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Supplementary Material Available: Listings of crystal data, bond distances, bond angles, positional parameters, and anisotropic thermal parameters for $H_2Ru_6(CO)_{17}$ (11 pages); listing of observed and calculated structure factors for $H_2Ru_6(CO)_{17}$ (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 ($R_2Si{=}SiR_2$) has prompted substantial activity in this field, both experimental[1] and theoretical.[2] Yet, the study of compounds containing double bonds to silicon is still in its infancy. For example, only aryl-, alkyl-, and $(Me_3Si)_2N$-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 $H_2Si{=}SiHR$ (**1**), R = Li, BeH, BH_2, H, CH_3, SiH_3, NH_2, OH, 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.

$H_2Si{=}SiH_2$ adopts, as reported previously,[2] a trans-bent conformation (**1b**, R = H) with $\theta_H = \theta_R = 12.9°$ and $r(Si{=}Si) = 2.132$ Å. However, the potential energy surface for trans bending 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 $H_2Si{=}SiH_2$ requires relatively little energy (e.g., 6.3 kcal mol^{-1} at MP3/6-31G*//6-31G* for $\theta_H = 60°$).

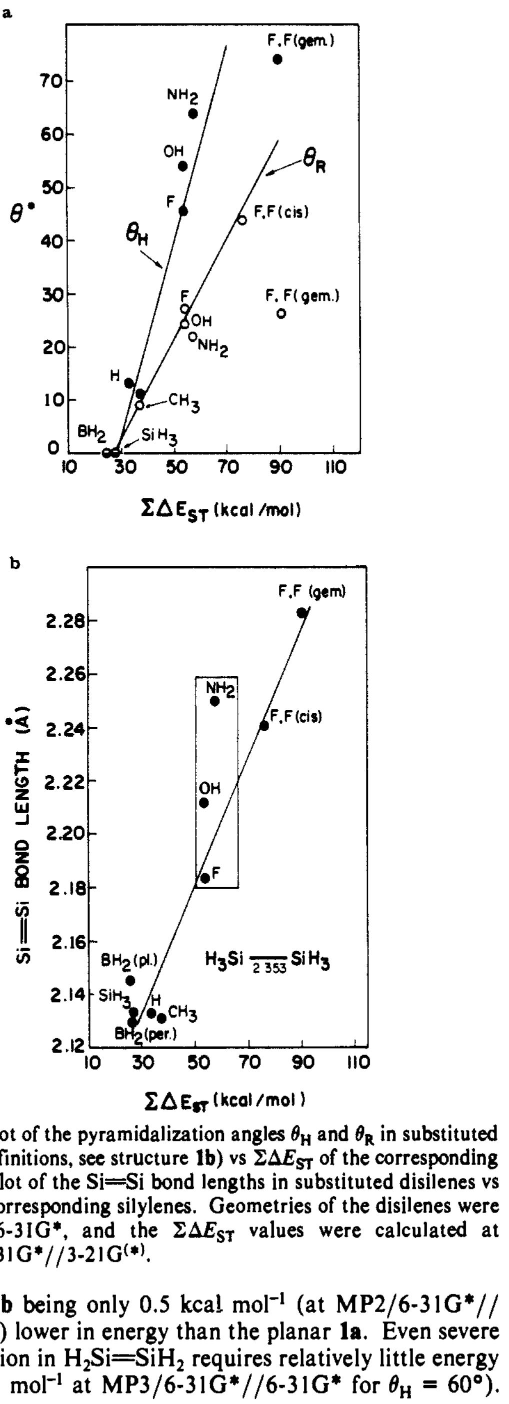
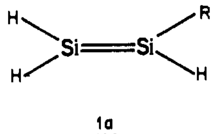
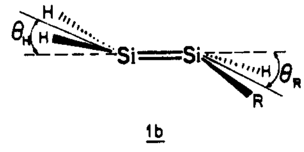


Figure 1. (a) Plot of the pyramidalization angles θ_H and θ_R in substituted disilenes (for definitions, see structure **1b**) vs $\Sigma\Delta E_{ST}$ of the corresponding silylenes. (b) Plot of the Si═Si bond lengths in substituted disilenes vs $\Sigma\Delta E_{ST}$ of the corresponding silylenes.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



1a



1b

The structures of the substituted disilenes **1** are strongly dependent on the substituent (Figure 1). With electropositive substituents (e.g., R = Li, BeH, 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**, R = H. In contrast, electronegative and π-donating substituents induce large deviations from planarity (Figure 1a); e.g., in $H_2Si{=}SiH(NH_2)$, $\theta_H = 64.1°$ and $\theta_R = 22.1°$. Disubstitution causes even larger distortions, and in $H_2Si{=}SiF_2$, $\theta_H = 73.6°$! The changes in the Si═Si bond length upon substitution are also very large (Figure 1b), much larger than in the corresponding substituted silenes[8] or olefins[9] (e.g., hydroxy sub-

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[1] Reviews: Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 17 and references cited therein. West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. West, R. *Pure Appl. Chem.* **1984**, *56*, 163.

[2] Review: Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 2, pp 129–136 and references cited therein.

[3] (a) Malrieu, J.-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916. (b) Trinquier, G.; Malrieu, J.-P. *Ibid.* **1987**, *109*, 5303. (c) Trinquier, G. *Ibid.* **1990**, *112*, 2130.

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[6] (a) Second-row elements: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.* **1973**, *28*, 213. (b) Third-row elements: Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

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[8] Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

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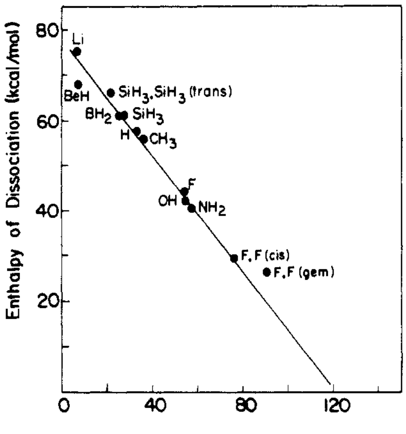

Figure 2. Plot of the dissociation energies of substituted disilenes to two singlet silylenes (MP3/6-31G*//6-31G* + ZPE at 6-31G*) vs $\Sigma\Delta E_{ST}$ of the corresponding silylenes (MP4SDTQ/6-31G*//3-21G(*)).

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 $H_2Si{=}SiH_2$, $\Sigma\Delta E_{ST} = 32.8$ kcal mol^{-1}) < (BDE = 57.2 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 dissociation 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 $\Delta G°$ 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(μ-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 $\Sigma\Delta E_{ST} \geq 120$ kcal mol^{-1} will dissociate spontaneously to two silylenes even at 0 K. An example is $F_2Si{=}SiF_2$ ($\Sigma\Delta E_{ST} = 147.6$ 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.

Acknowledgment. We thank Professor Robert West for many stimulating discussions and for sharing with us his unpublished results and Professors J.-P. Malrieu and G. Trinquier for helpful comments. This study was partially supported by the Venezuela Technion Society Research Fund and the Fund for the Promotion of Research at the Technion.

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(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 $\Sigma\Delta E_{ST} > 0.5E_{\sigma+\pi}$,[3a,b] where $E_{\sigma+\pi}$ 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, $E_{\sigma+\pi}$ = BDE + $\Sigma\Delta E_{ST}$ and the $\Sigma\Delta E_{ST} > 0.5E_{\sigma+\pi}$ condition suggested by MT becomes $\Sigma\Delta E_{ST} >$ BDE.

(12) MT also predict, using somewhat different values ($\Sigma\Delta E_{ST} = 38$ kcal mol^{-1}) > ($0.5E_{\sigma+\pi} = 37$ 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.

(15) The calculated (6-31G*) $\Delta S°$ for the dissociation of $H_2Si{=}SiH_2$ is (2 × 49.5) − 64.6 = 34.4 cal K^{-1} 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[†,1]

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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 reaction[2] (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 I is also potentially applicable to construction of a number of rings in one step, its application beyond bicyclization[3] 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 Chemical 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.