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Supplementary Material Available: Tables of final coordinates, thermal parameters, and bond distances and angles for **3** (6 pages), a table of observed and calculated structure factors for **3** (26 pages). Ordering information is given on any current masthead page.

Theoretical Search for the Silanone-to-Silylene Isomerization

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Summary: In view of the current experimental interest in the title reaction, the barrier for the 1,2-shift in $(\text{H}_3\text{Si})\text{HSi}=\text{O}$ to $\text{HSi}-\text{OSiH}_3$ is investigated by means of ab initio calculations with flexible basis sets and electron correlation. It is found that the 1,2-silyl shift takes place under relatively mild conditions.

Silicon-oxygen doubly bonded compounds, silanones, are currently of growing interest.¹ In a series of papers,² we have calculated that the parent silanone is kinetically stable to isomerization as well as unimolecular destruction.^{2a-c} It is of natural interest to investigate whether an appropriately substituted silanone would undergo isomerization.

Barton and co-workers³⁻⁵ have continued to search for such experimental evidence and recently found that the copolymerization of cyclotetrasiloxane and butadiene affords silacyclopentene.⁴ They attempted to interpret this finding

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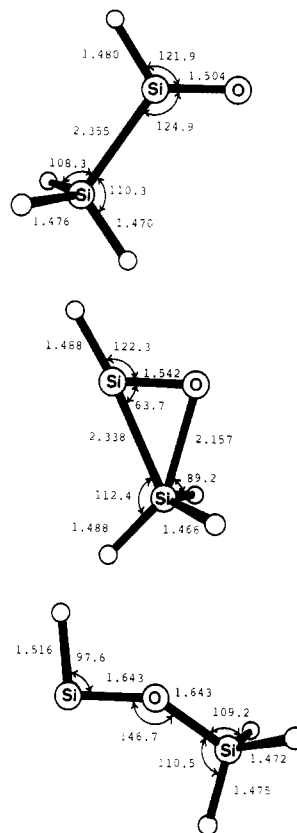


Figure 1. HF/6-31G* optimized geometries of **1**, **2**, and the transition state (middle) for the 1,2-silyl shift, in angstroms and degrees.

Table I. Barriers and Heats of Reaction (kcal/mol) for the 1,2-Silyl Shift in **1** to **2**

level of theory ^a	barrier	heat of reactn
HF/6-31G*	30.7	-31.6
HF/6-31G**	30.7	-31.6
HF/6-31+G(2d,p)	29.4	-27.6
MP2/6-31G**	25.1	-19.6
MP3/6-31G**	26.1	-25.0
MP4SDTQ/6-31G**	24.5	-19.5
MP2/6-31+G(2d,p)	23.5	-17.5
MP3/6-31+G(2d,p)	24.3	-23.0
MP4SDTQ/6-31+G(2d,p)	22.9	-18.0
+ ZPC	22.7	-18.0

^a For geometries, see Figure 1.

in terms of the silylsilanone to siloxysilylene isomerization via a 1,2-silyl shift. However, an alternative mechanism has also been suggested⁴ because a sizable barrier was calculated by us for the parent silanone.^{2a-c} We report now the ab initio calculations of the 1,2-silyl shift in $(\text{H}_3\text{Si})\text{HSi}=\text{O}$ (**1**) to $\text{HSi}-\text{OSiH}_3$ (**2**).

In this report, all geometries were fully optimized at the Hartree-Fock (HF) level with the 6-31G* basis set⁶ and identified as equilibrium or transition structures by calculating analytically the Hessian matrices. Energies were improved at the HF/6-31G* geometries with the larger basis sets and electron correlation. In the following, the symbol "/" means "at the geometry of".

In the isomerization of **1** to **2**, a relatively weak Si-Si bond is broken and a strong Si-O bond is formed. Reflecting this, the isomerization is ca. 18 kcal/mol exothermic (Table I), unlike the isomerization of the parent silanone which is approximately thermoneutral.^{2a-c} In

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addition, it is interesting to note that the isomerization of 1 to 2 proceeds via a least-motion path of C_s symmetry, as shown in Figure 1, while the parent silanone isomerizes via an out-of-plane path of C_1 symmetry.^{2a-c}

As Table I shows, the barrier for the 1,2-silyl shift in 1 to 2 is 30.7 kcal/mol at the HF/6-31G* level. Addition of a set of p-type polarization functions on hydrogens (i.e., HF/6-31G**//6-31G*) has no effect on the barrier height. On the other hand, the inclusion of a set of diffuse sp function⁷ and double sets of d-type polarization functions⁸ on heavy atoms (i.e., HF/6-31+G(2d,p)//6-31G*) lowers the HF/6-31G* barrier only by 1.3 kcal/mol. These suggest that at the HF level the further extension of the basis set has no significant effect on the barrier height.

Thus, the effect of electron correlation was incorporated by means of Møller-Plesset (MP) perturbation theory up to full fourth-order (MP4SDTQ)⁹ in the core-frozen approximation. As Table I shows, the MP calculations drop the HF barriers by ca. 6 kcal/mol: this dropping is rather insensitive to the order of perturbation. The most reliable energies at the MP4SDTQ/6-31+G(2d,p)//6-31G* level yield a barrier of 22.9 kcal/mol for the 1,2-silyl shift in 1 to 2. Zero-point correction (ZPC) made with the HF/6-31G* harmonic vibrational frequencies yields a final prediction of 22.7 kcal/mol for the classical barrier.

The predicted barrier is drastically small compared with that of 61 kcal/mol for the 1,2-H shift in the parent silanone. It appears that the relatively small barrier of 22.7 kcal/mol is readily surmountable at 610 °C where Barton and co-worker carried out their experiment:⁴ conventional transition-state theory allows us to estimate the rate constant on the order of $7.2 \times 10^5 \text{ s}^{-1}$ ($\Delta H^\ddagger = 20.8 \text{ kcal/mol}$ and $\Delta S^\ddagger = -8.3 \text{ eu}$)¹⁰ at the temperature. On the other hand, the reverse reaction 2 \rightarrow 1 is unlikely to proceed under mild conditions, as is apparent from Table I. In fact, no experimental evidence for the isomerization of siloxy-silylene to silylsilanone has been found.⁴

The relatively small barrier for the 1,2-silyl shift is probably ascribable to the hypervalent ability of the shifting silicon at the transition state.¹¹ At this point, it is instructive that the barrier for the 1,2-SiF₃ shift in (SiF₃)HSi=O to HSi—OSiF₃ was calculated to be 18.4 kcal/mol at the MP4SDTQ/6-31G**//6-31G* level and is 6.1 kcal/mol lower at the same level than that for the 1,2-SiH₃ shift. This lowering corresponds to the fact¹² that very electronegative substituents like F enhance the hypervalent bonding. In addition, it is important to note that the silicon atom in the SiF₃ group is more positively charged and thereby can interact more strongly with the negatively charged oxygen atom to be attacked.

In summary, we hope that the present calculations help obtain the definite experimental evidence for the interconversion of a silanone and a silylene.¹³ The further

details of this work together with some other 1,2-shifts will be published in due course.

Acknowledgment. All calculations were carried out at the Computer Center for the Institute for Molecular Science, by using the GAUSSIAN 82 program¹⁴ in the library program package.

(13) We have recently found that in the triplet state the 1,2-silyl shift proceeds without a significant barrier.

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Oxidative Syntheses of Cyclopentadienyl η^2 -Acyl Complexes and Stereospecific Conversion to an η^2 -Ylide Complex. X-ray Crystal Structures of Cp(NO)(I)Mo(η^2 -C(O)-*p*-tol) and Cp(NO)(I)Mo(η^2 -C(O)(PMe₃)-*p*-tol)

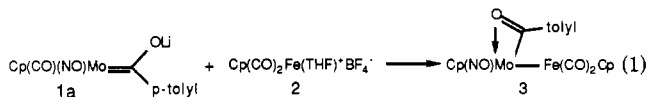
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Summary: Reaction of either Cp(NO)Mo(η^2 -C(O)-*p*-tol)-Fe(CO)₂Cp (3) (*p*-tol = *p*-tolyl) or Cp(CO)(NO)Mo=C(OLi)R (1) with I₂ gives the η^2 -acyl complexes Cp(NO)(I)Mo(η^2 -C(O)R) (4) (R = *p*-tol, 4-*t*-BuC₆H₄, Me). Oxidation of 4 (R = aryl) gives carboxylato complex 5, while reaction of 4 (R = *p*-tol) with PMe₃ gives at least a 95:5 ratio of diastereomers of the ylide complex Cp(NO)(I)Mo(η^2 -C(O)(PMe₃)-*p*-tol) (6).

The chemistry of transition-metal acyl complexes commands interest on the basis of their role in CO insertion reactions¹ and more recently in serving as templates for highly diastereoselective enolate reactions.² We recently reported the synthesis of two isomeric heterodinuclear μ -acyl compounds, *cis*- and *trans*-Cp(CO)Fe(μ -C(O)-*p*-tol)(μ -CO)Mo(NO)Cp, formed via reaction of Cp(CO)(NO)Mo=C(OLi)R (1a, R = *p*-tol) and Cp(CO)₂Fe(THF)⁺BF₄⁻ (2). During the course of this reaction we isolated a thermally unstable dinuclear intermediate and on the basis of spectroscopic data proposed the novel structure 3 shown in eq 1.³ In order to obtain additional



chemical evidence for this structure, we attempted to oxidatively cleave the proposed metal-metal bond with iodine to give Cp(CO)₂FeI and a perhaps more tractable molybdenum acyl complex. We report here (1) the successful

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(10) The thermodynamic quantities were evaluated with the statistical treatment, using the MP4SDTQ/6-31+G(2d,p)//6-31G* energies and the HF/6-31G* geometries and frequencies.

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