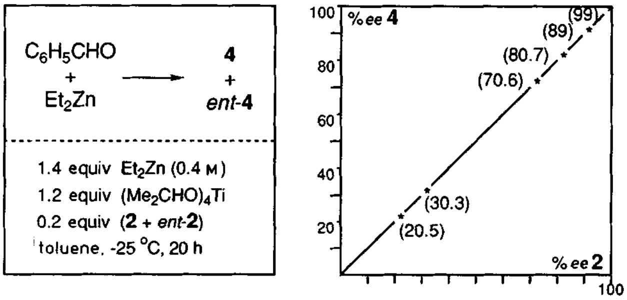

Fig. 2. Reactions of benzaldehyde with the DINOL derivative **2** of different enantiopurity. The molarity of Et_2Zn refers to the reaction mixture. Aliquots of (*R,R*)- and (*S,S*)-**3**, aryl = 2-$C_{10}H_7$, R = R′ = CH_3 were mixed for the preparation of **2** (see procedure). The numbers in brackets in the diagram were calculated from GC integrations measured with the samples of **4** obtained.

Experiments with aldehydes and zinc derivatives containing additional functional groups are under way.

Typical Procedure

8: Diol **3** (aryl = 2-$C_{10}H_7$, R = R′ = Me)[4], 0.933 g (1.4 mmol) is placed under argon in a dry 100 mL flask with side arm (serum cap). $Ti(OCHMe_2)_4$ (0.48 g, 1.7 mmol) and $PhCH_3$ (10 mL) are added by syringe, and after stirring at room temperature for 5 h the $PhCH_3$ and isopropanol are removed (40 °C/100–3 × 10^{-2} Torr). The solid residue is combined at room temperature with $PhCH_3$ (20 mL) and $Ti(OCHMe_2)_4$ (2.5 mL, 2.4 g, 8.4 mmol), and the solution cooled to − 25 °C (cryostat). Et_2Zn (4.2 mL, 8.4 mmol, 2 M in $PhCH_3$), and then 3-phenylpropanal (0.92 mL, 0.94 g, 7.0 mmol) are added dropwise. After 15 h at − 22 °C (TLC sampling) the reaction mixture is quenched with saturated aqueous NH_4Cl (10 mL), and Et_2O (40 mL) is added. Stirring for 30 min is followed by filtration through Celite, washing with saturated aqueous NaCl, drying over Na_2SO_4, and removal of the solvent. The residue is chromatographed through a short SiO_2 column (C_6H_{14}/Et_2O 3:1), and the resulting mixture of **3** and **8** heated in a Kugelrohr oven (100 °C air temp./0.3 mbar) to expel the alcohol **8**, the absence of which in the residue [14] is ascertained by NMR spectroscopy: 1.0 g colorless crystals, m.p. 40 °C.

Received: April 15, 1991 [Z 4578 IE]
German version: *Angew. Chem. 103* (1991) 1383

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[9] So far only mixtures of (*rac*-**5** and *epi*-**5**) and (*rac*-**6** and *epi*-**6**) have been described [6]. We determined the following properties ($[\alpha]_D^{RT}$ in $CHCl_3$): **5** M.p. 51 °C, $[\alpha]_D^{RT}$ = − 59.5; *epi*-**5**: *meso*-configuration, m.p. 114 °C, $[\alpha]_D^{RT}$ = + 0.3; **6**: M.p. 59 °C, $[\alpha]_D^{RT}$ = − 59.7).

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[12] **14** was freshly prepared by Swern oxidation from the corresponding alcohol; the enantiopurity of **14** was ≥ 85% (GC). Since all four stereoisomeric products could be seperated on a chiral capillary GC column [1 b, 7], the ratio **15**:**16** could be accurately determined, and extrapolated for enantiopure aldehyde. The isolated sample of **15** is levorotatory, that of **16** dextrorotatory.

[13] Nonlinear correlations between % *ee* and optical properties or enantioselectivities: A. Horeau, *Tetrahedron Lett. 1969*, 3121; C. Puchot, O. Samuel, E. Dunach, S. Zhao, C. Agami, H. B. Kagan, *J. Am. Chem. Soc. 108* (1986) 2353. For "chirality enhancement" in additions of Et_2Zn see the review [2] and references cited therein.

[14] **3** (aryl = 2-naphthyl, R = R′ = CH_3) holds on to **4** and **9** especially stubbornly. Cf. F. Toda, *Top. Curr. Chem. 149* (1988) 211, and earlier papers by *Toda*'s group cited therein.

The Radical Cations of Silaketene and Several Isomers of [C,H_2,Si,O]$^{\cdot\oplus}$: An Ab Initio MO Investigation**

By *Jan Hrušák, Ragampeta Srinivas, Diethard K. Böhme,* and *Helmut Schwarz**

Recently, during systematic studies of the gas-phase chemistry of unsaturated silicon molecules,[1] we produced a radical cation with the elemental composition [C,H_2,Si,O]$^{\cdot\oplus}$ by the electron-impact ionization of $Si(OCH_3)_4$.[2] Although it was possible in analogous cases to establish ion connectivities by using tandem mass spectrometry,[1] the [C,H_2,Si,O]$^{\cdot\oplus}$ ion derived from $Si(OCH_3)_4$ could not be characterized in this way with certainty. The analysis of the collisional-activation spectra pointed toward the presence of several structures such as **1** and **4**, and ab initio calculations revealed an energy surface rich in isomers. Here we present structures **1** to **4** which exhibit unusual structural features and show differences in geometry, symmetry, electronic structure, and order of stability from the "analogous" radical cations $CH_2{=}C{=}O^{\cdot\oplus}$ and $CH_2{=}O{=}C^{\cdot\oplus}$. These differences are also seen for the corresponding neutral molecules, and are much more pronounced than is implied by the similarities in Lewis structures.[3, 4]

$H_2SiCO^{\cdot +}$	$H_2SiOC^{\cdot +}$	$H_2CSiO^{\cdot +}$	$H_2COSi^{\cdot +}$
1	**2**	**3**	**4**

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. *R. Srinivas* is grateful to DAAD for a stipend und *D. K. Böhme* to the Humboldt Foundation for a Humboldt Senior Award.

All MO calculations were carried out with the GAUSSIAN 88 program package[5] within the unrestricted Hartree–Fock (UHF) formalism.[6] Stationary points were characterized by analyzing the force constant matrix. Complete geometry optimizations were accomplished with a 6-31G** basis set[7] and second-order Møller-Plesset perturbation theory (MP2).[8] Zero-point vibrational energies (ZPVE) were derived from harmonic frequencies calculated at the MP2/6-31G** level. The ZPVE were scaled by a factor of 0.89. The data for the energies obtained in this way (MP2/6-31G**//MP2/6-31** + ZPVE) for **1** to **4** are summarized in Table 1, and the geometric and electronic structures, as well as the relative stabilities of the $[C,H_2,Si,O]^{\cdot\oplus}$ radical ions, are adequately described[9] at this level of theory. This also follows from a comparison of calculated bond dissociation energies with experimentally available data.[2] Inconsistent results are obtained with smaller basis sets or when correlation effects are not included. On the other hand, an increase in the basis sets beyond 6-31G** does not seem necessary.

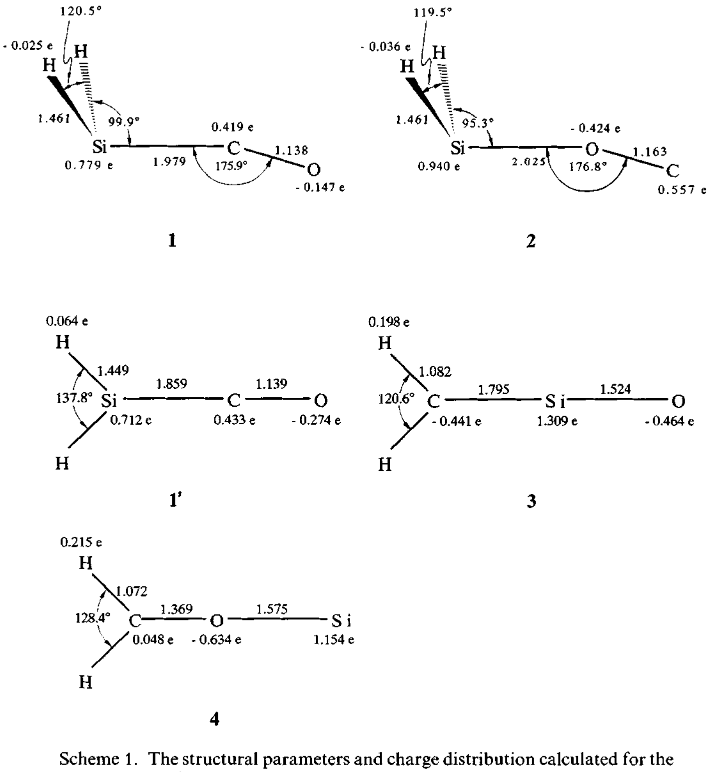
Table 1. Absolute [in Hartree] and relative energies [kcal mol^{-1}] for isomers of $[C, H_2, Si, O]^{\cdot\oplus}$ [a].

isomer	symmetry/ state	MP2/6-31G**// MP2/6-31G**	MP2/6-31G**// MP2/6-31G** + ZPE [b]
1	$C_s/{}^2A'$	− 402.876262 (5.7)	− 402.855192 (1.1)
1′ [c]	$C_{2v}/{}^2B_1$	− 402.865087 (12.7)	− 402.840662 (10.1)
2	$C_s/{}^2A'$	− 402.839944 (28.5)	− 402.817705 (24.5)
3	$C_{2v}/{}^2A_1$	− 402.838988 (29.1)	− 402.819463 (23.4)
4	$C_{2v}/{}^2A_1$	− 402.885364 (0.0)	− 402.856762 (0.0)

[a] For structural details see text and Scheme 1. [b] ZPVE: Zero-point vibrational energy. [c] The planar structure **1′** corrsponds to a transition state (one imaginary frequency) for the degenerate transformation **1** ⇄ **1′*** ⇄ **1**.

From many points of view, the radical cation of 1-silaketene ($H_2SiCO^{\cdot\oplus}$, **1**) is related to the neutral silaketene recently calculated by *Hamilton* and *Schaefer*.[10] The ketene-like *planar* C_{2v} structure **1′** (Scheme 1) is in both cases not a minimum but corresponds to a transition state of the degenerate isomerization **1** ⇄ **1′** ⇄ **1**. While for the neutral species an activation energy of 18.5 kcal mol^{-1} was calculated,[10] for the radical cations the energy difference between **1′** and **1** amounts to 9.0 kcal mol^{-1} (see Table 1). The imaginary frequency of the out-of-plane deformation is 598 cm^{-1} for the radical cation **1′** (Table 2) and 592 cm^{-1} for the neutral molecule.[10] Both the radical cation and the neutral form of **1** have a nonplanar C_s structure at the minimum. From a comparison of the vibrational frequencies (Table 2), the formal charges derived from the Mulliken population analysis and the geometrical details (Scheme 1) it follows that **1** corresponds to a complex of $SiH_2^{\cdot\oplus}$ and a largely "unperturbed" CO molecule. As is the case for the neutral species,[11] the Si–C bond can be understood in terms of an interaction between the empty p orbital of the silicon that is perpendicular to the SiH_2 plane and the pair of electrons on the carbon. A relatively long Si–C bond (1.979 Å) results. As expected, the unpaired electron occupies the sp^2-hybridized orbital of $SiH_2^{\cdot\oplus}$. In **1** Si is both the radical site (spin density $\varrho = 1.01$ e) and the center of charge ($q = 0.78$ e). The changes in structure which result as a consequence of the "complexation" of the $SiH_2^{\cdot\oplus}$ and CO parts are quite small compared with the structures of the separate building blocks: the C–O bond distance of 1.138 Å in **1** is not significantly shorter than that of the free CO (1.150 Å), and the Si–H bond is shortened by 0.008 Å and the HSiH angle is opened by 0.56 degrees. The vibrational frequencies summarized in Table 2 are also consistent with these changes in geometry. The energy for the dissociation of **1** into $SiH_2^{\cdot\oplus}$ and CO is 41.1 kcal mol^{-1}.

The coordination of $SiH_2^{\cdot\oplus}$ with the oxygen end of CO also results in a minimum in the energy surface for a nonplanar structure **2**. Although the isomer **2** is 23.4 kcal mol^{-1} less stable than **1**, the bond relationships and the geometries are



Scheme 1. The structural parameters and charge distribution calculated for the $[C, H_2, Si, O]^{\cdot\oplus}$ isomers **1**–**4**.

Table 2. Comparison of the vibrational frequencies of the planar and nonplanar silaketene radical cations (**1**) calculated at the MP2/6-31G**//MP2/6-31G** level with the CCSD results [10] for the neutral system[a].

system	vibration	cation ω_i[cm^{-1}]	neutral ω_i[cm^{-1}]
H_2Si-CO	torsion	271	270
	SiCO bending	293	280
	SiC stretching	410	410
	SiH_2 twisting	681	791
1	SiH_2 wagging	710	744
	SiH_2 scissoring	906	1021
	CO stretching	2261	2252
	SiH_2 asymm. stretching	2388	2200
	SiH_2 symm. stretching	2446	2200
H_2Si-CO	out-of-plane	−598	− 592
	in-plane linear bending	299	356
	out-of-plane linear bending	371	511
	Si-C stretching	551	732
1a	SiH_2 rocking	633	710
	SiH_2 scissoring	849	906
	CO stretching	2422	2202
	SiH_2 symm. stretching	2439	2448
	SiH_2 asymm. stretching	2516	2488
CO	CO stretching	2124	2245
SiH_2 [b]	SiH_2 bending	951	1072
	SiH_2 asymm. stretching	2334	2144
	SiH_2 symm. stretching	2414	2146

[a] For structural details see text and Scheme 1. [b] Calculated for the isolated cation and neutral species, respectively.

quite similar. The radical site and the charge are again mainly localized on the silicon ($\varrho = 0.98$ e; $q = 0.94$ e). The $\mathrm{SiH_2^{\cdot\oplus}}$ segment is strongly bent (95.3°), and the Si–H and C–O bond lengths of 1.461 and 1.163 Å, respectively, are very similar to those found for **1**. Furthermore, the analysis of the vibrational frequencies supports a description of **2** as a complex of $\mathrm{SiH_2^{\cdot\oplus}}$ and OC. The normal vibration of CO for **2** (2047 cm^{-1}) points towards an "unperturbed" CO bond, which is also consistent with the observed increase in the C–O bond length in **2** by 0.025 Å compared to **1**. The long Si–O separation of 2.025 Å and the low-lying frequency of 298 cm^{-1} for the SiO vibration correspond to a small perturbation. The symmetric and asymmetric SiH vibrations of 2383 and 2454 cm^{-1}, respectively, for **2** are very close to the vibrations of the free $\mathrm{SiH_2^{\cdot\oplus}}$ (2334 and 2414 cm^{-1}, respectively). We obtain a value for the energy of dissociation of **2** into $\mathrm{SiH_2^{\cdot\oplus}}$ and CO of 17.7 kcal mol^{-1}. As expected, the interaction of the empty p orbital of the $\mathrm{SiH_2^{\cdot\oplus}}$ fragment with a free electron pair on the oxygen is energetically less attractive than the interaction with the electron pair on the carbon atom of CO.

The radical cation of 2-silaketene ($\mathrm{H_2CSiO^{\cdot\oplus}}$, **3**) is a minimum on the energy surface. The energy of **3** is comparable to that of **2**. Several structural details deserve to be emphasized: 1) In contrast to **1** and **2**, the minimum in **3** can be described by a *planar* form with C_{2v} symmetry. 2) The Si–O bond in **3** of 1.524 Å is somewhat shorter than in the isolated $^2\Sigma^+$ $\mathrm{SiO^{\cdot\oplus}}$ (1.542 Å). This corresponds to an increase in the SiO vibrational frequency (1321 cm^{-1}) of 271 cm^{-1} compared to $\mathrm{SiO^{\cdot\oplus}}$. 3) The Si–C distance in **3**, 1.795 Å, lies between those of a Si–C bond in methylsilane (1.867 Å) and a Si–C double bond in silavinylidene (1.709 Å).[12] All of these data indicate that **3** formally corresponds to a silaketene derivative in which an electron has been removed from the Si–C double bond. The centers of spin and charge are formally separated in the resulting radical ion (a "distonic" ion[13]). The carbon atom carries the unpaired electron ($\varrho = 1.08$ e) and the silicon the charge ($q = 1.30$ e).

That the global minimum on the $[\mathrm{C,H_2,Si,O}]^{\cdot\oplus}$ energy surface corresponds to a planar C_{2v} structure $\mathrm{H_2COSi^{\cdot\oplus}}$ (**4**) is surprising, because in the ketene analogue the $\mathrm{H_2COC^{\cdot\oplus}}$ structure is about 63 kcal mol^{-1} more energetic than $\mathrm{H_2CCO^{\cdot\oplus}}$.[4c] It follows from the analysis of the geometry data and the charge distribution that **4** is not really a complex of $\mathrm{CH_2O/Si^{\cdot\oplus}}$ but a combination of $\mathrm{CH_2/OSi^{\cdot\oplus}}$. For example, the C–O separation in **4** of 1.369 Å clearly is larger than in a typical C–O double bond ($\mathrm{H_2CO}$: 1.208 Å), while the Si–O bond in **4** is only 0.033 Å longer than in isolated $^2\Sigma^+$ $\mathrm{SiO^{\cdot\oplus}}$. The C–H bond length and the HCH angle are also much closer to the parameters calculated for $^3\mathrm{CH_2}$ (1.073 Å and 131°, respectively). Like **3**, structure **4** represents a distonic ion. The carbon carries the spin (1.292 e) and the silicon the charge ($q = 1.154$ e). Attempts to localize a bent form for **4** were unsuccessful; the C_s structure found at the UHF level does not correspond to a stationary point at the MP2/6-31G** level.

Received: May 27, 1991 [Z 4652]
German version: *Angew. Chem. 103* (1991) 1396

CAS Registry numbers:
1, 136034-35-0; **3**, 136034-36-1; **4**, 136034-37-2; $\mathrm{SiH_2}$, 13825-90-6; $\mathrm{SiH_2^{\cdot+}}$, 28149-31-7; CO, 630-08-0; $\mathrm{CO^{\cdot+}}$, 12144-04-6.

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$\mathrm{K_2Cu_5Te_5}$, a Novel Mixed-Valence Layered Compound with Metallic Properties**

By *Younbong Park, Donald C. Degroot, Jon Schindler, Carl R. Kannewurf,* and *Mercouri G. Kanatzidis**

Since the discovery of high temperature superconductivity, mixed-valence Cu compounds have received considerable attention with the aim of discovering related materials with even higher transition temperatures. Although mixed-valence solid state Cu–chalcogenide compounds have been known for some time, they remain relatively rare. For example, the only mixed-valence compounds known so far are $\mathrm{Na_3Cu_4S_4}$,[1] $\mathrm{ACu_4Q_3}$ (A = K, Rb, Cs, Tl; Q = S, Se),[2] $\mathrm{A_3Cu_8S_6}$ (A = K, Rb),[3] $\mathrm{A_3Cu_8Se_6}$ (A = Rb, Cs),[4] $\mathrm{Cs_2Cu_5Se_4}$,[5] $\mathrm{TlCu_2Q_2}$ (Q = S, Se),[6] $\mathrm{TlCu_6S_4}$,[7] $\mathrm{Tl_5Cu_{14}Se_{10}}$.[8] Even though the a priori design of a superconducting material that has a high T_c is not yet possible, it is still worthwhile to pursue the synthesis of mixed-valence Cu compounds, since their electronic features generally play an important role for high electrical conductivity. Furthermore, compared with ternary sulfides and selenides, tellurides are even rarer. To the best of our knowledge, there are

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[**] Financial support from the Center for Fundamental Materials Research (CFMR) Michigan State University and the National Science Foundation (Presidential Young Investigator Award CHE-8958451) is gratefully acknowledged. The X-ray instrumentation was purchased in part with funds from the National Science Foundation (grant no. CHE-8908088). This work made use of the scanning electron microscope facilities of the Center for Electron Optics at Michigan State University.