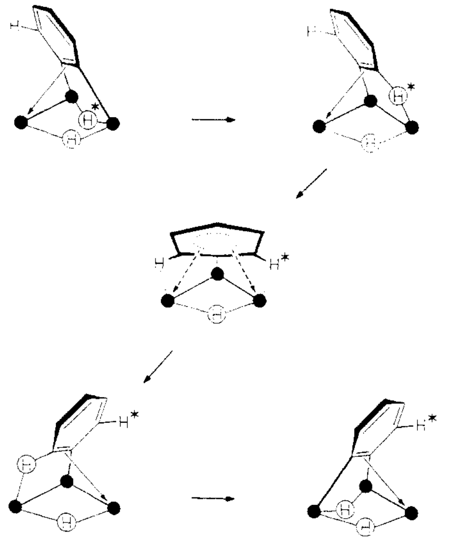
Scheme I



ring attachment to the Os_3 framework shifts in 1,2 steps concomitant with proton transfer *to* the metal from the ring for a C–H bond being broken and *from* the metal to the ring for a C–H bond being formed. Thus, in particular isomer **3a** can undergo a 1,2 shift either in one direction and regenerate itself or in the opposite direction and generate isomer **3b**. However, **3b** can only step in one direction, which immediately generates **3a**. The possibility of **3a** ↔ **3b** interconversion has been mentioned previously,[3,4] but our SST results provide direct evidence not only for the isomers **3a,b** but also for the "degenerate" cases of **1** and **2**.

We postulate the mechanism shown in Scheme I. A proton hops from a site associated with a pair of electrons between two Os atoms (Os–H–Os) to a site associated with a pair of electrons between a carbon atom and an osmium atom (C–H–Os) (an agostic[7] three-center, two-electron bond). This is followed by rolling of the aryl moiety such that a new C–H–Os bridge is created and the former is broken. Finally, exchange is completed by proton migration back to the Os–H–Os site. Since the presence of CO atomosphere has no effect on the rate, some π-bonding between the aryl moiety and the Os_3 framework must be maintained throughout the rearrangement.

Compound **2** was chosen as the simplest case for quantitative measurements. There was no measurable NOE at the ring proton sites upon irradiation of the hydride signal, so the rate constant could be determined readily from straightforward intensity and relaxation time measurements.[6,8] At 90 °C, the exchange rate constant k = 0.7 ± 0.05 s^{-1}, which corresponds to $\Delta G^{\ddagger}(363\ K) = 21.7 \pm 0.1$ kcal/mol. This $\Delta G^{\ddagger}$ value is similar to that recently determined for exchange between the two types of proton sites in $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ ($\Delta G^{\ddagger}$ = 24 kcal/mol),[10] consistent with rate-determining proton migration in both cases.

It has been suggested[1] that the pathway to benzyne complex **1** involves the formation first of a hydrido–phenyl complex with 10 CO ligands, i.e., $HOs_3(CO)_{10}(\mu\text{-}C_6H_5)$, which is then followed by CO loss and the second C–H bond scission. It is likely that the type of intermediate species proposed here, i.e., $HOs_3(CO)_9(\mu_3\text{-}C_6H_5)$, is the same as that involved in the latter step. Furthermore, the selective SST results for **1** rule out any rapid equilibrium with the η^6-benzene complex $Os_3(CO)_9(\mu_3,\eta^6\text{-}C_6H_6)$.[11] Thus, the hydrido–phenyl and benzene complexes of the $Os_3(CO)_9$ fragment do not readily interconvert. This contrasts with the demonstration of interconverting hydrido–phenyl and benzene complexes of a mononuclear rhodium fragment[12] but is reminiscent of the significant barrier observed between corresponding hydrido–vinyl and ethylene complexes of a mononuclear iridium center.[13] Further SST studies of CH/OsH exchange in hydridotriosmium hydrocarbyl complexes are in progress.

Acknowledgment. This research was supported by a National Science Foundation Grant (CHE 84-07233) to J.R.S. H.-J.K. thanks the Deutsche Forschungsgemeinschaft (Bonn) for a fellowship. The GE GN-500 FT-NMR spectrometer was purchased in part with funds from National Science Foundation Grant CHE 85-14500 to the School of Chemical Sciences at the University of Illinois.

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(7) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(8) The T_1 value for the C–H site was determined as T_1 = 3.99 s. The intensity ratio for the signal without and with irradiation of the hydride site was 3.79 ± 0.2. From these values,[9] k = 0.7 ± 0.05 s^{-1}. The free energy of activation from the Eyring equation is $\Delta G^{\ddagger}$ = 21.7 ± 0.1 kcal mol^{-1}.

(9) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; Chapter 7.

(10) VanderVelde, D. G.; Holmgren, J. S.; Shapley, J. R. *Inorg. Chem.* **1987**, *26*, 3077.

(11) Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1682. **Note Added in Proof.** The Cambridge group has observed the photochemical transformation of $Os_3(CO)_9(\mu_3,\eta^6\text{-}C_6H_6)$ into $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-}C_6H_4)$: Gallop, M. A., personal communication.

(12) Jones, W. D.; Feher, F. D. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

(13) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.

Some Interesting Properties in Silapropellanes and Derivatives. A Theoretical Study of Inverted Tetracoordinate Silicon

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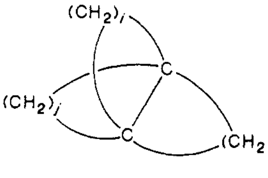
Summary: Ab initio calculations show that fully silicon-substituted propellanes, pentasila[1.1.1]propellane and octasila[2.2.2]propellane, are less strained than the corresponding carbon compounds and are interesting synthetic targets. Especially interesting is a drastic effect of trioxa substitution on the bridge bonding between the inverted tetracoordinate silicon atoms.

The [*i.j.k*]propellanes, which consist of three rings fused to a common carbon–carbon bond and may be regarded as hexasubstituted ethanes, have long been the subject of much experimental and theoretical interest.[1] The pro-



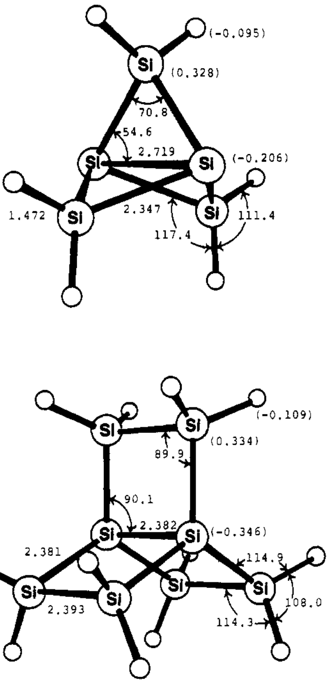


Figure 1. HF/6-31G* optimized geometries (in angstroms and degrees) and gross atomic charges (in parentheses) of **3** and **4** with D_{3h} symmetry. The total energies of **3** and **4** are −1448.017 96 and −2318.285 14 hartrees, respectively.

pellanes for small *i*, *j*, and *k* are of special interest in that they involve an inverted tetrahedral arrangement about the bridgehead carbon atoms and are highly strained. In the smallest [1.1.1]propellane (**1**)[2] four carbon–carbon bonds from the bridgehead are all directed into one hemisphere, while [2.2.2]propellane (**2**)[3] contains three coplanar carbon–carbon bonds 120° apart (i.e., a model for the S_N2 transition structure). The properties and reactivities of these tricyclic molecules with three- and four-membered rings have extensively been investigated.[4]

In view of recent interest in the silicon analogues[5,6] of polycyclic or polyhedral carbon compounds, we report here the first ab initio study of pentasila[1.1.1]propellane (**3**) and octasila[2.2.2]propellane (**4**). The aim of this work is to report what is characteristic of **3** and **4** compared with **1** and **2**. The optimized geometries of **3** and **4** obtained at the Hartree–Fock (HF) level with the split-valence d-polarized 6-31G* basis set[7,8] are shown in Figure 1, together with the gross atomic charges. For uniform comparison, all values cited here are those at the HF/6-31G* level.

The first point to be noted in Figure 1 is that the bridgehead silicon atoms in **3** and **4** are electron-attracting and bear net negative charges of −0.206e and −0.346e, respectively, despite the strong electropositive character of Si. To our knowledge, such negatively charged silicon has never been reported in the literature. For strained carbon compounds, it is demonstrated[9] that the more strained the carbon atoms, the greater the electronegativity.

Thus, we have calculated the strain energies of **3** and **4** from the homodesmotic reactions[10] by using the HF/6-31G* total energies. For comparison, we have also calculated the strain energies of **1** and **2** in the same way.[11]

$$\mathbf{3} + 7Si_2H_6 \rightarrow 2(SiH_3)_4Si + 3Si_3H_8$$

$$\mathbf{4} + 10Si_2H_6 \rightarrow 2(SiH_3)_4Si + 6Si_3H_8$$

It should be noted that the calculated strained energies of 104.3 and 96.0 kcal/mol for **1** and **2** agree reasonably well with the experimental values[9,12] of 98.0 and 89.0 kcal/mol, respectively; comparable accuracy would be expected for the calculated values of **3** (70.2 kcal/mol) and **4** (55.7 kcal/mol). It is interesting that silicon compounds **3** and **4** are calculated to be 34.1 and 40.3 kcal/mol less strained than carbon compounds **1** and **2**, respectively. The strain energy difference of 40.3 kcal/mol favoring **4** over **2** corresponds to the fact that the strain in three cyclotetrasilanes (3 × 16.7 kcal/mol) is 30 kcal/mol less than the strain in three cyclobutanes (3 × 26.7 kcal/mol), reflecting the additivity of strain per four-membered ring.[6] However, the smaller strain energy of **3** than **1** forms a contrast to the fact that the strain in three cyclotrisilanes (3 × 38.9 kcal/mol) is greater than that in three cyclopropanes (3 × 28.7 kcal/mol).[6] This may be ascribable to a considerable relief of strain due to the central bridge Si–Si bond stretching in **3**, as described later.

The second point to be noted in Figure 1 is that the central bridge (2.382 Å)[13] and peripheral (2.381 and 2.393 Å) Si–Si bonds in **4** are longer than a typical Si–Si bond (2.353 Å in disilane)[7] but are compared favorably with the Si–Si bonds in the strained four-membered rings of cyclotetrsilane (2.373 Å) and octasilacubane (2.396 Å).[6] Furthermore, it is interesting that the central bridge Si–Si bond in tricyclic **4** is rather shorter than that (2.399 Å) in bicyclo[2.2.0]hexasilane[14] (having two four-membered rings fused).

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(1) For reviews, see: (a) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379. (b) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978.

(2) For the first preparation, see: Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239.

(3) For the synthesis, see: (a) Eaton, P. E.; Temme, G. H. *J. Am. Chem. Soc.* **1973**, *95*, 7508. (b) Silverton, J. V.; Milne, G. W. A.; Eaton, P. E. Temme, G. H. *J. Am. Chem. Soc.* **1974**, *96*, 7429.

(4) See: a number of references in ref 1. For more recent papers, for example, see: (a) Wiberg, K. B. *Tetrahedron Lett.* **1985**, 599. (b) Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410. (c) Honegger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 7122. (d) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247. (e) Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257. (f) Pierini, A. B.; Reale, H. F.; Medrano, J. A. *J. Mol. Struct.* (*Theochem*) **1986**, *148*, 109. (g) Messmer, R. P.; Schultz, P. A. *J. Am. Chem. Soc.* **1986**, *108*, 7407.

(5) For the preparation of bicyclic silicon compounds, see: (a) Collins, S.; Duncan, J. A.; Kabe, Y.; Murakami, S.; Masamune, S. *Tetrahedron Lett.* **1985**, *26*, 2837. (b) Masamune, S.; Kabe, Y.; Collins, S.; Williams, D. J.; Jones, R. *J. Am. Chem. Soc.* **1985**, *107*, 5552. (c) Jones, R.; Williams, D. J.; Kabe, Y.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 173. (d) Kawase, T.; Batcheller, S. A.; Masamune, S. *Chem. Lett.* **1987**, 227. See also: (e) Fritz, G.; Wartanessian, S.; Matern, E.; Honle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1981**, *475*, 87. (f) Fritz, G.; Thomas, J. *J. Organomet. Chem.* **1984**, *271*, 107. (g) Yokelson, H. B.; Maxka, J.; Siegel, D. A.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4239.

(6) For a theoretical study of polyhedral silicon compounds, see: Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60.

(7) 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.

(8) Vibrational check was done at the HF/3-21G level.

(9) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001.

(10) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

(11) For the HF/6-31G* total energies of 1 and 2, see: Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227.

(12) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

(13) In the preliminary calculations, we have also located a minimum with a much longer central bridge bond as a result of the crossing in orbital energies of the symmetric (bonding) and asymmetric (antibonding) frontier orbitals. For the first example of the crossing that arises from the advantage of through-bond over through-space interactions, see: Stohrer, W.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779. The bond stretch isomer of 4 was calculated to be 30.7 kcal/mol more unstable at the HF/3-21G level; however, incorporation of electron correlation will be essential for the relative stability. For a recent study of bond stretch isomerism in the carbon counterpart, see: Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4133.

(14) Nagase, S.; Kudo, T., submitted for publication in *J. Chem. Soc., Chem. Commun.*

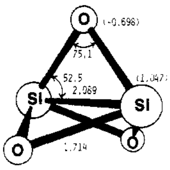

Figure 2. HF16-31G* optimized geometry (in angstroms and degrees) and gross atomic charges (in parentheses) of the trioxa-substituted **3** with D_{3h} symmetry. The total energy is −802.40867 hartrees.

On the other hand, the central bridge bond in **3** is considerably stretched to 2.719 Å,[15] though the peripheral Si–Si bond length of 2.347 Å is quite normal and very close to that in cyclotrisilane (2.341 Å).[6] Upon inclusion of electron correlation,[16] the stretching of the bridge bond in **3** will be further enhanced to have more singlet diradical character, as demonstrated in the corresponding carbon compound.[4d,f] In view of the fact that in silicon compounds three-membered rings are more strained than four-membered rings,[6,17–20] it is instructive to note that a long central bridge Si–Si bond (2.775 Å)[14] is also calculated in the closely related bicyclo[1.1.0]tetrasilane.[21–23]

The central bridge bond stretching in **3** (more strained than **4**) is probably due to inherently weak Si–Si bonds; the dissociation energies of Si–Si bonds are ca. 14 kcal/mol smaller than those of C–C bonds.[24] In addition, it may result from the electrostatic or exchange repulsion between the very dense electron clouds around the bridgehead positions. If this view is important, a proper replacement of the peripheral groups, which can remove the electron clouds around the bridgeheads and produce net positive charges on the bridgehead silicon atoms, will lead to a significant shortening of the central bridge bond: the accompanying orbital contraction around the bridgeheads is also suitable for the proximity of the two bridgehead silicon atoms. Thus, we have substituted the peripheral SiH_2 groups in **3** by the electronegative oxygen atoms, since a considerably short length (2.190 Å)[25] is calculated for the Si–Si bond in the three-membered ring of disilaoxirane.[26]

As Figure 2 shows, the trioxa substitution converts the charges on the bridgehead silicon atoms from −0.206e (negative) to +1.047e (positive) and permits the silicon atoms to approach each other by 0.630 Å. As a consequence, the central bridge bond length becomes unusually short (2.089 Å) in trioxa-substituted **3**.[27] The bridge bond length is shorter than the Si–Si double bond length (2.134 Å in trans-bent disilene)[28] and is rather comparable to the Si–Si triple bond length (2.083 Å in trans-bent disilyne).[29] The unusual shortening in silicon compounds provides an interesting contrast with that in carbon compounds.[30]

We think that silicon propellanes form fascinating synthetic targets. In addition, the nature of the bridge bonding in these compounds is an interesting theoretical challenge. A study along this line is in progress.

Acknowledgment. We are grateful to Prof. Schaefer for ref 20 and 26, to Prof. Schleyer for ref 23 and an interesting communication, and to Prof. Schoeller for ref 18b. Calculations were carried out at the Computer Center of the Institute of Molecular Science, using the GAUSSIAN 82 program.[31] This work was supported in part by a grant from the Ministry of Education, Science, and Culture in Japan.

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(15) The bond length is rather close to the nonbonding Si–Si bond length of 2.915 Å in bicyclo[1.1.1]pentasilane. In several ways we have tried to locate a second minimum with a shorter Si–Si bridge bond length. However, no second minimum of **3** could be located in the present calculations. The same conclusion has very recently been reached by Schleyer and Janoschek (private communication from Prof. Schleyer).

(16) The HOMO and LUMO are the Si–Si bonding and antibonding MO's between the bridgehead positions. The HOMO–LUMO energy gap is smaller in **3** than in **1**.

(17) Schleyer, P. v. R. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janoschek, R., Merenyi, R., Eds.; D.Reidel: Dordrecht, 1986; pp 69–81.

(18) (a) Schoeller, W. W.; Dabisch, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1706; (b) *Inorg. Chem.* **1987**, *26*, 1081.

(19) Sax, A. F. *Chem. Phys. Lett.* **1986**, *127*, 163; **1986**, *129*, 66.

(20) Grev, R. S.; Schaefer, H. F., submitted for publication in *J. Am. Chem. Soc.*

(21) Bicyclo[1.1.0]tetrasilane has also a minimum with a shorter central bridge bond (2.368 Å).[14] However, this isomer is 8.9 kcal/mol more unstable at the MP4SDTQ/6-31G*//6-31G* level.[14] In addition, it is calculated[23] that the shorter bond length isomer collapses to the bond stretch isomer almost without a barrier. For an argument against the presence of the more stable bond stretch isomer at the HF/6-31G* level, see: Collins, S.; Dutler, R.; Rauk, A. *J. Am. Chem. Soc.* **1987**, *109*, 2564.

(22) Dabisch, T.; Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1986**, 896.

(23) Schleyer, P. v. R.; Sax, A. F.; Kalcher, J.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364.

(24) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(25) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.

(26) Grev, R. S.; Schaefer, H. F., submitted for publication in *J. Am. Chem. Soc.*

(27) Also responsible for the shortening is the severe repulsion between the more negatively charged oxygen atoms as well as the strength of the Si–O bonds.

(28) Krogh-Jespersen, K. *J. Phys. Chem.* **1982**, *86*, 1492.

(29) Binkley, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 603.

(30) The trioxa substitution of the peripheral CH_2 groups in **1** shortens the central C–C bond only by 0.087 Å. However, note that the trioxa-substituted **1** is not a minimum but a transition structure, as characterized by a single imaginary frequency.[8]

(31) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Rahgavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fludre, E. M.; Pople, J. A. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.

Vinylidene Complexes from 1-Chloro-1-(trimethylsilyl)alkenes and the Coupling of Two Vinylidene Units at a Transition-Metal Center

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Summary: Photochemical reaction of MeCp(CO)$_3$Mn with 1-chloro-2-methyl-1-(trimethylsilyl)-1-propene (**1b**) yields the vinylidene complex MeCp(CO)$_2$Mn=C=CMe$_2$ (**2b**) as a major and the butatriene complex MeCp(CO)$_2$Mn(η^2-Me$_2$C=C=C=CMe$_2$) (**3**) as a minor product. **3** is exclusively obtained if MeCp(CO)$_2$Mn(THF) is reacted with **1b**. In the reaction of the THF complex and 1-chloro-2,2-diphenyl-1-(trimethylsilyl)ethene (**1a**) MeCp(CO)$_2$Mn=C=CPh$_2$ (**2a**) is formed instead.

In most preparative routes to transition-metal vinylidene complexes the vinylidene C=C bond is derived from either an acetylenic triple bond or a C—C single bond of suitable organometallic precursors.[1] There are only a few reports on the synthesis of vinylidene complexes from σ-vinyl metal complexes. For instance, Cp(PR$_3$)$_2$ClM=C=C(CN)$_2$ (M = Mo, W; Cp = η^5-C$_5$H$_5$) and related complexes have been obtained from Cp(CO)$_3$M—C(Cl)=C(CN)$_2$ by transfer of the halide from the α-carbon to the metal on heating the vinyl complexes with PR$_3$.[2] We have now

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(1) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

(2) King, R. B.; Saran, M. S. *J. Am. Chem. Soc.* **1973**, *98*, 1817.