Reaction of 1,1-Dimethylsilene with Formaldehyde**

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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. For example, silenes react with carbonyl compounds (in particular aromatic carbonyl compounds) in a Wittig-type reaction to give olefins (Scheme 1). [12–41] 1,2-Oxasilatanes have been postulated, and in some cases demonstrated, as intermediates in the formation of olefins. [44–6] The extremely unstable silanones formed in the fragmentation of the 1,2-oxasilatanes immediately react further to give cyclosiloxanes.

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-oxasilatane is exothermic by 67 kcalmol−1. The overall reaction, including fragmentation to ethene and silanone, is still exothermic by 30 kcalmol−1 [6] but the 1,2-oxasilatane 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). [11, 71]

We report here on the reaction of 1,1-dimethylsilene (1) with formaldehyde. This silene can be synthesized [10] in high yield by photolysis of (dimethylsilyldiazomethane) (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-lengths (λ > 305 nm) also resulted in elimination of N2 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 disilatane 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 CH2O could then be followed directly by IR spectroscopy: the intensity of the bands of CH2O 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% conversion the reaction stopped. The new product formed by warming the photolabile compound and rearranged quantitatively to 2,2-dimethyl-2-silapropanol (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 [18, 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. [113] 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 C3H7SiO isomers carried out at the MP2/6-31G(d,p) level shed light on the identity of 7. The calculated
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, but hitherto only been observed directly in one case by time-resolved spectroscopy. 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) 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 [D₄]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 SiH₂CH₂ + CH₂O 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 12 resembles the complex between silanones and CH₂O 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.

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 the formation of the oxasiletane 14, which lies 7.8 kcal mol⁻¹ above 13 and is formed by a 90° rotation of the CH₂O 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 oxasiletane 14.

Carbene 15 can exist as C₁-symmetrical gauche or C₁-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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[14] 8: IR (Ar, Zn) : 2974.6 (14, C-H str.), 2912.5 (4, C-H str.), 2752.4 (9, C-H str.), 2632.4 (32, aldehyde C-H str.), 1661.4 (51, C=O str.), 1370.2 (14), 1252.1 (64), 880.8 (58), 864.7 (100), 859.6 (63), 765.5 (14), 711.8 (15), 702.5 (7), 585.3 (9) cm⁻¹ (ref. intensity, assignment).

[15] 7: IR (Ar, Zn) : 2976.1 (13, C-H str.), 2766.4 (8, C-H str.), 2604.7 (25, C-H str. carbene), 1394.9 (25, OCH₃ bend), 1306.6 (67), 1254.9 (97), 862.6 (73), 850.5 (100), 795.7 (35), 688.0 (30), 522.1 (7) cm⁻¹ (ref. intensity, assignment).


[21] An exact description of the strongly zwitseronic 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 silaenone and formaldehyde has an energy barrier of 18 kcal mol⁻¹ (relative to 13), according to the results of CASSCF calculations.

**Strong Electronic Effects on Enantioselectivity in Rhodium-Catalyzed Hydroborations with Novel Pyrazole-Containing Ferroenyl Ligands**

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We have recently shown that chiral bidentate ferroenyl phosphonates 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.¹¹

Our two-step methodology for the synthesis of such ligands allows the incorporation of phosphono 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-ligands² of type 2, incorporating a phosphine and a pyrazole, an unprecedented combination in asymmetric catalysis,¹¹ and now report their use in the Rh-catalyzed hydroboration of styrenes with catecholborane.¹⁴ 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 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 3⁶ and the corresponding pyrazoles 4 in glacial acetic acid (Scheme 1). The results of 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 3 to 5 h. Workup and product analysis were carried out as previously reported.¹¹ Compared to some known systems,¹¹ 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 marginally altering its steric properties.¹⁷ 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

![Scheme 1. Synthesis of pyrazolyl-containing ferroenyl ligands. Cy = cyclohexyl. For R₁, R₂, R₃, A see Table 1.](image)