therefore, it is important to realize the importance of the difference between the type A and type B structures.

Acknowledgment. E.C. and Y.M. thank the Institut de Chimie Moléculaire d'Orsay (ICMO) for a grant that made possible part of this work and the CIRCE for providing computing facilities. Work at North Carolina State University was in part supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science under Grant DE-FG05-86-ER45259.

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SiC Agostic Interaction with Ti: Origin of Alkenyl Group Distortion in $Ti(C(SiH_2CH_3)=CH_2)X_2^+$. An ab Initio MO Study

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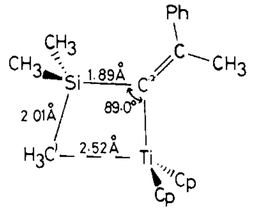
Abstract: We have optimized the structure of $Ti(C(SiH_2CH_3)=CH_2)(Cl)_2^+$ by an ab initio MO method and found a distorted alkenyl group with a small TiCSi bond angle, a long SiC^γ bond, and a short $Ti\cdots C^\gamma$ distance, all of which are in good agreement with the experiment on $Ti(C(Si(CH_3)_3)=C(C_6H_5)(CH_3))(Cp)_2^+$. Evidence has been found showing that the alkenyl group distortion is a consequence of the donative interaction from the CSi σ bond to a Ti vacant d orbital, similar to the $CH\cdots M$ agostic interaction, and thus it is proposed that this $SiC\cdots Ti$ interaction is called the βSiC agostic interaction. It is suggested that there exist various types of agostic interaction between varieties of σ bonds and the electron-deficient metal with varying structural distortion and stability depending on the donative bonds, metal, ligands, and coordination unsaturation.

Recently the first isolated intermediate $Ti(C(Si(CH_3)_3)=C(C_6H_5)(CH_3))(Cp)_2^+$ (**1**) of a Ziegler catalyst system has been reported by Eisch et al.[1] in the reaction of $C_6H_5C\equiv CSi(CH_3)_3$ with Cp_2TiCl_2 and CH_3AlCl_2. The X-ray structure of **1** shows an interesting distortion in the alkenyl group: a small TiCSi angle of 89° and a short distance between Ti and C^γ of 2.52 Å. They have ascribed this distortion to the hyperconjugation between the C^αSi σ bond and a Ti 4p vacant orbital. Although the electron deficiency of the central metal would surely create a driving force for distortion, it is not certain that such a hyperconjugation is operative. The C^αSi bond, which is expected to be longer upon hyperconjugation, is found experimentally not much longer than the standard CSi single bond length: 1.853 Å in vinylsilane[2a] and 1.867 Å in methylsilane.[2b] This is in contrast with the hyperconjugation between a C^αH bond and a metal vacant orbital found in the distorted carbene complexes.[3] The STO-3G calculations have given the long C^αH bond of 1.13–1.18 Å in the model titanium carbene complexes.[3] On the contrary, the SiC^γ bond length in **1** is longer by about 0.1 Å.



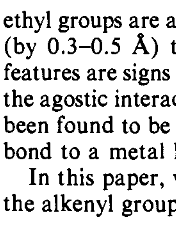
1

Table I. Relative Energy (in kcal/mol) of Optimized Structures and Assumed Structures with Undistorted Alkenyl Group

optimized structure		assumed structure		difference
5a	4.0	**10a**	18.1	14.1
5b	0.0[a]	**10b**	17.6	17.6
5c	14.0			

[a] The total energy is −2136.42895 hartrees.

It may be noted that the distortion of alkenyl group is similar to that of ethyl groups found experimentally in $Ti(C_2H_5)(dmpe)(Cl)_3$[4a] (**2**) or theoretically in $Ti(C_2H_5)(Cl)_2(PH_3)_2(H)$[5a] (**3**) and $Pd(C_2H_5)(H)(PH_3)^6$ (**4**). The MCC bond angles of the ethyl groups are about 90°, and their C^βH bonds are much longer (by 0.3–0.5 Å) than the normal CH bond. These structural features are signs of the intramolecular $CH\cdots M$ interaction, called the agostic interaction.[4c] The origin of the agostic interaction has been found to be the electron donative interaction from a CH σ bond to a metal low-lying vacant orbital.[5,6]



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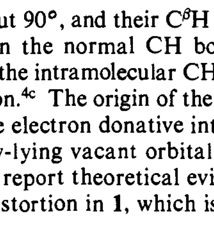

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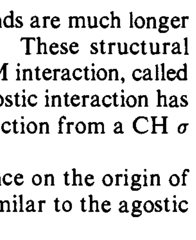

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In this paper, we report theoretical evidence on the origin of the alkenyl group distortion in **1**, which is similar to the agostic

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(1) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. J.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

(2) (a) O'Reilly, J. M.; Pierce, L *J. Chem. Phys.* **1961**, *34*, 1176. (b) Kilb, R. W.; Pierce, L. *Ibid.* **1957**, *27*, 108.

(3) Francl, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J. *Organometallics* **1983**, *2*, 281.

(4) (a) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 802. (b) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *Ibid.* **1982**, 1410. (c) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(5) (a) Koga, N.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4625. (b) Obara, S.; Koga, N.; Morokuma, K. *J. Organomet. Chem.* **1984**, *270*, C33.

(6) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

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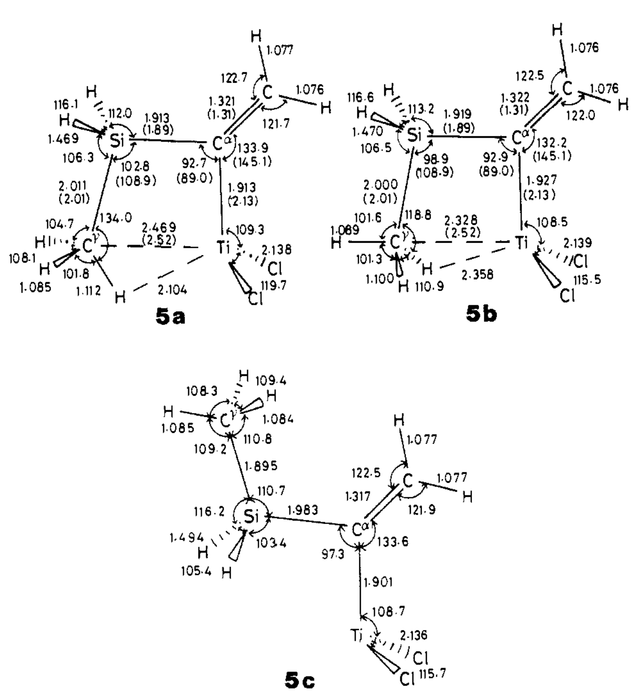


Figure 1. Optimized geometries (in Å and deg) of **5a**, **5b**, and **5c**. The numbers in parentheses are corresponding experimental values for **1**.[1]

interaction. We have determined with the ab initio MO method the structure of $Ti(C(SiH_2CH_3){=}CH_2)(Cl)_2^+$ (**5**), which is chosen as a model for **1**, and have found a distorted alkenyl group. Cp in **1** is replaced by chlorine and C_6H_5 and some CH_3's by H's. The replacement of Cp by chlorine has been used for dicyclopentadienyltitanacyclobutane, where the dichloro complex has been found to be a reasonable structural model.[7] We will discuss the electronic factor favoring the distortion.

Computational Methods

We used for the geometry optimization the restricted Hartree–Fock (RHF) energy gradient technique.[8] During the geometry optimization, the structures of the complexes were assumed to maintain in the C_s symmetry. The basis functions used for Ti were those of Huzinaga et al.,[9a] determined for the ^5F state and augmented by two p functions with the contraction (43321/4311/31). The 3-21G[9b,c] basis set was used for C, H, and Si and the STO-2G[9d] for Cl.

In most of the paper we did not consider a d orbital on Si, although it is known that the 3-21G basis set for second-row elements often gives a bond length longer than experiment.[9e] For instance, the calculated CSi bond length of CH_3SiH_3 is 1.917 Å with 3-21G and 1.883 Å with 3-21G$^{(*)}$ where a set of d orbitals is added to the Si basis functions,[9e] while the experimental CSi bond length of CH_3SiH_3 is 1.867 Å.[2b] Therefore, the present level of calculations gives a slightly longer CSi bond than experiment. However, an additional calculation with d functions, to be shown later, confirms that the conclusion obtained in the present study is independent on this basis set restriction.

Results and Discussions

Optimized Structure of $Ti(C(SiH_2CH_3){=}CH_2)(Cl)_2^+$ and Origin of Alkenyl Group Distortion. The three fully optimized geometries of $Ti(C(SiH_2CH_3){=}CH_2)(Cl)_2^+$ (**5a**, **5b**, and **5c**) are shown in Figure 1, and their relative energies are given in Table I. SiC^γ in **5a** and **5b** is syn with respect to TiC^α, and SiC^γ in **5c** is anti.

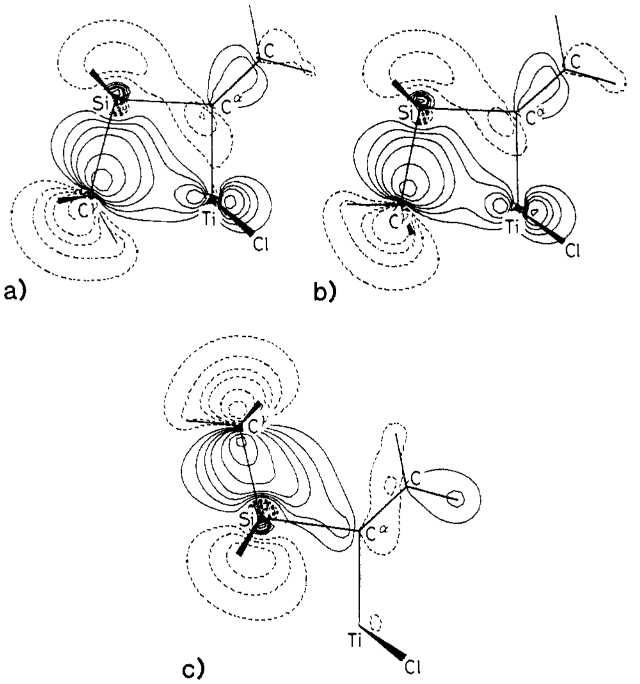


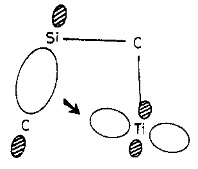
Figure 2. Contour maps of the MO 29a′ of (a) **5a** and (b) **5b** and (c) the MO 30a′ of **5c** in the molecular plane. The contours are ±0.025, ±0.050, ±0.075, ±0.10, ±0.15, ±0.20, ±0.25, ±0.30, ±0.35, and ±0.40 au, and solid and dotted lines denote positive and negative values, respectively.

The difference between **5a** and **5b** is in the conformation of the terminal methyl group; CH_3 in **5a** is eclipsed, with the in-plane $C^\gamma H$ toward Ti, and CH_3 in **5b** is staggered, with the in-plane $C^\gamma H$ away from Ti. CH_3 in **5c** is staggered.

In both **5a** and **5b**, one notices three structural features: (1) the distances between Ti and C^γ are short, (2) the TiCSi angles of 93° are much smaller than those expected for sp^2 hybridization (120°), and (3) the $C^\gamma Si$ distances of 2.01 and 2.00 Å are substantially (~0.1 Å) longer than that optimized for CH_3SiH_3 (1.917 Å). These features are in good agreement with experiment.[1]

The structure of **5c** is much different from **5a** and **5b**. While the SiC^γ bond length of 1.895 Å is shorter than that of **5a** and **5b** and is closer to that of CH_3SiH_3, the normal SiC^γ bond length, the $C^\alpha Si$ bond length of 1.983 Å is longer than that of **5a** and **5b**. The TiC^α bond length of 1.901 Å is also shorter. These differences of the structure of **5c** from those of **5a** and **5b** suggest that $SiC^\gamma H_3$ in **5a** and **5b** and $C^\alpha Si$ in **5c** interact with Ti.

In an electron-deficient transition-metal complex like **1**, there are low-lying vacant orbitals that tend to receive electrons from the ligands.[4-6] Since the CSi σ bond is diffuse in space and high in energy, the SiC^γ bond of **5a** and **5b** can easily interact with a Ti vacant d σ orbital, say d_{z^2}, as shown in **6**.[10] This donative



6

interaction would pull the SiC^γ bond closer to Ti and make it longer, consistent with the experiment. One finds in fact a canonical molecular orbital (29a′) of **5a** and **5b** shown in Figure 2, which demonstrates the importance of this interaction and is much

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(7) (a) Rappe, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 297. (b) Upton, T. H.; Rappe, A. K. *Ibid.* **1985**, *107*, 1206.

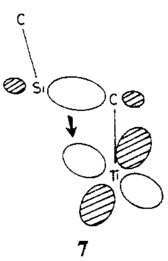
(8) We used the GAUSSIAN82 program: Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Pople, J. A. Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, PA, 1984.

(9) (a) Huzinaga, S.; Andzelm, J.; Kłobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets For Molecular Calculations*; Elsevier: Amsterdam, 1984. (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (c) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797. (d) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (e) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(10) A strong interaction between the CSi σ bond and the C=C π orbital in allylsilane cation radical has been found experimentally[10a,b] and theoretically.[10c] The cation center delocalizes into the CSi σ bond. (a) Kira, M.; Nakazawa, H.; Sakurai, H. *Chem. Lett.* **1985**, 1845. (b) Brumfield, M. A.; Quillen, S. L.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6855. (c) Morokuma, K.; Mizuuchi, S.; Koga, N., to be published.

different from a canonical molecular orbital of **5c** (30a′) representing the SiC$^{\gamma}$ bond. One can see a strong bonding interaction between the Ti d_{z^2} orbital and the SiC$^{\gamma}$ σ bond. The presence of bonding interaction is reflected also in the Ti–C$^{\gamma}$ overlap population: 0.288 in **5a** and 0.241 in **5b**.

In **5a** the electron donative interaction from C$^{\alpha}$Si to a Ti vacant d σ orbital, say d_{xz}, as shown in **7** takes place, instead of the electron-donative interaction from the SiC$^{\gamma}$ bond to a Ti d orbital.



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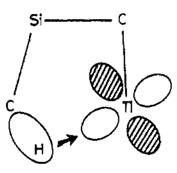
5c is higher in energy than **5a** and **5b** by 10 and 14 kcal/mol, respectively. This indicates that the SiC$^{\gamma}\cdots$Ti interaction in **5a** and **5b** is much stronger than the C$^{\alpha}$Si$\cdots$Ti interaction in **5c**. The TiCSi bond angle of **5c** is larger than that of **5a** and **5b**, presumably reflecting this difference. Though the C$^{\alpha}$Si$\cdots$Ti interaction might also be expected in **5a** and **5b**, the stronger SiC$^{\gamma}\cdots$Ti interaction takes place predominantly in them and thus Ti does not receive electron density from C$^{\alpha}$Si; no molecular orbital displaying a large C$^{\alpha}$Si$\cdots$Ti overlap has been found.

One also notices that the C$^{\gamma}$H bond distance directing toward the Ti atom, 1.112 Å in **5a** and 1.100 Å in **5b**, is longer than the other CH bond distances (1.085–1.089 Å). This is clear evidence[4-6] that the agostic interaction from a CH σ to a Ti d orbital is taking place as well. In **5a** the accepting orbital would be a dσ, say d_{xz}, orbital as shown in **8**, and in **5b** it would be a dπ, say $d_{xy} + d_{yz}$, orbital as shown in **9**.[11]



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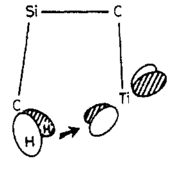


9

5b is more stable by 4 kcal/mol than **5a**; **5b** is a local minimum of the potential surface, i.e., an equilibrium structure, whereas **5a** is at the top of the conformational barrier for CH$_3$ rotation. One can take this as additional evidence that the SiC$^{\gamma}\cdots$Ti interaction is more important. If the C$^{\gamma}$H$\cdots$Ti agostic interaction were the most essential interaction in the present system, **5a** which has the shorter H$\cdots$Ti distance should be more stable than **5b**, opposite to what has been found. The structure of **5a** seems to have an unusual distorition; the SiC$^{\gamma}$H angle has opened up to 134°. The strong SiC$^{\gamma}\cdots$Ti interaction pulls the C$^{\gamma}$Si bond close to the Ti atom. As a result of this interaction, the C$^{\gamma}$H bond is forced to be very close to the Ti atom. In **5a** the H$\cdots$Ti distance (2.10 Å) is too close and the SiC$^{\gamma}$H angle opens to release the repulsion. **5b** where the C$^{\gamma}$H bond is staggered with the Ti atom has less repulsion and is more stable. One may say that the C$^{\gamma}$H$\cdots$Ti agostic interaction in **5** is caused by the structure change due to the SiC$^{\gamma}\cdots$Ti interaction.

One may notice that the calculated TiC$^{\alpha}$ bond lengths of 1.91 and 1.93 Å in **5a** and **5b**, respectively, are shorter than the experimental bond length of 2.13 Å, and one may suspect that this short bond might have artificially made the C$^{\gamma}\cdots$Ti distance too short. However, a geometry optimization under the constraint that TiC$^{\alpha}$ is 2.13 Å, the experimental bond length,[1] gave a similar distorted alkenyl group. This short bond distance is probably caused by the electronic and steric difference between the model Cl and the experimental Cp.

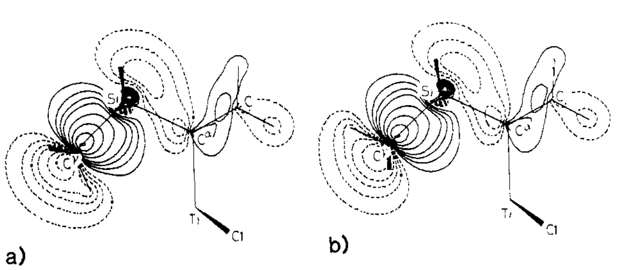
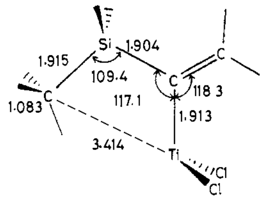
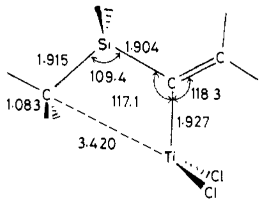


Figure 3. Contour maps of the MO 33a′ of (a) **10a** and (b) **10b** in the molecular plane. See Figure 2 for contour values.

In order to estimate the energy lowering due to the interactions, we have calculated the energy differences between the optimized structures, **5a** and **5b**, and the assumed structures with an undistorted alkenyl group, **10a** and **10b**, in which the structure of CH$_3$SiH$_2$C=CH$_2$ is constructed from the C$^{\gamma}$H$_3$ moiety of the CH$_3$SiH$_3$ optimized structure and the SiH$_2$C=CH$_2$ moiety of the SiH$_3$CH=CH$_2$ optimized structure and that of TiCl$_2$ is taken from **5a** and **5b**. The SiC$^{\gamma}$ bond orbitals of **10a** and **10b** show no trace of interaction with Ti, such as shown in Figure 3. The relative energies are shown in Table I. The net energy lowering, which should include the destabilization due to distortion as well as the stabilizing interactions, is 14 and 18 kcal/mol for **5a** and **5b**, respectively. The extra stability thus gained by the SiC$^{\gamma}\cdots$Ti interaction is probably one of the reasons why **1** became the first isolated intermediate of a Ziegler catalyst system.



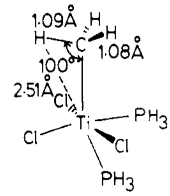
10a



10b

We have confirmed that this energy lowering does not depend on the basis set. When the polarization d functions with an exponent of 0.45 and 0.8 are added to Si and C,[9e,13a] respectively, as well as a diffuse sp function (exponent of 0.04) to C$^{\gamma}$,[13b] the energy lowering for **5b** was calculated to be 16 kcal/mol. In addition, one might worry about the poor basis set of Cl, STO-2G. Therefore, the energy lowering has been calculated by using the 3-21G for Cl with the above larger basis set to be 15 kcal/mol. The interaction is not influenced by the basis functions of Cl.

Comparison of Structure with Ti Ethyl and Methyl Complexes. We have previously studied the agostic interaction in Ti(C$_2$H$_5$)(PH$_3$)$_2$(Cl)$_2$(H) (**3**) and Ti(CH$_3$)(PH$_3$)$_2$(Cl)$_3$ (**11**). In the former complex, the C$^{\beta}$H$\cdots$Ti interaction takes place, giving rise to a longer C$^{\beta}$H bond, the small TiCC angle, and the short Ti$\cdots$H$^{\beta}$ distance. In the latter complex the C$^{\alpha}$H$\cdots$Ti interaction results in the small TiCH angle and the long C$^{\alpha}$H bond. The structures of ethyl and methyl groups in **3** and **11** are similar in character to that of the alkenyl group of the present complexes. The TiCC angle of **3** is 89° and the TiCH angle of **11** is 100°, while TiCSi



11

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[11] This is in a clear contrast with Pd(C$_2$H$_5$)(H)(PH$_3$) where the C$^{\beta}$H bond has to be in the molecular plane in order to have an agostic interaction with the only vacant d orbital.[6]

[12] In Ti(C$_2$H$_5$)(Cl)$_2$(H)(PH$_3$)$_2$ where only the agostic interaction takes place, the calculated H$^{\beta}\cdots$Ti distance is 2.230 Å.[5a]

[13] (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

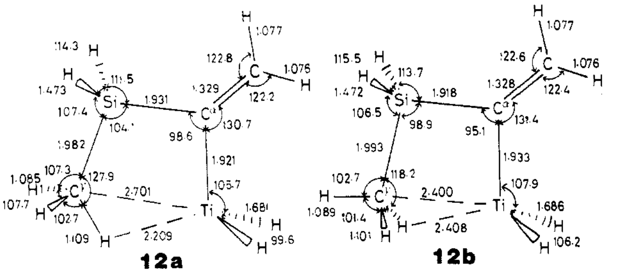


Figure 4. Optimized geometries (in Å and deg) of **12a** and **12b**.

angles of **5a** and **5b** in which the SiC$^\gamma$···Ti interaction takes place are 93° and the TiCSi angle of **5c** in which the C$^\alpha$Si···Ti interaction takes place is 97°.

The principal characteristic feature of the interaction, the electron donative interaction from a bond of the ligand to the central metal, is common in all cases. The present results indicate that such an electron donative interaction is not restricted to the CH···M interaction but can take place from various σ bonds. Although the term "agostic interaction" has been originally proposed to refer to the intramolecular CH···M interaction,[4c] the same term may be used to represent intramolecular donative interaction from other kinds of bonds as well. In addition, in order to state the electron donative bond explicitly, we propose that the name of the bond is added before the "agostic interaction". Thus the interaction for **5a** and **5b** is to be called the βSiC agostic interaction and that for **5c** and αCSi agostic interaction. In the same token, the agostic interaction of Ti ethyl and methyl complexes should be called the βCH agostic interaction and the αCH agostic interaction, respectively.

Effect of Ligand. Our previous theoretical studies on the CH agostic interaction of Ti ethyl and methyl complexes have revealed that the CH agostic interaction takes place under a delicate balance of ligand effects.[5,6] For instance, no agostic interaction has been found in $Ti(C_2H_5)(PH_3)_2(H)_3$[5a] and $Ti(CH_3)(PH_3)_2(H)_3$,[5b] where axial chlorides in agostic **3** and **11**, respectively, are replaced by hydrides. Therefore, we have replaced Cl ligands in **5a** and **5b** with H in order to investigate the effect of ligands on the βSiC agostic interaction.[14]

The optimized structures of $Ti(C(SiH_2CH_3){=}CH_2)(H)_2^+$ (**12**) are shown in Figure 4. One can see that the agostic interaction still takes place: long SiC$^\gamma$ bonds (1.982 and 1.993 Å in **12a** and **12b**, respectively), small TiCSi angles (98.6° and 95.1°), and short C$^\gamma$···Ti distances (2.701 and 2.400 Å). This situation is different from the above mentioned cases of **3** and **11**. The present complex is positively charged and the Ti atom is more electron deficient, and therefore **12** presumably has a larger electron-accepting and larger agostic interaction capability than the corresponding hydrides of **3** and **11**. However, the degree of the distortion is smaller than that of **5**, indicating that the hydride, more electron donative than the chloride, makes the electron-accepting Ti orbital higher in energy and the agostic interaction weaker.

Effect of Si. It is an interesting question whether Si is necessary for the interaction and whether the agostic interaction takes place between CC and Ti. Therefore, we have optimized the structure of $Ti(C(CH_2CH_3){=}CH_2)(Cl)_2^+$ (**13**) with a staggered terminal methyl group. The optimized structure shown in Figure 5 reveals the βCC agostic interaction: the long C$^\beta$C$^\gamma$ bond of 1.592 Å, the small TiCC angle of 93°, and the short TiC$^\gamma$ distance of 2.36 Å. In addition, a weak γCH agostic interaction takes place, two C$^\gamma$H bonds being slightly longer (1.100 Å) than usual.

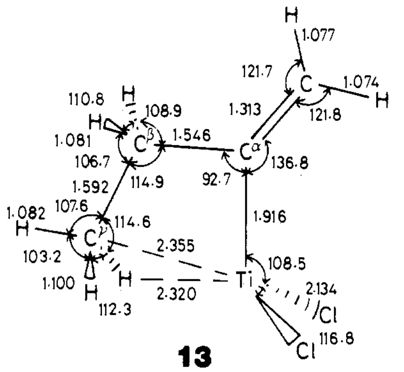


Figure 5. Optimized geometries (in Å and deg) of **13**.

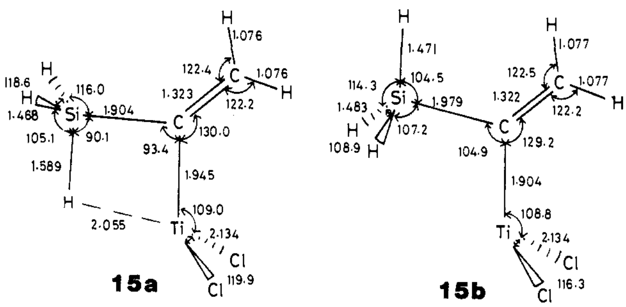
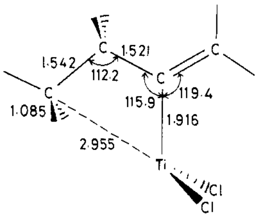


Figure 6. Optimized geometries (in Å and deg) of **15a** and **15b**.

We assumed again an undistorted structure, **14**, in which the structure of $CH_3CH_2C{=}CH_2$ was taken from that of the $CH_3CH_2CH{=}CH_2$ optimized structure, to estimate the interaction energy. The energy lowering thus obtained is 10 kcal/mol, about a half of that for **5b**. The silicon atom contributes substantially to the stability of **5**. This is probably due to the fact that the CSi σ bond is more diffuse in space and higher in energy than the CC σ bond and therefore more electron donating.



14

It is interesting to predict that even the CC bond, as well as the CH and the SiC bond, can interact with the central transition metal. The present complex is positively charged and Ti is very electron deficient. The electron-accepting ability of Ti is so strong that various agostic interactions might be possible.

We show an example of βSiH agostic interaction found in $Ti(C(SiH_3){=}CH_2)(Cl)_2^+$ (**15**). Its eclipsed optimized structure, **15a**, is shown in Figure 6 with the staggered optimized structure, **15b**. In **15a**, the TiCSi angle is small (93.4°), the interacting SiH bond (1.589 Å) is longer by 0.12 Å than the other SiH bonds, and the Ti···H distance is only 2.055 Å, indicating that the βSiH bond interacts with Ti very strongly.

The structure of **15b** is similar to that of **5c** in character; the CSi bond is longer, the TiC$^\alpha$ bond is shorter, and the TiCSi bond angle is larger than those in **15a**. These structural features indicate that here the C$^\alpha$Si bond, not SiH, interacts with Ti.

We have also determined the structures of **15a** and **15b** with the basis set in which the polarization function is added on Si.[9e] Calculations with the polarization function gave the C$^\alpha$Si bond of 1.865 Å, the TiCSi bond angle of 93.6°, and the interacting SiH bond of 1.564 Å for **15a** and the C$^\alpha$Si bond of 1.940 Å and the TiCSi bond angle of 105.7° for **15b**. The C$^\alpha$Si bonds are shorter by 0.040 Å than those determined without the polarization function. However, the C$^\alpha$Si bond of **15b** is still longer than the CSi bond in CH_3SiH_3, 1.883 Å, obtained with the same polarized basis set. The SiH bond and the TiCSi angle of **15a**, the signs of the interaction, are independent on the polarization function.

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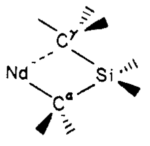
(14) A geometry optimization of $Ti(C(SiH_2CH_3){=}CH_2)(Cp)_2^+$, with the STO-2G basis set for the atoms in the Cp ring, gave an undistorted alkenyl group. It appears that the poor Cp basis set caused a large electron transfer from Cp to Ti, making the vacant Ti d orbitals too high in energy to interact strongly with the CSi σ bond. Also, the neglect of the electron correlation may affect the electronic structure of Cp-containing compounds.[14a,b] (a) Luthi, H. P.; Siegbahn, P. E. M.; Almlof, J.; Faegri, K., Jr.; Heiberg, A. *Chem. Phys. Lett.* **1984**, *111*, 1. (b) Taylor, T. E.; Hall, M. B. *Ibid.* **1985**, *114*, 338.

These results indicate that the SiC agostic interaction takes place regardless of the polarization function.

Concluding Remarks

We have optimized the structures of $Ti(C(SiH_2CH_3)=CH_2)(Cl)_2^+$, model of $Ti(C(Si(CH_3)_3)=C(CH_3))(C_6H_5)(Cp)_2^+$, to find the distorted alkenyl group that is the sign of the $SiC^{\gamma}\cdots Ti$ interaction. An analysis of geometries and molecular orbitals shows that the donative interaction from the SiC^{γ} σ bond to a Ti vacant d orbital is the major origin of alkenyl distortion, assisted by the CH → Ti d agostic interaction. The intramolecular $SiC^{\gamma}\cdots Ti$ interaction is similar in nature to the intramolecular $CH\cdots M$ interaction, called the agostic interaction. Therefore, the interaction found in the present study may be called the βSiC agostic interaction.

A similar distorted ligand, $CH[Si(CH_3)_3]_2$, in the neodymium complex, $NdCH[Si(CH_3)_3]_2Cp''_2Si(CH_3)_2$, **16** has been reported experimentally: a small NdCSi angle of 98° and a short $Nd\cdots C^{\gamma}$ distance of 2.90 Å.[15] The $Al_2(CH_3)_6$-like interaction between C and Nd has been suggested, as follow.



16

The structure of the $C^{\alpha}SiC^{\gamma}$ moiety in **16** resembles that of the alkenyl group in **5**. Since **16** is an electron-deficient complex, interactions similar to those we presented here are probably taking place in this lanthanide complex between the CSi σ bond and the Nd atom.

We also found the βCC agostic interaction in the optimized structure of $Ti(C(CH_2CH_3)=CH_2)(Cl)_2^+$ and the βSiH agostic interaction in the optimized structure of $Ti(C(SiH_3)=CH_2)(Cl)_2^+$. The βSiC agostic interaction is stronger than βCC agostic interaction, because the electron-donating ability of the SiC bond is stronger than the CC bond. It appears that the agostic interaction can take place between various σ bonds and vacant orbitals of an electron-deficient metal atom within a molecule. The extent of the structural distortion and stabilization, in competition with other conformational and structural energetics, would depend critically on the electron-donating ability of the σ bond and the electron-accepting ability of the metal as well as the ligands and the coordination unsaturation. Since these generalized agostic interactions are not known experimentally, they remain a prediction.

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Registry No. 1, 99248-82-5; **5**, 111524-71-1; **12**, 111524-72-2; **13**, 111524-73-3; **16**, 98690-06-3; $Ti(C(SiH_2CH_3)=CH_2)(Cp)_2^+$, 111524-74-4.

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Environmental Control of Product States in the Chemiluminescent Electron Transfer between Rubrene Radical Ions

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Abstract: Electrogenerated chemiluminescence (ecl) from the annihilation of rubrene anion and cation radicals has been studied in *N,N*-dimethylformamide solutions from −50 °C to room temperature. The magnetic enhancement of chemiluminescence declined toward lower temperatures. This result, together with the time dependence of ecl in triple-step experiments, suggests that ecl arises by both the S and T routes and that the T-route fraction declines at lower temperatures. Comparisons with the magnetic effect on ecl from a related system (the annihilation of the rubrene anion radical with the cation radical of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine) suggest that the T-route contribution to ecl in the rubrene system falls to about 10% near −40 °C. A new method for evaluating the relative ecl efficiency was developed. It showed that the efficiency generally rises in the rubrene system as the temperature is lowered, a result indicating that the change in the mechanistic balance is rooted in temperature-dependent branching ratios for production of singlet and triplet excited states in electron transfer. The efficiency of excited singlet production apparently doubles as the temperature drops over the working range. The concentration of supporting electrolyte also markedly influences the branching ratios for electron transfer.

The electrogenerated chemiluminescence (ecl) of rubrene has fascinated investigators for 2 decades, because it offers delicate energy balances in the two main steps of the chemiluminescence mechanism.[1,2] At least two distinct pathways to the emitting rubrene singlet ($^1R^*$) seem to exist, and their relative contributions are affected by the reaction environment. The system offers a rare opportunity to examine the manner in which extremely

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[1] The most complete and the most recent reviews of ecl are the following: (a) Faulkner, L. R. *MTP Int. Rev. Sci., Phys. Chem., Ser. Two* **1975**, *9*, 213. (b) Faulkner, L. R.; Bard, A. J. *Electroanal. Chem.* **1977**, *10*, 1. (c) Pragst, F. *Z. Chem.* **1978**, *18*, 41. (d) Faulkner, L. R. *Methods Enzymol.* **1978**, *57*, 494. (e) Park, S. M.; Tryk, D. A. *Rev. Chem. Intermed.* **1981**, *4*, 43. (f) Faulkner, L. R.; Glass, R. S. In *Chemical and Biological Generation of Excited States*; Adam, W., Cilento, G., Eds.; Academic Press: New York, 1982; Chapter 6. (g) Tachikawa, H.; Faulkner, L. R. In *Laboratory Techniques in Electroanalytical Chemistry*; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1984; Chapter 23.

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