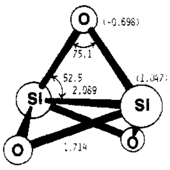

**Figure 2.** HF16-31G* optimized geometry (in angstroms and degrees) and gross atomic charges (in parentheses) of the trioxa-substituted **3** with $D_{3h}$ symmetry. The total energy is -802.40867 hartrees.

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.

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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.

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[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.

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[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]

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## 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 $MeCp(CO)_3Mn$ with 1-chloro-2-methyl-1-(trimethylsilyl)-1-propene (**1b**) yields the vinylidene complex $MeCp(CO)_2Mn{=}C{=}CMe_2$ (**2b**) as a major and the butatriene complex $MeCp(CO)_2Mn(\eta^2\text{-}Me_2C{=}C{=}C{=}CMe_2)$ (**3**) as a minor product. **3** is exclusively obtained if $MeCp(CO)_2Mn(THF)$ is reacted with **1b**. In the reaction of the THF complex and 1-chloro-2,2-diphenyl-1-(trimethylsilyl)ethene (**1a**) $MeCp(CO)_2Mn{=}C{=}CPh_2$ (**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, $Cp(PR_3)_2ClM{=}C{=}C(CN)_2$ (M = Mo, W; Cp = $\eta^5\text{-}C_5H_5$) and related complexes have been obtained from $Cp(CO)_3M{-}C(Cl){=}C(CN)_2$ 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.

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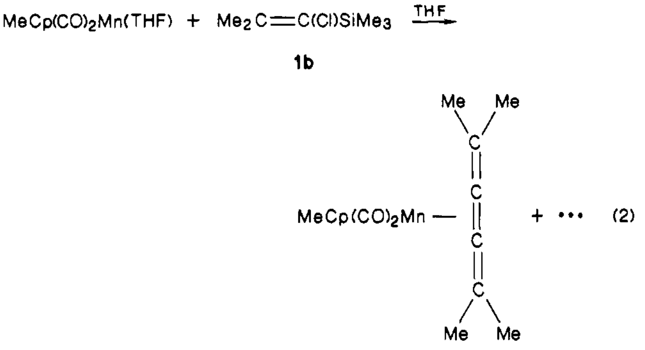
found an easy and efficient access to vinylidene complexes by treating 1-chloro-1-(trimethylsilyl)alkenes (**1**) with suitable transition-metal compounds.

On reaction of $\mathrm{MeCp(CO)_2Mn(THF)}$ (MeCp = $\eta^5$-$\mathrm{CH_3C_5H_4}$) (obtained by photochemical reaction of $\mathrm{MeCp(CO)_3Mn}$ in THF) with an equimolar amount of $\mathrm{Ph_2C{=}C(Cl)SiMe_3}$ (**1a**) in THF at room temperature the vinylidene complex **2a** is formed in good yield (eq 1). Surprisingly, the corresponding reaction of $\mathrm{Me_2C{=}C(Cl)SiMe_3}$ (**1b**) with the THF complex does not yield $\mathrm{MeCp(CO)_2Mn{=}C{=}CMe_2}$ (**2b**), but a complex (**3**), in which two dimethylvinylidene units are coupled to give a $\eta^2$-butatriene ligand (eq 2). However, **2b** is formed as a major product (together with some **3**) in the photochemical reaction of $\mathrm{MeCp(CO)_3Mn}$ with **1b** in pentane (eq 3). **2a**,**b** and **3** were separated from the reaction mixtures by column chromatography[3] and analytically[4] and spectroscopically[5] characterized. Spectra of **2a** correspond to those of $\mathrm{Cp(CO)_2Mn{=}C{=}CMe_2}$[6] or $\mathrm{Cp(CO)_2Mn{=}C{=}CHPh}$,[7] which have previously been prepared from $\mathrm{CpMn(CO)_3}$ and terminal acetylenes. The $^1$H NMR spectrum of **3** (equivalent methyl groups) indicates that the butatriene ligand is symmetrically bonded, i.e., that the central double bond is coordinated to the metal.

$$\mathrm{MeCp(CO)_2Mn(THF) + \underset{\mathbf{1a}}{Ph_2C{=}C(Cl)SiMe_3} \xrightarrow{THF} \underset{\mathbf{2a}}{MeCp(CO)_2Mn{=}C{=}CPh_2} + \ldots} \quad (1)$$



3

$$\mathrm{MeCp(CO)_3Mn} + \mathbf{1b} \xrightarrow[\text{pentane}]{h\nu} \underset{\mathbf{2b}}{\mathrm{MeCp(CO)_2Mn{=}C{=}CMe_2}} + \ldots \quad (3)$$

Whereas monosubstituted vinylidene ligands (C=CHR) are readily obtained from 1-alkynes,[1] preparative routes to complexes containing disubstituted vinylidene ligands ($\mathrm{C{=}CR_2}$) are less general. In particular, synthesis of $\mathrm{Cp(CO)_2Mn{=}C{=}CMe_2}$ was only achieved by a multistep procedure.[6] In contrast, our method for the preparation of **2** is very simple and uses readily accessible precursors for the vinylidene unit. Preliminary experiments show that vinylidene complexes of other metals can be analogously synthesized.

We believe that formation of **2a**,**b** involves oxidative addition of the chlorovinylsilane to the metal atom, followed by elimination of $\mathrm{Me_3SiCl}$. Since **2b** does not react with **1b** under the conditions employed in reaction 2 (room temperature, THF), **2b** cannot be a precursor to **3**. It seems reasonable to assume that **2** and **3** are formed from a common precursor. The outcome of the reaction is to a large extent determined by the $\beta$-substituents at the vinylidene unit.

If vinylidene complexes are prepared from 1-alkynes, in a few cases a second alkyne is incorporated into the vinylidene ligand to give butadienylidene ligands.[1] To the best of our knowledge, formation of a substituted butatriene ligand by metal-mediated coupling of two vinylidene units (eq 2) has not been observed previously.

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[3] Chromatography on silica at −20 °C with pentane or pentane/ether (100:1). Yields of the isolated complexes: **2a**, 54%; **2b**, 24%; **3**, 48% rel. $\mathrm{MeCp(CO)_3Mn}$ (96% rel. **1b**). In reaction 3 a carbonyl complex with $\nu$(CO) bands at 1964 and 1906 cm$^{-1}$ is formed as another minor product.

[4] Anal. Found (Calcd) for **2a**: C, 71.42 (71.74); H, 4.49 (4.65). Found (Calcd) for **2b**: C, 58.91 (59.03); H, 5.48 (5.37). Found (Calcd) for **3**: C, 64.21 (64.43); H, 6.54 (6.37).

[5] $^1$H NMR (60 MHz, $\delta$): **2a** ($\mathrm{CCl_4}$), 1.80 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 4.80 (m, 4 H, $\mathrm{C_5H_4}$), 7.57 (m, 6 H, $\mathrm{C_6H_5}$), 8.07 (m, 4 H, $\mathrm{C_6H_5}$); **2b** ($\mathrm{C_6D_6}$) 1.48 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 1.66 (s, 6 H, $\mathrm{C{=}C}\mathit{Me}_2$), 4.36 (m, 4 H, $\mathrm{C_5}\mathit{H}_4$); **3** ($\mathrm{C_6D_6}$), 1.33 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 2.29 (s, 12 H, $\mathrm{C{=}C}\mathit{Me}_2$), 4.19 (m, 4 H, $\mathrm{C_5}\mathit{H}_4$). IR (pentane, $\nu$(CO)): **2a**, 1981 (s), 1918 (m) cm$^{-1}$; **2b**, 1995 (s), 1939 (s) cm$^{-1}$; **3**, 1982 (s), 1928 (m) cm$^{-1}$. Mass spectra (70 eV): **2a** *m/e* (relative intensity) 368 (0.4, M), 312 (10, M − 2CO), 178 (100, $\mathrm{C_2Ph_2}$), 134 (36, MeCpMn); **3**, *m/e* (relative intensity) 298 (12, M), 242 (36, M − 2CO), 162 (27, MeCp(CO)Mn), 134 (100, MeCpMn), 108 (6, $\mathrm{C_4Me_4}$). Melting point: **2a** (orange), 55 °C dec; **3** (yellow), 59 °C; **2b**, red oil.

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# *Book Reviews*

**Ab Initio Molecular Orbital Theory.** By W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople. Wiley, New York. 1986. xviii + 548 pages. $79.95.

This book is to present-day ab initio calculations what its predecessor, *Approximate Molecular Orbital Theory* by Pople and Beveridge, was to semiempirical calculations 18 years ago. The authors present a thorough and very readable accounting of the methods, basis sets, and properties which can be investigated by using GAUSSIAN82 and its predecessors. The reader should recognize that only those methods which are available in the GAUSSIANxx programs are discussed in this book. Thus, methods such as multiconfigurational self-consistent field (MCSCF), generalized valence bond (GVB), and coupled electron pair approximation (CEPA) are not considered. Given those restrictions, however, the book is a very helpful guide to the methods developed by the authors and their co-workers as well as a useful survey of the results obtainable by those methods.

The presentation of the theoretical background and computational methodology, Chapters 2–4, is written at a readable level, with enough leading references for the reader to probe deeper into the theory if desired. Chapter 5 presents a "short-course" on how to use the GAUSSIANxx programs. Chapter 6 is a critical evaluation of the performance of the various basis sets and computational levels for a wide variety of physical properties. This chapter includes a very useful series of subsections which deal