2 h, the resultant yellow solution was filtered, the filtrate evaporated to dryness, and the residue dissolved in 5 mL of water. Addition of a stoichiometric amount of KPF_6 (0.099 g, 0.54 mmol) dissolved in 1 mL of water yielded the complex as a yellow solid. This product was washed with water and diethyl ether and dried under vacuum; yield 0.342 g (75%).

Solutions of the complex in CD_2Cl_2 show an uncomplicated ^1H NMR spectrum (at +20 °C), with methyl and methylene resonances appearing as broad singlets at δ +1.82 and +2.98, respectively, and a binomial septet at δ −8.42 (J_{HP} = 9.2 Hz) due to the hydride ligands coupled to six equivalent phosphorus atoms (Figure S1 in the supplementary material). This behavior is characteristic of a fluxional rhenium polyhydride complex. When these solutions are cooled to −100 °C, the Re*H* resonance broadens and approaches coalescence but we were unable to obtain the spectrum of the limiting static structure. Likewise, the P*Me* resonance broadened slightly but otherwise remained unchanged as the temperature was lowered. The $^{31}P\{^1H\}$ spectrum (recorded in CD_2Cl_2 at +20 °C) displays a singlet at δ −28.7 for the dmpm phosphorus atoms; this signal was also a singlet in ca. −80 °C. A selective 2DJ ^{31}P NMR experiment (Figure S1) shows the dmpm phosphorus resonance split into six peaks (J_{HP} = 9.2 Hz). This confirms the presence of five hydride ligands in the complex.

The X-ray crystal structure of $[Re_2H_5(dmpm)_3]PF_6$ was determined on a crystal grown from 1,2-dichloroethane/diisopropyl ether.[19-21] The key features of the structure of the $[Re_2H_5(dmpm)_3]^+$ cation are shown in Figure 1. While this species possesses no crystallographically imposed symmetry, it approximates C_s symmetry with the mirror plane encompassing the carbon atoms of the CH_2 groups of the three dmpm ligands and bisecting the Re–Re vector. The Re_2P_6 skeleton is essentially eclipsed. The most remarkable feature in this structure is the very long Re–Re distance of 3.5150 (4) Å, which clearly accords with the absence of any direct Re–Re bonding. We can view the structure as arising formally from the protonation of the neutral species $Re_2H_4(dmpm)_3$, in which the individual Re atoms have 15-electron counts, such that a three-center, two-electron Re–H–Re bonding interaction gives rise to a diamagnetic ground state. This structure differs from those of all other $[Re_2H_5]^+$ species that have been structurally characterized,[9-11] in which there is a $[HRe(\mu\text{-}H)_3ReH]$ unit and a very short Re–Re distance (2.58–2.60 Å). This $[Re_2H_5(dmpm)_3]^+$ structure likely represents one structural extreme in the series of terminal/bridging Re–H bond forming/breaking processes that presumably account for the fluxionality of this complex in solution.

The terminal Re–H bond lengths (1.6–1.8 (1) Å) are normal for M–H distances determined by X-ray crystallography;[22] the H⋯H distances are long (ca. 1.7 Å) and show that this is a classical hydride structure. The apparent disparity in the measured Re–H(B) distances (1.53 (7) and 2.06 (7) Å), while greater than 3σ, is not considered to be significant in view of the difficulty of determining H atom positions in the presence of heavy metals by X-ray diffraction.[23] Whatever the details of the Re–H–Re bonding, this complex is electronically unsaturated to an extent unusual for the heavier transition elements. It can be expected to be very reactive, although it has the remarkable property of being stable in air and water.[24] We find that it reacts with CO in 1-propanol to afford the carbonyl complex $[Re_2(\mu\text{-}H)(\mu\text{-}dmpm)_3(CO)_4]PF_6$ in which each Re atom has two terminal CO ligands bound to it and the structure of the $[Re_2(\mu\text{-}H)(\mu\text{-}dmpm)_3]$ unit of the parent cation is retained.[25] Studies on the reactivity of $[Re_2H_5(dmpm)_3]PF_6$ are being undertaken, and full details will be reported in due course.

Acknowledgment. Support from the National Science Foundation, through Grant No. CHE88-07444 to R.A.W. and Grant No. CHE86-15556 for the purchase of the microVAX II computer and diffractometer, is gratefully acknowledged. We also acknowledge the National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 8714258) for funds for the purchase of the NMR spectrometers.

Supplementary Material Available: A listing of atomic positional parameters for the structure of $[Re_2H_5(dmpm)_3]PF_6$ and a figure (Figure S1) showing some of the NMR spectral properties of this complex (5 pages). Ordering information is given on any current masthead page.

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[19] Yellow crystals of $[Re_2H_5(dmpm)_3]PF_6$ are monoclinic, space group $P2_1/n$, with a = 9.288 (1) Å, b = 24.515 (3) Å, c = 13.761 (3) Å, β = 93.23 (1)°, V = 3128 (1) Å^3, Z = 4, and d_{calcd} = 1.976 g/cm^3. X-ray data were collected at −100 °C on a 0.36 × 0.15 × 0.13 mm crystal for 5499 independent reflections having 4° < 2θ < 50° on an Enraf-Nonius diffractometer using graphite-crystal-monochromated Mo Kα radiation (λ = 0.71073 Å). Lorentz and polarization corrections were applied to the data. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were identified in succeeding difference Fourier syntheses. The five hydride ligands were located following anisotropic refinement of all non-hydrogen atoms. Hydrogen atoms of the dmpm ligands were included at fixed positions. An empirical absorption correction was applied,[20] but no correction for extinction was made. The non-hydrogen atoms of the dirhenium complex and the atoms of the PF_6^- anion were refined anisotropically; corrections for anomalous scattering were applied to these atoms.[21] The final residuals were R = 0.030 (R_w = 0.039) for 4476 data with $I > 3\sigma(I)$.

[20] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

[21] (a) Cromer, D. T. *International Tables for X-ray Crystallography*: Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution, see: Cromer, D. T.; Waber, J. T. *Ibid.* Table 2.2B.

[22] Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757.

[23] Interestingly, if such a difference was real it could be considered as evidence for a structure in which the two Re atoms had different electron counts, i.e., 14-electron and 16-electron. In this event, the species would show some resemblance to the unsymmetrical complex $(Me_2NH)(CO)_4Re(\mu\text{-}H)Re(CO)_4Cl$, which is formally composed of 18-electron and 16-electron fragments: Adams, R. D.; Kuhns, J. D. *Polyhedron* **1988**, *7*, 2543.

[24] A solution of $[Re_2H_5(dmpm)_3]^+$ in D_2O shows a Re*H* resonance as a binomial septet at δ −9.0 (J_{HP} = 8.7 Hz).

[25] This has been confirmed by a single-crystal X-ray structure analysis which shows the Re–Re distance to be 3.3625 (4) Å: Fanwick, P. E., unpublished results.

Formation and Characterization of an 84-Electron Hexaruthenium Cluster: Spontaneous Decarbonylation of $H_2Ru_6(CO)_{18}$ To Form $H_2Ru_6(CO)_{17}$

Deborah A. McCarthy, Jeanette A. Krause, and
Sheldon G. Shore*

Evans Laboratory, The Ohio State University
Columbus, Ohio 43210

Received June 18, 1990

Reported herein are the preparation and characterization of $H_2Ru_6(CO)_{17}$, a cluster that contains an equal number of vertices and skeletal electron pairs.[1] It is formed through the loss of CO from $H_2Ru_6(CO)_{18}$ (eq 1).

$$H_2Ru_6(CO)_{18} \xrightarrow{\text{room temperature}} H_2Ru_6(CO)_{17} + CO \qquad (1)$$

Although $H_2Ru_6(CO)_{18}$ was first reported some 20 years ago and has been studied in several laboratories,[2-6] its spontaneous decarbonylation at room temperature is a previously unrecognized

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[2] Churchill, M. R.; Wormald, J.; Knight, J.; Mays, J. M. *J. Chem. Soc. D* **1970**, 458.

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[4] Churchill, M. R.; Wormald, J. *J. Am. Chem. Soc.* **1971**, *93*, 5670.

[5] Knight, J.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1022.

[6] Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980**, 383.

property. It is likely that the formation of $H_2Ru_6(CO)_{17}$ from $H_2Ru_6(CO)_{18}$ was undetected earlier because these compounds are visually indistinguishable, both are a deep purple color, and their IR spectra[7] are virtually identical except for two weak bands below 2000 cm^{-1} in the spectrum of $H_2Ru_6(CO)_{17}$. Our clue that $H_2Ru_6(CO)_{18}$ decomposes was provided by the appearance of a new signal in the ^1H NMR spectrum in $CDCl_3$ of a sample that had been stored as a solid for 3 months at room temperature. The ^1H NMR signals of $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$ are so closely spaced (0.02 ppm) that the presence of two signals was revealed only under conditions of high resolution. The only positive means for distinguishing between these two clusters proved to be X-ray crystallography and mass spectrometry.

The starting point for the preparation, identification, and characterization of $H_2Ru_6(CO)_{17}$ was a freshly prepared sample of $H_2Ru_6(CO)_{18}$, fractionally crystallized from CH_2Cl_2, that was shown to be authentic by elemental analysis calculated for $H_2Ru_6C_{18}O_{18}$ (Calcd: C, 19.40; H, 0.18. Found: C, 19.38; H, 0.18.) and by comparison of published cell dimensions and space group data[4] with that obtained from a single crystal of the sample. The crystal was dissolved in $CDCl_3$. It produced a single sharp proton NMR resonance at −15.60 ppm at 25 °C (δ_{TMS} = 0.00 ppm). NMR spectra of $H_2Ru_6(CO)_{18}$ have not been reported previously. The FAB mass spectrum of $H_2Ru_6(CO)_{18}$ contains a maximum intensity peak of m/e = 1118 in the parent envelope and a distribution of peak intensities in the envelope that are in accord with that predicted for natural abundance isotopic distribution.[8]

Solution samples of $H_2Ru_6(CO)_{18}$, in CH_2Cl_2, allowed to stand for 3–4 weeks in the absence of air contain approximately equal amounts of $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$ plus minor amounts of $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ based on ^1H NMR spectra ($CDCl_3$ 25 °C). On the other hand, solution samples of $H_2Ru_6(CO)_{18}$ standing in air at room temperature for 2–3 h show noticeable conversion to a mixture of $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$. Solid samples of pure $H_2Ru_6(CO)_{18}$ stored under vacuum or N_2 decompose to $H_2Ru_6(CO)_{17}$, $H_2Ru_4(CO)_{13}$, and $H_4Ru_4(CO)_{12}$ though much more slowly than solutions of the cluster.

Although $H_2Ru_6(CO)_{17}$ and $H_2Ru_6(CO)_{18}$ are only slightly soluble in common solvents, they can be separated by careful fractional crystallization, from CH_2Cl_2. From fractional crystallization combined with FAB mass spectrometry it was shown that very small quantities (<2 mg) of $H_2Ru_6(CO)_{17}$ are produced in the initial preparation of $H_2Ru_6(CO)_{18}$ (~40 mg).

Crystals of $H_2Ru_6(CO)_{17}$ were obtained at the interface of a layered solution of $H_2Ru_6(CO)_{17}$ in CH_2Cl_2 and hexanes. Thirty-one crystals were isolated and subjected to the Search–Index programs on an Enraf-Nonius CAD4 X-ray diffractometer; they all indexed to give the same unit cell. One of the crystals was subjected to a full X-ray structure determination and shown to be $H_2Ru_6(CO)_{17}$.[9] The cluster was further identified by elemental analysis for $H_2Ru_6C_{17}O_{17}$ (Calcd: C, 18.83; H, 0.19. Found: C, 18.78; H, 0.21.) and by FAB mass spectrometry. The FAB mass spectrum contains a maximum intensity peak of m/e = 1086 in the parent envelope and a distribution of peak intensities in the envelope in accord with that predicted[8] for natural abundance isotopic distribution. The ^1H NMR spectrum, −15.58 ppm ($CDCl_3$, 25 °C), was obtained from the single crystal employed in the X-ray analysis. IR spectrum (CH_2Cl_2, 25 °C): ν_{CO} 2060 (s), 2054 (s), 2006 (w), 1940 (vw, br), 1871 (vw) cm^{-1}.

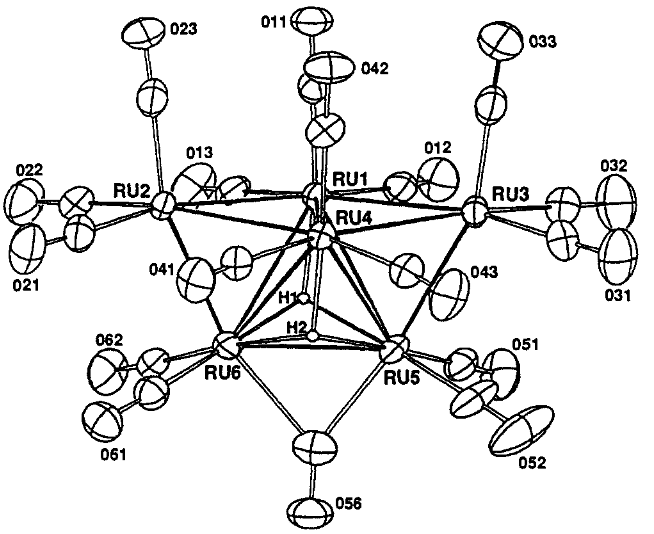

Figure 1. Molecular structure of $H_2Ru_6(CO)_{17}$ (ORTEP plot with 50% probability ellipsoids). Metal–metal bond distances (Å): Ru(1)–Ru(2) = 2.833 (1), Ru(1)–Ru(3) = 2.833 (1), Ru(1)–Ru(4) = 2.753 (1), Ru(1)–Ru(5) = 2.999 (1), Ru(1)–Ru(6) = 2.999 (1), Ru(2)–Ru(4) = 2.851 (1), Ru(2)–Ru(6) = 2.690 (1), Ru(3)–Ru(4) = 2.850 (1), Ru(3)–Ru(5) = 2.708 (1), Ru(4)–Ru(5) = 2.993 (1), Ru(4)–Ru(6) = 3.009 (1), Ru(5)–Ru(6) = 2.643 (1). Ru–H bond distances (Å): Ru(1)–H(1) = 1.81 (8), Ru(5)–H(1) = 2.01 (7), Ru(6)–H(1) = 1.86 (7), Ru(4)–H(2) = 1.78 (6), Ru(5)–H(2) = 1.98 (6), Ru(6)–H(2) = 1.92 (8). Ru–C_{bridge} bond distances (Å): Ru(5)–C(56) = 2.102 (9), Ru(6)–C(56) = 2.209 (9). Average[11] Ru–C_{axial} bond distance (Å): 1.900 (9). Average[11] Ru–$C_{equatorial}$ bond distance (Å): 1.902 (26). Average[11] Ru–C_{radial} bond distance (Å): 1.855 (9).

The $H_2Ru_6(CO)_{17}$ molecule possesses near C_{2v} symmetry (Figure 1). It contains an Ru_6 core which can be described as a bicapped tetrahedron (alternatively a monocapped trigonal bipyramid). Six skeletal electron pairs are associated with the core. This cluster belongs to a class of clusters in which the number of skeletal electron pairs is equal to the number of vertices.[1] It contains 84 valence electrons compared to the 86 valence electrons associated with octahedral transition-metal clusters. A related cluster, $Os_6(CO)_{18}$, also contains six skeletal electron pairs and has a like shaped metal core.[10] The hydrogen atoms were located in the X-ray Fourier difference map and refined. They cap the Ru(1)–Ru(5)–Ru(6) and Ru(4)–Ru(5)–Ru(6) faces. The cluster edge Ru(5)–Ru(6) is spanned by a carbonyl group. The arrangement is slightly asymmetric.

When either $H_2Ru_6(CO)_{17}$ or $H_2Ru_6(CO)_{18}$ reacted with excess CO at 1 atm in CH_2Cl_2 at room temperature, the clusters fragmented and formed $Ru_3(CO)_{12}$ as identified by IR spectroscopy. Reaction of $H_2Ru_6(CO)_{17}$ with 1.5 equiv of CO also resulted in some cluster fragmentation, forming $H_2Ru_4(CO)_{13}$ and $Ru_3(CO)_{12}$ identified by ^1H NMR and IR spectroscopy. Comparison of FAB mass spectra obtained on the sample before and after reaction with 1.5 equiv of CO indicated that a small amount of $H_2Ru_6(CO)_{18}$ was present in the reaction products. Deprotonation of $H_2Ru_6(CO)_{18}$ by PPNCl in CH_2Cl_2 produced $[PPN][HRu_6(CO)_{18}]$, whereas the products of the reaction of PPNCl with $H_2Ru_6(CO)_{17}$ indicated fragmentation of the cluster as evidenced by the ^1H NMR and IR spectra of the products. In this case the major product was $H_4Ru_4(CO)_{12}$, with small amounts of $H_2Ru_4(CO)_{13}$ and $Ru_3(CO)_{12}$ being formed. Additional studies are currently in progress on reactions of $H_2Ru_6(CO)_{17}$.

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(7) The IR spectrum of $H_2Ru_6(CO)_{18}$ obtained in this laboratory is in excellent agreement with spectra reported earlier.[2,3,5,6]

(8) Norton, J.; Scott, C. Colorado State University, Ft. Collins, CO.

(9) Crysial data for $H_2Ru_6(CO)_{17}$ (−40 °C): space group $P\bar{1}$, a = 8.131 (4) Å, b = 10.996 (3) Å, c = 15.350 (2) Å, = 93.58 (2)°, β = 97.89 (2)°, α = 109.33 (3)°, V = 1274.13 Å^3, ρ(calcd) = 2.827 g cm^{-3}, MW = 1090, Z = 2, μ = 34.8 cm^{-1}. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation. All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Crystallographic computations were carried out on a PDP 11/44 computer using the SDP (Structure Determination Package). The structure was solved by a combination of the direct method MULTAN 11/82 and difference Fourier syntheses. Full-matrix least-squares refinements were employed. R_F = 0.028 and R_{wF} = 0.032 (369 variable parameters refined) for 3181 reflections $[(I \geq 3\sigma(I)]$ of 5831 independent reflections collected over the 2θ range $4° \leq 2\theta \leq 55°$. Largest peak, e Å^{-3} = 0.69; largest shift/esd final cycle = 0.03.

(10) Mason, R.; Thomas, K. M.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802.

(11) Esd's on mean bond lengths, shown in brackets, are derived from $[\sum_{i=1}^{n}(d_i - \bar{d})^2/(n-1)]^{1/2}$, where d_i is the ith bond length and $\bar{d}$ is the mean of N equivalent bond lengths.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant CHE 88-00515. FAB mass spectra and NMR spectra were obtained at The Ohio State University Chemical Instrumentation Center (funded in part by National Science Foundation Grant No. 79-10019 and National Institutes of Health Grant No. 1 S10 PRO140518-01A).

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

Miriam Karni and Yitzhak Apeloig*

Department of Chemistry
Technion—Israel Institute of Technology
Haifa 32000, Israel

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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 $\theta_H = 60°$).

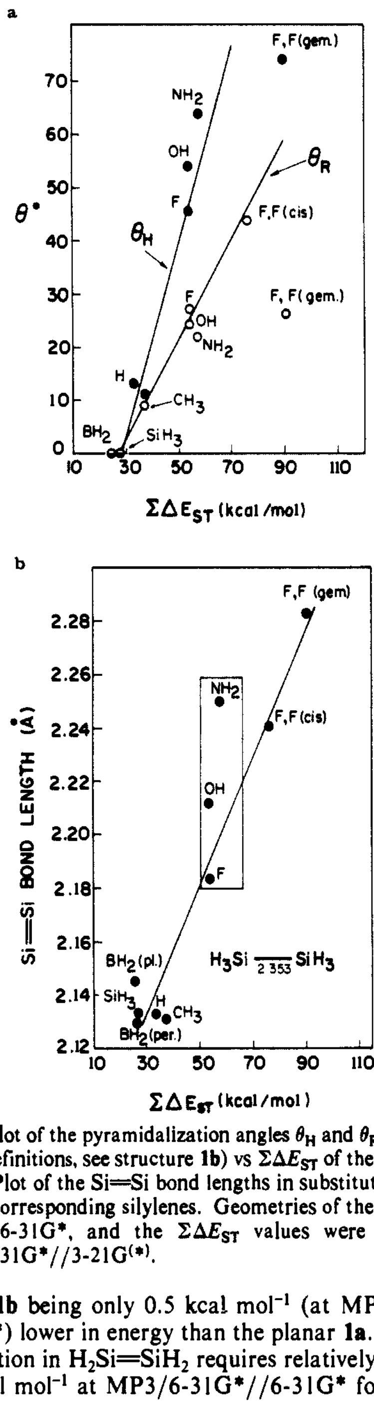
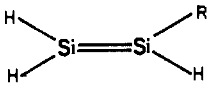
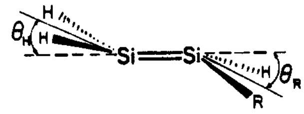


Figure 1. (a) Plot of the pyramidalization angles θ_H and θ_R in substituted disilenes (for definitions, see structure **1b**) vs $\Sigma\Delta E_{ST}$ of the corresponding silylenes. (b) Plot of the Si=Si bond lengths in substituted disilenes vs $\Sigma\Delta E_{ST}$ of the corresponding silylenes. 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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