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Supplementary Material Available: Listings of crystal data, bond distances, bond angles, positional parameters, and anisotropic thermal parameters for $\text{H}_2\text{Ru}_6(\text{CO})_{17}$ (11 pages); listing of observed and calculated structure factors for $\text{H}_2\text{Ru}_6(\text{CO})_{17}$ (32 pages). Ordering information is given on any current masthead page.

Substituent Effects on the Geometries and Energies of the Si=Si Double Bond

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The recent isolation of stable disilenes ($\text{R}_2\text{Si}=\text{SiR}_2$) has prompted substantial activity in this field, both experimental¹ and theoretical.² Yet, the study of compounds containing double bonds to silicon is still in its infancy. For example, only aryl-, alkyl-, and $(\text{Me}_2\text{Si})_2\text{N}$ -substituted disilenes have been isolated to date,¹ and thus little is known experimentally on the effect of heteroatom substitution on the properties of the Si=Si double bond. Malrieu and Trinquier (MT) have recently applied qualitative valence-bond and molecular orbital arguments to analyze this question,³ but the quantitative computational data that is available is limited and nonsystematic.⁴ We present here the results of the first systematic ab initio study of substituted disilenes, which shows that the substituents affect the isoelectronic Si=Si and C=C bonds in different ways, causing unprecedented large changes in both the structures and the energies of disilenes.

A series of disilenes $\text{H}_2\text{Si}=\text{SiHR}$ (**1**), $\text{R} = \text{Li}, \text{BeH}, \text{BH}_2, \text{H}, \text{CH}_3, \text{SiH}_3, \text{NH}_2, \text{OH}, \text{and F}$, and several disubstituted disilenes were calculated by ab initio methods using the GAUSSIAN 86 series of programs.⁵ Geometries were fully optimized with the 6-31G* basis set,⁶ and energies were evaluated at MP3/6-31G*⁷ a level of theory that includes part of the electron correlation energy.

$\text{H}_2\text{Si}=\text{SiH}_2$ adopts, as reported previously,² a trans-bent conformation (**1b**, $\text{R} = \text{H}$) with $\theta_{\text{H}} = \theta_{\text{R}} = 12.9^\circ$ and $r(\text{Si}=\text{Si}) = 2.132 \text{ \AA}$. However, the potential energy surface for trans bending

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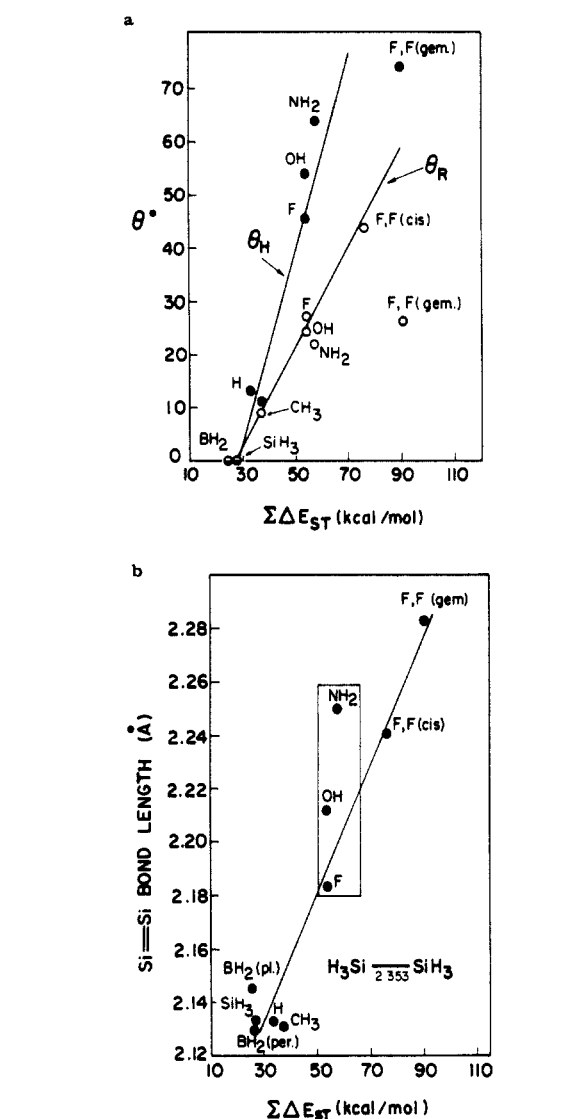
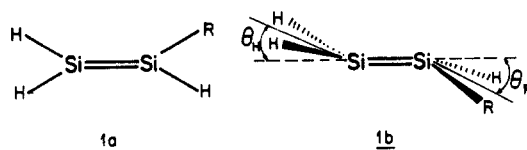


Figure 1. (a) Plot of the pyramidalization angles θ_{H} and θ_{R} in substituted disilenes (for definitions, see structure **1b**) vs $\Sigma \Delta E_{\text{ST}}$ of the corresponding silylenes. (b) Plot of the Si=Si bond lengths in substituted disilenes vs $\Sigma \Delta E_{\text{ST}}$ of the corresponding silylenes. Geometries of the disilenes were optimized at 6-31G*, and the $\Sigma \Delta E_{\text{ST}}$ values were calculated at MP4SDTQ/6-31G**//3-21G**.

is very flat, **1b** being only 0.5 kcal mol⁻¹ (at MP2/6-31G**//MP2/6-31G*) lower in energy than the planar **1a**. Even severe pyramidalization in $\text{H}_2\text{Si}=\text{SiH}_2$ requires relatively little energy (e.g., 6.3 kcal mol⁻¹ at MP3/6-31G**//6-31G* for $\theta_{\text{H}} = 60^\circ$).



The structures of the substituted disilenes **1** are strongly dependent on the substituent (Figure 1). With electropositive substituents (e.g., $\text{R} = \text{Li}, \text{BeH}, \text{BH}_2$, and SiH_3), the disilenes are planar and the Si=Si bond length is similar to or slightly longer than that in **1**, $\text{R} = \text{H}$. In contrast, electronegative and π -donating substituents induce large deviations from planarity (Figure 1a); e.g., in $\text{H}_2\text{Si}=\text{SiH}(\text{NH}_2)$, $\theta_{\text{H}} = 64.1^\circ$ and $\theta_{\text{R}} = 22.1^\circ$. Disubstitution causes even larger distortions, and in $\text{H}_2\text{Si}=\text{SiF}_2$, $\theta_{\text{H}} = 73.6^\circ$! The changes in the Si=Si bond length upon substitution are also very large (Figure 1b), much larger than in the corresponding substituted silenes⁸ or olefins⁹ (e.g., hydroxy sub-

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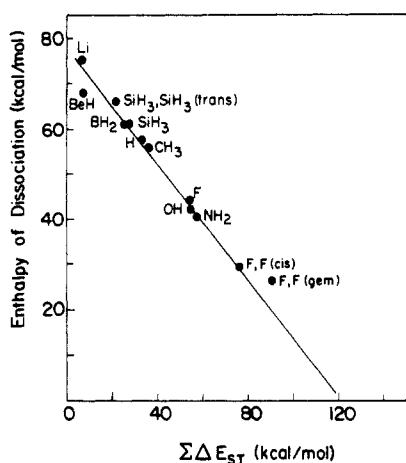


Figure 2. Plot of the dissociation energies of substituted disilenes to two singlet silylenes (MP3/6-31G*//6-31G* + ZPE at 6-31G*) vs $\Sigma\Delta E_{ST}$ of the corresponding silylenes (MP4SDTQ/6-31G*//3-21G(*)).

stitution elongates the Si=Si bond by 0.079 Å, compared to only 0.028 Å in $H_2Si=CH_2$ ⁸ and 0.001 Å in ethylene).

The degree of pyramidalization (θ) and the Si=Si bond distance in substituted disilenes correlate (Figure 1, parts a and b, respectively) with $\Sigma\Delta E_{ST}$, the sum of the singlet-triplet energy differences in the silylenes that formally compose the disilene (i.e., R_1R_2Si : and R_3R_4Si : for $R_1R_2Si=SiR_3R_4$).¹⁰ A correlation between θ and $\Sigma\Delta E_{ST}$ was previously suggested by Malrieu and Trinquier using qualitative VB and MO analysis,³ leading to the prediction that disilenes are trans-bent when $\Sigma\Delta E_{ST} > BDE$ (BDE = bond dissociation energy of a substituted disilene to the corresponding singlet silylenes).¹¹ This prediction is generally supported by our calculations, except for the region where the bending potential is flat; e.g., $H_2Si=SiH_2$ and $H_2Si=SiHCH_3$ are calculated to be trans-bent (Figure 1a) although $\Sigma\Delta E_{ST} < BDE$ [for $H_2Si=SiH_2$, $\Sigma\Delta E_{ST} = 32.8 \text{ kcal mol}^{-1}$] ($BDE = 57.2 \text{ kcal mol}^{-1}$).¹²

Most recently Liang and Allen suggested that the geometries of disilenes are dictated by the substituents' electronegativities: the more electronegative substituents induce larger distortions.^{4a} We find that in addition to electronegativity the π -donation ability of the substituent is also important. Thus, $r(Si=Si)$ and θ_H decrease (θ_R increases slightly) along the series $1b$, $R = NH_2 \rightarrow OH \rightarrow F$ (Figure 1, parts a and b), while the electronegativity of R increases. Changes in the geometries of disilenes are better predicted by $\Sigma\Delta E_{ST}$ of the corresponding silylenes, which are influenced by both the electronegativity and the π -donation ability of the substituents, than by the substituents' electronegativities.

The BDEs of substituted disilenes also correlate linearly with $\Sigma\Delta E_{ST}$ (Figure 2).¹³ The changes in the BDEs of disilenes upon substitution are dramatic. Thus, the calculated BDE of *cis*- $FHSi=SiHF$ of 29.5 kcal mol⁻¹ is only half of the BDE of $H_2Si=SiH_2$ (57.2 kcal mol⁻¹).¹⁴

The correlation between $\Sigma\Delta E_{ST}$ and the BDE of disilenes can be used to predict the thermodynamic stabilities toward disso-

ciation of unknown disilenes and for deciding which disilenes are reasonable targets for synthesis. For example, according to Figure 2 the BDE of $(HO)HSi=SiH(OH)$ is as low as ca. 30 kcal mol⁻¹. As entropy favors dissociation, the ΔG° for the reaction $(HO)HSi=SiH(OH) \rightarrow 2(HO)HSi$: is even lower, only ca. 20 kcal mol⁻¹ at 298 K.¹⁵ The isolation of dialkoxydisilenes is expected therefore to be extremely difficult, even at low temperatures.¹⁶ Note that as the DBE decreases, other possible Si_2R_4 isomers [e.g., bridged $RSi(\mu-R_2)SiR$] may compete with the classical disilene geometry (e.g., $FHSi=SiHF$ for which BDE = 27.6 kcal mol⁻¹).^{3c,17} Figure 2 also predicts that a substituted disilene for which $\Sigma\Delta E_{ST} \geq 120 \text{ kcal mol}^{-1}$ will dissociate spontaneously to two silylenes even at 0 K. An example is $F_2Si=SiF_2$ ($\Sigma\Delta E_{ST} = 147.6 \text{ kcal mol}^{-1}$), which was found not to be a minimum on the Si_2F_4 potential energy surface.^{3a,4b}

The finding that *silyl substitution increases the DBE of disilenes* [Figure 2, e.g., the BDE of $(H_3Si)HSi=SiH(SiH_3)$ is calculated to be 8.7 kcal mol⁻¹ higher than that of $H_2Si=SiH_2$] is of special significance, because it suggests that disilenes such as $(R_3Si)_2Si=Si(SiR_3)_2$ should have a relatively high thermodynamic stability, making them interesting goals for synthesis.

In conclusion, both the geometries and the bond dissociation energies of substituted disilenes correlate with $\Sigma\Delta E_{ST}$ of the corresponding silylenes. This correlation can be used to predict the structures and the BDEs of yet unknown disilenes and to find which disilenes are capable of existence.

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(15) The calculated (6-31G*) ΔS° for the dissociation of $H_2Si=SiH_2$ is $(2 \times 49.5) - 64.6 = 34.4 \text{ cal K}^{-1} \text{ mol}^{-1}$.

(16) In agreement, attempts to synthesize such disilenes were indeed so far unsuccessful (R. West, personal communication).

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One-Step Construction of Fused Tricyclic and Tetracyclic Structures from Acyclic Precursors via Cyclic Carbopalladation[†]

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Construction of two or more rings in one synthetic operation is an attractive synthetic strategy. Among the most noteworthy examples is W. S. Johnson's cationic polyene cyclization reaction² (an example of "crochet"-mode cyclization), which has been applied to bi- through tetracyclization. Although a conceptually distinct "zipper"-mode cyclization strategy schematically shown in Scheme 1 is also potentially applicable to construction of a number of rings in one step, its application beyond bicyclization³ has been very limited.⁴

[†] This paper is dedicated to the memory of Professor J. K. Stille.

(1) The critical results described in this paper were orally presented. (a) Zhang, Y.; Negishi, E. Presented at the 5th IUPAC Symposium on Organometallic Chemistry Directed towards Organic Synthesis, Florence, Italy, Oct 1-6, 1989; OP-B07. (b) Negishi, E. Presented at the 1989 International Congress of Pacific Basin Societies, Honolulu, HI, Dec 17-22, 1989; ORGN 711.

(2) For tetracyclization of polyenes, see: Johnson, W. S.; Wiedhaup, K.; Brady, S. F.; Olson, G. L. *J. Am. Chem. Soc.* 1974, 96, 3979.

(3) In addition to numerous organometallic bicyclization reactions, we have recently reported some examples of bicyclization reactions producing fused bicycles via cyclic carbopalladation: Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* 1989, 111, 3454.

(9) Heinrich, N.; Koch, W.; Frenking, G.; Schwarz, H. *J. Am. Chem. Soc.* 1986, 108, 593.

(10) Of the silylenes studied, $HSiLi$ and $HSiBeH$ are the only ground-state triplets, and they were therefore not included in Figure 1. $H_2Si=SiHLi$ and $H_2Si=SiHBeH$ are both planar, with Si=Si bond lengths of 2.159 and 2.145 Å, respectively.

(11) According to Malrieu and Trinquier, doubly bonded species are trans-bent when $\Sigma\Delta E_{ST} > 0.5E_{\sigma+\sigma}$ ^{3a,b} where $E_{\sigma+\sigma}$ is the binding energy of the disilene relative to the corresponding two divalent triplet silylenes. When the divalent fragments are singlets (i.e., $\Sigma\Delta E_{ST} > 0$), as for most silylenes, $E_{\sigma+\sigma} = BDE + \Sigma\Delta E_{ST}$ and the $\Sigma\Delta E_{ST} > 0.5E_{\sigma+\sigma}$ condition suggested by MT becomes $\Sigma\Delta E_{ST} > BDE$.

(12) MT also predict, using somewhat different values ($\Sigma\Delta E_{ST} = 38 \text{ kcal mol}^{-1}$) ($0.5E_{\sigma+\sigma} = 37 \text{ kcal mol}^{-1}$), that $H_2Si=SiH_2$ is trans-bent.^{3b}

(13) A similar correlation was suggested for substituted olefins: Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* 1986, 90, 998. Carter, E. A.; Goddard, W. A., III. *J. Chem. Phys.* 1988, 88, 1752.

(14) Note that while the Carter-Goddard equation suggests a slope of -1,¹³ we obtain in Figure 2 a slope of -0.62.