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A novel product pattern in the palladium(II)-catalyzed decomposition of a (1-diazo-2-oxoalkyl)silane *

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Abstract

Elimination of dinitrogen from (3,3-dimethyl-1-diazo-2-oxobutyl)-(tert-butyl)dimethylsilane catalyzed by palladium(II) chloride bis(acetonitrile), bis[(η^3-allyl)chloropalladium] or palladium(II) acetate gives the butatriene derivatives (E)- and (Z)-1,4-di[((tert-butyl)dimethylsilyl)oxy]-2,2,7,7-tetramethyl-3,4,5-octatriene, which are the formal dimers of an alkylidene carbene. The siloxyalkene (^{t}Bu)[Me$_2$(^{t}Bu)SiO]C=CHCl is also formed, with a yield which parallels the amount of catalyst. Similarly, (^{t}Bu)[Me$_2$(^{t}Bu)SiO]C=CH(OAc) is a by product, when the decomposition of the same diazoketone is catalyzed by palladium(II) acetate. The structure of the (E) isomer of the bis(siloxy)-3,4,5-octatriene derivative was determined by an X-ray diffraction study.

Key words: Palladium; Silicon; Diazo

1. Introduction

The various procedures (thermolysis, photolysis, and transition-metal catalysis) for elimination of dinitrogen from (1-diazo-2-oxoalkyl)silanes **1** involve a range of reaction pathways. Thermolysis involves a surprisingly facile 1,3-(C → O) silyl shift, resulting in the formation of diazoalkenes **2** (Scheme 1). Under the conditions of this rearrangement, the diazocumulenes **2** can be trapped [1], but they readily lose N_2 to form β-siloxyalkylidene carbenes 3, which react intramolecularly to form stable products such as **5** and **6** [2,3]. Photochemical decomposition of **1** (R^2,R^3 = alkyl or aryl) consistently yields silyl ketenes **4**, formed by a Wolff rearrangement [4]. In appropriate cases, carbenic γ-C–H insertion leading to 2-silylcyclobutanones can occur concurrently.

The copper(I)-triflate-catalyzed decomposition of silylated diazoketones **1a-1c**, like the photolysis, normally gives the ketenes **4** [4] (Scheme 2). In contrast, 1-oxa-2-sila-4-cyclopentene (**6d**) is the sole product obtained from **1d**, irrespective of whether CuOTf (OTf = OSO_2CF_3; triflate = trifluoromethanesulfonate) [4], Cu(OTf)$_2$ [5a], bis[(η^3-allyl)chloropalladium] [5a] or rhodium(II) perfluorobutyrate [5b] is used as catalyst. Thus catalytic decomposition of **1d** at room temperature and thermal N_2 elimination both yield the same heterocycle **6d**. Since the catalytic decomposition occurs at a temperature at which **1d** is still thermally stable, we can account for its formation with the usual concepts of metal carbene chemistry, namely carbenoid C–H insertion resulting in an acylsilirane (**7**) which immediately rearranges to **6d** (Scheme 2).

We now report an unprecedented product pattern that is observed when the N_2 elimination from diazoketone **1b** is induced by various palladium(II) catalysts.

2. Results

Decomposition of the diazoketone **1b** by the homogeneous catalysts bis[(η^3-allyl]chloropalladium(II)] or dichloropalladium(II) bis(acetonitrile) at room temperature gave a mixture of products which, according to the ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra, consisted mainly of 1-oxa-2-sila-4-cyclopentene (**6b**), butatriene derivatives (E)- and (Z)-**8**, and chloroalkene (Z)-**9** (Scheme 3). These products could not be resolved by column chromatography on silica

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* Dedicated to Prof. O.J. Scherer on the occasion of his 60th birthday.

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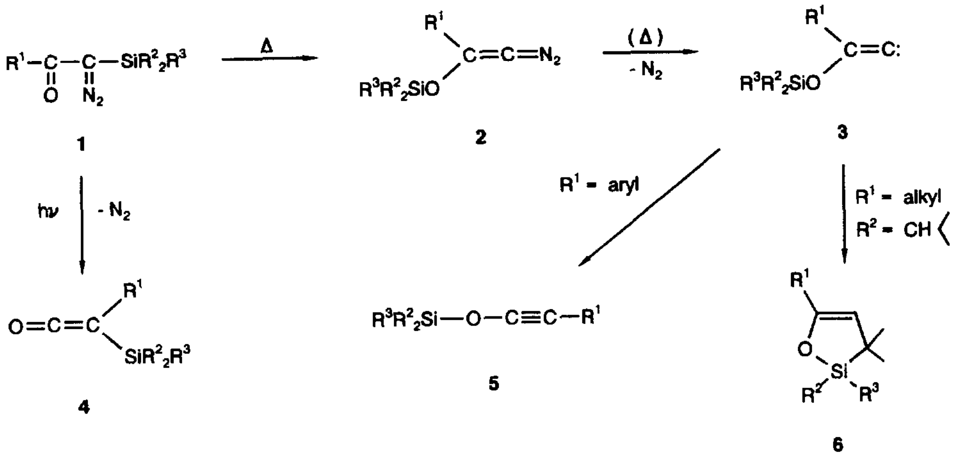
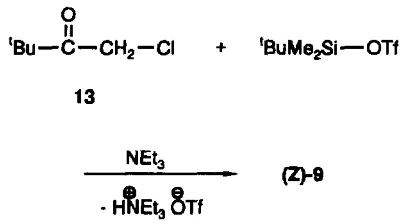


Scheme 1.

gel, but separation was achieved (although incompletely in several cases) by fractional Kugelrohr distillation.

The bis(siloxy)butatrienes (E)- and (Z)-**8** were isolated as a mixture from which pure (E)-**8** was obtained by crystallization. The constitution of this cumulene was evident from its ^1H and ^{13}C NMR and mass spectra, and the (E) configuration was established by an X-ray structure analysis (see below). Under modified work-up conditions, (E)-**8** was isolated by crystallization directly from the reaction mixture from which palladium-containing material had been removed by filtration through silica gel. When this purification procedure was carried out, partial or complete hydrolysis of **6b** occurred, and silanol **11** was obtained (*vide infra*).

Compound **9** was identified by comparison of its ^1H and ^{13}C NMR data with those for an authentic sample prepared independently by silylation of α-chloroketone **13**, which gave only one diastereomer of **9**:



$$ {}^tBu-\overset{\overset{O}{\|}}{C}-CH_2-Cl \quad + \quad {}^tBuMe_2Si-OTf \xrightarrow[-\,H\overset{\oplus}{N}Et_3\,\overset{\ominus}{O}Tf]{NEt_3} (Z)\text{-}9 $$

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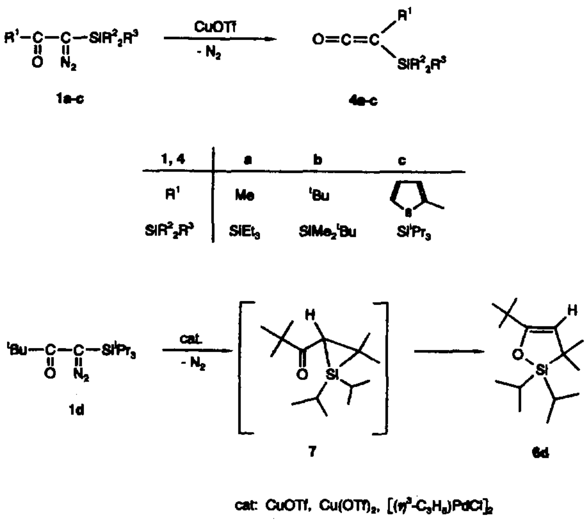
By analogy, with the outcome of the corresponding silylation of α-bromoketones [6], it would be expected to be the thermodynamically favored [7] (Z) isomer. This assignment was confirmed by a nuclear Overhauser effect experiment (see Section 3).

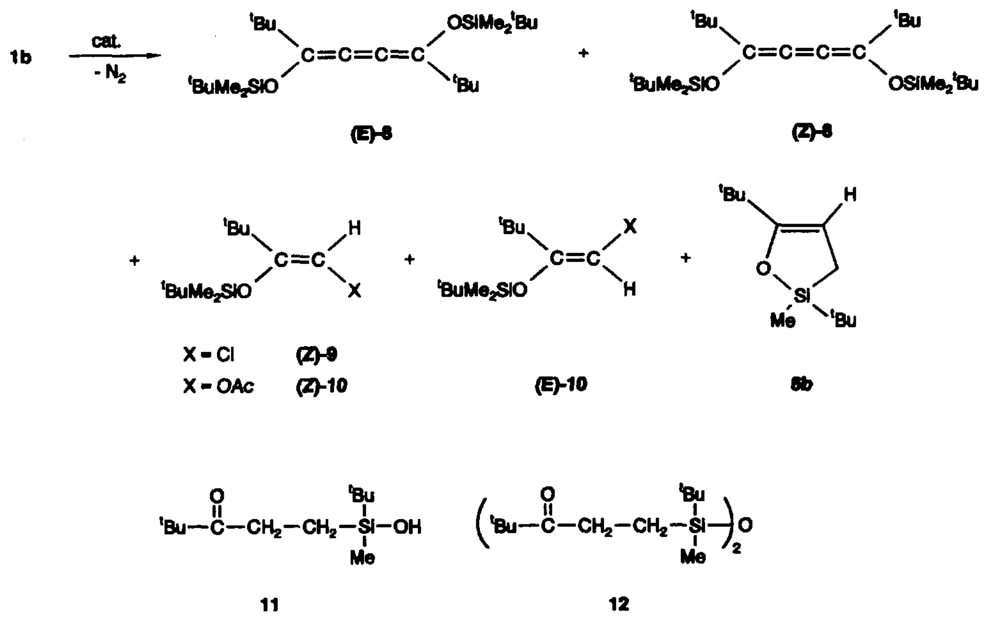
Clearly, the chlorine atom incorporated in **9** stems from the chloropalladium catalyst. The yield of **9** approximately parallels the amount of catalyst used, and metallic palladium is formed in all the reactions. Thus the chloropalladium catalysts mentioned so far must undergo a stoichiometric reaction with **1b** to give the chloroalkene **9**. Increasing the supply of chloride ions by addition of LiCl results in a correspondingly enhanced yield of **9** (Table 1, rows 5 and 6). In keeping with these observations, the enol acetate **10** (5 : 1 mixture of diastereomers) rather than **9** is found in the reaction mixture when the chloropalladium catalysts are replaced by palladium(II) acetate.

In the case of the decomposition of **1b** by $PdCl_2$–$2CH_3CN$, the yield of **8** is distinctly higher at 55–60°C than at room temperature (Table 1, rows 3–5). At higher temperatures, the catalytic process is sufficiently fast largely to replace the thermal decomposition of **1b**, leading to **6b** depicted in Scheme 1. This is no longer



cat: CuOTf, $Cu(OTf)_2$, $[(\eta^3\text{-}C_3H_5)PdCl]_2$

Scheme 2.



Scheme 3. For catalysts, products and yields, see Table 1.

true when $PdCl_2$ is used as catalyst. In contrast with the bis(acetonitrile) complex, it does not form a homogeneous solution, and the reaction at 20°C proceeds very slowly. At 60°C, the catalytic process, which again produces a considerable amount of butatrienes (Z)- and (E)-**8**, is still rather slow, and the major product

TABLE 1. Catalytic decomposition of **1b** by various palladium catalysts and by $(PPh_3)_2Rh(CO)Cl$ in benzene or tetrahydrofuran

Row	Catalyst (mol%)	Reaction temperature (°C)	Reaction time (h)	Yield [a] (%)			
				6b, **11** or **12**	**8** [b]	**9** [c]	**10** [d]
1	$[(\eta^3\text{-}C_3H_5)PdCl]_2$ (7)	20	5	(**6b** [e])	22	14 [f]	
2	$[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2.5)	50	2		20	4 [f]	
3	$PdCl_2 \cdot 2CH_3CN$ (5)	20	12	(**6b** [e])	22	10 [f]	
4	$PdCl_2 \cdot 2CH_3CN$ (5)	60	2	(**6b** [e])	35	6 [f]	
5	$PdCl_2 \cdot 2CH_3CN$ (6.5)	55 [g]	1	11(**6b**)	33	7 [f]	
6	$PdCl_2 \cdot 2CH_3CN$ (6.5) + LiCl (6.2)	55 [g]	1.2	9(**12**)	24	20	
7	$PdCl_2$ (5)	20	72		< 5	Trace	
8	$PdCl_2$ (5)	60	22	57(**11**)	32		
9	$Pd(OOCCH_3)_2$ (5)	20	12	≈ 2(**6b**)	30	≈ 6	
10	$(PPh_3)_2Rh(CO)Cl$ (5)	20	48		3		
11	$(PPh_3)_2Rh(CO)Cl$ (5)	60	18	40(**11**)	5		

[a] Yields of isolated products are given in most cases; for work up conditions, see Section 3. Since complete separation of the products and/or purification in several cases was not possible and, because of some loss of material (especially of **6b** and **10**) due to unavoidable partial hydrolysis, the true yields certainly differ by a few per cent.

[b] A mixture of diastereomers is obtained in all cases (E):(Z), 1:1.1). The yields given here are for the diastereomer composite. Only the (E) isomer can be obtained in pure form by fractional crystallization. For rows 1–3, the total yield has been calculated from the amount of the pure (E) isomer obtained, taking into account the (Z)-to-(E) ratio of 1.1 in the original reaction mixture.

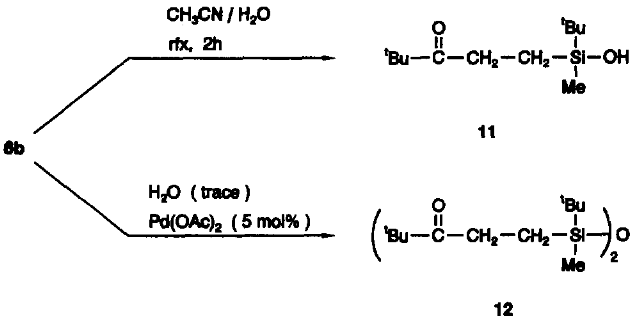
[c] Only one diastereomer is obtained (presumably the (Z) isomer).

[d] Diastereomer composite (5:1).

[e] Detected by ^1H NMR spectroscopy in the reaction mixture (about 5–7%), but not isolated.

[f] Accompanied by an unknown compound (about 10–20%; see Section 3).

[g] In THF.

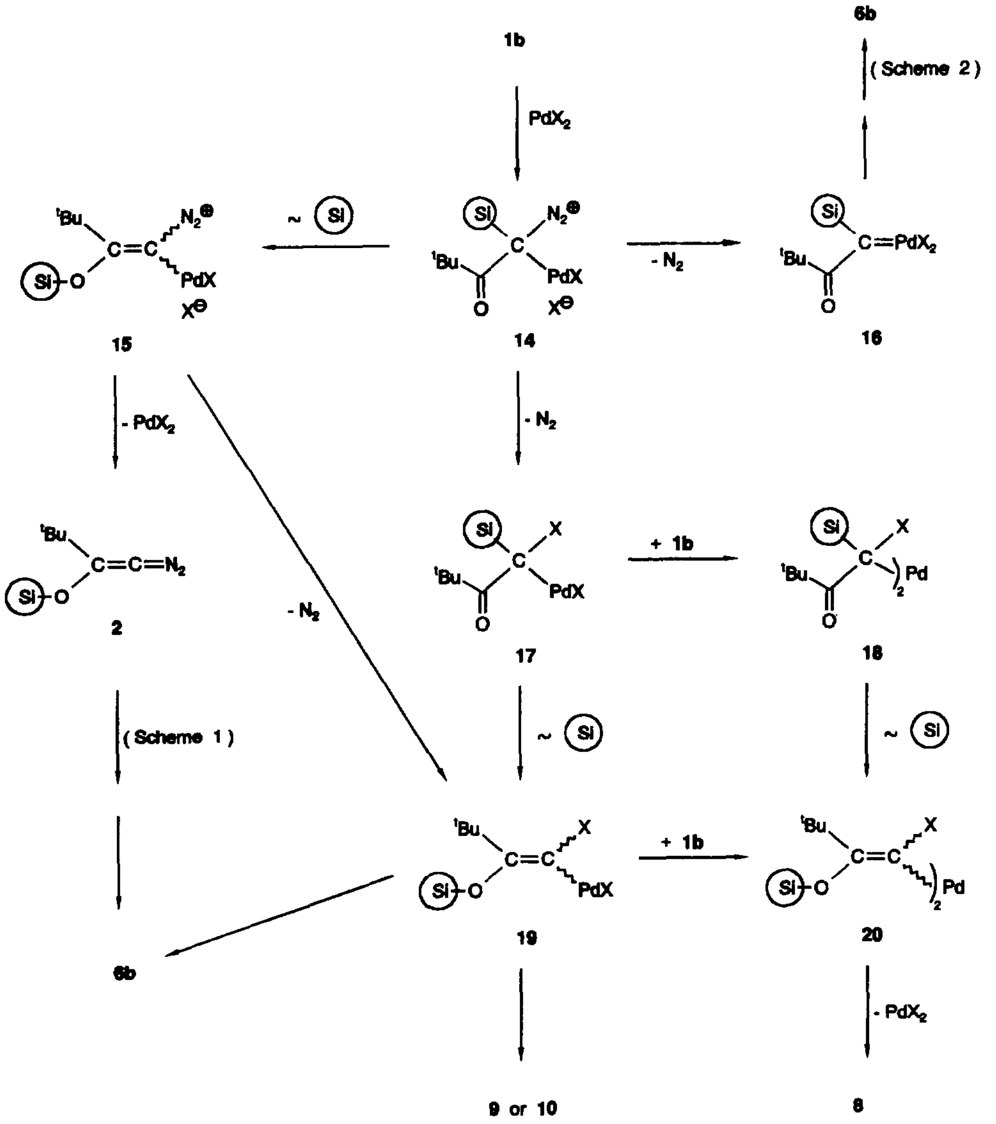


Scheme 4.

obtained is the silanol **11**, which again arises from hydrolysis of **6b** during the chromatographic work-up.

Although we cannot definitely decide whether **6b** has been formed by the thermal (Scheme 1) or a metal carbene pathway, the former route seems very likely in view of the fact that the long reaction time is sufficient for complete thermal decomposition of **1b** [3]. The same arguments apply to the decomposition of **1b** by $(PPh_3)_2Rh(CO)Cl$ as catalyst (Table 1, rows 10 and 11).

The cyclic silyl enolether **6b** was detected by ^1H NMR spectroscopy in most of the crude product mix-



Scheme 5. X = Cl or OAc. Additional ligands of palladium are omitted for clarity.

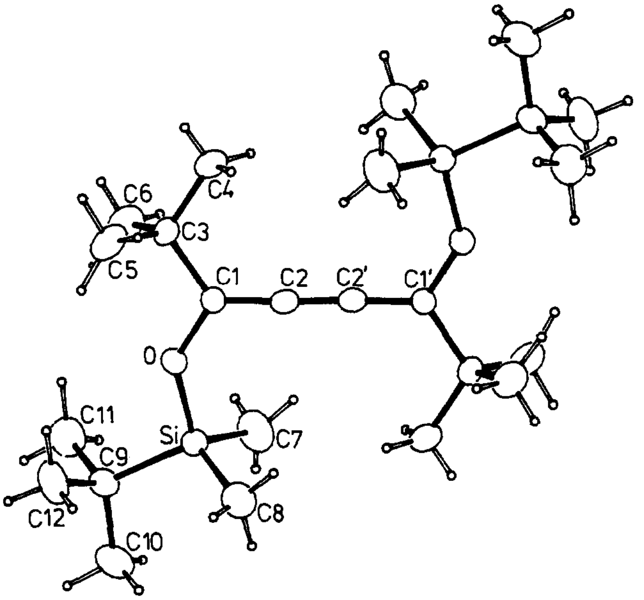


Fig. 1. ORTEP plot of (E)-**8**. The size of the ellipsoids of thermal vibration corresponds to a 33% probability.

tures listed in Table 1; it was usually hydrolyzed during the work-up, and the silanol **11** or disiloxane **12** was isolated. As a rule, the silanol **11** was obtained when work-up included a chromatographic purification step on a silica gel column, whereas the disiloxane **12** appeared to result from a palladium-assisted hydrolytic cleavage of **6b**. In independent experiments (Scheme 4), we found that the hydrolysis of the cyclic silyl enolether **6b** in acetonitrile–water yields the silanol **11**. In contrast, treatment of **6b** with a catalytic amount of palladium(II) acetate in the presence of only adventitious traces of water (in "dry" benzene), followed by work-up involving distillation in the presence of the palladium catalyst, yields the disiloxane **12**. In the latter case, we observed approximately 30% conversion of **6b** after 12 h at room temperature.

TABLE 2. Positional parameters of non-hydrogen atoms in (E)-**8**; standard deviations are given in parentheses

Atom	*x*	*y*	*z*
Si	0.2294(1)	0.1650(1)	0.7246(2)
O	0.3656(2)	0.2173(2)	0.8684(4)
C(1)	0.4820(3)	0.1672(3)	0.9448(5)
C(2)	0.4925(3)	0.0534(3)	0.9814(6)
C(3)	0.5961(3)	0.2554(3)	0.9938(5)
C(4)	0.7261(4)	0.1960(3)	1.0717(7)
C(5)	0.5491(4)	0.3559(3)	1.1579(7)
C(6)	0.6213(4)	0.3068(4)	0.7919(7)
C(7)	0.2832(4)	0.0536(4)	0.5072(7)
C(8)	0.1171(4)	0.0976(4)	0.8928(7)
C(9)	0.1422(3)	0.2997(3)	0.6280(5)
C(10)	0.0059(4)	0.2654(4)	0.5119(7)
C(11)	0.2315(4)	0.3544(4)	0.4804(7)
C(12)	0.1140(4)	0.3932(4)	0.8162(7)

2.1. Reaction mechanism

The Pd-assisted transformation of **1b** into **6b**, **8**, **9** and **10** involve a 1,3(C → O) silyl shift, and so participation of Pd-substituted β-siloxyalkylidene species in the reaction pathways appears likely. A possible mechanistic scheme is shown in Scheme 5 for the decomposition of **1b** by PdX_2 (X = Cl or OAc).

Diazoacetonitrile [8] and bis(trifluoromethyl)diazomethane [9] insert with loss of N_2 into the Pd–Cl bond of L_2PdCl_2 (L = PPh_3, PhCN) or $[(\eta^3\text{-}C_3H_5)PdCl]_2$. The analogous reaction of **1b** would furnish the σ-alkylpalladium complexes **17** and **18**, which then could rearrange to the σ-vinylpalladium complexes **19** and **20**. For the transformation of **19** into **9** or **10**, hydride transfer (RPdX → RPdH) followed by reductive elimination of Pd(0) is conceivable. Whereas solvent molecules could provide the hydride ion in the experiments conducted in tetrahydrofuran (THF), the hydride source is not immediately obvious in the other cases listed in Table 1. Furthermore, comparison of rows 4 and 5 (Table 1) shows that a change in the solvent from benzene to THF does not affect the yield of **9**. Therefore a different reaction pathway, not yet identified, must be assumed to account for the formation of **9** and **10**.

Complex **20**, assumed to be the precursor of butatriene **8**, could be formed from both **18** and **19**. For the transformation of **20** into **8**, the mechanism could correspond to that proposed for Ni(0)-induced dehalogenative coupling of 2-aryl-1,1-dibromoalkenes to give the corresponding butatrienes [10,11]. A certain similarity to the photochemical formation of butatriene complexes from $MeCp(CO)_3Mn$ and (α-chlorovinyl)silanes ($R'_3Si(Cl)C{=}CR_2$) [12] is also noteworthy.

In Scheme 4 it is suggested that a 1:1 organyl–palladium complex is involved in the formation of **9** (or **10**) and a 2:1 complex in that of **8**. This is supported by the markedly increased yield of **9** in the presence of an excess of LiCl, since an enhanced concentration of chloride ions should stabilize any RPdX species towards nucleophilic attack by **1b**. The mode of formation of heterocycle **6b** also remains a matter for speculation. The enhanced yield in the cases requiring elevated temperature and long reaction times (Table 1, rows 8 and 11) is likely to result from an uncatalyzed thermal transformation of **1b** (see Section 1). However, since **1b** is stable at room temperature, formation of **6b** under these conditions requires an alternative explanation. One possibility is the metal–carbene pathway

TABLE 3. Selected bond lengths, bond angles and torsion angles in (E)-**8**

	Bond length (Å)		Bond length (Å)		Bond length (Å)
Si–O	1.645(2)	Si–(C9)	1.869(2)	C(1)–C(3)	1.508(3)
Si–C(7)	1.835(4)	O–C(1)	1.343(2)	C(2)–C(2′)	1.260(4)
Si–C(8)	1.829(3)	C(1)–C(2)	1.332(3)		
	Bond angle (°)		Bond angle (°)		
O–S1–C(7)	109.6(2)	Si–O–C(1)	134.1(1)		
O–Si–C(8)	109.4(2)	O–C(1)–C(2)	123.3(2)		
O–Si–C(9)	104.6(1)	O–C(1)–C(3)	112.4(2)		
C(7)–Si–C(8)	110.4(2)	C(2)–C(1)–C(3)	124.2(2)		
C(7)–Si–C(9)	112.7(2)	C(1)–C(2)–C(2′)	177.7(3)		
C(8)–Si–C(9)	110.0(2)				
	Torsion angle (°)		Torsion angle (°)		
C(2)–C(1)–C(3)–C(4)	4.7	C(2)–C(1)–O–Si	−24.9		

(**14** → **16** → **6b**) that we proposed previously for the analogous transformation of **1d** under copper or palladium catalysis (see Scheme 2). In the light of the current results, however, the possibility cannot be excluded that the aliphatic diazonium salt **14** undergoes 1,3-silyl displacement prior to loss of dinitrogen, so that the alkenediazonium salt **15** is formed rather than **17**. Loss of PdX_2 from **15** would yield the diazoalkene **2**, which is known to decompose readily to **6b** in a purely thermal reaction (compare Scheme 1). The alkenediazonium salt **15** may be a precursor not only of **2** but also of **19**, namely by a nucleophilic vinylic substitution of N_2 by Cl.

The above discussion has shown that a variety of mechanistic possibilities can account for the products obtained in the Pd-assisted transformation of **1b**. At present, it is not possible to identify the exact pathway leading to each product (including the order of events such as loss of N_2 and silyl shift), in particular since no reaction intermediates have been observed directly.

2.2. X-ray structure analysis of (E)-8

Figure 1 shows the structure of the molecule. Atomic coordinates are given in Table 2 and bond distances and angles in Table 3. In the crystal the molecule is centrosymmetric. The cumulene unit of (E)-**8** has a planar, nearly linear geometry as indicated by the following data: C(1)–C(2)–C(2′) angle 177.7(3)°; sum of valence angles at C(1), 355.9°; no atom defining the least-squares plane C(1)–C(2)–C(3)–O–C(1′)–C(2′)–C(3′)–O′ deviates by more than 3.5σ. For comparison, high level calculations predict that the parent butatriene is linear–planar [13]. This geometry has been found experimentally for a tetraalkyl-substituted butatriene [14], whereas tetraphenylbutatriene is somewhat twisted around the cumulenic axis [15]. The remaining atoms in (E)-**8** are outside the plane defined by the cumulene skeleton. For example, C(4) deviates by 0.065 Å and Si by 0.446 Å from the plane defined by O, C(1), C(2) and C(3). The presence of a short central double bond (1.260(4) Å) in the cumulene unit is in agreement with previous reports [14,15,16 *]. In fact, the value found closely matches those calculated for butatriene itself [13] or observed experimentally for a tetraalkyl-substituted butatriene [14].

3. Experimental details

^1H NMR (200 and 400 MHz) and ^{13}C NMR spectra (100.6 MHz) were recorded in $CDCl_3$: ^1H NMR, $CHCl_3$ as internal standard, $\delta(CHCl_3) = 7.27$ ppm; ^{13}C NMR, $CDCl_3$ as internal standard, $\delta(CDCl_3) = 77.0$ ppm. Column chromatography was done on a silica gel column (particle size, 0.063–0.2 mm) or on a Merck Lobar column (LiChroprep Si-60; 40-63 μm). $[(\eta^3\text{-}C_3H_5)\text{-}PdCl]_2$, $PdCl_2$ and $PdCl_2 \cdot 2CH_3CN$ were purchased from Merck, and $Pd(OAc)_2$ from Janssen.

3.1. Catalytic decomposition of the diazoketone 1b; general procedure (see Table 1 for more details)

Under argon a solution of **1b** [3] (3–6 mmol) in dry benzene or THF (5–10 ml) was added at room temperature during 30 min (or at 50–60 °C during 3 min) to a stirred solution (suspension in the case of $PdCl_2$) of the catalyst (2.5–7 mol.%) in the same solvent (10 ml). Stirring was continued until N_2 evolution had ceased, and the solvent evaporated at about 0.01 Torr. Subse-

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* A reference number with an asterisk indicates a note in the list of references.

quent work-up procedure for the various rows in Table 1 were as follows.

3.1.1. Table 1, row 1

The residue was dissolved in pentane (2 ml); two crystallizations at −30°C yielded pure (E)-**8**. The combined mother liquors were concentrated and subjected to Kugelrohr distillation at 60°C (0.02 Torr) to give **9**. This product, which was identified by comparison of its ^{1}H and ^{13}C NMR data with that of an independently prepared sample (see below), was accompanied by an unidentified product that showed the following NMR signals. ^{1}H NMR: 5.70 (s) ppm. ^{13}C NMR: 118.8 (^1J(C,H) = 179 Hz); 143 ppm. Upon the assumption that the singlet at $\delta \doteq 5.70$ ppm in the ^{1}H NMR spectrum corresponds to one proton, the yield of the minor product was calculated to be about 10–20 mol.% of that of **9**.

3.1.2. Table 1, rows 2–4, 7, 8, 10 and 11

The black semisolid residue was passed through a silica gel column (20–40 g of silica gel; eluent, ether: petroleum ether, 2:8 v/v) to remove metallic palladium and other palladium-containing material. Pure (E)-**8** was obtained by two crystallizations from petroleum ether at −30°C. The mother liquor was concentrated and subjected to Kugelrohr distillation to give **9** (60–65°C (0.02 Torr)) (this product was accompanied by a small amount of an unidentified compound, see above), **11** (about 170°C (0.02 Torr)) and residual (E)- and (Z)-**8** (240 °C(0.02 Torr)).

3.1.3. Table 1, row 5

The black semisolid residue was fractionated by Kugelrohr distillation.

(a) At 60–65°C (0.02 Torr), a mixture (0.20 g) of **6b**, (Z)-**9** and presumably 1,3-di(tert-butyl)-1,1,3,3-tetramethyldisiloxane (^{1}H NMR (200 MHz): −0.01 ($SiMe_2$), 0.84 ($Si{-}CMe_3$) ppm) in a molar ratio (^{1}H NMR) of 1:0.65:0.86 was obtained.

(b) At 240°C (0.02 Torr), a mixture of (E)- and (Z)-**8** was obtained (yield, 33%), and this was processed further as described in Section 3.1.4 for row 6.

3.1.4. Table 1, row 6

The black semisolid residue was fractionated by Kugelrohr distillation.

(a) At 60–65°C (0.02 Torr), (Z)-**9** was obtained as a colorless oil with a 22% yield. The compound was identified by comparison of its spectra (^{1}H and ^{13}C NMR) with those of a sample prepared independently (see below). The ^{1}H NMR (200 MHz) spectrum showed signals from impurities at $\delta = 0.0$–0.1 ppm and $\delta = 0.8$–1.2 ppm.

(b) At 110°C (0.02 Torr), a colorless oil was obtained that according to its NMR spectra (^{1}H, ^{13}C) consisted mostly of disiloxane **12** (yield, about 9%) and traces of (Z)-**9**. Compound **12** was identified by comparison (NMR and IR) with a sample prepared independently (see below).

(c) At 240°C (0.02 Torr), a pale-yellow oil was obtained which was a mixture of (E)- and (Z)-**8** (yield, 24%) in a ratio of 1:1.1 as indicated by integration of relevant ^{13}C NMR signals. On standing, colorless crystals of (E)-**8** separated. Some of (E)-**8** was isolated by repeated fractional crystallization from pentane. The oily residue obtained after removal of the solvent consisted of (Z)-**8**, a smaller amount of (E)-**8** and some impurities (^{1}H NMR gave multiplets at $\delta = 0.8$–1.3 ppm).

3.2. Decomposition of 1b catalyzed by palladium(II) acetate (Table 1, row 9)

A solution of **1b** (0.76 g, 3.2 mmol) in benzene (10 ml) was added dropwise during 1 h to a solution of palladium(II) acetate (0.035 g, 5 mol%) in benzene (10 ml). After 12 h, evolution of nitrogen had ceased. The solvent was evaporated off at 0.001 Torr (10°C), and the black residue fractionated by Kugelrohr distillation at 60–65°C × (0.02 Torr) and 240°C (0.02 Torr). The lower-boiling fraction (0.12 g) was a colorless liquid consisting mainly of **6b**, **10** (two isomers, 5:1), **12** and presumably 1,3-di(tert-butyl)-1,1,3,3-tetramethyldisiloxane (^{1}H NMR (200 MHz): −0.01 ($SiMe_2$), 0.84 ($Si{-}CMe_3$) ppm) (molar ratio according to ^{1}H NMR, 1:2.5:0.6:0.8). From this mixture, enol acetate (**10**) (0.05 g) was isolated by Lobar column chromatography (eluent, ether:petroleum ether, 1:9), but it was accompanied by small amounts of a product of hydrolysis. The high-boiling fraction (0.20 g) consisted mainly of a mixture of (E)-**8** and (Z)-**8** ((E):(Z), 1:1.1 according to ^{13}C NMR integration); the presence of some impurities was indicated by multiplets in the region $\delta = 0.8$–1.3 ppm in the ^{1}H NMR spectrum. Pure (E)-**8** was obtained by repeated crystallization from pentane at −30°C.

3.3. Spectroscopic and analytical data for 6b, 8 and 10

3.3.1. 2,5-Di(tert-butyl)-2-methyl-1-oxa-2-sila-4-cyclopentene (6b)

This compound was synthesized independently by thermolysis of **1b** [3]. ^{13}C NMR: −5.5 (SiMe); 10.7 (t, $^1J = 126$ Hz, C-3); 18.2 ($Si{-}CMe_3$); 25.2 ($Si{-}CMe_3$); 27.8 (CMe_3 at C-5); 34.3 (CMe_3 at C-5); 93.6 (dt, $^1J = 166$ Hz, $^2J = 6.9$ Hz, C-4); 167.5 (C-5) ppm.

3.3.2. *(E)-1,4-di[((tert-butyl)dimethylsilyl)oxy]-2,2,7,7-tetramethyl-3,4,5-octatriene*

[(E-**8**)]: melting point 132°C. IR (KBr): −1603 m, 1260 m, 1143 s, 900 s, 827 m, 781 m cm^{-1}. ^{1}H NMR (200 MHz): 0.17 (SiMe$_2$); 0.93 (Si–CMe$_3$); 1.13 (C–CMe$_3$) ppm. ^{13}C NMR: −4.6 (SiMe$_2$); 18.5 (Si–*C*Me$_3$), 25.8 (Si–C*Me*$_3$); 28.9 (C–C*Me*$_3$); 37.5 (C–*C*Me$_3$); 135.8 (=*C*–OSi; signal is broadened by ^3J(C,H) coupling), 145.8 (*C*=C–OSi) ppm. Mass spectroscopy (MS) (electron impact (EI), 70 eV): *m/z* 424 (M$^+$), 409, 147, 115, 75, 73, 57. Anal. Found: C, 67.6; H, 11.64. $C_{24}H_{48}O_2Si_2$ (424.8) calcd: C, 67.9; H, 11.39%.

(Z)-8: This compound was isolated only as the major constituent of an oil that also contained (E)-**8** and some impurities that gave rise to multiplets at $\delta = 0.8$–1.3 ppm in the ^{1}H NMR spectrum. ^{1}H NMR (200 MHz): 0.19 (SiMe$_2$); 0.93 (Si–CMe$_3$); 1.10 (C–CMe$_3$) ppm. ^{13}C NMR: −4.2 (SiMe$_2$); 18.5 (Si–*C*Me$_3$); 25.8 (Si–C*Me*$_3$); 28.9 (C–C*Me*$_3$); 37.6 (C–*C*Me$_3$); 135.0 (=*C*–OSi), 145.6 (*C*=C–OSi) ppm.

3.3.3. *{(Z)- and (E)-3,3-Dimethyl-2-[((tert-butyl)dimethylsilyl)oxy]-1-butenyl} acetate ((Z)-10, (E)-10)*

A 5:1 mixture of two diastereomers was obtained. ^{1}H NMR (200 MHz), major isomer–minor isomer: 0.18–0.16 (SiMe$_2$); 0.96–0.90 (Si–CMe$_3$); 1.07–1.09 (C–CMe$_3$); 2.12–2.09 (CO–Me); 6.73–6.69 (=CH) ppm. ^{13}C NMR, major isomer: −3.8 (SiMe$_2$); 18.9 (Si–*C*Me$_3$); 25.8 (CO–*Me*); 26.1 (Si–C*Me*$_3$); 27.9 (C–C*Me*$_3$); 35.2 (C–*C*Me$_3$); 115.5 ($J = 194$ Hz, =CH); 147.1 (*C*=CH); 167.3 (C=O) ppm. The mixture of (Z)-**10** and (E)-**10** was accompanied by small amounts of a product that gave the following NMR data. ^{1}H NMR (200 MHz): 1.14 (s, CMe$_3$); 4.49 (s, CH$_2$) ppm. ^{13}C NMR: 25.8 (C*Me*$_3$); 42.8 (*C*Me$_3$); 65.5 ($J = 140.2$ Hz, CH$_2$); 212.9 (C=O) ppm. These data point to 3,3-dimethyl-2-oxo-1-butanol (a likely product of hydrolysis of **10**); however, for an independently prepared [17] sample of this compound, we obtained the following slightly different NMR values ^{1}H (400 MHz): 1.19 (s, 9H); 4.42 (s, 2H) ppm. ^{13}C NMR: 26.0 (C*Me*$_3$); 41.9 (*C*Me$_3$); 63.6 ($J = 144$ Hz, CH$_2$); 215.0 (C=O) ppm. Another possible hydrolysis product (3,3-dimethyl-2-oxobutyl) acetate was excluded on the basis of published NMR data ($\delta(CH_2) = 4.88$ ppm [18]) and the absence of several expected ^{1}H and ^{13}C NMR signals.

3.4. *(Z)-1-Chloro-3,3-dimethyl-2-[(tert-butyl)dimethylsilyl]oxy-1-butene ((Z)-9)*

A mixture of 1-chloro-3,3-dimethyl-2-butanone (**13**) [19] (1.09 g, 8.2 mmol), (tert-butyl)dimethylsilyl trifluoromethanesulfonate (2.15 g, 8.2 mmol) and triethylamine (0.83 g, 8.2 mmol) was stirred for 5 h. After addition of pentane (15 ml), triethylammonium trifluoromethanesulfonate was separated and the solvent evaporated from the solution. The residue was distilled at 60°C (0.001 Torr) (yield, 1.00 g (57%)). IR (film): ν(C=C) 1610s, 1455s, 1390s, 1305s, 1250s, 1225s, 1160s, 1135s, 1060s cm^{-1}. ^{1}H NMR (200 MHz): 0.26 (s, SiMe$_2$); 0.97 (s, Si–CMe$_3$); 1.08 (s, C–CMe$_3$); 5.27 (s, =CH) ppm. An intensity enhancement of 11% for the =CH signal was observed on irradiation at the C–CMe$_3$ resonance. ^{13}C NMR: −2.9 (SiMe); 19.2 (Si–*C*Me$_3$); 26.3 (Si–C*Me*$_3$); 28.2 (C–C*Me*$_3$); 37.4 (C–*C*Me$_3$); 92.9 (=CH, ^1J(C,H) = 195 Hz); 159.8 (C-2). Anal. Found: C, 57.2; H, 10.3. $C_{12}H_{25}ClOSi$ (248.9) calcd: C, 57.91; H, 10.12%.

3.5. *(tert-Butyl)-(4,4-dimethyl-3-oxopentyl)-methylsilanol (11)*

A solution of **6b** (0.59 g, 2.8 mmol) in a mixture of acetonitrile (40 ml) and water (2 ml) was refluxed for 2 h. After addition of chloroform (60 ml), the mixture was dried over MgSO$_4$. Then it was filtered, and the solvents were removed at 20°C (0.002 Torr). Kugelrohr distillation of the residue at 180°C (0.04 Torr) yielded **11** as a colorless oil (0.26 g, (40%)). IR (film): ν(OH) 3450s, br, 1700vs, 1465s, 1360s, 1255s, 1175s, 1075s, 980s, 860–825vs br cm^{-1}. ^{1}H NMR (200 MHz): −0.01 (s, Si–Me); 0.55–about 0.9 (m, Si–CH$_2$); 0.87 (s, Si–CMe$_3$); 1.10 (CO–CMe$_3$); 2.60 (mc, CO–CH$_2$) ppm. ^{13}C NMR: −5.7 (Si–Me); 6.6 (Si–CH$_2$); 17.9 (Si–*C*Me$_3$); 25.7 (C*Me*$_3$); 26.3 (C*Me*$_3$); 30.5 (CO–*C*H$_2$), 43.8 (CO–*C*Me$_3$), 217.8 (CO) ppm. Anal. Found: C, 62.2; H, 11.2, $C_{12}H_{26}O_2Si$ (230.4) calcd: C, 62.6; H, 11.4%.

3.6. *Preparation of 1,3-di(tert-butyl)-1,3-dimethyl-1,3-bis(4,4-dimethyl-3-oxopentyl)disiloxane (12) from 6b*

The mixture of **6b** (0.45 g, 2.1 mmol) and palladium(II) acetate (25 mg, 5 mol%) in dry benzene was stirred at room temperature for 12 h, after which about 30% of **6b** had been consumed (^{1}H NMR). The solvent was removed at 20°C (0.002 Torr), and the remaining oil kept in a Kugelrohr apparatus for 24 h at 20°C (0.002 Torr) to remove all starting material **6b**. Kugelrohr distillation of the residue at 140°C (0.015 Torr) yielded 70 mg (15% based on the initial amount of **6b**) of disiloxane **12**. IR (film): ν(C=O) 1700vs, 1250s, 1170s, 1080–1035vs br cm^{-1}. ^{1}H NMR (200 MHz): 0.01 (s, Si–Me); 0.77 (mc, Si–CH$_2$); 0.87 (s, ^{t}Bu), 1.10 (s, CO–CMe$_3$), 2.40–2.65 (m, CH$_2$–CO) ppm. ^{13}C NMR: −4.4 (Si–Me); 7.56/7.66 (Si–CH$_2$); 18.6 (Si–*C*Me$_3$); 26.1 (Si–C*Me*$_3$); 26.6 (C*Me*$_3$); 30.6 (*C*H$_2$–CO); 44.0 (CO–*C*Me$_3$); 216.2 (C=O) ppm. MS (EI, 70 eV): *m/z* 385.2 (100%, M$^+$−^{t}Bu), 287.2 (26), 213.2 (35). Anal. Found: C, 64.5; H, 11.2. $C_{24}H_{50}O_3Si_2$ (442.8) calcd: C, 65.1; H, 11.4%.

3.7. X-Ray crystal structure analysis of (E)-8

3.7.1. Crystal data

This was as follows: Triclinic; space group, $P\bar{1}$; $a = 9.761(3)$ Å, $b = 11.274(2)$ Å and $c = 6.363(1)$ Å; $\alpha = 97.41(2)°$, $\beta = 93.76(3)°$ and $\gamma = 88.08(2)°$; $Z = 1$; $D_x = 1.02$ g cm^{-3}; crystal size, 0.65 mm × 0.30 mm × 0.15 mm.

3.7.2. Data collection

A total of 1488 independent reflections were measured in the range $2.0° \leqslant \theta \leqslant 21°$ (diffractometer Enraf–Nonius CAD4; monochromated Mo Kα radiation; ω–2θ scan; scan width, $0.95 + 0.35(\tan\theta)°$.) An overall intensity loss of 1% was observed and was taken into account by a linear correction.

3.7.3. Structure solution and refinement

The structure was solved by direct methods (MULTAN) and refined by a full-matrix least-squares method. All H atoms were located in a difference Fourier map and refined with isotropic temperature factors. Refinement converged at $R = 0.043$, $R_W = 0.043$ (1196 reflections with $I > 2.5\,\sigma(I)$, $w = [\Sigma(F_{obs})^2 + (0.015\,F_{obs})^2]^{-1}$), 223 variables, shift-to-error ratio of 1.1 or less and a residual electron density of 0.17 e Å^{-3} [19*,20*].

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20 Further crystal structure data have been deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Enquiries should be accompanied by the depository number CSD-56390, the names of the authors, and the journal citation.