(CHO), 134.86, 135.69, 137.46, 137.99 (HC=CH). ^{29}Si NMR ($CDCl_3$): δ −17.56, −12.84 ($SiCl_2OPr^i$), 12.89, 17.24 ($SiEt_2$). MS (70 eV): *m/e* 418 (0%, M^+), 375 (1.08), 319 (2.97), 253 (12.28), 57 (100). Anal. Found: C, 57.32; H, 8.77. Calcd for $C_{20}H_{38}Cl_2OSi_2$ (419.59): C, 57.25; H, 8.65.

Acknowledgment. We were supported by the Fonds der Chemischen Industrie and Stiftung Volkswagenwerk. We thank Wacker Chemie GmbH for organosilicon compounds and Prof. Dr. R. West for helpful discussions.

Supplementary Material Available: Tables of bond lengths and angles, least-squares planes, atomic coordinates, root-mean-square amplitudes of thermal vibration, and thermal parameters for compound **25** (15 pages). Ordering information is given on any current masthead page.

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Transition-Metal-Catalyzed Decomposition of Silylated Diazoacetic Esters: Influence of Silicon Substituents, Catalyst, and Solvent on Product Formation

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The catalytic decomposition of silylated diazo esters, $R^1R^2R^3SiC(N_2)COOMe$ ($R^1R^2R^3Si$ = Me_3Si, Et_3Si, Me_2tBuSi, iPr_3Si, Ph_2tBuSi, $Me_3SiSiMe_2$), by copper(I) triflate, dirhodium tetraacetate, and dirhodium tetrakis(perfluorobutyrate) ($Rh_2(pfb)_4$) in inert solvents has been studied. The efficiency of the catalysts is CuOTf > $Rh_2(pfb)_4$ ≫ $Rh_2(OAc)_4$. With $Rh_2(pfb)_4$, ketenes $R^2R^3(OMe)SiC(R^1){=}C{=}O$ are formed in all cases. With CuOTf, the formal carbene dimers, azines, 5,5-dimethoxy-3,4-bis($SiR^1R^2R^3$)-2(5*H*)-furanones, and the ketenes mentioned before can be obtained; the result depends on the nature of the silyl substituent and on the solvent (carbon tetrachloride or toluene). The X-ray crystal structures of (*E*)-**2a** ($C_{12}H_{24}O_4Si_2$, orthorhombic space group *Pbca*, a = 8.987 (1) Å, b = 12.076 (1) Å, c = 15.329 (7) Å, Z = 4) and of **4d** ($C_{24}H_{48}O_4Si_2$, monoclinic space group $P2_1/c$, a = 15.220 (4) Å, b = 8.503 (3) Å, c = 22.247 (3) Å, β = 103.75 (2)°, Z = 4) have been determined.

In the last few years, transition-metal-catalyzed decomposition of diazocarbonyl and related diazo compounds has become a standard tool in synthetic organic chemistry, especially since significant progress has been made in terms of efficient chemo-, stereo-, and even enantioselective inter- and intramolecular reactions derived from metal–carbene intermediates.[1] α-Diazo-α-silylcarbonyl compounds have hardly participated in this development, except for some α-diazo-α-silyl ketones, the Cu- or Pd-assisted decomposition of which resulted in intramolecular carbene chemistry.[2–4]

Extrusion of dinitrogen from silylated diazoacetic esters has so far been induced by UV irradiation or by thermal means in nearly all cases.[5] Photolysis of ethyl diazo(trimethylsilyl)acetate generates the corresponding carbene, which is able to cyclopropanate alkenes and to insert into alkane C–H bonds.[6] When the same diazo compound is photolyzed in an alcohol, a complex mechanistic scenery arises, which is dominated by direct carbene interaction with the alcohol, Wolff rearrangement, and a 1,2(Si→C)-methyl shift resulting in a silene.[7] This silene is prone to further rearrangement but can be trapped by the alcohol present. The carbene → silene isomerization constitutes the exclusive pathway when ethyl diazo(pentamethyldisilanyl)acetate is photolyzed in an inert solvent.[8]

With the fact in mind that the mode of decomposition of diazo compounds very often alters the yields, the identity, and the diastereomer ratio of the products, we embarked on the transition-metal-catalyzed decomposition of various silylated methyl diazoacetates, all of which are easily accessible by electrophilic substitution of methyl diazoacetate with silyl triflates. The purpose of this study was to reveal the steric and electronic influence of silicon-attached substituents on the decomposition and subsequent carbene chemistry of these diazo esters. In particular, the following questions were to be answered: (a) What catalyst is needed for efficient decomposition, when sterically demanding silyl groups are present? (b) Does steric shielding by the silyl group entail different carbene-derived products? (c) Is the 1,2(Si→C)-substituent shift observed for the free carbenes also possible in the corresponding metal–carbene intermediates?

Results

Decomposition of Silylated Methyl Diazoacetates 1 in the Absence of a Trapping Reagent. Diazo esters **1a–f** were chosen for the present study since the size of

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[2] Brückmann, R.; Schneider, K.; Maas, G. *Tetrahedron* **1989**, *45*, 5517.

[3] Fronda, A.; Maas, G. *Angew. Chem.* **1989**, *101*, 1750; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1663.

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[5] For a review on silyl carbenes, see: Tomioka, H. In *Methoden der Organischen Chemie* (*Houben-Weyl*); Regitz, M., Ed.; Thieme: Stuttgart, Germany, 1989; Vol. 19b, Part 2, pp 1410–1450.

[6] (a) Schöllkopf, U.; Rieber, N. *Angew. Chem.* **1967**, *79*, 906; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 884. (b) Schöllkopf, U.; Hoppe, D.; Rieber, N.; Jacobs, V. *Liebigs Ann. Chem.* **1969**, *730*, 1.

[7] (a) Ando, W.; Hagiwara, T.; Migita, T. *J. Am. Chem. Soc.* **1973**, *95*, 7518. (b) Ando, W.; Sekiguchi, A.; Hagiwara, T.; Migita, T.; Chowdhry, V.; Westheimer, F. H.; Kammula, S. L.; Green, M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6393.

[8] Ando, W.; Sekiguchi, A.; Sato, T. *J. Am. Chem. Soc.* **1981**, *103*, 5573.

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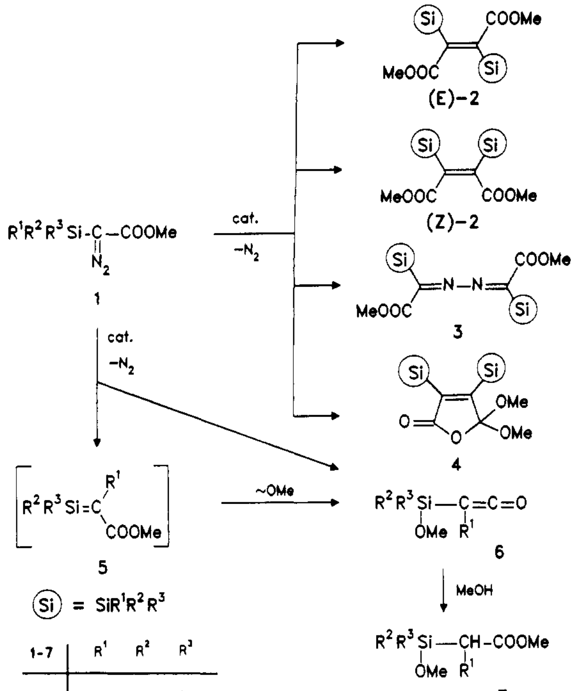
Scheme I



1-7	R¹	R²	R³
a	Me	Me	Me
b	Et	Et	Et
c	Me	Me	*t*-Bu
d	*i*-Pr	*i*-Pr	*i*-Pr
e	Ph	Ph	*t*-Bu
f	Me	Me	$SiMe_3$

their silyl groups varies over a broad range and since they contain silicon-attached substituents with significantly different abilities to undergo a 1,2-shift to a neighboring carbene center ($SiMe_3$ > Ph > alkyl according to previous experience[5]). Furthermore, we utilized those decomposition catalysts that have emerged as the most potent ones in recent years,[1,9] namely copper(I) triflate (CuOTf), dirhodium tetraacetate ($Rh_2(OAc)_4$), and dirhodium tetrakis(perfluorobutyrate) ($Rh_2(pfb)_4$). As will be seen, all three catalysts are suitable for the present purpose, although to a different extent and, in a number of cases, with different results. On the other hand, the diazo esters **1** were decomposed by palladium(II) acetate or by the (μ-allyl)palladium chloride dimer neither in toluene at room temperature nor in refluxing toluene; in the latter case, formation of a palladium mirror occurred, but without evolution of dinitrogen, and the diazo compound was recovered unchanged.

The transition-metal-catalyzed decomposition of **1a–f** was carried out by slowly adding the diazo compound to a solution of the catalyst in the appropriate solvent. The products obtained are summarized in Scheme I. It turned out that not only the identity of the silyl group but also the catalyst and even the solvent determine which product is being formed.

Catalysis by Copper(I) Triflate. This catalyst is known to decompose diazoacetates under exceptionally mild conditions,[10] and even disubstituted diazo compounds (e.g. dimethyl diazomalonate[11]) are readily decomposed at room temperature. In line with these facts, all diazoesters **1a–f** are decomposed smoothly at room temperature by CuOTf, no matter how bulky the silyl group is. However, the choice of solvent is crucial for product formation (Table I).

Table I. Products and Yields of CuOTf-Catalyzed Decomposition of Silylated Diazoacetates 1

diazo compd	$SiR^1R^2R^3$	products (yields,[a] %) solvent CCl_4, 20 °C	products (yields,[a] %) solvent toluene, 20 °C
1a	$SiMe_3$	(*E*)-**2a** (95)	(*E*)-**2a** (51); (*Z*)-**2a** (8)
1b	$SiEt_3$	(*E*)-**2b** (64)	(*E*)-**2b**[b] (36); **4b**[b] (36)
1c	$SiMe_2tBu$	(*E*)-**2c** (43); **3c** (23)	(*E*)-**2c** (40); **4c** (40)
1d	$SiiPr_3$	*c*	**4d** (31)
1e	$SiPh_2tBu$		**6e** (23)
1f	$SiMe_2SiMe_3$		**6f** (40)

[a] Yields of isolated products are given. [b] A mixture of (*E*)-**2b** and **4b** was obtained, which could not be separated. [c] See text.

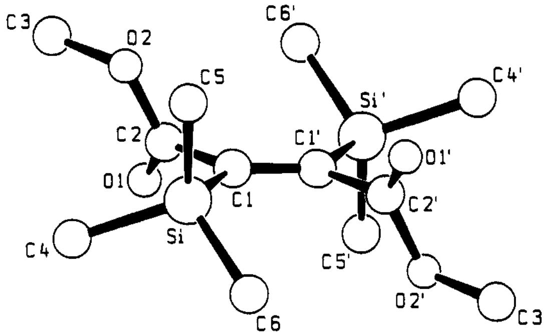


Figure 1. SCHAKAL plot of (*E*)-**2a**. The molecule has a crystallographic inversion center. Selected bond lengths (Å) and angles (deg): C1–C1′ = 1.34 (1), C1–Si = 1.891 (7), C1–C2 = 1.495 (9), C2–O1 = 1.179 (7); C1′–C1–Si = 128.8 (7), C1′–C1–C2 = 116.3 (8), Si–C1–C2 = 114.8 (4). The torsion angle C1′–C1–C2–O1 is 65.4 (8)°.

When **1a,b** were decomposed in *tetrachloromethane*, the *E* isomers of the formal carbene dimers ((*E*)-**2a**, (*E*)-**2b**) were isolated as the sole products. Decomposition of **1c** in the same solvent produced azine **3c** in addition to the carbene dimer (*E*)-**2c**. From the triisopropylsilyl derivative **1d**, a complex reaction mixture resulted, which could not be separated chromatographically; furthermore, the results obtained were not fully reproducible in repeated runs. The azine **3d** could be obtained by fractional crystallization in up to 26% yield, whereas alkene **2d** was not detected (^{13}C NMR) in any case.

In *toluene* as the solvent, different product patterns arise. In the case of **1a**, the formal carbene dimer (*E*)-**2a** is now accompanied by a minor amount of its *Z* isomer. The two alkenes can be separated chromatographically, but the stereochemical assignment cannot be derived firmly from the NMR, UV, and IR spectra due to their very close similarity (see Experimental Section). Isomer (*Z*)-**2a** had been synthesized before by Pd-assisted addition of $Me_3SiSiMe_3$ to dimethyl acetylenedicarboxylate,[12] but the configurational assignment had been based merely on the assumption of a syn addition rather than proven rigorously. In order to let the stereochemical assignment rest upon an undisputable fact rather than on this (admittedly reasonable and well-precedented) mechanistic assumption or on the melting point criterion[13] ((*E*)-**2a**, mp 128 °C; (*Z*)-**2a**, mp 63 °C), we carried out an X-ray structure analysis, which unambiguously proved the *E* configuration of the major isomer (Figure 1).

Decomposition reactions of **1c** and **1d** yield, besides the usual olefinic carbene dimer (**2b,c**, *E* isomers exclusively),

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(9) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695.

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(11) De March, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4952.

(12) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931.

(13) Cis-1,2-disubstituted alkenes typically have lower melting points than the trans isomers: Eliel, E. L. *Stereochemie der Kohlenstoffverbindungen*; Verlag Chemie: Weinheim, Germany, 1966; p 392.

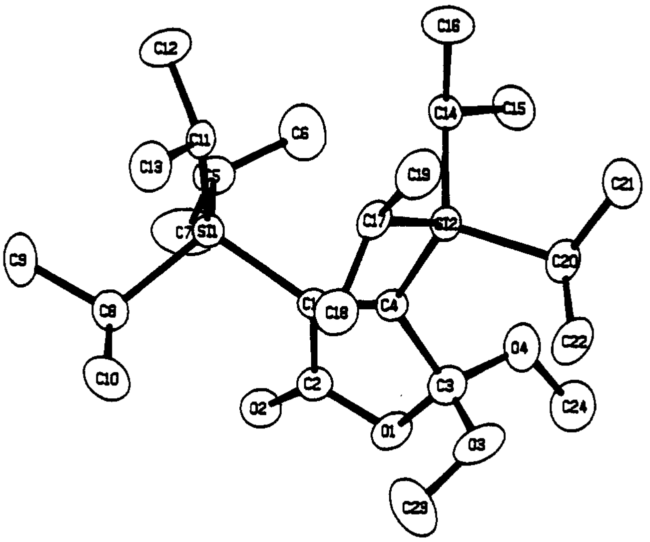
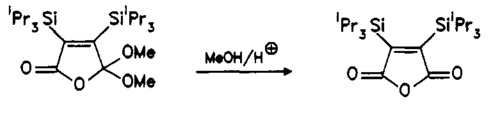


Figure 2. ORTEP plot of **4d**. The ellipsoids of thermal vibration represent a 27% probability. Selected bond lengths (Å) and angles (deg): C1–Si1 = 1.906 (4), C1–C4 = 1.358 (5), C4–Si2 = 1.927 (4), C1–C2 = 1.503 (6), C2–O1 = 1.349 (5), C2–O2 = 1.187 (5), C3–O1 = 1.436 (5), C3–C4 = 1.529 (6); C4–C1–Si1 = 140.5 (3), Si1–C1–C2 = 112.5 (3), C1–C4–Si2 = 133.3 (3). Torsion angles (deg): Si1–C1–C4–Si2 = –0.5, Si1–C1–C2–O2 = –1.5.

another carbene dimer of unusual constitution (**4b,c**). From **1d**, the corresponding derivative **4d** was the only product isolated. The constitution of **4d** was established by an X-ray structure analysis (Figure 2). In agreement with its chemical nature as a maleic anhydride acetal, acidic hydrolysis cleanly produced bis(triisopropylsilyl)maleic anhydride (**8**).



4d 8

The sole products isolated from CuOTf-catalyzed decomposition of **1e,f** in toluene were identified as ketenes by their IR spectra. ^{13}C NMR spectra clearly show that structures **6e,f** must be assigned to these ketenes. Had the ketenes arising from a Wolff rearrangement been formed, the integrity of the original $SiR^1R^2R^3$ groups would not have been changed, and the methoxy group would have been found at the terminal cumulenic carbon atom. Ketenes **6e,f** may arise from short-lived silene intermediates **5** by a fast 1,3-methoxy migration or directly from a metal–carbene intermediate (see Discussion).

Catalysis by Rh(II) Carboxylates. $Rh_2(OAc)_4$ is known as a highly active catalyst which usually decomposes diazoacetates and diazomethyl ketones at room temperature and 2-diazo-1,3-dicarbonyl as well as other disubstituted diazo compounds at elevated temperatures (typically 60–80 °C).[1] However, decomposition of the silylated diazoacetates **1a–c** by this catalyst requires the temperature of refluxing toluene, whereas no reaction seems to occur in benzene at 80 °C (**1b**: 94% recovered after 3 h). The sterically most shielded diazo ester in our series, **1d**, is inert to decomposition even under such forcing conditions. On the other hand, the more electrophilic $Rh_2(pfb)_4$[14] smoothly decomposes all of the silylated diazo esters except **1d** at room temperature.

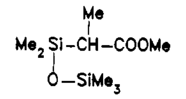
Table II. Products and Yields of Rh(II) Carboxylate Catalyzed Decomposition of Silylated Diazoacetates 1

	$SiR^1R^2R^3$			products (yields,[a] %)	
	R^1	R^2	R^3	$Rh_2(OAc)_4$, toluene, 110 °C	$Rh_2(pfb)_4$, toluene, 20 °C
1a	Me	Me	Me	(*E*)-**2a** (19); (*Z*)-**2a** (7)	*b*
1b	Et	Et	Et	(*E*)-**2b** (43)	**6b** (45) (→**7b**, quant)
1c	Me	Me	*t*Bu	*c*	**6c** (→**7c** (48[d]))
1d	*i*Pr	*i*Pr	*i*Pr	no reacn	no reacn
1e	Ph	Ph	*t*Bu		**6e** (50) (→**7e**, quant)
1f	Me	Me	$SiMe_3$		**6f** (45)

[a] Yields of isolated products are given. [b] See text. [c] Inseparable mixture of products. [d] Ketene **6c** was not isolated; yield based on **1c**.

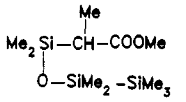
The products obtained with the two rhodium catalysts are different (Table II). Decomposition of **1a,b** by $Rh_2(OAc)_4$ leads to the olefinic carbene dimers ((*E*)-**2a**, (*Z*)-**2a**, (*E*)-**2b**, respectively) as the only isolated products. By comparing these results with those obtained with CuOTf as the catalyst (toluene, 20 °C; see above), we note that the yield of (*E*)-**2a** is considerably higher in the latter case and that **4b** is formed from **1b** only with CuOTf, not with $Rh_2(OAc)_4$.

Most remarkably, $Rh_2(pfb)_4$ catalysis produces ketenes **6** in all cases, except for **1d**, which is inert to catalytic decomposition at 20 °C. Ketenes **6b,c,e,f** are stable enough to be isolated by bulb-to-bulb distillation; however, **6b,c,e** could not be obtained analytically pure in this way and, therefore, were transformed into methyl silylacetates **7b,c,e** by addition of methanol. Decomposition of **1a** in toluene as well as in dichloromethane resulted in very unclean reaction mixtures, which did contain a ketene (IR: 2090 cm^{-1}). This ketene decomposed on attempted distillation, and even after a methanol quench, no product could be isolated in pure form. The only (albeit low-yield) product identified by NMR in the toluene reaction was the carbenoid C/H insertion product, $C_6H_5CH_2CH(SiMe_3)COOMe$. From the dichloromethane reaction, two fractions were obtained in minor yield by distillation, which according to GC–MS and NMR evidence consisted mainly of the esters **9a,b** in different ratios. Obviously, these products are derived from the expected ester **7a**,[7b] which is unstable under the workup conditions (i.e. heat and the presence of unremovable catalytic $Rh_2(pfb)_4$).



$Me_2Si(OSiMe_3)–CH(Me)–COOMe$

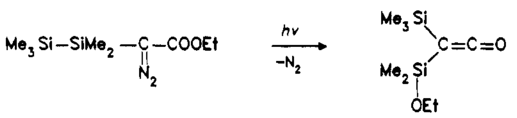
9a



$Me_2Si(OSiMe_2–SiMe_3)–CH(Me)–COOMe$

9b

Ando et al.[8] have obtained ketene **6g** in high yield by photolysis of **1g**. In contrast, photolysis of **1b,d** in benzene with 300-nm light led to product mixtures, which we could not separate by distillation or by column chromatography. The NMR spectra of the crude product mixture from **1b** indicated the presence of a minor amount of ketene **6b**, whereas only the azine **3d**, but no ketene **6d**, could be identified in the second case. These observations underline the superiority of $Rh_2(pfb)_4$ as a catalyst for the synthesis of ketenes **6**.



$Me_3Si–SiMe_2–C(=N_2)–COOEt \xrightarrow[-N_2]{h\nu} (Me_3Si)(Me_2Si(OEt))C=C=O$

1g 6g

Discussion

Efficiency of the Catalyst. It is evident from the present studies that both CuOTf and $Rh_2(pfb)_4$ are highly

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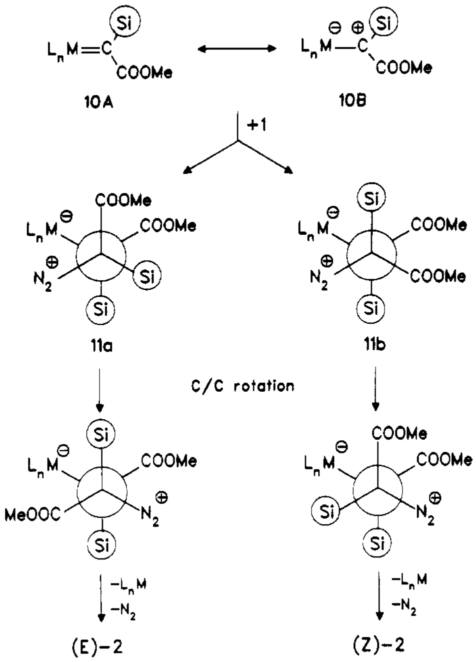
efficient catalysts for decomposition of diazoacetates bearing a sterically demanding substituent at the diazo carbon atom. $Rh_2(OAc)_4$ is rather inappropriate for this purpose, since a considerably higher temperature must be applied and product yields are lower. Both rhodium catalysts fail to decompose **1d**, the compound with the sterically most shielded diazo function in our series. Thus, CuOTf emerges as the most versatile catalyst for the decomposition of sterically hindered diazo compounds. The higher decomposition temperature needed for $Rh_2(OAc)_4$ as compared to that for $Rh_2(pfb)_4$ cannot be attributed to different steric interactions, since both rhodium carboxylates are of the same structural type (i.e. dinuclear complexes with four carboxylate bridges). Rather, the higher electrophilicity of $Rh_2(pfb)_4$[14] facilitates an attack at the vacant coordination site of one metal atom by the electron-rich diazo carbon atom; this interaction is supposed to constitute the first step on the way to a metal–carbene intermediate.[1a,b] There is convincing evidence that such intermediates are actively involved in the product-determining step.

Influence of Catalyst and Solvent on Product Formation. When other stabilization routes are unproductive, the presumed metal–carbene intermediates **10** are converted into the formal carbene dimers **2** and/or azines **3**. Whether the *E* or *Z* isomer of the carbene dimer is formed preferentially depends in general on the diazo compound[1b,15] and eventually also on the reaction conditions (e.g. catalyst concentration for $Cu(acac)_2$-catalyzed decomposition of ethyl diazoacetate[16]). In a number of cases, the thermodynamically less favored carbene dimer is formed preferentially. In our experiments, however, we have observed the predominant or exclusive formation of the sterically less encumbered isomers of (*E*)-**2**; only from **1a**, bearing the smallest silyl group in our series, did we also obtain the second stereoisomer (*Z*)-**2a** as a minor product.

Mechanisms for both the dimer[16–18] and the azine[18] formation have been proposed. Since our catalyst:diazo ratios were rather low, we follow the proposal that both olefins and azines result from an interaction between a metal–carbene intermediate (**10**) and excess diazo ester **1** (Scheme II). In our cases, two intermediates (**11a,b**) result from this interaction, which yield alkenes (*E*)-**2** and (*Z*)-**2**, respectively, after C–C bond rotation to bring the two departing groups in an antiperiplanar relation. Provided that the steric interaction between a silyl group and the metal substituent at two neighboring carbon atoms is more severe than that between two silyl groups, intermediate **11a** is energetically more favorable, and hence, the (*E*)-alkene is formed predominantly. As the silyl groups become larger (**1a,b** → **1c** → **1d**), steric interactions hinder the formation of **11**, and the attack of **10** at the terminal nitrogen of **1**, resulting in azine formation, takes over.

Scheme II suggests that the *E*:*Z* ratio of **2** also depends on the steric demand of the metal substituent. For **2a**, one does indeed observe different *E*:*Z* ratios, when the CuOTf–benzene complex in either carbon tetrachloride or toluene or $Rh_2(OAc)_4$ is used as catalyst (Tables I and II). A ready rationalization of the observed differences is not possible, since nothing is known about the structure of the presumed metal–carbene intermediates.[19] The solvent effect on the ratio (*E*)-**2a**:(*Z*)-**2a** in the CuOTf reaction seems to indicate that the coordination sphere of copper in CCl_4 is sterically more demanding than in toluene, so that **11a** is preferred over **11b**. Taking into account that both the triflate anion and solvent molecules can act as weakly coordinating ligands of the copper atom,[20,21] this difference may be caused by the different ability of the solvent molecules (toluene[22] or CCl_4[23,24]) to enter the coordination sphere of the copper atom with concomitant displacement of a triflate group.

Scheme II



In contrast to the intermolecular reaction pathways discussed so far, the products **6a–f** obtained from $Rh_2(pfb)_4$-catalyzed decomposition of the diazo compounds **1** result from an intramolecular reaction mode. Silene intermediates **5** may or may not be the precursors of ketenes **6**. A discussion of the possible reaction pathways must take into account that, in a metal carbene derived from $Rh_2(pfb)_4$, the degree of metal to carbon π back-bonding is even lower than for other rhodium carbenes with less

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(19) The copper– or rhodium–carbene complexes, which are often invoked in carbenoid transformations of diazo compounds, have never been observed directly. The only exception is the copper–methylene complex, which has been isolated in argon and nitrogen matrices at 12 K: Chang, S.-C.; Kafafi, Z. H.; Hauge, R. H.; Billups, W. E.; Margrave, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 4508.

(20) Copper(I) triflate is highly ionized (ion pair) even in nonaqueous solvents. The electrophilic copper atom thus formed can accept other ligands usually considered as relatively weak; examples are represented by the complex $(CuOTf)_2$·(benzene)[10] and by complexes of CuOTf with one to three olefin molecules.[21]

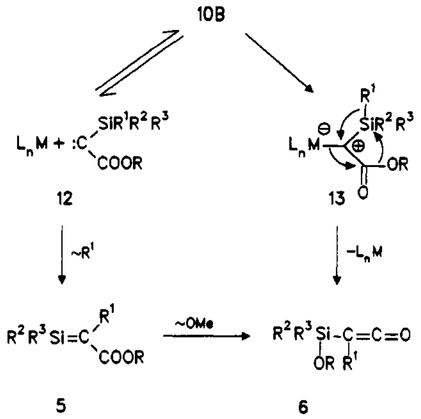
(21) (a) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889. (b) Evers, J. T. M.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 423. Spee, T.; Mackor, A. *J. Am. Chem. Soc.* **1981**, *103*, 6901.

(22) For the simultaneous coordination of triflate and π ligands in the solid state, see the X-ray crystal structures of $(CuOTf)_2$·(benzene) and $(CuOTf)_2$·(cyclohexene): (a) Dines, M. B.; Bird, P. H. *J. Chem. Soc. D* **1969**, 1054. (b) Timmermans, P. J. J. A.; Mackor, A.; Spek, A. L.; Kojić-Prodić, B. *J. Organomet. Chem.* **1984**, *276*, 287.

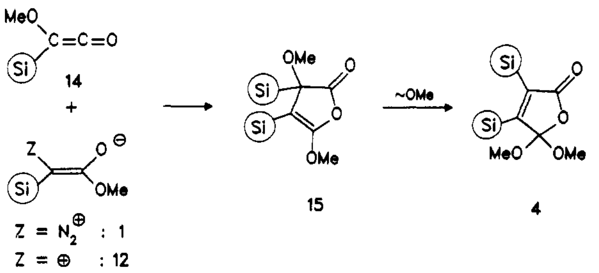
(23) (a) For the coordination chemistry of halocarbons, see: Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89. (b) Dichloromethane complexes of Ag^+ and $[Cp(NO)(PPh_3)Re]^+$ salts with weakly coordinating anions have only recently been described: Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P., Frye, J. S.; Anderson, P. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349. Fernândez, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.

(24) In analogy to the findings cited in ref 23b, CCl_4 could act as a ligand at the copper atom, also. However, this coordination mode has not been substantiated so far.

Scheme III



Scheme IV



electron-withdrawing carboxylate ligands,[25] a situation adequately described by resonance structure **10B** (see Scheme II). This feature may explain why the degree of chemoselectivity in certain cases (including the present study) is different for rhodium carbenes derived from $Rh_2(pfb)_4$ as compared to those derived from other dinuclear Rh(II) catalysts.[26]

It has been proposed recently that metal carbenes produced from rhodium(II) perfluorocarboxylates and diazomalonates are in equilibrium with the free carbene and the rhodium catalyst.[27] In analogy, we may postulate that metal carbene **10B**, derived from $Rh_2(pfb)_4$, easily dissociates to furnish carbene **12**, which than rearranges to silene **5** (Scheme III). In fact, when **12** (R^1 = $SiMe_3$, R = OEt rather than OMe) was generated by photolysis of **1g**, the corresponding silene **5** was produced as an intermediate that rearranged to ketene **6g** in solution[8] and was observable under matrix isolation conditions.[28] In contrast to these literature reports, the photolysis of silylated diazo esters **1b**,**d** did not reproduce the results obtained with $Rh_2(pfb)_4$ catalysis. Therefore, we propose a rearrangement of the rhodium carbene as depicted in **13**, which leads to ketene **6** without the intervention of the transient silene **5**. In contrast to the carbene → silene isomerization (**12** → **5**), this rearrangement has a cationic component, namely a Wagner–Meerwein type 1,2(Si→C)-migration, probably with internal nucleophilic participation by the methoxy group.[29]

A possible reaction sequence explaining the formation of maleic anhydride acetals **4b**–**d** from the CuOTf-catalyzed decomposition of **1b**–**d** in toluene is given in Scheme IV. The heterocyclic framework is obtained by a cycloaddition between the ketene **16** and the "enolate part" of the diazo ester **1** (or, alternatively, the ketocarbene dipole). The 2,3-dihydro-2-furanone **15** so obtained isomerizes to the final product by a 1,3-shift of an alkoxy group, probably with catalysis by CuOTf acting as a Lewis acid. Interestingly, a heterocycle isostructural with **15** (COOMe instead of silyl) has been obtained as a minor product from bis(methoxycarbonyl)carbene generated thermally from dimethyl diazomalonate.[30,31] This example shows that the cycloaddition process proposed in Scheme IV is possible without assistance by a catalyst. However, it is quite reasonable to assume that CuOTf, due to its Lewis acid character, is actively involved in the process. For example, it may activate the ketene by coordination to the carbonyl oxygen, much in the same way as it activates nitriles for oxazole formation with diazocarbonyl compounds.[1a]

Ketene **14** is the result of a Wolff rearrangement of diazo ester **1**. Thus, we are faced with the surprising observation that the presumed metal carbenes formed from **1** and $Rh_2(pfb)_4$ ultimately lead to ketenes **6** (by migration of a silicon-attached substituent to the carbene center), whereas the metal carbenes obtained from **1b**,**c**,**d** and CuOTf yield the isomeric ketenes **16** (by methoxy migration to the carbene center). On the other hand, both catalysts promote the formation of ketenes **6e**,**f**. Although copper catalysts in general suppress the Wolff rearrangement of diazocarbonyl compounds,[32] we have recently found[2] that CuOTf effectively promotes this rearrangement for (1-diazo-2-oxoalkyl)silanes, compounds closely related to the silylated diazo esters **1**. However, we do not see an obvious explanation for the nonuniform behavior in the series **1a**–**f** nor can we explain why toluene favors the Wolff rearrangement of **1b**–**d**, whereas carbon tetrachloride supports carbene dimer and/or azine formation. A solvent-induced change of chemoselectivity in rhodium-mediated reactions of diazocarbonyl compounds has been observed only recently in a few cases.[33] Solvent polarity cannot make the difference in our case, since the polarities of carbon tetrachloride and toluene are nearly the same.[34] As already discussed, it is perhaps the different coordination spheres of the copper atom created by molecules of the two solvents that determine the further fate of the primarily formed metal–carbene intermediate.

Experimental Section

General Information. ^{1}H NMR spectra: Varian EM 390 (90 MHz), Bruker WP 200 (200 MHz), Bruker AM 400 (400 MHz); TMS (δ 0.0) or chloroform (δ 7.24) as internal standard. ^{13}C NMR spectra: Bruker AM 400 (100.6 MHz); solvent signals were used as internal standard; δ($CDCl_3$) 77.0, δ(C_6D_6) 128.0. All NMR spectra were recorded in $CDCl_3$, if not stated otherwise. IR

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(28) Sekiguchi, A.; Ando, W.; Hondo, K. *Tetrahedron Lett.* **1985**, *26*, 2337.

(29) In the absence of nucleophilic participation, a tertiary silicenium ion would result from the cationic 1,2(Si→C)-migration of R^1. Theory predicts that a tertiary silicenium ion (R_3Si^+) is more stable than the isomeric α-silylcarbenium ion and that a 1,2(Si→C)-methyl shift taking place in the latter cation has only a small activation barrier. Recently, the first solvolysis experiment triggering such a process has been described: Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1987**, *109*, 272.

(30) Pomerantz, M.; Levanon, M. *Tetrahedron Lett.* **1991**, *32*, 995.

(31) To a larger extent, an isomeric heterocycle was formed which resulted from the cycloaddition reaction with opposite regiochemistry. This isomer was obtained exclusively when dimethyl diazomalonate was photolyzed in 1,4-dichlorobenzene at 65–100 °C; see: Eichhorn, K.; Hoge, R.; Maas, G.; Regitz, M. *Chem. Ber.* **1977**, *110*, 3272.

(32) Meier, H.; Zeller, K.-P. *Angew. Chem.* **1975**, *87*, 52; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.

(33) Padwa, A.; Austin, D. J.; Xu, S. L. *J. Org. Chem.* **1992**, *57*, 1330 and references cited therein.

(34) $E_T(30)$ (CCl_4) = 32.5 kcal/mol; $E_T(30)$ (toluene) = 33.9 kcal/mol; see: Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, Germany, 1979.

spectra: Perkin-Elmer IR 397; wavenumbers (cm^{-1}) are given. Mass spectra: Finnigan MAT90; GC unit Varian 3400 (fused silica capillary column J&W DB-5, inner diameter 0.25 mm, length 30 m; oven temperature 100–200 °C). Elemental analyses: Perkin-Elmer EA 2400. Melting points: Mettler FP5 and FP51. Single-crystal X-ray diffraction: Enraf-Nonius CAD4 diffractometer. Analytical HPLC: Merck/Hitachi LiChromatograph with L-6200 gradient pump, UV detector, and D-2000 integrator; column silica gel Si-60, 5 μm, eluant *tert*-butyl methyl ether/hexane (1/4). Preparative chromatographic separations were carried out by standard column chromatography (silica gel, 0.063–0.2 mm) or on Merck Lobar columns (LiChroprep Si-60, particle size 40–63 μm).

The following silylated diazo esters were prepared by literature procedures from methyl diazoacetate and the corresponding silyl triflate: **1a**,[35] **1c**,[35] **1d**,[35] **1f**.[36] The copper(I) triflate–benzene complex[10] and dirhodium(II) tetrakis(perfluorobutyrate)[37] were synthesized by literature procedures. Rhodium(II) acetate was prepared from rhodium(III) chloride.[38]

Methyl Diazo(triethylsilyl)acetate (1b). The compound was obtained from methyl diazoacetate and triethylsilyl triflate in analogy to a literature procedure:[35] yield 75%; bp 47 °C/0.01 Torr (Kugelrohr). For alternative syntheses, see ref 39.

Methyl (*tert*-Butyldiphenylsilyl)diazoacetate (1e). A solution of *tert*-butyldiphenylsilyl triflate (3.88 g, 10.0 mmol) in ether (10 mL) is slowly added at 0 °C to a solution of methyl diazoacetate[40] (1.00 g, 10.0 mmol) and ethyldiisopropylamine (1.74 mL, 10.0 mmol) in anhydrous ether (50 mL). The mixture is allowed to assume room temperature, stirred overnight, filtered, and passed over $MgSO_4$ (15 g). The solvent is removed at 12 Torr, and the residue is purified by flash column chromatography over silica gel (eluant diethyl ether/petroleum ether, 2/8 v/v): yield 2.71 g (80%) of a rather viscous yellow oil. ^1H NMR: δ 1.16 (s, *t*Bu), 3.62 (s, OMe), 7.29–7.79 (m, Ph). ^{13}C NMR: δ 19.4 (CMe_3), 29.0 (CMe_3), 44.3 (CN_2), 52.6 (OMe), 127.9 (d), 129.9 (d), 132.1 (s), 135.8 (d), 169.5 (C=O). IR (film): 2090 ($C{=}N_2$), 1680 cm^{-1} (C=O). Anal. Calcd for $C_{19}H_{22}N_2O_2Si$ (M_r 338.5): C, 67.42; H, 6.55; N, 8.28. Found: C, 66.3; H, 6.55; N, 8.3.

Decomposition of Diazo Esters 1 Catalyzed by CuOTf: General Procedure. Under an argon atmosphere, a solution of diazo ester **1** (2.6–7.5 mmol) in CCl_4 or toluene (20 mL) is added dropwise over a period of 2–3 h to a mixture of $CuO_3SCF_3{\cdot}0.5C_6H_6$ (3–5 mol %) in the same solvent (30 mL). When evolution of dinitrogen has ceased, the mixture is filtered over $MgSO_4$ (ca. 15 g), and the solvent is removed at 12 Torr. The residue is further processed as specified below.

Decomposition of 1a in CCl_4. The crude product mixture obtained from **1a** (0.50 g, 2.9 mmol) and catalyst (3 mol %) is dissolved in petroleum ether (10 mL). After filtration and evaporation of the solvent, a colorless solid is left, which after recrystallization from pentane at −10 °C yields pure dimethyl bis(trimethylsilyl)fumarate ((*E*)-**2a**): yield 0.40 g (95%); mp 128 °C. ^1H NMR: δ 0.17 (s, 9 H), 3.73 (s, 3 H). ^{13}C NMR: δ −1.2 (SiMe), 51.3 (OMe), 154.2 (C=C), 171.8 (C=O). IR (KBr pellet): 1705 cm^{-1} (C=O). UV (CH_3CN): λ_{max} 208.0 nm (ϵ = 10 730). Anal. Calcd for $C_{12}H_{24}O_4Si_2$ (M_r 288.5): C, 49.96; H, 8.39. Found: C, 49.2; H, 8.0.

Decomposition of 1b in CCl_4. The crude product mixture obtained from **1b** (1.60 g, 7.5 mmol) and catalyst (4 mol %) is separated by column chromatography (silica gel; eluant diethyl ether/petroleum ether, 2/8 v/v). The product so obtained is dimethyl bis(triethylsilyl)fumarate ((*E*)-**2b**): yield 0.90 g (64%); bp 90 °C/0.01 Torr (Kugelrohr). ^1H NMR: δ 0.41–1.23 (m, 15 H), 3.68 (s, 3 H). ^{13}C NMR: δ 3.3 ($SiCH_2$), 7.2 (CH_2Me), 51.2 (OMe), 152.6 (C=C), 171.0 (C=O). IR (film): 1725 cm^{-1} (C=O). UV (CH_3CN): λ_{max} 213.4 nm (ϵ = 6770). Anal. Calcd for $C_{18}H_{36}O_4Si_2$ (M_r 372.6): C, 58.01; H, 9.74. Found: C, 57.6; H, 9.7.

Decomposition of 1c in CCl_4. The crude product mixture obtained from **1c** (0.55 g, 2.6 mmol) and catalyst (3.9 mol %) is separated by column chromatography (silica gel, eluant diethyl ether/petroleum ether, 3/7 v/v). The first fraction yields dimethyl bis(*tert*-butyldimethylsilyl)fumarate ((*E*)-**2c**): yield 0.18 g (37%); bp 100 °C/0.01 Torr (Kugelrohr). ^1H NMR: δ 0.03 (s, $SiMe_2$), 0.85 (Si*t*Bu), 3.62 (OMe). ^{13}C NMR: δ −4.8 (SiMe), 18.2 (CMe_3), 27.4 (CMe_3), 51.0 (OMe), 152.0 (C=C), 171.9 (C=O). IR (film): 1730 cm^{-1} (C=O). UV (CH_3CN): λ_{max} 217.5 nm (ϵ = 7790). Anal. Calcd for $C_{18}H_{36}O_4Si_2$ (M_r 372.6): C, 58.01; H, 9.74. Found: C, 58.2; H. 9.6. The second fraction is a viscous yellow oil (0.15 g), which constitutes a 20/80 mixture of (*E*)-**2b** (see above, total yield 43%) and dimethyl 1,4-bis(*tert*-butyldimethylsilyl)-2,3-diaza-1,3-butadiene-1,4-dicarboxylate (**3c**, 23%). The latter product was identified by the following NMR data. ^1H NMR: δ 0.10 (s, $SiMe_2$), 0.90 (s, Si*t*Bu), 3.70 (s, OMe). ^{13}C NMR: δ 17.3 (CMe_3), 26.3 (CMe_3), 51.4 (OMe), 167.3, 169.9 (C=N, C=O).

Decomposition of 1a in Toluene. The product mixture obtained from **1a** (0.50 g, 2.9 mmol) and catalyst (6.6 mol %) is separated by Lobar column chromatography (eluant diethyl ether/petroleum ether, 2/8 v/v). The first fraction contains (*E*)-**2a** (0.21 g, 51%), mp 128 °C. The second fraction yields dimethyl 1,2-bis(trimethylsilyl)maleate ((*Z*)-**2a**): yield 0.07 g (8%); mp 63 °C (lit.[12] mp 64–65 °C). ^1H NMR: δ 0.24 ($SiMe_3$), 3.67 (OMe). ^{13}C NMR: δ 0.1 ($SiMe_3$), 51.6 (OMe), 153.5 (C=C), 172.2 (C=O). IR (KBr): 1720 cm^{-1} (C=O). UV (CH_3CN): λ_{max} 207.2 nm (ϵ = 9850). Anal. Calcd for $C_{12}H_{24}O_4Si_2$ (M_r 288.5): C, 49.96; H, 8.39. Found: C, 49.8; H, 8.3.

Decomposition of 1b in Toluene. The product mixture obtained from **1b** (1.10 g, 5.1 mmol) and catalyst (3 mol %) is fractionated by column chromatography (silica gel, eluant diethyl ether/petroleum ether, 2/8 v/v). A colorless oil is obtained (0.69 g) which constitutes a 1:1 mixture of (*E*)-**2b** and **4b** (NMR). Separation of the two compounds by chromatography or distillation was not possible. ^{13}C NMR of 3,4-bis(triethylsilyl)-5,5-dimethoxy-2(5*H*)-furanone (**4b**): δ 3.1 (CH_2), 7.3 (CH_2Me), 51.0 (OMe), 123.4 (C-5), 144.5 (C-4), 171.8, 175.8 (C-3, C=O). IR (film): 1770 cm^{-1} (C=O).

Decomposition of 1c in Toluene. The product mixture obtained from **1c** (1.00 g, 4.7 mmol) and catalyst (3.4 mol %) is separated by column chromatography (silica gel, eluant diethyl ether/petroleum ether, 3/7 v/v). A yellow oil (0.70 g) is obtained which is a 1:1 mixture (NMR) of (*E*)-**2c** and **4c**. When this mixture stands, crystallization of **4c** begins, which is completed by addition of methanol and cooling at −10 °C. The crystals are collected and washed with cold methanol (yield 0.35 g, 40%); the filtrate is concentrated and subjected to Kugelrohr distillation at 100 °C/0.01 Torr: yield 0.35 g (40%) of (*E*)-**2c**. Data for 3,4-bis(*tert*-butyldimethylsilyl)-5,5-dimethoxy-2(5*H*)-furanone (**4c**) are as follows. Mp: 75 °C. ^1H NMR: δ 0.29 (s, 6 H, $SiMe_2$), 0.37 (s, 6 H, $SiMe_2$), 0.94 (s, 18 H, Si*t*Bu), 3.34 (s, 6 H, OMe). ^{13}C NMR: δ −2.30 ($SiMe_2$), −2.16 ($SiMe_2$), 17.6 (CMe_3), 27.8 (CMe_3), 28.3 (CMe_3), 51.0 (OMe), 123.2 (C-5), 145.4 (C-3), 171.8, 174.0 (C-4, C=O). IR (KBr pellet): 1745 cm^{-1} (C=O). Anal. Calcd for $C_{18}H_{36}O_4Si_2$ (M_r 372.6): C, 58.01; H, 9.74. Found: C, 57.9; H, 9.59.

Decomposition of 1d in Toluene. The crude product obtained from **1d** (1.79 g, 7.0 mmol) and catalyst (4.5 mol %) is purified by column chromatography (silica gel; eluant diethyl ether/petroleum ether, 3/7 v/v). An oil is obtained which crystallizes after 2–3 days. The crystals are washed with a small amount of cold methanol: yield 0.49 g (31%) of 3,4-bis(triisopropylsilyl)-5,5-dimethoxy-2(5*H*)-furanone (**4d**); mp 66 °C. ^1H NMR: δ 1.11 and 1.16 (2 × d, each 3 H, $SiCHMe_2$), 1.43 (sept, SiCH), 1.60 (sept, SiCH), 3.36 (6 H, OMe). ^{13}C NMR: δ 12.9 (SiCH), 14.9 (SiCH), 19.5 ($CHMe_2$), 51.1 (OMe), 123.2 (C-5), 144.8 (C-3), 172.4, 178.7 (C-4, C=O). IR (KBr pellet): 1750 cm^{-1} (C=O). Anal. Calcd for $C_{24}H_{48}O_4Si_2$ (M_r 456.8): C, 63.1; H, 10.59. Found: C, 62.9; H, 10.5.

Bis(triisopropylsilyl)maleic Anhydride (8). A solution of **4d** (0.20 g, 0.44 mmol) and 1 N hydrochloric acid (0.05 mL) in

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(40) Searle, N. E. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 424.

methanol (3 mL) is refluxed for 5 days. The solvent is replaced by diethyl ether, and this solution is washed with water and dried ($MgSO_4$). Removal of the solvent gives **8**: yield 0.16 g (89%); mp 211 °C. ^1H NMR: δ 1.18 (d, SiCH*Me*$_2$), 1.61 (sept, SiCH). ^{13}C NMR: δ 13.1 (SiCH), 19.4 (SiCH*Me*$_2$), 162.5 (C=C), 169.2 (C=O). IR (KBr pellet): 1740 cm^{-1} (C=O). Anal. Calcd for $C_{22}H_{42}O_3Si_2$ (M_r 410.6): C, 64.36; H, 10.31. Found: C, 64.5; H, 10.6.

Decomposition of 1a by Rhodium(II) Acetate. A solution of **3a** (0.36 g, 2.1 mmol) in toluene (20 mL) is added over a period of 2 h to refluxing toluene (50 mL) containing rhodium(II) acetate (0.043 g, 4.7 mol %). After filtration over neutral Al_2O_3 (15 g), the solvent is evaporated, and the residue is distilled (Kugelrohr). At 90 °C/0.002 Torr, a mixture of (*E*)-**2a** and (*Z*)-**2a** is obtained (0.078 g, 26%, *E*/*Z* = 2.7/1). The isomers can be separated by Lobar column chromatography; their spectroscopic data are identical with the values given above.

Decomposition of 1b by Rhodium(II) Acetate. A solution of **3c** (2.40 g, 11.2 mmol) in toluene (10 mL) is added over a period of 2 h to refluxing toluene (50 mL) containing rhodium(II) acetate (0.12 g, 5 mol %). The mixture is kept at reflux temperature for another 12 h, brought to room temperature, and filtered over $MgSO_4$ (15 g). The solvent is evaporated, and the residue is subjected to Kugelrohr distillation. A fraction boiling at 60 °C/0.01 Torr (0.12 g) shows several TLC spots and is discarded. At 90 °C/0.01 Torr, (*E*)-**2b** (0.90 g, 43%) is obtained (see above for spectral data).

Decomposition of Diazo Esters 1 by Rhodium(II) Perfluorobutyrate: General Procedure. The solution of diazo ester **1** (5–8 mmol) in toluene (15 mL) is added over a period of 2–3 h to a stirred solution of $Rh_2(pfb)_4$ (3–5 mol %) in toluene (40 mL). After an additional reaction time of 12 h, the catalyst is partly removed by filtration over $MgSO_4$, and the solvent is evaporated at 40 °C/12 Torr. Further workup is detailed below.

Decomposition of 1a. The reaction is carried out with **1a** (0.55 g) in dichloromethane (40 mL). The crude product mixture is stirred in methanol (5 mL) for 30 min. The solvent is evaporated, and the residue is subjected to Kugelrohr distillation at 0.01 Torr. Extensive loss of material occurs. Two minor fractions are obtained at 70 °C (50 mg) and 110 °C (20 mg), both of which consist of several products according to GC–MS and NMR. The major components in both cases are methyl 2-{dimethyl[(trimethylsilyl)oxy]silyl}propionate (**9a**) and methyl 2-{dimethyl[(dimethyl((trimethylsilyl)oxy)silyl)oxy]silyl}propionate (**9b**). The major component of both fractions shows the following NMR signals (200 MHz, $CDCl_3$): δ 0.22 ($SiMe_3$), 0.37 ($SiMe_2$), 1.28 (d, CH*Me*), 2.11 (q, C*H*Me), 3.48 (s, COOMe). Mass spectra (EI): **9a** ($C_9H_{22}O_3Si_2$, M_r 234.5), *m*/*e* 235, 219, 179, 163 (100%), 149, 133; **9b** ($C_{11}H_{28}O_4Si_3$, M_r 308.6), 309, 293, 291, 253, 237 (100%).

Decomposition of 1b. Kugelrohr distillation of the crude product mixture at 100 °C/0.5 Torr yields (diethylmethoxysilyl)ethylketene (**6b**; yield ca. 50%), which is not analytically pure, however. ^1H NMR: δ 0.38–1.04 (m, 10 H, $SiEt_2$), 1.11 (t, 3 H, CH_2), 1.97 (q, 2 H, CH_2), 3.44 (s, 3 H, OMe). IR (film): 2080 cm^{-1} (C=C=O).

The ketene is kept in excess methanol for 30 min, the solvent is removed, and the residue is distilled at 100 °C/0.5 Torr (Kugelrohr). Thus, methyl 2-(diethylmethoxysilyl)butyrate (**7b**; yield 45% based on **1b**) is obtained as a colorless oil. ^1H NMR: δ 0.46–1.16 (m, 13 H, $SiEt_2$, CH_3), 1.36–2.24 (m, 3 H, CH, CH_2), 3.49 and 3.56 (2 × s, 3 H each, SiOMe and COOMe). ^{13}C NMR: δ 3.5, 3.7 ($SiCH_2$), 6.3 ($SiCH_2CH_3$), 14.9 (C-4), 19.6 (C-3), 38.3 (C-2), 50.9 and 51.0 (SiOMe and COOMe), 175.3 (C=O). IR (film): 1715 cm^{-1} (C=O). Anal. Calcd for $C_{10}H_{22}O_3Si$ (M_r 218.4): C, 55.0; H, 10.16. Found: C, 53.8; H, 9.8.

Decomposition of 1c. The crude product mixture is treated with excess methanol for 30 min. The solvent is evaporated, and from the residual oil, methyl 2-(*tert*-butylmethoxymethylsilyl)propionate (**7c**; yield 47%) is isolated by Kugelrohr distillation at 75 °C/0.1 Torr. ^1H NMR (mixture of diastereomers, ca. 7/6 ratio): major diastereomer, δ 0.13 (s, SiMe), 0.91 (s, *t*Bu), 1.26 (d, CHC*H*$_3$), 2.33 (q, CH), 3.50, 3.63 (SiOMe, COOMe); minor diastereomer, δ 0.21 (s, SiMe), 0.91 (s, *t*Bu), 1.24 (d, CHC*H*$_3$), 2.33 (q, CH), 3.46, 3.60 (SiOMe, COOMe). IR (film): 1710 cm^{-1} (C=O). The ^1H NMR spectrum indicates an impurity, and a correct elemental analysis could not be obtained; attempts to further purify the oil by repeated Kugelrohr distillations proved unsuccessful.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2) for the Non-Hydrogen Atoms of (*E*)-2a

	x	*y*	*z*	*B*(eq)^a
Si	8459 (2)	−42 (2)	1254 (1)	3.96 (3)
O1	7833 (5)	367 (3)	−1147 (3)	5.3 (1)
O2	8133 (5)	1789 (3)	−240 (3)	5.3 (1)
C1	9331 (6)	164 (4)	143 (4)	3.7 (1)
C2	8361 (7)	739 (5)	−508 (4)	3.6 (1)
C3	7112 (8)	2431 (6)	−764 (5)	7.1 (2)
C4	6416 (8)	−51 (8)	1063 (5)	8.1 (2)
C5	8979 (8)	1106 (6)	1959 (4)	5.6 (2)
C6	8975 (9)	−1388 (6)	1738 (5)	7.0 (2)

^{a} $B(\mathrm{eq}) = {}^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for the Non-Hydrogen Atoms of 4d

	x	*y*	*z*	*U*(eq)^a
Si1	6752 (1)	3214 (1)	1840 (1)	47 (1)
Si2	7839 (1)	2233 (2)	335 (1)	46 (1)
O1	9246 (2)	1248 (6)	2150 (2)	78 (1)
O2	8431 (2)	1913 (5)	2801 (1)	72 (1)
O3	9878 (2)	1791 (7)	1366 (2)	99 (2)
O4	9053 (3)	−345 (5)	1279 (2)	85 (1)
C1	7851 (3)	2403 (6)	1695 (2)	41 (1)
C2	8498 (3)	1873 (7)	2280 (2)	55 (2)
C3	9145 (4)	1250 (9)	1492 (2)	74 (2)
C4	8242 (3)	2063 (6)	1222 (2)	46 (2)
C5	6131 (4)	1516 (8)	2096 (2)	64 (2)
C6	6080 (5)	94 (8)	1690 (3)	99 (2)
C7	6425 (5)	1033 (10)	2766 (3)	119 (3)
C8	7068 (4)	4673 (8)	2492 (3)	71 (2)
C9	6230 (5)	5409 (10)	2661 (3)	107 (3)
C10	7759 (5)	5897 (9)	2446 (3)	104 (3)
C11	6004 (3)	4109 (2)	1116 (2)	54 (2)
C12	4999 (4)	3777 (9)	1033 (3)	91 (3)
C13	6153 (5)	5857 (8)	1037 (3)	84 (2)
C14	6753 (3)	1080 (7)	160 (2)	54 (2)
C15	6895 (4)	−692 (7)	228 (3)	78 (2)
C16	6062 (4)	1473 (9)	−439 (3)	89 (2)
C17	7647 (3)	4371 (7)	126 (2)	56 (2)
C18	8352 (4)	5472 (7)	506 (3)	79 (2)
C19	7516 (4)	4715 (8)	−570 (3)	84 (2)
C20	8690 (4)	1342 (7)	−60 (2)	63 (2)
C21	8276 (5)	776 (9)	−717 (3)	93 (2)
C22	9529 (4)	2288 (9)	−49 (3)	85 (2)
C23	10227 (1)	3302 (2)	1670 (1)	112 (3)
C24	9724 (5)	−1379 (9)	1547 (3)	93 (3)

^{a} *U*(eq) defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Decomposition of 1e. Column chromatography of the oily reaction product (silica gel, eluant chloroform) yields (*tert*-butylmethoxyphenylsilyl)phenylketene (**6e**) as a colorless oil (yield 50%). ^1H NMR: δ 0.88 (s, *t*Bu), 3.56 (s, OMe), 6.9–7.7 (m, Ph). ^{13}C NMR: δ 20.5, 20.9 (*C*Me$_3$, *C*=C=O), 26.6 (C*Me*$_3$), 52.6 (OMe), 125.0, 127.8, 128.6, 128.9, 130.0, 134.9 (all d), 130.5 (s), 132.5 (s), 182.9 (C=*C*=O). IR (film): 2085 cm^{-1} (C=C=O). The compound could not be obtained analytically pure.

A solution of **6e** in methanol is refluxed for 2 h. After evaporation of the solvent, methyl (*tert*-butylmethoxyphenylsilyl)phenylacetate is obtained (yield 49% based on **1e**) as a 7/6 mixture of diastereomers. ^1H NMR: δ 0.90, 1.07 (2 × s, *t*Bu), 3.55, 3.69, 3.74, 3.75 (4 × s, SiOMe and COOMe), 4.05, 4.06 (2 × s, CH), 7.2–7.8 (m, Ph). ^{13}C NMR (diastereomer composite; for the 20–53 ppm region, signals of the major isomer are given first): δ 20.0, 20.7 (*C*Me$_3$), 26.4, 26.8 (C*Me*$_3$), 43.4, 43.7 (C-2), 51.4, 52.9, 51.6, 53.0 (SiOMe and COOMe), 132.0, 132.3, 135.3, 135.5 (all s), 125.8, 126.2, 127.3, 127.4, 127.8, 128.1, 129.5, 129.7, 129.9, 132.3, 134.9, 135.0 (all d), 173.0 (C=O). Anal. Calcd for $C_{20}H_{26}O_3Si$ (M_r 342.5): C, 70.1; H, 7.65. Found: C, 69.8; H, 7.61.

Decomposition of 1f. The crude product mixture consists mainly (ca. 80%) of ketene **6f**. Kugelrohr distillation at 40 °C/0.5 Torr yields pure **6f** in 45% yield as a colorless oil. ^1H NMR and IR data agree with literature[6] values. ^{13}C NMR (C_6D_6): δ −3.2 ($C{=}C{=}O$), 0.3, 0.8 ($SiMe_3$ and $SiMe_2$), 49.7 (OMe), 168.1 ($C{=}O$).

X-ray Crystal Structure Analysis of (*E*)-2a. Crystal Data: $C_{12}H_{24}O_4Si_2$, molecular mass 288.5, orthorhombic, space group *Pbca*, $a = 8.987$ (1) Å, $b = 12.076$ (1) Å, $c = 15.329$ (7) Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, $d_{calcd} = 1.15$ g cm^{-3}.

Data Collection: crystal size 0.45 × 0.15 × 0.30 mm, monochromatized Mo Kα radiation, 1366 reflections measured in the range $4.0 \le 2\theta \le 46.0°$, 1153 unique reflections, $\omega/2\theta$ scan, scan width $(1.30 + 0.35(\tan\theta))°$.

Structure Solution and Refinement.[41] Structure solution was by direct methods (MULTAN) and refinement by a full-matrix least-squares method. H atoms were localized in a ΔF map and were refined (with *B* fixed) except for H3C and H4A. With 653 reflections ($I > 2.5\sigma(I)$) and 122 variables, refinement converged at $R = 0.062$, $R_w = 0.067$, $w = [\sigma(F_o)^2 + (0.04F_o)^2]^{-1}$ (shift/error ratio ≤0.75, residual electron density ≤0.58). Positional and thermal parameters for non-hydrogen atoms are given in Table III.

X-ray Crystal Structure Analysis of 4d. Crystal Data: $C_{24}H_{48}O_4Si_2$, molecular mass 456.8, monoclinic, space group $P2_1/c$, $a = 15.220$ (4) Å, $b = 8.503$ (3) Å $c = 22.247$ (3) Å, $\beta = 103.75$ (2)°, $Z = 4$, $d_{calcd} = 1.08$ g cm^{-3}.

Data Collection: crystal size 0.52 × 0.30 × 0.20 mm, monochromatized Mo Kα radiation, 2792 independent reflections in the range $4.0 \le 2\theta \le 41.0°$, $\omega/2\theta$ scan, scan width $(0.85 + 0.35(\tan\theta))°$.

Structure Solution and Refinement.[41] Structure solution was by direct methods (MULTAN) and refinement by a full-matrix least-squares method. H atoms were partly localized in a ΔF map and refined isotropically, and partly calculated and not refined. With 2169 reflections ($I > 2\sigma(I)$) and 463 variables, refinement converged at $R = 0.056$ and $R_w = 0.054$ (unit weights, shift/error ratio ≤1.60, residual electron density ≤1.06). Positional and thermal parameters for non-hydrogen atoms are given in Table IV.

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Supplementary Material Available: Tables of crystal data, data collection, and structure solution and refinement, atomic and thermal parameters, and bond distances and angles for compounds (*E*)-**2a** and **4d** (9 pages). Ordering information is given on any current masthead page.

OM920337C

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Hypervalent Monoorganyl- and Diorganyltin(IV) Fluoride Complexes: A ^{19}F and ^{119}Sn Study of Inter- and Intramolecular Dynamics in Solution

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Reactions of fluoride ion with diorganyltin(IV) dichlorides R_2SnCl_2 (R = Ph, Me, ^nBu, ^tBu) and monoorganyltin(IV) halides $RSnCl_3$ (R = Ph, Me, ^nBu) in dichloromethane solution have been studied using variable-temperature ^{19}F and ^{119}Sn NMR spectroscopy. A number of hypervalent tin species are identified in solution including $[Ph_2SnF_3]^-$, $[Ph_2SnClF_2]^-$, and $[Ph_2SnCl_2F]^-$, which are stereochemically rigid on the NMR time scale at −100 °C but fluxional at about −80 °C. The fluoride in $[Ph_2SnCl_2F]^-$ and $[Ph_2SnClF_2]^-$ shows a smaller apicophilicity than the chloride. Addition of fluoride ion causes appreciable R group migration for R = Ph.

Introduction

The poor solubility of organylfluorostannanes has largely restricted their study to investigations of solid compounds. A common feature of this class of compounds in the solid state is coordination expansion of the tin atom which is achieved by fluoride bridges which in turn often results in formation of polymeric materials. For example, dimethyldifluorostannane is a sheetlike polymer[1] containing six-coordinate tin whereas trimethylfluorostannane is probably a chain type polymer[2] containing five-coordinate tin. The crystal structure determination of triphenylfluorostannane has only recently been reported[3] and indicates a polymeric chain. Solid-state ^{119}Sn NMR studies have confirmed five coordination for trimethylfluorostannane, as well as for triisobutylfluorostannane and triphenylfluorostannane.[4] Trimesitylfluorostannane is monomeric in the solid state and contains four-coordinate tin,[5] presumably because the bulky organyl substituent prevents fluoride bridging. Vibrational and ^{119}Sn Mössbauer spectroscopies imply that methyltrifluorostannane contains both bridging and terminal fluorides such that the tin is six-coordinate.[6]

The Lewis acidity of organylfluorostannanes is demonstrated by their reaction with additional fluoride ion to

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