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Competitive Alkylidene Transfer to Olefins and Alkylidene-to-Olefin Interconversion of the Electrophilic Iron Carbene Complexes $[FeCp(CO)(L)(=CHR)]^+$ (L = CO, PH_3; R = Me, Et): A Theoretical Study[†]

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The ethylidene and propylidene transfer to olefins as well as the intramolecular alkylidene-to-olefin isomerization of the cationic alkylidene complexes $[FeCp(CO)(L)(=CHR)]^+$ (L = CO, PH_3; R = Me, Et) has been investigated by means of DFT/B3LYP calculations. It was found that both processes are thermodynamically very favorable independent of the co-ligand L and the substituent R. Kinetically, the ethylidene transfer onto ethylene is slightly favored over the intramolecular ethylidene isomerization by 4.5 and 1.9 kcal/mol for L = CO and PH_3, respectively. Accordingly, these pathways are strongly competitive with one another. For the propylidene complex the reactivity is reversed and the propylidene-to-propylene interconversion becomes the dominating process. The energy barrier for the propylidene transfer process is almost twice as high as the one for the propylidene isomerization. viz., 17.7 and 9.7 kcal/mol. With regard to stereoselectivity, for the ethylidene transfer of $[FeCp(CO)_2(=CHMe)]^+$ to propylene the formation of the *cis* dimethylcyclopropane is slightly favored. All reactions studied are strongly frontier orbital controlled, and charges do not play a significant role.

Introduction

Alkylidene complexes of the type $[FeCp(CO)_2(=CRR')]^+$ (R, R′ = H, alkyl, aryl) are one of the most reactive carbenes, as far as their electrophilicity at the carbene carbon atom is concerned.[1−4] They are typically too unstable to be isolated or even to be observed by NMR spectroscopy. Their existence is implied by the transfer of an alkylidene moiety to an olefin substrate. Isolated or at least spectroscopically characterized examples include the benzylidene complex $[FeCp(CO)_2(=CHPh)]^+$,[1e] the cyclopropylmethylidene complex $[FeCp(CO)_2(=CH(c\text{-}C_3H_5)]^+$,[1f] and the methyl-ethylidene complex $[FeCp(CO)_2(=CMe_2)]^+$.[2] However, iron alkylidene complexes can be generated and reacted in situ with alkenes to give cyclopropanes under very mild conditions (path a, Scheme 1).[5] Unfortunately, due to the strongly electrophilic nature of the carbene carbon atom, facile β-hydrogen and, in some cases, even β-alkyl or aryl migration[3] takes place (these reactions are formally 1,2 migrations analogous to Wagner−Meerwein rearrangements in carbenium ions), forming the thermodynamically more stable olefin complexes (path b, Scheme 1). This competitive process severely diminishes the yield of cyclopropanes and thus the usefulness of $[FeCp(CO)_2(=CRR')]^+$ complexes as carbene transfer reagents. Interestingly, in the presence of γ-hydrogen atoms, e.g., in the case of propylidene complexes, alkylidene transfer is almost completely suppressed and the alkylidene-to-olefin interconversion becomes the predominant process.[1e] According to experimental data,[1e] the mechanism of the alkylidene transfer process appears to proceed via a direct attack of the olefin at the electrophilic carbene carbon atom. A metal-mediated process through the intermediacy of a metallacyclobutadiene complex involving dissociation of a CO ligand to initiate olefin attack at the metal center seems less likely. Thus, to gain a deeper understanding of such alkylidene transfer reactions and how carbene-to-olefin isomerizations proceed and how these processes can be controlled in terms of yield and selectively, it is essential to establish how the nature of the co-ligands and the substituents at the carbene carbon atom affect thermodynamics and reaction barriers.

In the present contribution we attempt to establish a reasonable mechanistic proposal for the ethylidene and propylidene transfer to olefins and the competitive alkylidene-to-olefin interconversion of the electrophilic cationic carbene complexes $[FeCp(CO)(L)(=CHR)]^+$ (L

[†] This article is dedicated to the memory of Prof. Roland Schmid (1945−2004), my former mentor, respected colleague, and friend.

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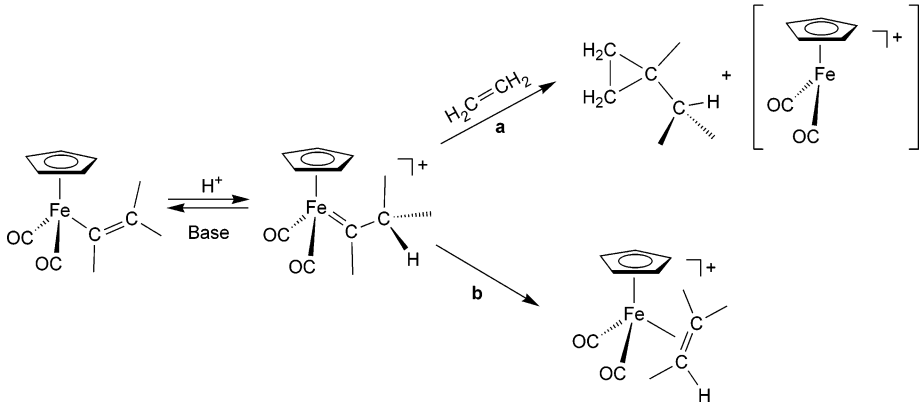
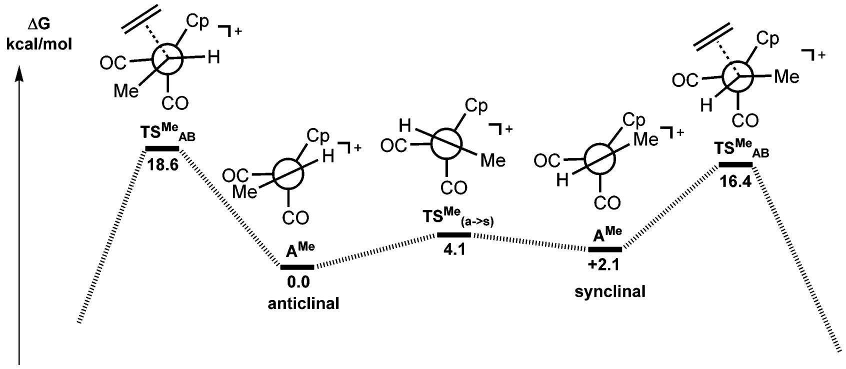
10.1021/om049374h CCC: $27.50

Scheme 1



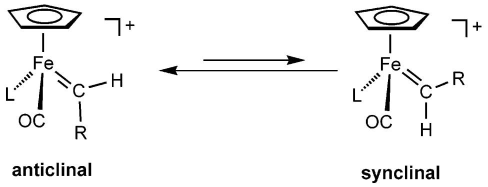
Scheme 2. Reaction Profile of the Computed Relative Gibbs Free Energies (kcal/mol) for the Interconversion of the *Anticlinal* and *Synclinal* Isomers of $[FeCp(CO)_2(=CHMe)]^+$ (A^{Me}) and the Addition of Ethylene to These Isomers



= CO, PH_3; R = Me, Et) by means of DFT/B3LYP calculations.

Results and Discussion

The relative Gibbs free energies (in kcal/mol) and geometries of the cationic alkylidene complexes $[FeCp(CO)(L)(=CHR)]^+$ (L = CO, PH_3; R = Me, Et) have been determined by means of DFT/B3LYP[6] calculations using Gaussian98.[7] The lowest energy conformation for these complexes, in agreement with experimental findings,[8] has the H–C–R plane of the carbene ligand perpendicular to the Cp ring with an *anticlinal* orientation being more stable by 2–4 kcal/mol than a *synclinal* one depending on the co-ligand L and the substituent R. On the basis of low-temperature ^1H NMR studies,[8] the energy barrier $\Delta G_{exp}^{\ddagger}$ of the interconversion between *anticlinal* and *synclinal* isomers has been estimated to be smaller than 7–8 kcal/mol. It has also been observed[8] that the reactivity of the *synclinal* isomer is greater than the *anticlinal* isomer. An explanation for the higher reactivity of the *synclinal* isomer has been given by Davies and Seemann[9] from a conformational analysis of the transition states and initial products formed from methoxide addition to the benzylidene complex $[FeCp(CO)(PPh_3)(=CHPh)]^+$.



The same reactivity pattern has been found for complex $[FeCp(CO)_2(=CHMe)]^+$. The Gibbs free activation energy for the *anticlinal*-to-*synclinal* interconversion is small, being merely 4.1 kcal/mol. The transition state $\mathbf{TS^{Me}_{AB}}$ for the ethylene addition to $\mathbf{A^{Me}}$ (anticlinal) and $\mathbf{A^{Me}}$ (synclinal) clearly reveals that the energy barrier is lower for the less populated *synclinal* isomer as predicted by Davies and Seemann (Scheme 2). Accordingly, the *synclinal* isomers are intrinsically more reactive and have been chosen as the starting point for all our calculations.

The geometries of $[FeCp(CO)_2(=CHMe)]^+$ ($\mathbf{A^{Me}}$) and $[FeCp(CO)_2(=CHEt)]^+$ ($\mathbf{A^{Et}}$) with selected bond dis-

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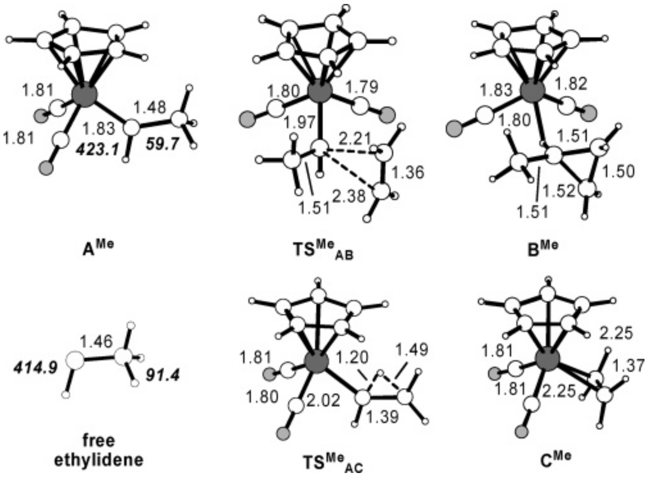


Figure 1. Optimized B3LYP geometries of the equilibrium structures and transition states **A$^{\mathrm{Me}}$**, **B$^{\mathrm{Me}}$**, **C$^{\mathrm{Me}}$**, **TS$^{\mathrm{Me}}_{\mathrm{AB}}$**, and **TS$^{\mathrm{Me}}_{\mathrm{AC}}$** (distances in Å) and calculated (DFT-GIAO) ^{13}C chemical shifts δ (in ppm relative to TMS) for **A$^{\mathrm{Me}}$** (italics).

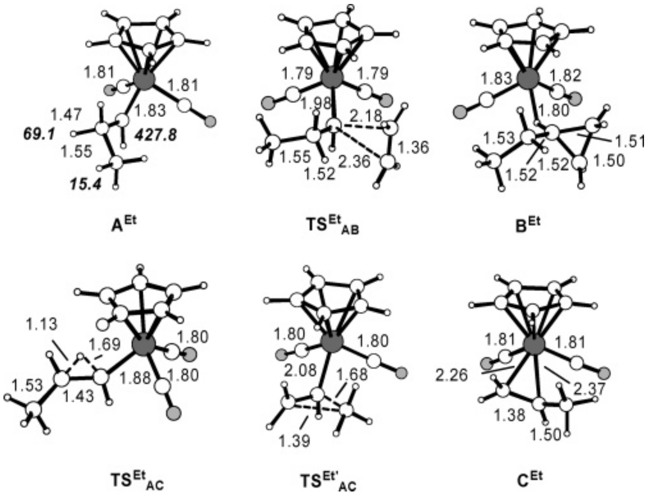


Figure 2. Optimized B3LYP geometries of the equilibrium structures and transition states **A$^{\mathrm{Et}}$**, **B$^{\mathrm{Et}}$**, **C$^{\mathrm{Et}}$**, **TS$^{\mathrm{Et}}_{\mathrm{AB}}$**, **TS$^{\mathrm{Et'}}_{\mathrm{AC}}$**, and **TS$^{\mathrm{Et}}_{\mathrm{AC}}$** (distances in Å) and calculated (DFT-GIAO) ^{13}C chemical shifts δ (in ppm relative to TMS) for **A$^{\mathrm{Et}}$** (italics).

tances are depicted in Figures 1 and 2. In addition GIAO calculations based on the optimum DFT models of [FeCp(CO)$_2$(=CHMe)]$^+$, [FeCp(CO)$_2$(=CHEt)]$^+$, and [FeCp(CO)(PH$_3$)(=CHMe)]$^+$ have been performed revealing ^{13}C NMR chemical shifts of the carbene carbon atoms downfield shifted as much as 423.1, 427.8, and 411.3 ppm, respectively. These enormous values are in good agreement with the experimental values of similar compounds such as [FeCp(CO)$_2$(=CMe$_2$)]$^+$ and [FeCp(CO)(PPh$_3$)(=CMe$_2$)]$^+$, giving rise to resonances at 419.0 and 406.5 ppm, respectively.[3] For comparison, the ^{13}C NMR resonance of the illusive free singlet ethylidene CHMe is calculated to be 414.9 ppm (Figure 1). Most noteworthy, organic carbenium ions do not exhibit comparable downfield shifts.[10] In fact, according to GIAO calculations the carbenium ion [HCHMe]$^+$ gives rise to a signal at 315 ppm. Accordingly, the large chemical shifts clearly do not reflect a positive charge on the carbene carbon atom. As can be seen in Figure 3, the NPA charges in the optimized geometries of **A$^{\mathrm{Me}}$**, **A$^{\mathrm{Et}}$**, and free CHMe are −0.02, −0.02, and −0.07, respectively. Instead, the large downfield shifts can be traced back to a strong localization of the LUMO on the carbene carbon atom in conjunction with a small energy gap between the LUMO and the Fe−C σ-orbitals.[11] As an example, the LUMO of [FeCp(CO)$_2$(=CHMe)]$^+$ (**A$^{\mathrm{Me}}$**) and the free ethylidene HCCH$_3$ is shown in Figure 4. Accordingly the structure of iron alkylidene complexes may be described best by resonance structure **A**.

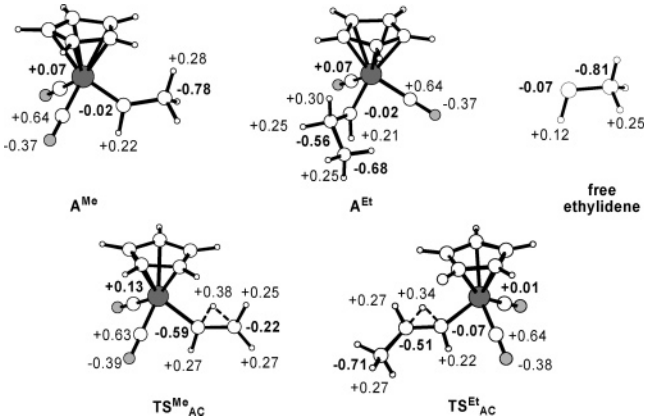


Figure 3. NPA charge distribution in the optimized geometries of the equilibrium structures and transition states **A$^{\mathrm{Me}}$**, **A$^{\mathrm{Et}}$**, **TS$^{\mathrm{Me}}_{\mathrm{AC}}$**, and **TS$^{\mathrm{Et}}_{\mathrm{AC}}$** and the free singlet carbene CHMe.

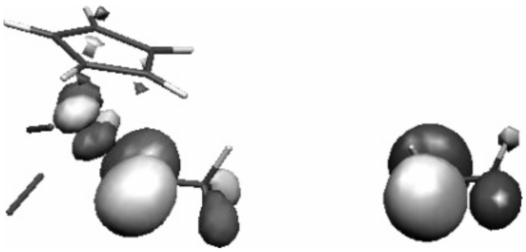
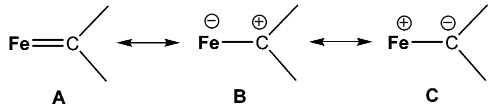


Figure 4. LUMOs of [FeCp(CO)$_2$(=CHMe)]$^+$ (**A$^{\mathrm{Me}}$**) and the free singlet carbene CHMe.



A conceivable pathway for the direct transfer of the ethylidene moiety of [FeCp(CO)(L)(=CHMe)]$^+$ (**A$^{\mathrm{Me}}$**) to ethylene to form the respective cyclopropane complex [FeCp(CO)(L)(η^2(C,H)-*c*-CH(Me)CH$_2$CH$_2$)]$^+$ (**B$^{\mathrm{Me}}$**) is shown in Scheme 3. The detailed structures of complexes **A$^{\mathrm{Me}}$** and **B$^{\mathrm{Me}}$** and the transition state connecting them are displayed in Figure 1. The reaction is exergonic independent of whether L = CO or PH$_3$, releasing 8.7 and 8.3 kcal/mol, respectively. The Gibbs free activation energy is 16.4 kcal/mol for L = CO, whereas with the more electron-donating phosphine ligand PH$_3$ the energy barrier increases to 21.8 kcal/mol, making this process slightly less favorable. This reaction requires no vacant coordination site at the metal center; that is, neither dissociation of the CO or PH$_3$ ligands, respectively, nor an η^5 to η^3 ring slippage process of the

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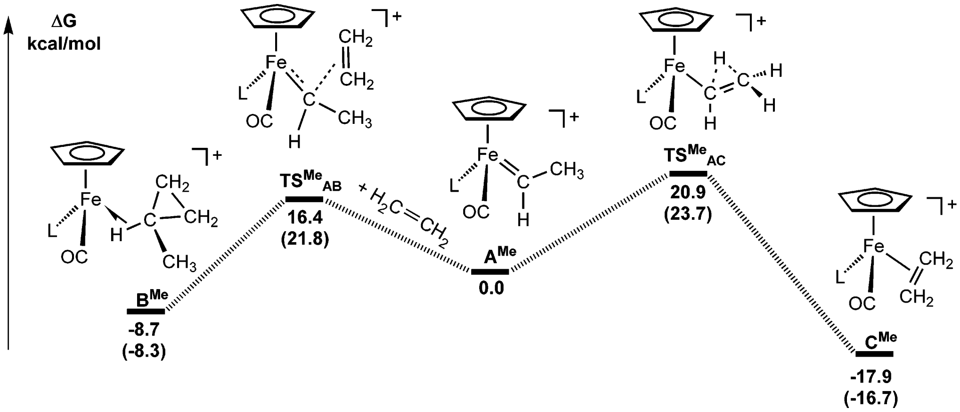
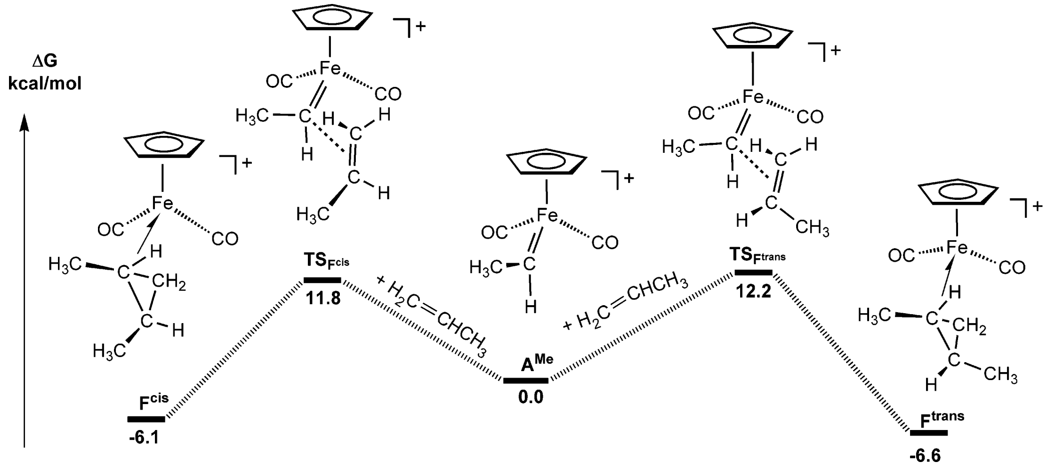
Scheme 3. Reaction Profile of the Computed Relative Gibbs Free Energies (kcal/mol) for the Ethylidene Transfer of $[FeCp(CO)(L)(=CHMe)]^+$ (A^{Me}) (L = Co, PH_3) to Ethylene and the Competitive Interconversion to the Olefin Complex $[FeCp(CO)(L)(\eta^2\text{-}CH_2{=}CH_2)]^+$ (C^{Me})[a]



[a] The numbers in parenthesis are for L = PH_3.

Scheme 4. Reaction Profile of the Computed Relative Gibbs Free Energies (kcal/mol) for the Ethylidene Transfer of $[FeCp(CO)_2(=CHMe)]^+$ (A^{Me}) to Propylene



Cp ligand is necessary. In the transition state $\mathbf{TS^{Me}_{AB}}$ the incoming ethylene molecule approaches the carbene carbon atom in a slightly unsymmetrical mode, with C−C bond distances between the olefin and the carbene carbon atom of 2.21 and 2.38 Å. Accordingly, the two new C−C bonds are essentially formed in a synchronous mode. At the same time the Fe−C bond becomes significantly longer with concomitant pyramidalization of the carbene carbon atom. The C−C bond of the ethylene molecule in the transition state is 1.36 Å, being hardly different from the C−C bond in the free molecule (1.33 Å). In the final product $\mathbf{B^{Me}}$ the methylcyclopropane is only weakly coordinated via an agostic interaction and can be easily liberated.

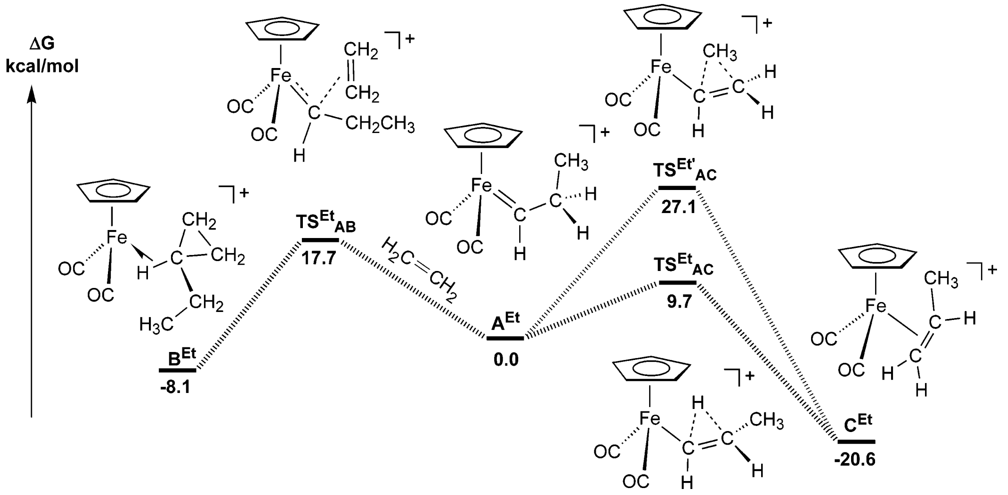
With regard to the stereoselectivity of cyclopropanation reactions it has been observed that iron alkylidene complexes $[FeCp(CO)_2(=CRR')]^+$ exhibit very little to moderate stereoselectivities with monosubstituted terminal olefins. Internal olefins, on the other hand, proceed in most cases with high selectivity in a *cis* fashion.[1,2] We have thus investigated the transfer of ethylidene to propylene with the energy profile shown in Scheme 4. As a result, the formation of the *cis* cyclopropane complex is slightly favored over the *trans* product with an energy difference of merely 0.4 kcal/mol, thus reproducing the experimental trend.

The reactivity of the propylidene complex $[FeCp(CO)_2(=CHEt)]^+$ ($\mathbf{A^{Et}}$) toward ethylene is very similar to that of the iron ethylidene complex $\mathbf{A^{Me}}$. The formation of the cyclopropane complex $[FeCp(CO)(L)(\eta^2(C,H)\text{-}c\text{-}CH(Et)CH_2CH_2)]^+$ ($\mathbf{B^{Et}}$) is exergonic by 8.1 kcal/mol, with an energy barrier of 17.7 kcal/mol (Scheme 5). The detailed structures of all complexes and transition states involved are depicted in Figure 2.

Next we investigated the competitive intramolecular 1,2-hydrogen migration processes to afford the ethylene and propylene complexes $[FeCp(CO)(L)(\eta^2\text{-}CH_2{=}CH_2)]^+$ ($\mathbf{C^{Me}}$) and $[FeCp(CO)(L)(\eta^2\text{-}CH_2{=}CHMe)]^+$ ($\mathbf{C^{Et}}$) as depicted in Schemes 3 and 4. The detailed structures of all complexes and transition states are displayed in Figures 1 and 2. In addition, NPA charges and Wiberg indices (WI) for selected complexes are given in Figures 3 and 5. Instead of distances, the WIs measure the bond strengths, allowing easy comparisons of equivalent bonds within the reacting molecules, and are more sensitive to changes in bond order than are distances.

The carbene-to-olefin interconversion is thermodynamically very favorable in both cases, i.e., independent of the substituent on the carbene carbon atom. During the formation of the olefin complexes $\mathbf{C^{Me}}$ (with L = CO or PH_3) and $\mathbf{C^{Et}}$ 17.9, 16.7, and 20.6 kcal/mol, respectively, are released. Kinetically, however, a striking

Scheme 5. Reaction Profile of the Computed Relative Gibbs Free Energies (kcal/mol) for the Propylidene Transfer of $[FeCp(CO)_2(=CHEt)]^+$ (A^{Et}) to Ethylene and the Competitive Interconversion to the Olefin Complex $[FeCp(CO)_2(\eta^2\text{-}CH_2{=}CHMe)]^+$ (C^{Et}) via Both H and CH_3 Migration



difference between the ethylidene and propylidene complexes is observed. While the Gibbs free activation energies for the formation of $\mathbf{C^{Me}}$ (with L = CO or PH_3) are 20.9 and 23.7 kcal/mol, the energy barrier for the formation of $\mathbf{C^{Et}}$ drops to 9.7 kcal/mol. For comparison, the energy barriers of the competing ethylidene and propylidene transfer to ethylene are almost twice as high, being 17.7 and 16.4 kcal/mol, respectively (Schemes 3 and 4). Gratifyingly, these results are in full agreement with experimental results reported by Brookhart and co-workers, who have shown that propylidene complexes rapidly isomerize to give the respective olefin complexes even at −40 °C ($t_{1/2}$ ca. 1 h).[1e] It is thus obvious that cyclopropane formation is strongly competitive with the carbene rearrangement process. Moreover, it has to be noted that both solvation and tunneling effects[12] may be also important in hydrogen shift reactions and could lower these activation barriers even further. Such effects are not taken into account by the present DFT calculations.

Such a difference in activation energies has been explained by viewing the isomerization as hydride migration to a carbenium ion center with accumulating substantial positive charge on the β-carbon atom in the transition state. Consequently, carbenium ion stabilizing substituents such as alkyl groups would be expected to lower the energy barrier and accelerate the hydride migration.[1e]

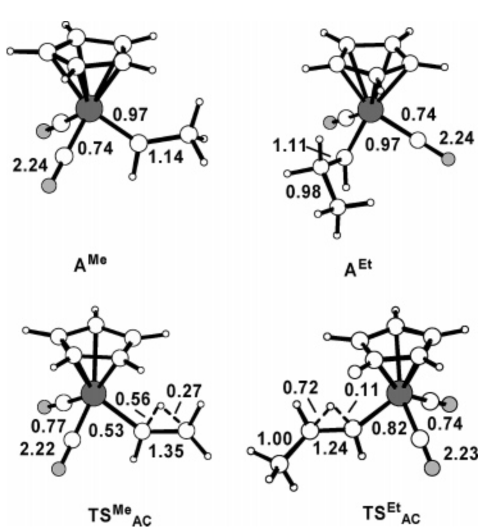


Figure 5. Wiberg indices in the optimized geometries of the equilibrium structures and transition states $\mathbf{A^{Me}}$, $\mathbf{A^{Et}}$, $\mathbf{TS^{Me}_{AC}}$, and $\mathbf{TS^{Et}_{AC}}$.

To establish whether this assumption is reasonable or not, we first took a closer look at the progress of the hydrogen migration by using NPA charges and WIs. Surprisingly, the charge distribution in the carbene moiety of the alkylidene precursors $\mathbf{A^{Me}}$ and $\mathbf{A^{Et}}$ is very similar to that in the free ethylidene molecule with essentially no charge localized on the Fe and the carbene carbon atoms, being +0.07 and −0.02, respectively (Figure 3). Accordingly, the carbene carbon atom is not electrophilic as far as the charge is concerned. The Fe−C carbenic bonds in complexes $\mathbf{A^{Me}}$ and $\mathbf{A^{Et}}$ exhibit WIs of 0.97, in agreement with a metal carbon double bond.[13]

On going from $\mathbf{A^{Me}}$ to $\mathbf{TS^{Me}_{AC}}$, a substantial negative charge is induced onto the carbene carbon atom (−0.59), while the positive charge at the metal center increases slightly to +0.13. At the same time, the negative charge of the β-carbon atom is lowered from −0.78 in $\mathbf{A^{Me}}$ to −0.22 in $\mathbf{TS^{Me}_{AC}}$. The charge redistribution is accompanied by a significant decrease of the Fe−C bond strength, as indicated by a WI value of 0.53. Most interestingly, the NPA charge of the migrating hydrogen atom $\mathbf{TS^{Me}_{AC}}$ is +0.38, indicating a protonic rather than a hydridic character. In $\mathbf{TS^{Me}_{AC}}$ the migrating hydrogen atom is asymmetrically bound, with the new C−H bond being already formed to a large extent as suggested by the short C−H distance of 1.20 Å, corroborated by the Wiberg indices. Accordingly, $\mathbf{TS^{Me}_{AC}}$ may be classified as a late and polar transition state.

The situation is quite different for the rearrangement of $\mathbf{A^{Et}}$. In the course of the hydrogen migration essentially hardly any charge redistributions take place, as can be seen from Figure 3. The migrating hydrogen

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(12) For tunneling in hydrogen shift reactions see: Hess, B. A., Jr. *J. Org. Chem.* **2001**, *66*, 5897, and references therein.

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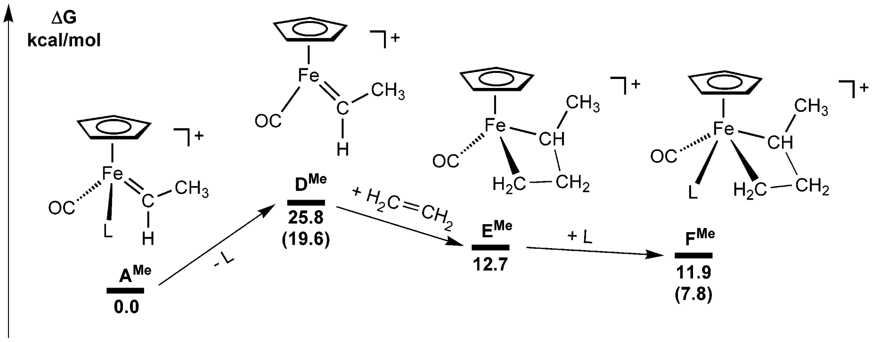
Scheme 6. Computed Relative Gibbs Free Energies (kcal/mol) for the Formation of the Metallacyclobutane Complexes $[FeCp(CO)(CH(Me)CH_2CH_2)]^+$ (E^{Me}) and $[FeCp(CO)(L)(CH(Me)CH_2CH_2)]^+$ (F^{Me}) via $[FeCp(CO)(=CHMe)]^+$ (D^{Me}) Involving Dissociation of L (CO, PH_3)[a]



[a] The numbers in parenthesis are for L = PH_3.

atom also bears a positive NPA charge of +0.34. The Fe−C bond in **TS^{Et}_{AC}** is only slightly weakened and is still carbenic, as indicated by the short bond distance of 1.88 Å and the WI of 0.82 (Figures 2 and 5). The β-C−H bond to be cleaved is still intact, being 1.13 Å, while the new C−H bond to be formed is still weak, being 1.69 Å. This is also apparent from the respective WIs of 0.72 and 0.11. Therefore, in contrast to **TS^{Me}_{AC}**, **TS^{Et}_{AC}** may be viewed as an early transition state. According to the Hammond postulate,[14] an early transition state for an exothermic reaction means a lower activation energy.

The enhanced reactivity of the propylidene complex may also be rationalized by taking a closer look at the hyperconjugation between the occupied p_z-orbitals of the alkylidene carbon atoms of **A^{Me}**, **A^{Et}**, **TS^{Me}_{AC}**, and **TS^{Et}_{AC}**. Relevant orbital interactions are shown in Figure 6. In contrast to **A^{Me}** and **TS^{Me}_{AC}**, there is a high-lying occupied orbital (**II**) in **A^{Et}** and **TS^{Et}_{AC}** featuring an unfavorable antibonding interaction between the p_z-orbitals of the β- and γ-carbon atoms. A weakening of this antibonding interaction and, thus, a significant lowering of the energy barrier are achieved in **TS^{Et}_{AC}** by removing electron density from the p_z-orbital of the β-carbon atom. Removal of electron density from this orbital, however, is counterbalanced by transferring electron density back via other conjugated orthogonal lying p-orbitals (not shown in Figure 6), and therefore no charge redistributions are observed.

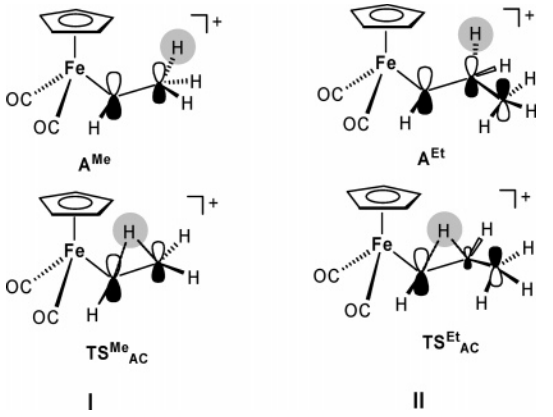


Figure 6. Selected hyperconjugated occupied p-orbitals of $[FeCp(CO)_2(=CHMe)]^+$ (**A^{Me}**) and $[FeCp(CO)_2(=CHEt)]^+$ (**A^{Et}**) and the respective transition states **TS^{Me}_{AC}** and **TS^{Et}_{AC}**.

It has to be noted that the formation of the propylene complex **C^{Et}** can also be achieved by migration of a methyl group, as shown in Scheme 4. However, the energy barrier for this process is comparatively high, being 27.1 kcal/mol. It is thus safe to assume that as long as β-H atoms are present, a 1,2-methyl shift is unlikely to compete with 1,2-hydrogen migration.

Finally, we considered the intermediacy of metallacyclobutane complexes along the pathway to cyclopropane complexes (Scheme 6). The formation of a discrete Fe(IV) metallacycle requires dissociation of L (L = CO, PH_3) to open up a free coordination site at Fe to give the 16e alkylidene $[FeCp(CO)(=CHMe)]^+$ (**D^{Me}**). This process is thermodynamically very unfavorable, i.e., strongly endergonic by 25.8 and 19.6 kcal/mol for L = CO and PH_3, respectively. Note that, depending on the substituents R, the Gibbs free activation energies for the direct addition of an olefin to the alkylidene moiety of $[FeCp(CO)_2(=CHR)]^+$ is in the range 9.7−17.7 kcal/mol. Therefore, this pathway is considered to be less likely in the case of L = CO. On the other hand, with L = PH_3 (especially with bulky phosphines) dissociation will be much more accessible and the alternative metallacyclobutane pathway may become feasible. In both cases, once the free coordination site is created, coordination of ethylene leads readily to the formation of the coordinatively unsaturated metallacyclobutadiene $[FeCp(CO)(CH(Me)CH_2CH_2)]^+$ (**E^{Me}**), which in the presence of L forms the more stable 18e metallacycle $[FeCp(CO)(L)(CH(Me)CH_2CH_2)]^+$ (**F^{Me}**).

Conclusions

The ethylidene and propylidene transfer to olefins as well as the intramolecular alkylidene-to-olefin isomerization of the cationic alkylidene complexes $[FeCp(CO)(L)(=CHR)]^+$ (L = CO, PH_3; R = Me, Et) are orbital- rather than charge-controlled reactions. The LUMO of the alkylidene complexes is essentially centered at the carbene carbon atom and, in contrast to common beliefs, bears no positive charge on the carbene carbon atom (unlike carbenium ions). The NPA charge of the alkylidene complexes is −0.02, which is more or less the same charge as found for the free ethylidene molecule. Likewise, the ^{13}C spectra of complexes $[FeCp(CO)_2(=CHMe)]^+$ and the free CHMe are very similar, being

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(14) Hammond, G. S. *J. Am. Chem. Soc.* **1954**, *77*, 334.

419.0 and 414.9 ppm, respectively, while the corresponding carbenium ion $[HCHMe]^+$ exhibits a characteristic resonance at 315 ppm.

It was found that both processes are thermodynamically very favorable independent of the co-ligand L or the substituent R. Kinetically, the ethylidene transfer reaction is only slightly favored over the ethylidene isomerization, and these processes are thus strongly competitive with one another. In the case of the propylidene complex this trend is reversed and intramolecular rearrangement of the propylidene moiety is the dominating process. Therefore, iron complexes of the type $[FeCp(CO)(L)({=}CHR)]^+$ with R = alkyl groups, especially if they contain γ-C−H bonds, are not good candidates for alkylidene transfer reactions. Most promising in this regard may thus be benzylidene complexes, as has been demonstrated by Brookhart and co-workers.[1]

Experimental Section

Computational Details. All calculations were performed using the Gaussian98 software package.[7] The geometries of the model complexes and the transition states were optimized at the B3LYP level[15] with the Stuttgart/Dresden ECP (SDD) basis set to describe the electrons of the Fe atom.[16,17] For all other atoms the 6-31G(d,p) basis set was employed.[18] Transition state optimizations were performed with the synchronous transit-guided quasi-Newton method (STQN) developed by Schlegel et al.[19] Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. The vibrational eigenvectors corresponding to the reaction coordinate (with imaginary frequency) of all transition states were visually checked to confirm the connectivity of transition states with the reactants and the products. No IRC calculations were performed. All geometries were optimized without symmetry constraints. A natural population analysis (NPA)[20] and the resulting Wiberg indices[21] were used for a detailed study of the electronic structure and bonding of the optimized species.

^{13}C chemical shifts were calculated at the B3LYP level of theory for the optimized structures of $[FeCp(CO)_2({=}CHMe)]^+$, $[FeCp(CO)_2({=}CHEt)]^+$, and $[FeCp(CO)(PH_3)({=}CHMe)]^+$ using the gauge-independent atomic orbital (GIAO) method in Gaussian 98 with the same basis sets as above. Chemical shifts are given with respect to $Si(Me_3)_4$ (TMS) at the same computational level.

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