, ^3J = 5.3 Hz, ^4J = 1.4 Hz, 1 H, 6-H), 7.74 (dd, ^3J = 7.0 Hz, ^4J = 1.4 Hz, 1 H, 4-H). − ^{13}C NMR (50.32 MHz): δ = 22.08 (CMe_3), 27.05 (CMe_3), 50.87 (OMe), 118.24 (C-3), 103.57 (C-5), 150.73 (C-4), 152.87 (C-6), 169.68 (C=O). − GC-MS (EI, 70 eV): *m*/*z* (%) = 268 (19) [M$^+$], 237 (7), 211 (100), 155 (19).

Methyl 2,2-Di-*tert*-butyl-4-methyl-2*H*-1,2-oxasiline-3-carboxylate (3g) and Methyl 4-Acetyl-2,2-di-*tert*-butyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (4g): A solution of **1g** (888 mg, 3.0 mmol) in dichloromethane (10 mL) was added gradually during 1 h to a suspension of copper(I) triflate benzene complex (76 mg, 10 mol%) in the same solvent (20 mL). During the reaction, air was bubbled through the solution. After stirring for 14 h, the solution was filtered over aluminum oxide [8 g, further elution with dichloromethane (30 mL)]. The residue obtained after evaporation of the solvent was separated by column chromatography [silica gel (30 g), petroleum ether/ether (9:1)]. The first product obtained was **3g** [colorless oil; yield 169 mg (20%)], followed by **4g** [colorless oil, yield: 54 mg (6%)].

Data for **3g**: M.p. 130°C/0.004 mbar. − IR (film): ṽ = 1712 (C=O), 1615, 1286, 1262, 1207, 1115 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 0.94 (s, 18 H, *t*Bu), 2.16 (s, 3 H, 4-Me), 3.62 (s, 3 H, OMe), 4.97 (d, 1 H, 5-H), 6.63 (d, 1 H, 6-H). − ^{13}C NMR (125.77 MHz): δ = 22.50 (CMe_3), 23.42 (4-Me), 27.44 (CMe_3), 50.27 (OMe), 109.72 (C-5), 113.29 (C-3), 150.04 (C-6), 160.80 (C-4), 169.98 (C=O). − ^{29}Si{^{1}H} NMR: δ = −8.3. − GC-MS (EI, 70 eV): *m*/*z* (%) = 282 (12) [M$^+$], 251 (6), 225 (100), 169 (9), 165(7). − $C_{15}H_{26}O_3Si$ (282.5): calcd. C 63.78, H 9.28; found C 63.86, H 9.08.

Data for **4g**: B.p. 110°C/0.026 mbar. − IR (film): ṽ = 2933, 2859, 1710 (broad, C=O), 1257, 1065 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 1.06 (s, 18 H, *t*Bu), 2.33 (s, 3 H, COMe), 3.80 (s, 3 H, COOMe), 4.81 (s, 2 H, OCH_2). − ^{13}C NMR (125.77 MHz): δ = 21.63 (CMe_3), 27.04 (CMe_3), 29.18 (CO*Me*), 51.94 (COO*Me*), 72.96 (C-5), 133.73 (C-3), 163.00 (C-4), 168.20 (*C*OO), 199.09 (Me*C*=O). − MS (EI, 70 eV): *m*/*z* = 298 (9) [M$^+$], 267 (6), 241 (81), 209 (8), 185 (11), 171 (14), 43 (100). − $C_{15}H_{26}O_4Si$ (298.4): calcd. C 60.37, H 8.78; found C 58.78, H 8.81.

$Rh_2(OAc)_4$-Mediated Decomposition of 1d. − 3d and Methyl 4-Acetyl-2,2-diisopropyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (4d): A solution of **1d** (850 mg, 3.0 mmol) in xylene (10 mL) was added gradually during 1 h to a suspension of dirhodium tetraacetate (66 mg, 5 mol%) in the same solvent (10 mL) kept at reflux temperature. During the reaction, air was bubbled through the mixture. After cooling to room temp., the mixture was filtered over aluminum oxide [10 g, further elution with 100 mL of petroleum ether/ether (9:1)]. The residue obtained after evaporation of the solvent was separated by column chromatography [silica gel (30 g), petroleum ether/ether (1:1)] to give first **3d** [colorless oil; yield 46 mg (6%)] and then **4d** [colorless oil; yield: 91 mg (11%)].

Data for **4d**: B.p. 120°C/0.026 mbar. − IR (KBr): ṽ = 1721 (C=O), 1712 (C=O) 1259, 1074 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 1.03 (d, 6 H, CH*Me*), 1.06 (d, 6 H, CH*Me*), 1.22 (sept, 2 H, C*H*Me), 2.36 (s, 3 H, COMe), 3.78 (s, 3 H, COOMe), 4.82 (s, 2 H, OCH_2). − ^{13}C NMR (125.76 MHz): δ = 13.08 (*C*HMe), 16.58/16.62 (CHMe_2), 29.33 (CO*Me*), 52.01 (COO*Me*), 72.95 (OCH_2), 132.09 (C-3), 164.59 (C-4), 167.66 (COO), 199.66 (C=O). − ^{29}Si{^{1}H} NMR: δ = 38.2. − MS (EI, 70 eV): *m*/*z* (%) = 270 (3) [M$^+$], 255 (4), 242 (7), 227 (23) 199 (9), 171 (9), 157 (16). − $C_{13}H_{22}O_4Si$ (270.4): calcd. C 57.75, H 8.20; found C 57.74, H 8.25.

Catalytic Decomposition of Diazoacetates 1a,b,c,d,e with Dirhodium Tetrakis(tetrafluorobutyrate)

Methyl 2,2,5,6-Tetramethyl-2*H*-1,2-oxasiline-3-carboxylate (3a) and Methyl 5-Acetyl-2,2,5-trimethyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (5a): A solution of **1a** (412 mg, 1.4 mmol) in dichloromethane (10 mL) was added gradually during 1 h to a solution of dirhodium tetrakis(tetrafluorobutyrate) (29 mg, 2 mol%) in the same solvent (30 mL). After stirring for 14 h, the solvent was replaced by petroleum ether, and the solution obtained after centrifugation was concentrated and subjected to bulb-to-bulb distillation. The fraction obtained at 93°C/0.015 mbar was submitted to colum chromatography [silica gel (27 g), petroleum ether/ether (8:2)]. The first fraction furnished **3a** (pale yellow oil, yield: 134 mg, 45%), the second fraction contained **5a** (colorless oil; yield: 31 mg, 10%).

Data for **3a**: M.p. 70°C/0.018 mbar. − IR (film): ṽ = 1712 (C=O), 1686, 1529, 1433, 1299, 1231, 1182 cm^{-1}. − ^{1}H NMR (200.13 MHz): δ = 0.35 (s, 6 H, $SiMe_2$), 1.80 (s, 3 H, 5-Me), 1.95 (s, 3 H, 6-Me), 3.73 (s, 3 H, OMe), 7.56 (d, 1 H, 4-H). − ^{13}C NMR (50.32 MHz): δ = 1.02 ($SiMe_2$), 17.83 (5-Me), 20.36 (6-Me), 51.20 (OMe), 106.20 (C-5), 116.56 (C-3), 155.83 (C-4), 157.13 (C-6), 169.96 (C=O). − GC-MS (EI, 70 eV): *m*/*z* (%) = 212 (100) [M$^+$], 197 (55), 184 (40), 169 (97), 139 (51). − $C_{10}H_{16}O_3Si$ (212.3): calcd. C 56.57, H 7.60; found C 56.35, H 7.61.

Data for **5a**: B.p. 70°C/0.018 mbar. − IR (film): ṽ = 1728 (C=O), 1710 cm^{-1}. − ^{1}H NMR (200.13 MHz): δ = 0.40 (s, 3 H, SiMe), 0.44 (s, 3 H, SiMe), 1.46 (s, 3 H, 5-Me), 2.20 (s, 3 H, COMe), 3.76 (s, 3 H, COOMe), 7.55 (s, 1 H, =CH). − ^{13}C NMR (50.32 MHz): δ = 0.03 (SiMe), 0.84 (SiMe), 25.09 (5-Me), 25.49 (CO*Me*), 51.84 (COO*Me*), 92.01 (s, C-5), 135.33 (C-3), 161.28 (=CH), 166.46 (COO), 209.53 (Me*C*=O). − ^{29}Si{^{1}H} NMR: δ = 30.94. − MS (EI, 70 eV): *m*/*z* = 228 (2) [M$^+$], 197 (5), 185 (100). − $C_{10}H_{16}O_4Si$ (228.3): calcd. C 52.61, H 7.06; found C 52.35, H 7.06.

Methyl 2,2-Diisopropyl-5,6-dimethyl-2*H*-1,2-oxasiline-3-carboxylate (3c): A solution of **1c** (500 mg, 1.7 mmol) in dichloromethane (10 mL) was added gradually during 1 h to a solution of dirhodium tetrakis(tetrafluorobutyrate) (56 mg, 3 mol%) in the same solvent (30 mL). After stirring for 14 h, the solvent was replaced by petroleum ether, and the solution was filtered over aluminum oxide [10 g, further elution with petroleum ether (100 mL)]. After removal of the solvent, **3c** was left as a colorless oil; yield: 225 mg (50%); b.p. 93°C/0.015 mbar. − IR (film): ṽ = 1712 (C=O), 1686, 1527, 1230 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 0.98 (d, 6 H, CH*Me*), 1.01 (d, 6 H, CH*Me*), 1.12 (sept, 2 H, SiCH), 1.95 (s, 3 H, Me), 1.78 (s, 3 H, Me), 3.71 (s, 3 H, OMe), 7.69 (s, 1 H, =CH). − ^{13}C NMR (50.32 MHz): δ = 13.67 (SiC), 16.41 (CH*Me*), 16.90 (CH*Me*), 17.70 (5-Me), 20.08 (6-Me), 50.89 (OMe), 105.76 (C-5), 113.32 (SiC), 157.54 (=CH), 158.16 (C-6), 170.16 (C=O). − ^{29}Si{^{1}H} NMR: δ = 11.31. − MS (CI, CH_4, 120 eV): *m*/*z* (%) = 297 (22) [MEt$^+$], 269 (100) [MH$^+$], 237 (24) [MH$^+$], 225 (68). − $C_{14}H_{24}O_3Si$ (268.4): calcd. C 62.64, H 9.01; found C 61.96, H 8.93.

By an analogous procedure, **3b** was obtained from **1b** (yield: 32%) and **3d** from **1d** (yield: 52%); see above for spectroscopic data.

Methyl 5-Acetyl-2,2-diisopropyl-5-methyl-2,5-dihydro-1,2-oxasilole-3-carboxylate (5): When **3c** was submitted to column chromatogra-

phy [silica gel, petroleum ether/ether (9:1)] or left in $CDCl_3$ solution saturated with air, complete transformation into **5c** took place; bp. 75°C/0.02 mbar (Kugelrohr). − IR (film): $\tilde{\nu}$ = 1729 (C=O), 1711 (C=O) cm^{-1}. − ^1H NMR (500.14 MHz): δ = 1.01 (d, 3 H, CH*Me*$_2$), 1.04 (d, 3 H, CH*Me*$_2$), 1.07 (d, 6 H, CH*Me*$_2$), 1.20 (sept, 2 H, SiCH), 1.47 (s, 3 H, 5-Me, 2.27 (s, 3 H, MeCO), 3.75 (s, 3 H, OMe), 7.73 (s, 1 H, 4-H). − ^{13}C NMR (125.76 MHz): δ = 12.52 (SiCH), 13.18 (SiCH), 16.93/17.21/13.32/17.38 (CH*Me*), 25.01 (*Me*CO), 25.94 (5-Me), 51.70 (OMe), 91.48 (C-5), 132.47 (C-3), 162.25 (C-4), 166.77 (COO), 209.74 (s, C=O). − $^{29}Si\{^1H\}$ NMR: δ = 33.55. − MS (EI, 70 eV): *m*/*z* (%) = 284 (0.5) [M^+], 241 (100), 198 (2), 181 (9), 171 (5). − $C_{14}H_{24}O_4Si$ (284.4): calcd. C 59.12, H 8.50; found C 58.74, H 8.45.

Methyl 2,2-Diisopropyl-2,5,6,7,8,9-hexahydrocyclohepta[*e*][1,2]oxasiline-3-carboxylate (3e) and Methyl 2,2-Diisopropyl-6-oxo-2-silaspiro[4.6]undec-3-ene-3-carboxylate (5e): By a procedure analogous to the one described above for **1a**, decomposition of **1e** (265 mg, 0.79 mmol) furnished **3e** as a pale-yellow oil (93 mg, 38%) and **5e** as a colorless oil (20 mg, 8%).

Data for **3e**: M.p. 130°C/0.024 mbar. − IR (film): $\tilde{\nu}$ = 1708 (C=O), 1518 cm^{-1}. − ^1H NMR (200.13 MHz): δ = 1.00 (t, 12 H, CH*Me*$_2$), 1.13 (sept, 2 H, C*H*Me$_2$), 1.50 (m$_c$, 2 H, CH$_2$), 1.56 (m$_c$, 2 H, CH$_2$), 1.72 (m$_c$, 2 H, CH$_2$), 2.28 (m$_c$, 2 H, CH$_2$), 2.42 (m$_c$, 2 H, CH$_2$), 3.71 (s, 3 H, OMe), 7.71 (s, 1 H, =CH). − ^{13}C NMR (50.32 MHz): δ = 13.85 (*C*HMe$_2$), 16.54 (CH*Me*), 17.00 (CH*Me*), 25.14/27.60/32.07/33.31/37.01 (5× CH$_2$), 50.99 (OMe), 111.71 (C-3), 113.46 (C-4a), 158.22 (C-4), 166.72 (C-9a), 170.50 (COO). − $^{29}Si\{^1H\}$ NMR: δ = 11.51. − GC-MS (EI, 70 eV): *m*/*z* (%) = 308 (23) [M^+], 265 (100). − $C_{17}H_{28}O_3Si$ (308.5): calcd. C 61.19, H 9.18; found C 61.15, H 8.85.

Data for **5e**: B.p. 130°C/0.024 mbar. − IR (film): $\tilde{\nu}$ = 1709 (C=O), 1710, 1518, 1232 cm^{-1}. − ^1H NMR (200.13 MHz): δ = 0.95−1.07 (3× d, 12 H, CH*Me*$_2$), 1.19 (sept, 2 H, C*H*Me$_2$), 1.80 (m$_C$, 8 H, CH$_2$), 2.37 (m$_C$, 1 H, CH$_2$), 2.91 (m$_C$, 1 H, CH$_2$), 3.74 (s, 3 H, OMe), 7.85 (s, 1 H, =CH). − ^{13}C NMR (50.32 MHz): δ = 12.41/12.83 (*C*HMe), 16.93/17.13/17.19/17.32 (CH*Me*$_2$), 23.32/24.91/27.80/38.47/40.78 (5 x CH$_2$), 51.66 (OMe), 93.91 (C-5), 130.96 (C-3), 162.66 (C-4), 166.70 (s, COO), 211.74 (C=O). − MS (CI, CH_4, 100 eV): *m*/*z* (%) = 365 (0.2) [MAllyl$^+$], 353 (20) [MEt$^+$], 325 (100) [M^+], 293 (8), 281 (26), 253 (7). − $C_{17}H_{28}O_4Si$ (324.59): calcd. C 62.93, H 8.70; found C 62.65, H 8.35.

Decomposition of Diazoacetates 1a,d,e with Copper(I) Chloride; General Procedure: To a solution of the diazoacetate in THF (50 mL) was added copper(I) chloride (20 mol%), and the mixture was heated at reflux for 24 h. After cooling, unsoluble parts were separated by centrifugation. The solvent was evaporated, and the residue was treated with petroleum ether (40 mL). Unsoluble parts were separated again by centrifugation. Evaporation of the solvent and bulb-to-bulb distillation of the residue gave **6**.

6-Methoxy-1,1,3,3-tetramethyl-1H,3*H*-furo[3,4-*c*][1,2]oxasilole (6a): The crude product mixture obtained from **1a** (1.00 g, 4.16 mmol) yielded after two bulb-to-bulb distillations at 110°C/0.018 mbar a colorless oil, which consisted according to GC-MS of **6a** (ca. 50%, calculated yield ca. 17%) and five major byproducts. − ^1H NMR (200.13 MHz): δ = 0.39 (s, 6 H, SiMe$_2$), 1.49 (s, 6 H, CMe$_2$), 3.81 (s, 3 H, OMe), 6.69 (s, 1 H, =CH). − ^{13}C NMR (50.32 MHz): δ = 2.31 (SiMe$_2$), 32.14 (C*Me*$_2$), 57.76 (OMe), 76.82 (*C*Me$_2$), 87.97 (C-6a), 122.70 (=CH), 145.84 (C-3a), 160.65 (C-6). − $^{29}Si\{^1H\}$ NMR: δ = 13.54. − MS (CI, CH_4, 120 eV): *m*/*z* (%) = 253 (2) [MAllyl$^+$], 241 (4) [MEt$^+$], 213 (100) [MH$^+$], 197 (46) [M^+ − Me], 195 (20), 185 (4), 167 (4), 155 (2), 139 (3).

1,1-Diisopropyl-6-methoxy-3,3-dimethyl-1*H*,3*H*-furo[3,4-*c*][1,2]-oxasilole (6c): The crude product mixture obtained from **1c** (2.65 g, 9.4 mmol) yielded **6c** (1.45 g, 58%) after bulb-to-bulb distillation at 80°C/0.015 mbar as a colorless oil. − IR (film): $\tilde{\nu}$ = 2943, 2865, 1618, 1601, 1578, 1345 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 1.04 (d, 6 H, CH*Me*), 1.07 (d, 6 H, CH*Me*) 1.13 (m$_c$, 2 H, SiCH), 1.50 (s, 6 H, CMe$_2$), 3.84 (s, 3 H, OMe), 6.70 (s, 1 H, =CH). − ^{13}C NMR (125.76 MHz): δ = 13.22 (SiCH), 17.31 (CH*Me*), 17.57 (CH*Me*), 32.00 (C*Me*$_2$), 58.04 (OMe), 76.36 (C-3), 84.97 (C-6a), 122.80 (=CH), 146.49 (C-4a), 160.72 (C-6). − $^{29}Si\{^1H\}$ NMR: δ = 19.71. − MS (CI, CH_4, 100 eV): *m*/*z* (%) = 309 (2) [MAllyl$^+$], 297 (9) [MEt$^+$], 269 (100) [MH$^+$], 254 (26) [MH$^+$ − Me], 225 (65) [M^+ − *i*Pr]. − MS (EI, 70 eV): *m*/*z* (%) = 268 (38) [M^+], 253 (8), 238 (2), 225 (100) M^+ − *i*Pr], 207 (51), 183 (12), 167 (7), 139 (8), 119 (10), 91 (17). − $C_{14}H_{24}O_3Si$ (268.4): calcd. C 62.64, H 9.01; found C 61.43, H 8.91.

1,1-Diisopropyl-6-methoxyspiro{cyclohexane-1,3′-[3*H*]furo[3,4-*c*]-[1,2]oxasilole} (6e): The crude product mixture obtained from **1e** (0.58 g, 1.71 mmol) yielded **6e** (0.32 g, 61%) after bulb-to-bulb distillation at 110°C/0.004 mbar as a colorless oil. − IR (KBr): $\tilde{\nu}$ = 2934, 2861, 1599, 1577, 1462, 1438, 1339, 1256, 1063, 1036 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 1.02 (d, 6 H, CH*Me*) 1.06 (d, 6 H, CH*Me*), 1.10 (sept, 2 H, SiCH), 1.41−1.52 (m, 4 H, CH$_2$), 1.60−1.66 (m, 2 H, CH$_2$), 1.69−1.78 (m, 4 H, CH$_2$), 3.83 (s, 3 H, OMe), 6.76 (s, 1 H, =CH). − ^{13}C NMR (125.77 MHz): δ = 13.29 (SiCH), 17.42/17.70 (SiCH*Me*), 22.64 (CH$_2$), 25.15 (CH$_2$), 40.21 (CH$_2$), 58.07 (OMe), 78.38 (spiro-C), 85.35 (C-6a), 123.00 (=CH), 145.54 (C-3a), 160.73 (C-6). − $^{29}Si\{^1H\}$ NMR: δ = 18.32. − $C_{17}H_{28}O_3Si$ (308.5): calcd. C 66.19, H 9.15; found C 66.34, H 9.08.

X-ray Crystal Structure Determination of 2c[40]. − Crystal Data: $C_{28}H_{48}O_6Si_2$; *M* = 536.8 g/mol; triclinic space group $P\bar{1}$, *a* = 8.795(1), *b* = 9.563(2), *c* = 9.941(2) Å, α = 76.84(2), β = 84.56(2), γ = 82.16(2)°; *V* = 804.8(2) Å^3; *Z* = 1; $d_{calcd.}$ = 1.108 Mg/m^3, μ(Mo-K_a) = 0.14 mm^{-1}. − *Data Collection:* *T* = 295 K, crystal size 0.38 × 0.23 × 0.08 mm, diffractometer Stoe-IPDS, radiation Mo-K_a; Θ range 2.11−25.97°; 7973 reflections collected, 2930 independent reflections (R_{int} = 0.0521). − *Structure Solution and Refinement:* Structure solution by direct methods (program SHELXS-97), full-matrix least-squares refinement on *F* (program SHELXL-97) with 2930 reflections and 203 variables (5 restraints). Hydrogen atoms are in calculated positions and were refined as riding atoms. *R* = 0.1234 (0.0556), R_w = 0.1629 (0.1379) for all reflections [reflections with $I > 2\sigma(I)$]; residual electron density ≤ 0.34 e Å^{-3}. The ester group and the two Si-*i*Pr groups are disordered. For the ester group, two sets of positions, both with occupancy factors of 0.5, were refined. For one of the isopropyl groups (C9,C10,C11), two sets of positions were refined (occupance factors of 0.85 and 0.15, no hydrogen atoms included for the minor site), while the disorder of the second Si−*i*Pr group could not be resolved reasonably.

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