the "imidazole tailed picket-fence" porphyrin,[5,35] Fe[Piv$_3$-(5ClmP)Por], and Fe(PocPivP)(1-MeIm) (Ic) shows that the CO affinity of the pocket porphyrin is smaller by almost two orders of magnitude. The oxygen affinities are quite similar. These results dramatically illustrate the effect that steric encumbrance can play in regulating CO binding in otherwise similar ferrous porphyrins.

It is tempting to compare the M, $P_{1/2}^{CO}$, and $P_{1/2}^{O_2}$ values for the pocket porphyrin models with those for hemoproteins. The O_2 affinities of both the picket-fence and pocket models are similar to that of myoglobin, but only the sterically encumbered pocket porphyrin has a CO affinity approaching that[36] of Hb and Mb. Our findings strongly suggest that distal side steric effects play a role in regulating CO-binding affinities in hemoproteins. We hope to augment this study with structural determinations, allowing us to assess to what degree the observed reductions in CO binding are reflected in tilting and/or bending of the FeCO unit.

Acknowledgment. We thank Kenneth Doxsee for helpful discussions and Professor Daryle Busch (Ohio State) for communicating results prior to publication. Mass spectral data were obtained at the Midwest Center for Mass Spectrometry, The University of Nebraska—Lincoln, and at the Middle Atlantic Mass Spectrometry Laboratory, The Johns Hopkins University, Baltimore, Maryland. Both facilities are supported under the National Science Foundation Regional Instrumentation Facilities Program. Our work was supported by the National Instutes of Health (Grant CM17880) and the National Science Foundation (Grants CHE78-09443 and CHE77-22722).

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(36) The roughly 10-fold higher CO affinity of Hb (R) vs. Mb can make these comparisons difficult. For example, on the basis of model compound behavior Romberg and Kassner[19] infer a distal steric effect in Mb; Traylor and Berzinis[14] claim the same data show no steric effect in Hb (R). We hypothesize that the essentials of binding in Hb and Mb are the same, and because of complexities introduced by pH, salts, etc., in Hb, we generally prefer comparisons with Mb. An advantage of model studies such as ours is that they can focus on the effect of one specific variable and yield results without *requiring* comparisons to natural systems.

Theoretical Challenge to the Experimentally Determined Geometrical Structure of Dimethylsilaethylene

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Received October 10, 1980

In a recent communication to this journal, Mahaffy, Gutowsky, and Montgomery[1] (MGM) presented an experimental molecular structure for 1,1-dimethylsilaethylene (DMSE), on the basis of their electron diffraction data. Their work was of particular interest, inasmuch as it represented the first experimental structural study of any molecule containing a carbon–silicon double bond.[2] The most significant finding of MGM was an extremely long Si═C double bond, namely, 1.83 ± 0.04 Å, or only 0.08 Å shorter than their observed Si–C single bond, 1.91 ± 0.02 Å. For comparison, the typical C═C double bond (1.35 Å) is 0.19 Å shorter than the typical C–C single bond (1.54 Å). If this long Si═C distance of 1.83 Å is correct, one would likely infer that the π bond in DMSE is exceptionally weak.

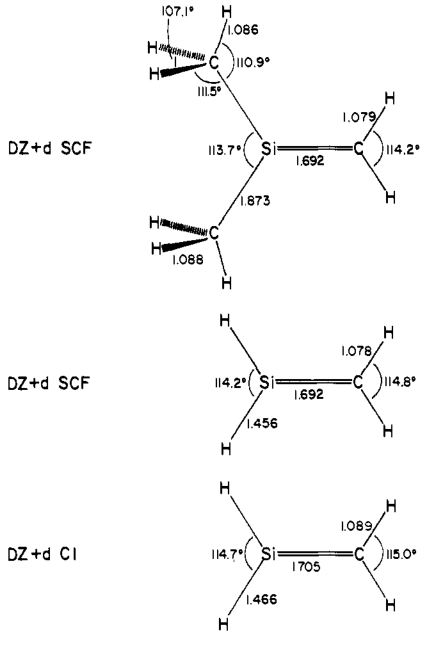

Figure 1. Theoretical equilibrium geometries for 1,1-dimethylsilaethylene (DMSE) and the parent unsubstituted silaethylene.

MGM noted an apparent discrepancy between theory and experiment. For the parent unsubstituted silaethylene $H_2Si{=}CH_2$, MGM cited about a dozen quantum mechanical predications[3,4] of thee Si═C bond distance, and these vary from 1.63 Å to 1.75 Å. Of these the most complete study[4] was carried out at the self-consistent-field (SCF) level of theory and employed a double-zeta (DZ) basis set of contracted Gaussian functions. Since the predicted Si═C bond distance of 1.715 Å is so much less than the experimental DMSE value of 1.83 Å, one is logically left with three alternatives: (a) the two methyl substituents greatly increase the Si═C distance in DMSE relative to the parent $H_2Si{=}CH_2$; (b) the theoretical predictions for the Si═C bond distance in $H_2Si{=}CH_2$ are all incorrect; (c) the experimental Si═C distance is DMSE is in error. Of course it is also possible that some superposition of these three effects might lead to the 0.115-Å gap between theory for $H_2Si{=}CH_2$ and experiment for DMSE.

In the present communication we report results which drastically reduce the possibility that points (a) or (b) above could be responsible for the discrepancy between theory and experiment. First, an explicit optimization of the geometrical structure of DMSE has been completed. Furthermore, this equilibrium geometry was determined at a level of theory higher than any previous structural optimization of even the parent $H_2Si{=}CH_2$. To the double-zeta (DZ) basis[5] used by Hood and Schaefer[4] was added a set of d functions on each heavy atom. These polarization functions were assigned orbital exponents $\alpha = 0.75$ (carbon) and $\alpha = 0.60$ (silicon). The designation of this DZ + d basis set is then Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), and H(4s/2s).

The predicted theoretical structure for DMSE is seen in Figure 1. The relative orientations of the two methyl groups was arbitrarily chosen to maintain point group C_{2v}, but the barriers to

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rotation about these Si–C single bonds should be quite small. Figure 1 shows that the predicted Si=C bond distance, 1.692 Å, falls far outside the range 1.83 ± 0.04 Å provided by the experimental electron-diffraction study.[1] The predicted Si–C single bond distance, 1.873 Å, is also shorter than experiment, 1.91 ± 0.02 Å, but in this case the disagreement is much less severe. None of the other geometrical parameters of DMSE were determined by MGM,[1] but the predicted theoretical values are all quite consistent with chemical intuition.[6] Furthermore, a steadily increasing body of comparisons[7,8] between theory and experiment would suggest a typical reliability of ± 0.01 Å for bond distances predicted at the DZ + d SCF level of theory.

For an assessment of the relationship between the structures of DMSE and the parent silaethylene, the latter equilibrium geometry was theoretically determined in a manner precisely the same as that described above for DMSE. This DZ + d SCF structure for the parent is illustrated in the middle of Figure 1. Figure 1 shows that at the DZ + d SCF level of theory, the Si=C bond distances of $H_2Si{=}CH_2$ and $(CH_3)_2Si{=}CH_2$ are *identicial (1.692 Å) to within one-thousandth of an angstrom.* This would certainly appear to dispense with the possibility, suggested by MGM,[1] that the Si=C distance is significantly longer in DMSE.

The only remaining satisfactory explanation of the experimental DMSE geometry is that the DZ + d SCF level of theory systematically predicts Si=C distances much too short. This possibility has been examined by explicitly determining the structure of $H_2Si{=}CH_2$ using highly correlated[9] wave functions. Using the DZ + d basis set, configuration interaction (CI) was carried out including all single and double excitations relative to the Hartree–Fock reference configuration. With the six core orbitals [C(1s), Si(1s,2s,$2p_x$,$2p_y$,$2p_z$)] constrained to be doubly occupied in all configurations, this approach yields a total 6920 $^1A_1$ configurations.

The DZ + d CI structure of silaethylene shown at the bottom of Figure 2 demostrates clearly that electron correlation has little effect on the predicted Si=C bond distance. The theoretical distance is 1.705 Å, or only 0.013 Å longer than the analogous SCF result. For the above-discussed comparison of the silaethylene and DMSE structures, one anticipates that the DMSE Si=C bond distance will also be ~1.70 Å.

On the basis of previous experience,[7,8] we suggest that the exact (unknown) Si=C bond distance r_e for the unsubstituted silaethylene is 1.705 ± 0.03 Å. To our thinking this prediction causes serious doubt upon the assumptions made by MGM[1] in extracting the Si=C distance in DMSE from the reported electron-diffraction data.[10]

It should be noted that theoretical geometry predictions for molecules containing the second-row atoms Al, Si, P, S, and Cl have been much less thoroughly calibrated then those for hydrocarbons and other first-row molecules.[7-9] However, the most complete comparison, that of Collins, Schleyer, Binkley, and Pople,[11] suggests that even without polarization functions and CI, a double-zeta basis set is unlikely to yield bond distance errors greater than 0.1 Å. Furthermore, for thioformaldehyde (isoelectronic with silaethylene), our DZ basis set yields a C=S bond distance of 1.637 Å,[12] in reasonable agreement with experiment,[13] 1.611 Å. For the same molecule, with a DZ basis set augmented by sulfur d functions, Flood and boggs[14] predicted r_e(C=S) = 1.600 Å. Therefore it appears extremely unlikely that the level of theory employed here results in a large error in the C=Si bond distance of DMSE.

Acknowledgment. The research on dimetylsilaethylene was carried out at the University of Texas and supported by the National Science Foundation and the Robert A. Welch Foundation. The research on silaethylene was carried out at the University of California and supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract W-7405-Eng-48.

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Metal Vapor Microsolution Optical Spectroscopy

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Received January 26, 1981

The synthetic utility of transition-metal vapors for the production of organometallic materials is now well recognized,[1] and experimental methodologies for combining metal vapor and ligands are widely documented.[2] In the earliest experiments a cocondensation procedure was adopted in which both reagents, under low-pressure conditions, were simultaneously deposited onto a cooled (static or rotary) surface held at cryogenic temperatures (usually 77 K for macropreparative[3] and 4.2–20 K for matrix spectroscopic experiments[4]).

In an effort to surmount the sampling problems associated with involatile or temperature-sensitive ligands, solid-state reactions, condensed-phase inhomogeneities, uncertainties in melt-down chemistry, and general handling of products, the metal vapor–rotary solution reactor was developed.[5] The synthetic versatility of this kind of device has been subsequently demonstrated in a variety of solution-phase organometallic preparations[6] and is ideally suited for combining metal vapors with liquid polymers[7] and

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