Journal of Organometallic Chemistry, 96 (1975) 195—198

THE SILAFULVENE: A POTENTIALLY STABLE COMPOUND CONTAINING A DOUBLE CARBON—SILICON BOND

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(Received March 5th, 1975)

Summary

Two conformations of dimethylsilafulvene are calculated via a CNDO/2 procedure. One of them is planar while in the other the CH_3—Si—CH_3 plane is perpendicular to the cyclopentadienyl ring plane. The conformation energies differ by 19.8 kcal/mol.

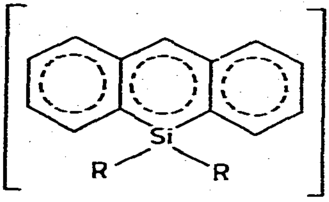
The synthesis of compounds containing a Group IVB element—carbon double bond has been and remains an attractive problem, but as yet no compounds with a double p_π—p_π C=Si bond have been synthesised [1]. They have been postulated as short-lived intermediates in the thermolysis of tetramethylsilane [2] or molecules containing a silicon in the cycle [3]. Thermolysis of silacyclobutanes [4] and a liquid-phase photolysis of monosilacyclobutanes [5] are the most convenient ways to unstable species of the type $R_2Si{=}CH_2$. Unlike double-bonded carbon compounds, the Si=C species are very reactive and hardly isolable as monomers. This may be attributed to a high polarity of carbon—silicon bonds [6]. The species may be stable at lower temperatures only. Barton and McIntosh studied pyrolysis products of 1,1-dimethyl-1-silacyclobutane at −196°C using IR. The band at 1407 cm^{-1} was ascribed to $(CH_3)_2Si{=}CH_2$ [7]. Identification of species of this kind is usually based on either isolating the dimerisation products [3,8] (1,3-disilacyclobutanes) or applying traps such as H_2O, NH_3, CH_3OD or RR′CHCN [3,5,9].

Thermodynamic calculations show that the p_π—p_π C=Si bonding energy (33 ± 5 kcal/mol) is approximately one half that of the C=C bond [10]. This may be due to a decrease in the overlap integrals $\langle p_\pi^{Si} | p_\pi^{C} \rangle$, resulting from the fact that the C—Si bond is ca. 0.4 Å shorter than the carbon—carbon bond [11].

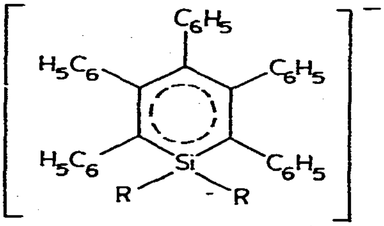
No stable heteroaromatic molecules containing trigonal Si, Ge or Sn atoms in the cycle have been obtained either, although compounds of a similar type were obtained for Group V elements [12]. Intense radical cations of silabenzene

[13] or silaanthracene formed in a mass spectrometer were reported. Orlov [14] points out the similarity between thermolysis and parent ion degradations occurring under electron impact conditions.

Anions with a C=Si bond are known. They are iso-π-electron analogues of aromatic hydrocarbons and their closed 6π-electron systems are formed due to participation of vacant silicon $3d$ orbitals [13,15]. UV and NMR spectra of the anions I and II synthesised by Yutzi [15] and by Märkl and Mertz [13] indicate clearly that the π-system is indeed closed. Jaffé [21] discussed double bonds but involving vacant d-orbitals.

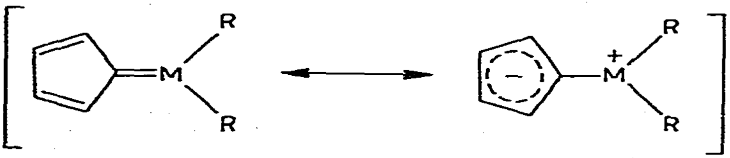


(I)



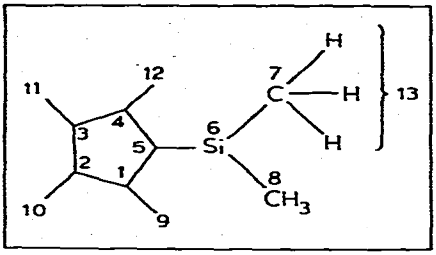
(II)

We studied mass spectra of bis(trimethylsilyl)cyclopentadiene (III) and its ring-deuterated derivative, III-d_4 [16], at various ionisation or photoionisation energies. The compounds III and III-d_4 bombarded at 70 or at 10.2 eV lead to the ions $[C_5D_5Si(CH_3)_2]^+$ (m/e 126) and $[C_5H_5Si(CH_3)_2]^+$ (m/e 122), both being satisfactorily stable. Further degradation of both the ions is essentially similar to degradation of the dimethylfulvene parent ion [17]. This suggests to us that the respective neutral molecules, $C_5H_4M(CH_3)_2$ (M = Si, Ge, Sn), might be stable. An additional stabilisation may be contributed by the participation of the ylide structure (IVb) that stabilises and causes some aromaticity of the usual fulvenes. The effect in silafulvene might be even more pronounced, owing to the lower electronegativity of silicon.

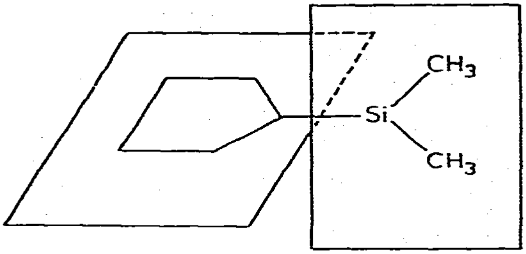


(a) (IV) (b)

To test the assumption above, we have calculated the energies of two dimethylsilafulvene conformations, Va and Vb, via a CNDO/2 technique [18]. The conformation Va is planar and the p_π—p_π carbon/silicon overlap should be at its maximum. In Vb the CH_3—Si—CH_3 plane is perpendicular to the ring plane and the p_π orbitals are orthogonal. The difference between the total energies of the conformations gives us the barrier to rotation around the C=Si bond and may serve as a measure of the p_π—p_π bonding. The cycle geometry was assumed similar to that in dimethylfulvene [19], the C=Si bond length was varied until the total energy minimum achieved in both cases, the vacant $3d$ orbitals being neglected. The results are listed in Table 1.



(Va)



(Vb)

The energy difference is 19.8 kcal/mol and thus agrees with the value of the p_π—p_π C=Si bonding [10]. It should be remembered that the CNDO/2 method used more often that not gives lower conformation energies than experiment [20]. The conformation Va is, as expected, more stable. The total ground-state dipole moment is close to the values found in dicyclopentadienyls, suggesting that structure IVb contributes appreciably. Another favourable feature is that in Va the C—Si bond ($r_{5,6}$) is 0.138 Å shorter than is the H_3C—Si bond ($r_{6,7}$). In Vb, the C—Si bond is 0.098 Å longer than in Va.

These data suggest that p_π—p_π bonding in metalated fulvene molecules may be rather significant. The additional stabilisation due to the ylide structure allows us to hope that stable compounds of the type may be synthesised when appropriate radicals at the metal and appropriate substituents in the ring are found. Preliminary results obtained in this laboratory show that the defiantly elusive C=Si compounds may yield eventually to persistence.

TABLE 1

TOTAL ENERGIES, BOND LENGTHS, CHARGE DENSITIES AND DIPOLE MOMENTS, FOR CONFORMATIONS Va AND Vb OF DIMETHYLSILAFULVENE, AS CALCULATED VIA A CNDO/2 TECHNIQUE. FOR NUMBERING OF ATOMS, SEE STRUCTURE Va

Parameter	Va	Vb	Comment
E_{total} (eV)	—1653.77	—1652.91	
$r_{5,6}$ (Å)	1.962	2.060	
$r_{6,7} = r_{6,8}$	2.10	2.10	The parameters of $C_5H_4C(CH_3)_2$ [19]
$r_{1,5}$	1.475	1.475	
$r_{1,2}$	1.347	1.347	
$r_{2,3}$	1.462	1.462	
$\langle r_{CH} \rangle$	1.111	1.111	The mean $\langle r_{CH} \rangle$ calculated via CNDO/2.
μ (D)	5.47	6.83	
q_1	—0.03	—0.01	
q_2	—0.03	—0.06	
q_5	—0.12	—0.19	
q_6	0.45	0.60	
q_7	—0.13	—0.15	
q_9	—0.03	—0.05	
q_{10}	—0.02	—0.03	
q_{13}	0.02	0.03	

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