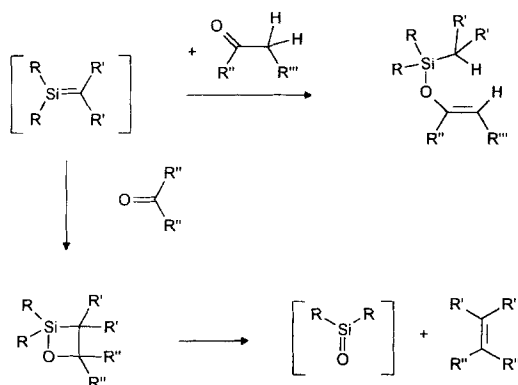# Reaction of 1,1-Dimethylsilene with Formaldehyde**

Martin Trommer, Wolfram Sander,*
Carl-Henrik Ottosson, and Dieter Cremer*

*Dedicated to Professor Paul von Ragué Schleyer
on the occasion of his 65th birthday*

In contrast to C—C double bonds, Si—C double bonds are strongly polar and labile and thus undergo reactions with polar molecules that are unknown in olefin chemistry.[1] For example, silenes react with carbonyl compounds (in particular aromatic carbonyl compounds) in a Wittig-type reaction to give olefins (Scheme 1).[2–4] 1,2-Oxasiletanes have been postulated, and in some cases demonstrated, as intermediates in the formation of olefins.[4–6] The extremely unstable silanones formed in the fragmentation of the 1,2-oxasiletanes immediately react further to give cyclosiloxanes.

Scheme 1.

According to the results of our CCSD(T)/6-31G(d,p) calculations the reaction of silene with formaldehyde leading to formation of 1,2-oxasiletane is exothermic by 67 kcal mol^{-1}. The overall reaction, including fragmentation to ethene and silanone, is still exothermic by 30 kcal mol^{-1},[6] but the 1,2-oxasiletane lies in such a deep energy well that it can be detected as an intermediate.

The reaction of silenes with carbonyl compounds having an α-H atom follows another route. Here, the main product is a silyl enol ether formed by migration of an H atom (Scheme 1).[1a, 7]

We report here on the reaction of 1,1-dimethylsilene (1) with formaldehyde. This silene can be synthesized[8] in high yield by photolysis of (dimethylsilyl)diazomethane (2) and is very suitable for the investigation of simple silenes that are not stabilized by bulky substituents (Scheme 2).

Irradiation (λ = 360 nm) of 2 in an argon matrix at 10 K[9] led to formation of the silene 1 and the diazirine 3. The carbene 4 was too short lived to be detected by IR or UV/Vis spectroscopy, even under conditions of matrix isolation. Irradiation at shorter wave-

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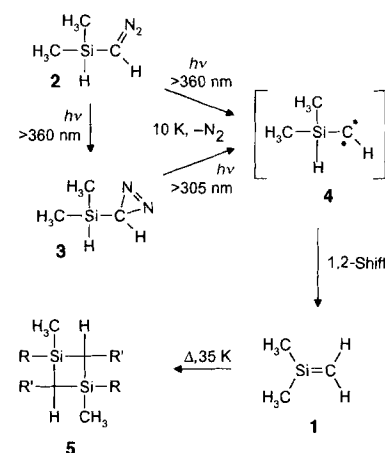
Scheme 2.

length (λ > 305 nm) also resulted in elimination of N$_2$ from 3, and 1 was formed in almost quantitative yield (IR detection). When the matrix was annealed at 30–40 K, 1 dimerized within a few hours to give disiletane 5 as the main product.[10–13]

In the photolysis of 2 (λ > 305 nm, 10 K) in a matrix containing 0.6% formaldehyde, 1 was still formed as the main product, but small amounts of other reaction products were now observed by IR spectroscopy. When the matrix was warmed to 30–35 K after photolysis of 2 at 10 K, the reaction between 1 and CH$_2$O could then be followed directly by IR spectroscopy: the intensity of the bands of CH$_2$O and 1 decreased markedly within a few hours, and the new product 7 was formed in addition to small amounts of dimer 5 (Scheme 3). After about 70%
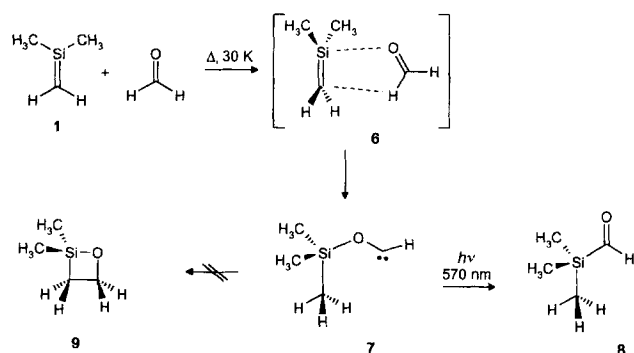
Scheme 3.

conversion the reaction stopped. The new product formed by warming the matrix was extremely photolabile and rearranged quantitatively to 2,2-dimethyl-2-silapropanal (8) within a few minutes' irradiation (λ > 570 nm) (Fig. 1). Comparison of the most intense bands at 2624 (aldehyde C—H str.), 1661 (C=O str.), 1252, and 851 cm^{-1} with those of an authentic matrix-isolated sample[8, 14] allowed 8 to be identified.

The photolabile compound 7 shows an intense IR absorption at 2605 cm^{-1}, the position and intensity of which resemble that of the OC—H stretching vibration of aldehydes.[15] However, this functional group can be excluded because of the absence of a C=O vibration. Other bands of high intensity are found at 1306, 1254, and 850 cm^{-1} in the range of Si—O and Si—C stretching vibrations. Ab initio calculations of the vibrational spectra of a series of C$_4$H$_{10}$SiO isomers carried out at the MP2/6-31G(d,p) level shed light on the identity of 7. The calculated
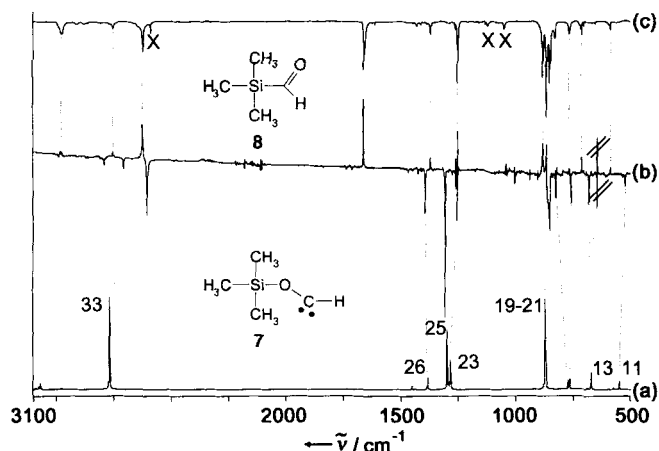
Fig. 1. a) IR spectrum of trimethylsiloxycarbene (7) from ab initio calculations at the MP2/6-31G(d,p) level. b) IR difference spectrum of the photoisomerization 7 → 8 (λ = 570 nm) at 10 K; bands of 7 (pointing downwards) disappear to be replaced by bands of 8 (pointing upwards). c) IR reference spectrum of 8 at 10 K. To match the experimental spectrum, the calculated spectrum was scaled with a factor of 0.95 and simulated with a Lorentz band form with a half-bandwidth of 2 cm⁻¹. Bands marked X are due to residual solvent.

Scheme 4. Energies of some C_2OSiH_6 isomers, relative to the energy of 12, calculated at the MP2/6-31G(d,p) and CCSD(T) levels.

spectrum of trimethylsiloxycarbene was in very good agreement with that of 7 (Fig. 1), whereas no correlation was found for 2,2-dimethyl-1,2-oxasiletane (9).

The formation of siloxycarbenes as short-lived intermediates in the irradiation of silylcarbonyl compounds has frequently been postulated,[16, 17] but hitherto only been observed directly in one case by time-resolved spectroscopy.[18, 19] Under the conditions of matrix isolation ($T < 40$ K) 7 is thermally stable.

For comparison, 2-silapropene (10) and 2-methyl-2-sila-2-butene (11)[12, 13] were treated with formaldehyde under similar conditions. Whereas the silapropene reacted with formaldehyde analogously to 1—although quantitatively and markedly faster at 35 K—no thermal reaction was observed with the silabutene. The reactivity of the silene towards formaldehyde therefore drops with increasing number of methyl substituents. Because of the large kinetic isotope effect, reaction of silapropene with [D_2]formaldehyde could not be measured (no reaction after 12 h at 35 K).

Results from CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p) calculations for the system $SiH_2CH_2 + CH_2O$ show that the thermal reaction to form carbene 15 takes place via the van der Waals complex 13 and the intermediate diradical or zwitterion 17 (Scheme 4). The van der Waals complex[20] resembles the complex between silanones and CH_2O,[8] but the bonding is considerably weaker than that in the latter complex (8 kcal mol⁻¹, Scheme 4). Intermediate 17 sits in an extremely shallow well (0.3 kcal mol⁻¹ deep) on the energy hypersurface 6.2 kcal mol⁻¹ above the van der Waals complex 13, so that 17 effectively corresponds to a transition state, from which carbene 15 is formed by a proton shift.[21]

The transformation of complex 13 via 17 to carbene 15 also takes place at low temperature, as a result of the excess energy of 8 kcal mol⁻¹ and slow dissipation of energy in the argon matrix. On the other hand, the remaining excess energy of the van der Waals complex 13 is insufficient to allow access to the transition state for formation of the oxasiletane 14, which lies 7.8 kcal mol⁻¹ above 13 and is formed by a 90° rotation of the
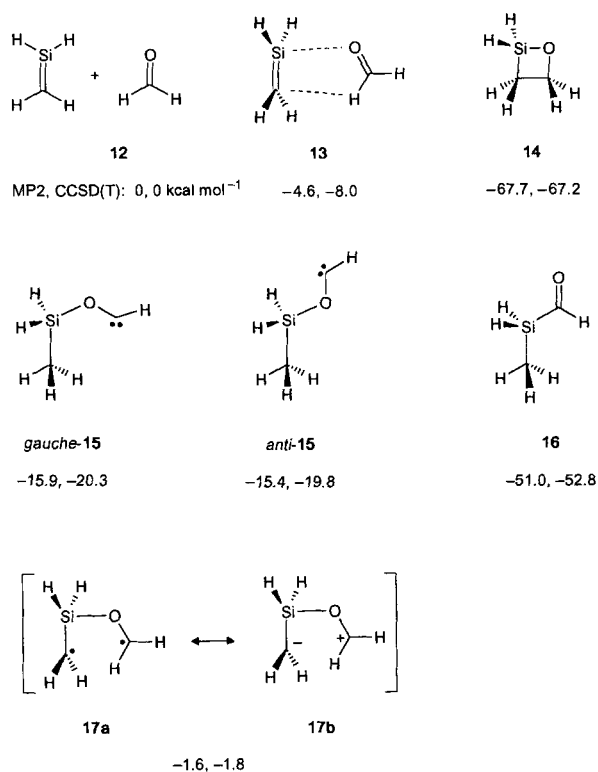
CH_2O group in 17. An energy difference of 1.6 kcal mol⁻¹ in the respective barriers is therefore responsible for the fact that carbene 15 is formed rather than silaoxetane 14.[22]

Carbene 15 can exist as C_1-symmetrical gauche or C_s-symmetrical anti conformer, although the former is more stable by 0.5 kcal mol⁻¹. The energy barrier for the rearrangement 15 → 16 is 4.7 kcal mol⁻¹; the reaction is exothermic by 33 kcal mol⁻¹ and therefore irreversible. The results of the ab initio calculations are consistent with the experimental results and explain the formation of the carbene 15 in place of the anticipated oxasiletane 14. Further experiments will show to what extent the new type of reaction between silenes and formaldehyde reported here is restricted to a matrix environment or whether it can also take place in solution.

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with a Bruker IFS-66 FT-IR spectrometer in the range 4000–400 cm⁻¹ with a resolution of 1 cm⁻¹. Description of the matrix isolation equipment: W. Sander, *J. Org. Chem.* **1989**, *54*, 333–339.

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[14] **8**: IR (Ar, 10 K): ṽ = 2974.6 (14, C-H str.), 2912.5 (4, C-H str.), 2752.4 (9, C-H str.), 2624.2 (32, aldehyde C-H str.), 1661.4 (51, C=O str.), 1370.2 (14), 1252.1 (64), 880.8 (58), 864.7 (100), 850.6 (63), 765.5 (14), 711.8 (15), 702.5 (7), 585.3 (9) cm⁻¹ (rel. intensity, assignment).

[15] **7**: IR (Ar, 10 K): ṽ = 2791 (13, C-H str.), 2706.4 (8, C-H str.), 2604.7 (25, C-H str. carbene), 1393.2 (25, OCH bend), 1306.6 (67), 1254.9 (97), 862.6 (73), 850.5 (100), 759.7 (35), 680.8 (30), 522.1 (7) cm⁻¹ (rel. intensity, assignment).

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[21] An exact description of the strongly zwitterionic compound **17** requires extensive MR-CI calculations (10 electrons, 10 active MOs), which are beyond the scope of the current work.

[22] The concerted [2 + 2] cycloaddition of silaethene and formaldehyde has an energy barrier of 18 kcal mol⁻¹ (relative to **13**), according to the results of CCSD(T) calculations.
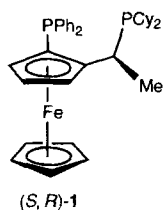
Strong Electronic Effects on Enantioselectivity in Rhodium-Catalyzed Hydroborations with Novel Pyrazole-Containing Ferrocenyl Ligands

Anita Schnyder, Lukas Hintermann, and Antonio Togni*

We have recently shown that chiral bidentate ferrocenyl phosphanes of type **1**, which contain two sterically and electronically different ligating fragments, are able to ensure high enantioselectivities in a variety of transition-metal-catalyzed reactions.[1] Our two-step methodology for the synthesis of such ligands allows the incorporation of phosphano groups with virtually no limitations. This ligand system provides an opportunity for studying steric and electronic effects due to the chiral inducing agent on stereoselectivity.

We then extended our concept to P,N-ligands[2] of type **2**, incorporating a phosphane and a pyrazole, an unprecedented combination in asymmetric catalysis,[3] and now report their use in the Rh-catalyzed hydroboration of styrenes with catecholborane.[4] The most striking finding relates to the observation of large electronic effects on the enantioselectivity of this reaction.[5] Furthermore, the different electronic properties of the

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pyrazole and phosphane fragments exert opposite influences: high enantioselectivities are obtained when both the N-ligand is a good σ-*donor* and the P-ligand a good π-*acceptor* (vide infra).

The new ligands **2** were easily prepared in moderate yields starting from ferrocenyl amines of type **3**[6] and the corresponding pyrazoles **4** in glacial acetic acid (Scheme 1). The results of
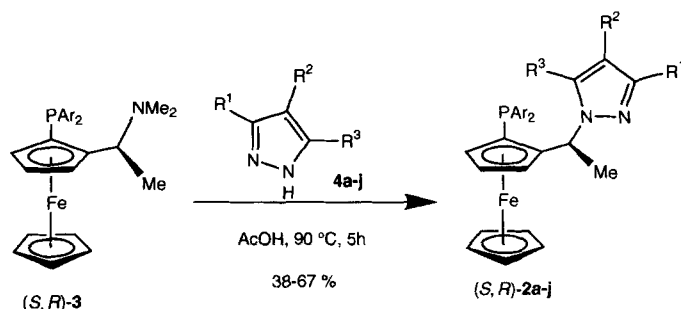
Scheme 1. Synthesis of pyrazolyl-containing ferrocenyl ligands. Cy = cyclohexyl. For R¹, R², R³, Ar see Table 1.

the catalytic hydroboration experiments (Scheme 2) are summarized in Table 1. The reactions were conducted at room temperature in THF, with 1 mol% of the catalyst (formed in situ from [Rh(1,5-cod)₂]BF₄ and 1.1 equiv of the ligand). Complete conversion of the substrate styrene was found to take place within
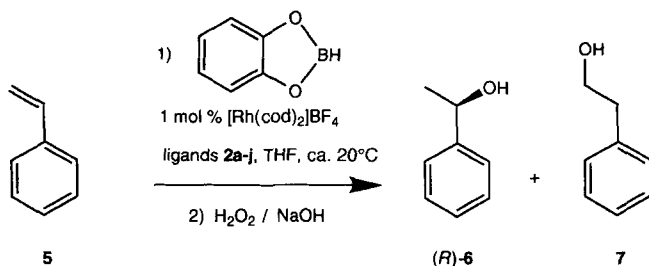
Scheme 2. The Rh-catalyzed hydroboration of styrene with catecholborane. cod = cyclooctadiene.

3 to 5 h. Workup and product analysis were carried out as previously reported.[1a] Compared to some known systems,[4] our catalysts proved to be less regioselective and afforded relatively high amounts of the achiral linear alcohol. On the other hand, in some cases the enantioselectivity for the desired branched product **6** reaches very high and unprecedented values (up to 98.0% *ee*). Thus, the ligand containing the 3,5-dimethylpyrazolyl fragment (**2a**) affords an *ee* of 95.1% (Table 1, entry 1). Similar values were obtained with ligands **2c** and **2f**, which contain the extra substituent 4-methyl and 4-bromo, respectively (entries 3 and 6). Increasing the size of the groups in positions 3 and 5 from methyl to isopropyl lead to a lower enantioselectivity (91.6%, entry 5); the *steric* properties of those substituents are therefore crucial.

Replacement of the methyl groups by the strong σ-accepting trifluoromethyl fragments at positions 3 and 5 of the pyrazole should engender an *electronic* modification of the ligand, whilst only marginally altering its steric properties.[7] Thus ligand **2b** led to a drastically different stereochemical outcome when used under the exact same conditions. Whereas the regioselectivity dropped by only a few percent (from 66:34 to 61:39 branched to linear), the enantioselectivity dropped to 33.4% *ee* (from