

Metal and Ancillary Ligand Structural Effects on Ethylene Insertion Processes at Cationic Group 4 Centers. A Systematic, Comparative Quantum Chemical Investigation at Various *ab Initio* Levels

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Ethylene insertion into the metal–methyl bonds of group 4 (Ti, Zr) $(C_5H_5)_2MCH_3^+$ and $H_2Si(C_5H_4)(^tBuN)MCH_3^+$ catalyst cations has been investigated at the *ab initio* level, employing DZV- and DZP-quality basis sets together with Moller–Plesset perturbative and coupled-cluster single-double excitation wave function expansions. All reactions are found to proceed from reactants to products via intermediate π -complexes and subsequent Cossee–Arlman four-center transition state structures. Enthalpic barriers for the insertion step strongly depend on the nature of the ancillary ligand and metal, with ΔH^\ddagger increasing in the order $(C_5H_5)_2TiCH_3^+ < (C_5H_5)_2ZrCH_3^+ \approx H_2Si(C_5H_4)(^tBuN)TiCH_3^+ < H_2Si(C_5H_4)(^tBuN)-ZrCH_3^+$. Furthermore, metallocene $H_2Si <$ bridging has the effect of increasing the electrophilicity toward ethylene. The observed ethylene activation/insertion structural and energetic trends may be rationalized using qualitative electronic structure arguments, ancillary ligand steric hindrance, and metal ionic radius. Electron correlation effects are found in all cases to play a crucial role in predicting reaction energetics. Reasonable, incremental convergence in computed energies is obtained for Zr systems and for the $H_2Si(C_5H_4)(^tBuN)TiCH_3^+$ cation upon increasing the calculational level (MP2 \rightarrow MP3 \rightarrow MP4-SDQ \rightarrow CCSD). In contrast, fluctuations in results are found for the $(C_5H_5)_2TiCH_3^+$ cations, indicating the desirability of high-level calculations.

Introduction

Considerable scientific interest in α -olefin polymerization processes is currently fueled by the desire to rationally design and produce new generations of group 4 (or other transition metal) complex + cocatalyst combinations displaying improved activity, productivity, selectivity, and thermal stability.¹ Both bis-cyclopentadienyl² and mono-cyclopentadienyl-amido (generally known as constrained geometry catalysts, CGC)³ single-site catalysts have been extensively studied by varying the metal, ancillary ligand substituents, cocatalyst, reaction solvent, and other operating parameters. From

these, a considerable body of empirical structure–activity correlations has begun to emerge.^{1,4} Nevertheless, a quantitative understanding of the relationship between the structure of the active site ion pairs and catalytic properties is far from realization.^{1–4} In this regard, theoretical studies have been of great relevance to the experimental community in understanding basic polymerization mechanisms and in rationalizing trends

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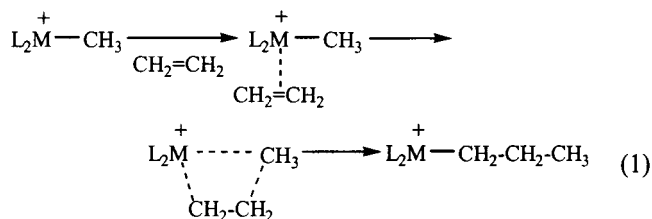
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in kinetics and selectivities. A number of systems have now been investigated theoretically using the naked catalyst cation approach.^{5–9} However, only recently have studies appeared in which counteranion and solvent effects are explicitly included, and these show that both counteranion and solvent strongly influence elementary reactions in single-site polymerization processes, in agreement with experiment.^{10–12} While the cation–anion pairs are generally strongly interacting, it is also found that increasing the solvent dielectric constant and lengthening the growing polymer chain substantially weakens the cation–anion interaction and that the active center thereby acquires some characteristics of the naked cation.^{10a} Therefore, high-level studies of naked cations are of relevance in partitioning effects due

to the active cationic center versus those attributable to the counteranion and solvent. Although it is widely accepted that such catalytic processes involve Cossee–Arlman scenarios (eq 1), quantitative issues associated with the existence of intermediate π -complexes and with details of insertion barriers remain unresolved and of great interest.^{1,13}



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The only experimental studies of truly naked cations and their reactions with olefins have been by mass spectrometric techniques in the gas phase.¹⁴ Among the theoretical studies of naked cations, substantial efforts have been made at the ab initio level. Thus, Morokuma et al.^{6a,b,e} used ab initio and molecular mechanics methodologies to analyze elementary reactions of ethylene insertion into $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{MCH}_3^+$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) and $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{fluorenyl})\text{ZrCH}_3^+$ complexes. Goddard et al.^{6d} reported on the relationships between structural variations and tacticity control for the $(\text{C}_5\text{H}_5)_2\text{TiCH}_3^+$ model cation. Density functional (DFT) methodologies have been similarly applied to several aspects of olefin insertion reactions into $(\text{C}_5\text{H}_5)_2\text{TiR}^+$ ($\text{R} = \text{CH}_3$ and C_2H_5), Cp_2ZrR^+ ($\text{Cp} =$ variously substituted cyclopentadienyl ring; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9,$ and C_5H_{11}), $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCH}_3^+$, $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)\text{NHMCH}_3^+$ ($\text{M} = \text{Ti}, \text{Zr},$ and Hf), and $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{HN})\text{TiR}^+$ ($\text{R} = \text{C}_2\text{H}_5$ and C_3H_7) complexes.^{6c,7,8} Brintzinger et al.⁹ have also focused on interesting aspects of olefin insertion at $(\text{C}_5\text{H}_5)_2\text{ZrR}^+$, while Ahlrichs et al.^{6c} stressed the importance of dynamic electron correlation at the ab initio MP2 and DFT levels to predict olefin insertion pathways in complexes containing first-row transition metals. As the lowest energy pathway, they identified a direct insertion process without an intermediate π -complex or energetic insertion barrier in $(\text{C}_5\text{H}_5)_2\text{TiCH}_3^+$. Similar conclusions in terms of negligible π -complex formation and negligible energy barrier to insertion have been reached by Car–Parrinello DFT methods for the case of insertion at $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3^+$.^{8d}

The conclusions to emerge from the breadth of the recent literature are that there are significant discrepancies, even at a qualitative level, concerning the energetics of olefin insertion at metallocene $(\text{C}_5\text{H}_5)_2\text{MCH}_3^+$ cations and that no theoretical ab initio studies are available for mono-cyclopentadienyl-amido Zr cations.^{5–9,10b} Importantly, the published conclusions are not uniform in terms of energetic trends versus the level

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of theory adopted. Therefore, certain requirements become mandatory to reliably deal with any detailed theoretical modeling of organogroup 4 catalysts. The highest possible level of theory, large basis sets, and methods to account for high-order electron correlation are required in the case of catalysts containing transition metal (especially first-row transition metal) reactive centers and nearly degenerate transition states. Nevertheless, the large number of atoms in “real world” catalytic systems (cation–anion–solvent) often precludes such very high-level calculations, and studies on selected simpler systems using accurate formalisms (MP3, MP4, CCSD, etc.) should be useful to calibrate more tractable single reference MP2 calculations with moderate basis sets.¹⁰ In this context, we report here state-of-the-art ab initio level calculations on ethylene activation and insertion reactions involving $(C_5H_5)_2MCH_3^+$ and $H_2Si(C_5H_4)(^tBuN)MCH_3^+$ naked cations ($M = Ti$ and Zr). The goals of the present investigation then are the following:

(1) Collect uniform computational data on catalytic reactions promoted by the $(C_5H_5)_2MCH_3^+$ and $H_2Si(C_5H_4)(^tBuN)MCH_3^+$ cation series. This information when combined with data on real, solvated cation–anion systems should render feasible a reliable partitioning of effects due to the metal active site versus those due to the counteranion/solvent;

(2) Compare and contrast data on model systems using CCSD, MP4, and MP3 wave function expansions and/or double- ζ plus polarization function basis sets to calibrate calculations on “real” catalysts using MP2 wave functions and simpler double- ζ quality basis sets;

(3) Compare and contrast ab initio structural and energetic data on $(C_5H_5)_2MCH_3^+$ and $H_2Si(C_5H_4)(^tBuN)MCH_3^+$ with previously reported data;

(4) Uniformly analyze structural and electronic factors that ultimately govern olefin insertion energetics in the present, closely related metallocene and CGC catalysts;

(5) Compare and contrast MP3, MP4, and CCSD calculations with our earlier MP2 results^{10b} on $H_2Si(C_5H_4)(^tBuN)TiCH_3^+$ with data on the related $(C_5H_5)_2MCH_3^+$ and $H_2Si(C_5H_4)(^tBuN)ZrCH_3^+$ cations;

(6) Establish a broad, consistent database of naked cation molecular and electronic structures and olefin reaction coordinates to later compare with systems containing the counteranion;

(7) Present the results in a manner informative to both the theoretical and experimental communities.

Computational Details

The effective core potentials (ECP) of Hay and Wadt,¹⁵ which explicitly treat semicore s and p electrons and a basis set contracted as [541/511/41] and [541/521/31], were used for the Ti and Zr atoms, respectively. The standard all-electron 6-31G basis was used for the remaining atoms.¹⁶ This basis set will be indicated as DZV. Cartesian 6 d-type and 10 f-type basis functions have been used. Geometry optimization used analytical gradient techniques within the restricted Hartree–Fock (HF) formalism, and the threshold adopted for the convergence

was 0.0004 Hartree/Bohr on the gradient. No local symmetry and no geometrical constraints were imposed in optimization. The “distinguished reaction coordinate procedure” (also known as the linear transit method) was used for determining the transition state geometry in the ethylene insertion process, and the reaction coordinate was associated with the vector along the newly formed C–C σ -bond ($TiCH_3 \cdots CH_2=CH_2$).

Correlation effects were evaluated adopting MP2, MP3, MP4-SDQ, and coupled-cluster single and double excitation (CCSD) wave functions where all valence electrons, including the semicore metal s and p, are correlated. The use of CCSD procedures within a single reference configuration approach can, in principle, partially resolve the degeneracy problem associated with the transition state structure.¹⁷ To investigate the reliability of the DZV basis set and electron correlation on computed energies and geometries, a more flexible basis set (DZP) and MP2 geometry optimization were adopted to study ethylene activation/insertion at the $(C_5H_5)_2TiCH_3^+$ and $H_2Si(C_5H_4)(^tBuN)TiCH_3^+$ species. Two sets of test calculations were performed: (i) geometry optimization at the MP2 level using the DZV basis set (DZV/MP2/MP2) and (ii) geometry optimization at the MP2 level using the DZP basis set (DZP/MP2/MP2). In the DZP basis set, the all-electron 6-31G basis, included with a set of “f” polarization ($\alpha = 0.8$) functions, was adopted for the Ti atom.¹⁸ The 6-31G basis set on all carbon atoms was complemented with a set of “d” polarization functions ($\alpha = 0.8$), while the basis for the hydrogen atoms of reactive groups (CH_3 and CH_2CH_2) also included a set of “p” polarization functions ($\alpha = 1.1$). The DZP basis set is the standard 6-31G* in which a set of “p” polarization functions is added to hydrogen atoms of the reactive centers.

All the calculations were performed using the HONDO 95.3¹⁹ and G94 codes²⁰ on IBM-SP and Origin 2000 systems.

Results and Discussion

Molecular Structures of Naked Cations. The $H_2Si(C_5H_4)(^tBuN)ZrCH_3^+$ cation adopts a pseudo-trigonal pyramidal arrangement around the metal center (Figure 1). The Zr–CH₃ vector is displaced by an angle θ from the $Cp_{\text{centr}}-Zr-N$ plane ($\theta = 51.4^\circ$ at the HF level, $\theta \sim 60^\circ$ at the MP2 level; Figures 1, 2). The structure with a pseudo-planar-trigonal arrangement (C_s symmetry) lies slightly higher in energy (0.5 and 2.8 kcal/mol at HF and MP2 levels, respectively). The potential energy profile describing bending of the Zr–CH₃ vector from the pseudo-planar C_s structure (Figure 2) exhibits two symmetric minima at $\theta = 60^\circ$ and -60° (at the MP2 level) separated by a maximum of ~ 2.8 kcal/mol. This contrasts with the low-energy “coplanar” geometry found for the homologous $H_2Si(C_5H_4)(^tBuN)-TiCH_3^+$ cation having a single minimum with the Ti–CH₃ bond lying in the $Cp_{\text{centr}}-Ti-N$ plane (Figures 1, 2).^{10b}

Orbital arguments provide a convincing explanation for the flexibility of the M–CH₃ bond vector in CGC cations as well as in $(C_5H_5)_2MCH_3^+$ complexes. In both

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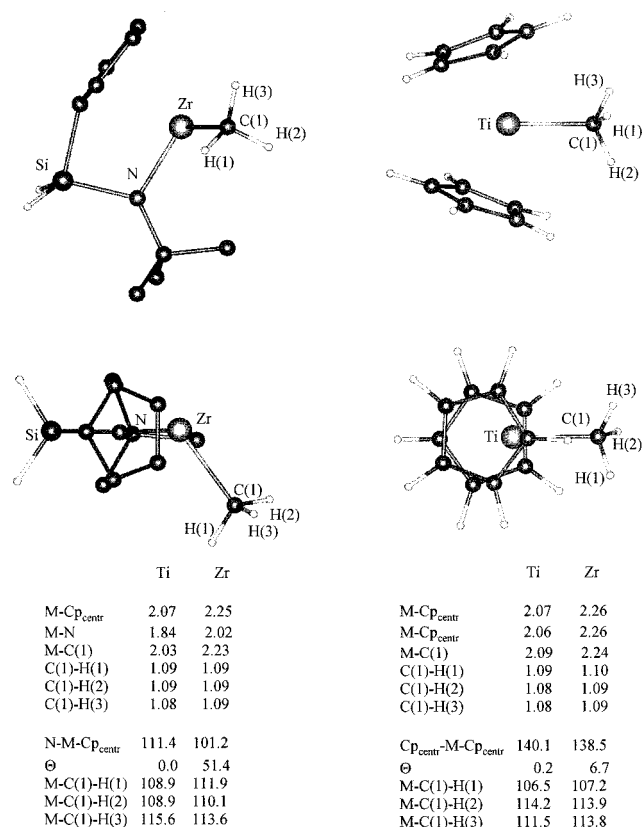


Figure 1. HF optimized structures of $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(^t\text{BuN})\text{ZrCH}_3^+$ and $(\text{C}_5\text{H}_5)_2\text{TiCH}_3^+$ methyl cations (distances in Å, angles in deg). Hydrogen atoms on the $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(^t\text{BuN})$ ligand have been omitted for ease of viewing. \emptyset defines the angle between the plane $\text{Cp}_{\text{centr}}\text{-M-N}$ (in CGC systems) or $\text{Cp}_{\text{centr}}\text{-M-Cp}_{\text{centr}}$ (in metallocenes) and the M-CH_3 vector.

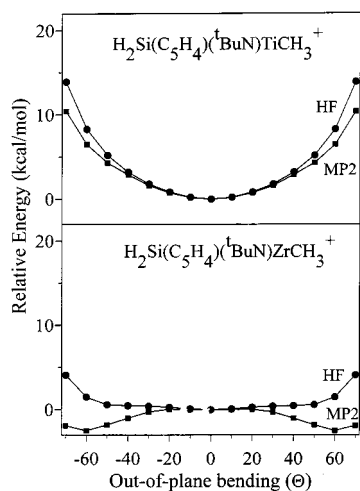
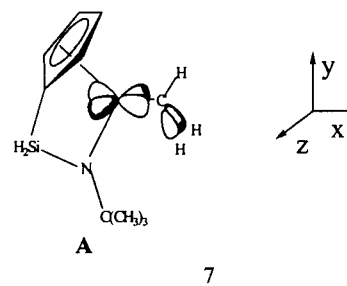


Figure 2. Potential energy profile for out of the $\text{Cp}_{\text{centr}}\text{-M-N}$ plane bending of the M-CH_3 vector in $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(^t\text{BuN})\text{MCH}_3^+$ ($\text{M} = \text{Ti}$ and Zr) complexes.

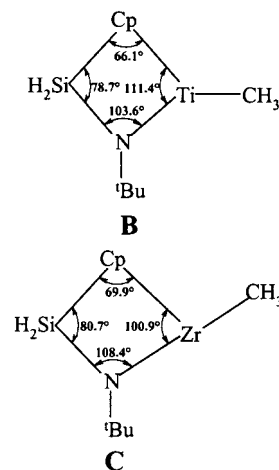
systems, the two $\sigma_{\text{M-CH}_3}$ bonds of the neutral dimethyl precursor predominantly involve the d_{xz} (out-of-phase combination) and $d_{x^2-y^2}$ (in-phase combination) metal orbitals. Upon methide abstraction by a Lewis acid cocatalyst such as $\text{B}(\text{C}_6\text{F}_5)_3$,^{1a,10} a vacant orbital site is created at the metal center. The remaining CH_3 group can interact either with the $d_{x^2-y^2}$ metal orbital, thus resulting in a trigonal planar structure (C_s symmetry), or with the d_{xz} metal orbital, leading to a pyramidal

structure. However, α -agostic interactions involving methyl $\sigma_{\text{C-H}}$ bonds and vacant metal orbitals of appropriate symmetry can be effective in flattening the displacement potential energy surface in these naked cations. In the C_s -symmetric Ti-CGC cation, the $\sigma_{\text{Ti-CH}_3}$ bond involves the $\text{Ti } d_{x^2-y^2}$ orbital, while the d_{xz} orbital acts as an electron acceptor site for α -agostic interactions (**A**) with the localized C(1)-H(1) and C(1)-H(2) bonds. These electronic structure features account for the longer bond lengths (0.01 Å with respect to C(1)-H(3)) as well as the Ti-C(1)-H(1) and Ti-C(1)-H(2) bond angle distortion (7° with respect Ti-C(1)-H(3)). In the bent Zr homologue, the CH_3 group has nearly exact local C_3 symmetry, hence negligible α -agostic interactions. This is in agreement with DFT-BP86 trends observed for $(\text{CH}_3)_2\text{MC}_2\text{H}_5^+$, $(\text{NH}_2)_2\text{MC}_2\text{H}_5^+$, and $(\text{OH})_2\text{MC}_2\text{H}_5^+$ model complexes which indicate dimin-



ishing agostic interactions as one moves down the Ti-triad because the empty d orbital energies of the $\text{L}_2\text{MC}_2\text{H}_5^+$ fragment rise as the triad is descended.^{7c}

The computed $\text{CGC Zr-Cp}_{\text{centr}}$, Zr-N , and Zr-C(1)H_3 distances are ~ 0.18 Å longer than those found in the homologous Ti cation, in qualitative agreement with differences in ionic radii. Furthermore, the bond angles



and bond lengths associated with the $\text{H}_2\text{Si}<$ moiety of the planar pseudo-four-membered ring defined by the $\text{Cp}_{\text{centr}}\text{-Si-N-M}$ vertices are slightly perturbed on passing from the Ti to Zr catalysts (**B**, **C**). Elongation of the $\text{Zr-Cp}_{\text{centr}}$ and Zr-N bonds compresses the $\text{Cp}_{\text{centr}}\text{-Zr-N}$ angle and simultaneously expands both the Si-N-Zr and $\text{Si-Cp}_{\text{centr}}\text{-Zr}$ angles. This observation agrees well with experimental diffraction data reported for $(\text{CH}_3)_2\text{Si}[(\text{CH}_3)_4\text{C}_5](^t\text{BuN})\text{MCl}_2$ complexes, where $\text{Cp}_{\text{centr}}\text{-M-N}$ angles of 107.6° and 102.0° have been reported for Ti and Zr complexes, respectively.^{3f} It therefore transpires that the different structural

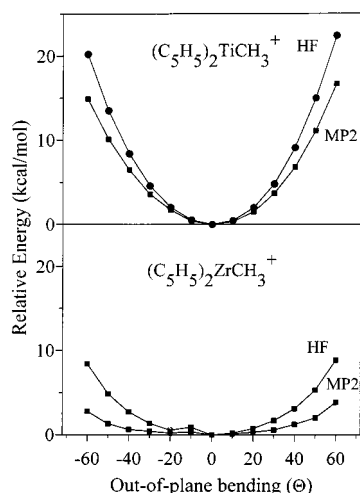
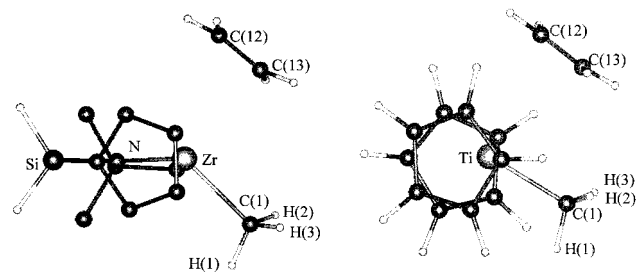
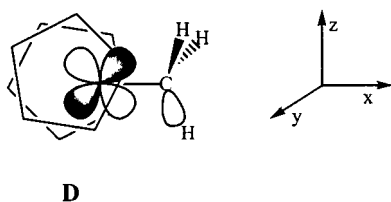


Figure 3. Potential energy profile for out of the $\text{Cp}_{\text{centr}}-\text{M}-\text{Cp}_{\text{centr}}$ plane bending of the $\text{M}-\text{CH}_3$ vector in $(\text{C}_5\text{H}_5)_2\text{MCH}_3^+$ ($\text{M} = \text{Ti}$ and Zr) complexes.

potential energy profiles (hence different minimum energy equilibrium structures) observed on passing from the Ti to Zr CGC cation are principally due to the reduction of the $\text{Cp}_{\text{centr}}-\text{M}-\text{N}$ angle and to the increased $\text{M}-\text{Cp}_{\text{centr}}$ and $\text{M}-\text{N}$ bond lengths. Both of these features relax crowding in the $\text{M}-\text{CH}_3$ region, thereby reducing interligand repulsive interactions upon $\text{M}-\text{CH}_3$ bending. Note that planar tricoordinate complexes are expected to be more stable in a simple VSEPR description. Similar effects have been reported at the GVB-CI ab initio level for $(\text{C}_5\text{H}_5)_2\text{TiCH}_3^+$ upon constraining the $\text{Cp}_{\text{centr}}-\text{Ti}-\text{Cp}_{\text{centr}}$ angle. A single energetic minimum is found for a soft ($\text{Cp}_{\text{centr}}-\text{Ti}-\text{Cp}_{\text{centr}} = 132.6^\circ$) out-of-plane bending process (~ 4 kcal/mol for a 50° bending), and three energetically close minima, located at 0° , 50° , and -30° , are observed upon compressing $\text{Cp}_{\text{centr}}-\text{Ti}-\text{Cp}_{\text{centr}}$ to 118° .^{6d}

In both unconstrained $(\text{C}_5\text{H}_5)_2\text{MCH}_3^+$ cations ($\text{M} = \text{Ti}, \text{Zr}$), the most stable computed structures (Figure 1) possess pseudo-trigonal planar geometries (the $\text{M}-\text{CH}_3$



| | Ti | Zr | | Ti | Zr |
|--|-------|-------|--|-------|-------|
| $\text{M}-\text{Cp}_{\text{centr}}$ | 2.11 | 2.27 | $\text{M}-\text{Cp}_{\text{centr}}$ | 2.10 | 2.28 |
| $\text{M}-\text{N}$ | 1.85 | 2.04 | $\text{M}-\text{Cp}_{\text{centr}}$ | 2.10 | 2.28 |
| $\text{M}-\text{C}(1)$ | 2.05 | 2.24 | $\text{M}-\text{C}(1)$ | 2.10 | 2.26 |
| $\text{M}-\text{C}(12)$ | 2.90 | 3.06 | $\text{M}-\text{C}(12)$ | 3.07 | 3.04 |
| $\text{M}-\text{C}(13)$ | 2.64 | 2.81 | $\text{M}-\text{C}(13)$ | 3.00 | 2.97 |
| $\text{C}(1)-\text{C}(13)$ | 3.22 | 3.78 | $\text{C}(1)-\text{C}(13)$ | 3.18 | 3.33 |
| $\text{C}(12)-\text{C}(13)$ | 1.34 | 1.34 | $\text{C}(12)-\text{C}(13)$ | 1.33 | 1.34 |
| $\text{C}(1)-\text{H}(1)$ | 1.09 | 1.09 | $\text{C}(1)-\text{H}(1)$ | 1.09 | 1.09 |
| $\text{C}(1)-\text{H}(2)$ | 1.09 | 1.09 | $\text{C}(1)-\text{H}(2)$ | 1.08 | 1.09 |
| $\text{C}(1)-\text{H}(3)$ | 1.09 | 1.09 | $\text{C}(1)-\text{H}(3)$ | 1.08 | 1.09 |
| $\text{N}-\text{M}-\text{Cp}_{\text{centr}}$ | 110.1 | 101.6 | $\text{Cp}_{\text{centr}}-\text{M}-\text{Cp}_{\text{centr}}$ | 135.3 | 133.1 |
| θ | 45.1 | 49.2 | θ | 40.3 | 45.8 |
| $\text{M}-\text{C}(12)-\text{C}(13)$ | 65.2 | 66.7 | $\text{M}-\text{C}(12)-\text{C}(13)$ | 74.5 | 74.3 |
| $\text{M}-\text{C}(1)-\text{H}(1)$ | 111.1 | 111.5 | $\text{M}-\text{C}(1)-\text{H}(1)$ | 109.0 | 110.4 |
| $\text{M}-\text{C}(1)-\text{H}(2)$ | 109.7 | 111.0 | $\text{M}-\text{C}(1)-\text{H}(2)$ | 111.2 | 112.0 |
| $\text{M}-\text{C}(1)-\text{H}(3)$ | 111.5 | 113.2 | $\text{M}-\text{C}(1)-\text{H}(3)$ | 111.0 | 111.9 |
| Φ | 4.0 | 0.4 | Φ | 16.3 | 16.2 |

Figure 4. HF optimized structures of $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{BuN})-\text{ZrCH}_3(\text{C}_2\text{H}_4)^+$ and $(\text{C}_5\text{H}_5)_2\text{TiCH}_3(\text{C}_2\text{H}_4)^+$ π -complexes (distances in Å, angles in deg). Hydrogen atoms on the $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{BuN})$ ligand have been omitted for ease of viewing. Φ indicates the $\text{M}-\text{C}(12)-\text{C}(13)-\text{C}(1)$ torsional angle.

metallocenes, with bond lengths and angles suggesting that only the $\text{C}(1)-\text{H}(1)$ bond is involved in an α -agostic interaction (**D**). This $\text{M}-\text{CH}_3$ spatial arrangement is different from that found in both $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{BuN})-\text{MCH}_3^+$ complexes and resembles the spatial arrangement of the transition state structure for the olefin insertion step. This aspect is of relevance to the reaction pathway for olefin insertion, as will be analyzed in a following section. Similar equilibrium geometries have been reported at the ab initio level for $(\text{C}_5\text{H}_5)_2\text{TiCH}_3^+$ and $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{MCH}_3^+$ ⁶ and at the DFT level for $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{HN})\text{ZrCH}_3^+$ cations^{7j-1} with only minor differences, possibly due either to differences in basis set or computational method. In contrast, different results have been reported at the DFT level for the $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3^+$, $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCH}_3^+$, and $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{HN})-\text{TiCH}_3^+$ cations,^{7j-1} with pyramidal arrangements found at the metal ($\theta = 45.8^\circ$, 53° , and 61.2° , respectively). Although the DFT methodology at both the LDA and BP86 levels adopted by Ziegler et al.⁷ generally identifies pyramidal structures for L_2MCH_3^+ species, note that the greater tendency of Zr derivatives toward pyramidal structures found in the present study is in agreement with a similar preference for pyramidal conformations observed for $(\text{CH}_3)_2\text{MCH}_3^+$, $(\text{NH}_2)_2\text{MCH}_3^+$, and $(\text{OH})_2\text{MCH}_3^+$ model complexes as one moves down the group 4 triad.^{7c}

Activated Olefin Complexes. The geometry and relevant metrical data for the intermediate CGC π -olefin complex $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{BuN})\text{ZrCH}_3\cdot\text{C}_2\text{H}_4^+$ along the insertion reaction coordinate are summarized in Figure 4 and compared with those of the Ti homologue. In both cases, the $\text{M}-\text{CH}_3$ bonds are located $\sim 40^\circ$ out the $\text{Cp}_{\text{centr}}-\text{M}-\text{N}$ plane. Thus, one metal site is occupied by the CH_3 group while the C_2H_4 engages the second site. The

vector lies a few degrees out of the $\text{Cp}_{\text{centr}}-\text{M}-\text{Cp}_{\text{centr}}$ plane), and the potential energy surfaces for $\text{M}-\text{CH}_3$ bending (Figure 3) exhibit a single minimum, although a somewhat flatter profile is apparent for the $\text{M} = \text{Zr}$ cation. Three noteworthy issues are evident upon inspecting Figures 1, 2, and 3: (i) flatter potential surfaces are always obtained at the MP2 level, (ii) Zr cations are more flexible than the Ti homologues with regard to $\text{M}-\text{CH}_3$ bending, and (iii) less sterically crowded ligand arrays, as found in CGC ligation, definitely favor bent Zr cation structures. Differences in agostic interactions upon changing from symmetrical metallocenes to CGC cations can be understood by considering the spatial arrangements of the $\text{C}(1)\text{H}_3$ groups. Similar arrangements are found in this study for both Ti and Zr

Table 1. π -Complexation, Insertion, and Product Formation Energies (kcal/mol) Computed at Various Levels for Ethylene Insertion into $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})\text{MCH}_3^+$ and $(\text{C}_5\text{H}_5)_2\text{MCH}_3^+$ Complexes (M = Ti with Zr values in parentheses)

| | π -complex | energy barrier | γ -agostic product | β -agostic product | β -agostic product |
|--|----------------|----------------|---------------------------|--------------------------|--------------------------|
| $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})\text{MCH}_3^+$ | | | | | |
| RHF/RHF | -18.4 (-21.4) | 18.1 (22.2) | -20.7 (-19.5) | -23.8 (-21.3) | -23.0 (-21.0) |
| MP2/RHF | -29.7 (-29.1) | 7.9 (14.6) | -33.8 (-29.2) | -33.7 (-28.6) | -32.8 (-28.4) |
| MP3/RHF | -27.4 (-28.0) | 12.2 (16.9) | -32.0 (-27.8) | | |
| MP4SDQ/RHF | -28.1 (-27.3) | 11.2 (17.0) | -31.3 (-26.7) | | |
| CCSD/RHF | -26.9 (-26.8) | 11.6 (17.0) | -30.3 (-25.8) | | |
| $(\text{C}_5\text{H}_5)_2\text{MCH}_3^+$ | | | | | |
| RHF/RHF | -5.7 (-15.0) | 19.5 (19.7) | -15.5 (-18.1) | -21.3 (-22.6) | -21.0 (-22.5) |
| MP2/RHF | -22.0 (-29.9) | 2.4 (8.0) | -23.6 (-31.6) | -37.0 (-37.7) | -36.3 (-37.2) |
| MP3/RHF | -13.5 (-26.1) | 13.0 (12.2) | -21.7 (-28.6) | | |
| MP4SDQ/RHF | -21.7 (-26.5) | 5.1 (11.3) | -22.0 (-28.4) | | |
| CCSD/RHF | -15.5 (-25.4) | 9.9 (11.7) | -20.3 (-27.1) | | |
| $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3^+$ | | | | | |
| DFT ^a | (-22.9) | (0.7) | (-30.6) | (-35.8) | |
| DFT ^b | (-14.7) | (6.2) | (-19.1) | | |
| $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{HN})\text{MCH}_3^+$ | | | | | |
| DFT ^a | -20.8 (-24.2) | 3.8 (5.1) | -33.6 (-32.4) | | |
| $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCH}_3^+$ | | | | | |
| DFT ^a | (-26.0) | (1.0) | (-32.3) | | |
| $(\text{C}_5\text{H}_5)_2\text{TiCH}_3^+$ | | | | | |
| RHF/RHF ^c | -5.3 | 17.8 | -21.7 | | |
| MP2/RHF ^c | -23.7 | no barrier | -32.3 | | |
| MP2/MP2 ^c | | no barrier | -45.1 | | |
| $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{MCH}_3^+$ | | | | | |
| RHF/RHF ^d | -13.0 (-19.0) | 14.3 (16.6) | -22.8 (-23.8) | -29.2 (-26.8) | |
| MP2/RHF ^d | -28.6 (-33.4) | 1.3 (6.0) | -34.7 (-38.4) | -43.1 (-40.9) | |
| MP3/RHF ^d | -20.9 (-29.4) | 10.9 (9.9) | -30.8 (-34.6) | -37.4 (-36.9) | |
| MP4(SDQ)/RHF ^d | -27.6 (-30.1) | 2.9 (9.2) | -32.6 (-34.6) | -39.7 (-36.6) | |
| RQCISD/RHF ^d | -21.9 (-29.1) | 7.1 (9.4) | -29.3 (-33.4) | -35.4 (-35.4) | |

^a References 7j–l. ^b References 8b,c. ^c Reference 6c. ^d References 6b,e.

differing M–C(12) and M–C(13) metal–ethylene contacts are indicative of asymmetric bonding induced by repulsive interactions with the Cp ring. Both Zr–C(12) and Zr–C(13) are ~ 0.16 Å longer than in the corresponding Ti homologue due to the differing metal ionic radii. In the $(\text{C}_5\text{H}_5)_2\text{MCH}_3\cdot\text{C}_2\text{H}_4^+$ complexes, the M–CH₃ vector is similarly displaced $\sim 40^\circ$ out of the Cp_{centr}–M–Cp_{centr} plane, thus favoring the ethylene coordination. The M–C₂H₄ bond distances are slightly longer than in the corresponding CGC complexes because of the greater ligand congestion about the metal center in the $(\text{C}_5\text{H}_5)_2\text{MCH}_3\cdot\text{C}_2\text{H}_4^+$ structures. The reduced strength (vs CGCM) of C₂H₄ coordination is also evident in the smaller C(12)=C(13) bond elongation (~ 0.02 Å for the CGC complex vs ~ 0.01 Å for the metallocene π -complex) since this metrical parameter is an index of the ethylene-to-metal dative donation strength. Again, the stronger ethylene-to-metal coordination in the CGC systems is in accord with the reduced crowding at the metal center and, hence, with the greater reactivity of the CGC system toward long chain α -olefin enchainment as well as ethylene copolymerization with sterically encumbered comonomers.³ Steric effects are similarly responsible for the longer metal–ethylene bond distances found in the $(\text{C}_5\text{H}_5)_2\text{TiCH}_3\cdot\text{C}_2\text{H}_4^+$ π -complex compared to the Zr homologue, despite the smaller Ti ionic radius. In fact, the short Ti–Cp bond lengths congest the ligation environment and preclude stronger ethylene coordination.^{12e} All these structural features reflect the computed trends in ethylene complexation energies (Table 1). In fact, almost identical energies are found for both CGC complexes, while a less exothermic reaction (~ 1 kcal/mol) is found in forming the $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3\cdot\text{C}_2\text{H}_4^+$ complex, and a further, predictable reduc-

tion (~ 8 kcal/mol) is observed for sterically hindered $(\text{C}_5\text{H}_5)_2\text{TiCH}_3\cdot\text{C}_2\text{H}_4^+$. These results agree well with data reported for a large series of model complexes.⁷ Thus, there is evidence that the strength of ethylene coordination depends on steric constraints at the metal site and increases almost monotonically in the cases of less encumbered systems ($(\text{C}_5\text{H}_5)_2\text{TiR}^+ < (\text{C}_5\text{H}_5)_2\text{ZrR}^+ < \text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{HN})\text{TiR}^+ < \text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{HN})\text{ZrR}^+$) despite the lower energies of empty metal d orbitals in Ti complexes versus those of Zr.⁷

In all of the present cationic π -olefin complexes, the other metal–ligand bond lengths are slightly longer ($\Delta(\text{M}–\text{Cp}) \approx +0.03$ Å, $\Delta(\text{M}–\text{N}) \approx +0.02$ Å, and $\Delta(\text{M}–\text{C}(1)) \approx +0.01$ Å) than in the corresponding naked cations, reflecting the greater molar volume, the reduced electron deficiency at the metal center, and the greater intergroup nonbonded repulsions. Finally, the methyl C(1)–H bond lengths and M–C(1)–H bond angles in the present π -olefin complexes are close to those expected for a locally C_{3v} symmetric M–C(1)H₃ group, thus indicating diminished α -agostic interactions.

Trends in geometrical parameters similar to the present were reported in ab initio studies of $(\text{C}_5\text{H}_5)_2\text{TiCH}_3^+$ ethylene complexes at the HF level.^{6c} However, shorter metal-to-ethylene contacts (~ 0.16 Å) than the present results were found for the corresponding $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{MCH}_3^+$ (M = Ti, Zr) π -olefin complexes.^{6b,e} The difference is likely due to the different basis sets used and/or to the $\text{H}_2\text{Si} <$ bridging which contracts the Cp_{centr}–M–Cp_{centr} angle and leaves increased space for ethylene coordination. Shorter (~ 0.3 Å) metal-to-ethylene contacts have been reported at the DFT-LDA level for both the $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{NH})\text{MCH}_3^+$ and $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3^+$

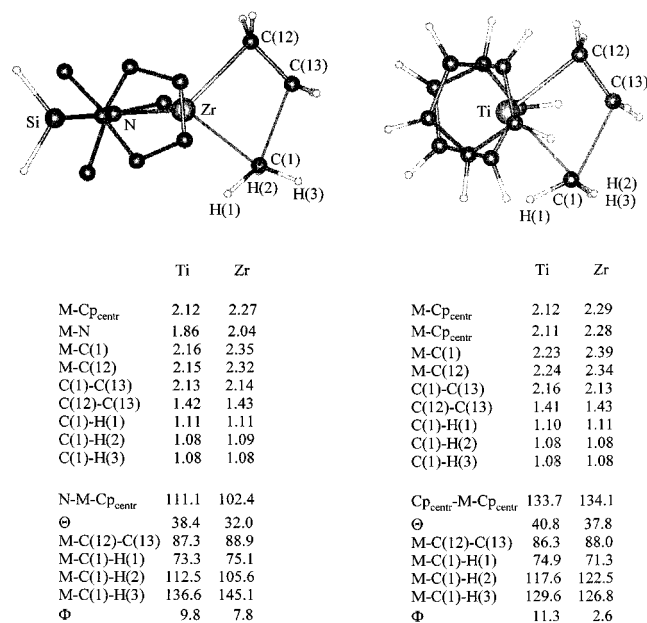


Figure 5. HF optimized structures of $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})\text{-Zr}(\text{C}_2\text{H}_4)\text{CH}_3^+$ and $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_2\text{H}_4)\text{CH}_3^+$ ethylene insertion transition states (distances in Å, angles in deg). Hydrogen atoms on the $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})$ ligand have been omitted for ease of viewing. \emptyset defines the angle between the plane $\text{Cp}_{\text{centr}}\text{-M-N}$ (in CGC systems) or $\text{Cp}_{\text{centr}}\text{-M-Cp}_{\text{centr}}$ (in metallocenes) and the $\text{M-C}(12)$ vector.

model π -olefin complexes, probably a consequence of the different computational approach.^{7j-1}

Olefin Insertion Transition State. The transition state for the ethylene insertion into CGCZr-CH_3^+ is found to involve a highly distorted $\text{Zr-C}(1)\text{H}_3$ conformation (Figure 5) compared to both the naked methyl cation and initial olefin π -complex. Two of the $\text{Zr-C}(1)\text{H}_3$ hydrogen atoms become pseudo-eclipsed with respect to the ethylene fragment, while the remaining H is involved in a strong α -agostic interaction. In fact, the interacting $\text{C}(1)\text{-H}(1)$ bond length (Figure 5) is computed to be significantly longer (1.11 Å) than the others (1.08 Å). The geometry of the four-membered $\text{Zr-C}(1)\text{-C}(13)\text{-C}(12)$ transition state exhibits a 7.8° folding angle along the $\text{C}(1)\text{-C}(13)$ internuclear vector, and the puckering arises from repulsive interactions between the methyl and ethylene hydrogen atoms. Comparing the Ti and Zr CGC homologues, minor structural differences are found except for longer (~ 0.18 Å) $\text{Zr-C}(1)$ and $\text{Zr-C}(12)$ bond lengths, mostly reflecting the greater Zr ionic radius. The olefin insertion transition state structures associated with the bicyclopentadienyl complexes (Figure 5) evidence similar rearrangements of $\text{M-C}(1)\text{H}_3$ hydrogen atoms and the involvement of a $\text{C}(1)\text{-H}(1)$ bond in an α -agostic interaction. In the case of the $(\text{C}_5\text{H}_5)_2\text{TiCH}_3^+$ cation, the newly formed $\text{C}(1)\text{-C}(13)$ bond distance at the transition state is slightly longer than in the other cases, including CGC systems. This is evidence of an earlier transition state and of a lower barrier to insertion.

The present transition state structures for olefin insertion closely resemble those found for $(\text{C}_5\text{H}_5)_2\text{-TiCH}_3^+$ ^{6c} and $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{MCH}_3^+$ ^{6b,e} at the HF level and for $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCH}_3^+$ ^{6b,e} at the MP2 level, even though a somewhat less puckered $\text{M-C}(12)\text{-C}(13)\text{-C}(1)$

Table 2. Computed *ab Initio* vs DFT Selected Internuclear Distances at the Transition State

| | | internuclear distance (Å) | |
|--|------------|---------------------------|------|
| | | <i>ab initio</i> | DFT |
| $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{NR})\text{Ti}(\text{C}_2\text{H}_4)\text{CH}_3^+$ | Ti-C(12) | 2.15 (2.27) ^a | 2.38 |
| | C(1)-C(13) | 2.13 (2.19) ^a | 3.00 |
| $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{NR})\text{Zr}(\text{C}_2\text{H}_4)\text{CH}_3^+$ | Zr-C(12) | 2.32 | 2.54 |
| | C(1)-C(13) | 2.14 | 3.09 |
| $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{C}_2\text{H}_4)\text{CH}_3^+$ | Zr-C(12) | 2.34 | 2.39 |
| | C(1)-C(13) | 2.13 | 2.28 |

^a Values in parentheses refer to calculations at the MP2 level adopting a DZP basis set (see text).

ring is found in the silyl-bridged metallocenes.^{6b,e} In that case, the near planarity may be due to constraints imposed either by the silylene bridging or by the adopted geometry optimization procedures. Interestingly enough, the present geometries are at some variance with DFT data as shown below. For example, DFT-LDA results for the insertion transition states of $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{HN})\text{MCH}_3(\text{C}_2\text{H}_4)^+$ indicate significantly longer $\text{C}(1)\text{-C}(13)$ and $\text{M-C}(12)$ contacts (Table 2).^{7j} The differences are probably artifacts of the local density approximation in the energy evaluation for geometry optimization, and more comparable data are obtained for the $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3^+$ cations.^{7k,1} In the case of $(\text{C}_5\text{H}_5)_2\text{-TiCH}_3^+$, both DFT-LDA and MP2 data reported by Ahlrichs et al.^{6e} indicate a negligible ethylene insertion barrier in marked contrast with the present results. However, the present results, at a higher level of theory (vide infra), follow the same trend, although an earlier transition state structure is generally obtained. This aspect will be analyzed in greater detail in the following sections.

Product Metal *n*-Propyl Cations. The initial direct insertion products are found in all cases to have γ -agostic structures with the $\text{C}(1)\text{H}_3$ chain-end group directed toward the cationic metal vacant coordination site (Figure 6). The $\text{M-CH}_2\text{CH}_2\text{CH}_3^+$ propyl chain can, however, easily rearrange to two other structures (β -agostic conformers) upon simple rotation ($\sim 120^\circ$) about the $\text{C}(12)\text{-C}(13)$ bond. The CGC β -agostic conformers (Figure 7; only one β -agostic conformer is shown) are close in energy ($\Delta E \approx 1$ kcal/mol; Table 1) to the γ -agostic structure. In contrast, the β -agostic conformers are considerably more stable in the case of metallocene cations (Figure 7; Table 1). In both CGCM and Cp_2M cases, the $\text{M-C}(12)$ bond is bent out of either the $\text{Cp}_{\text{centr}}\text{-M-N}$ or $\text{Cp}_{\text{centr}}\text{-M-Cp}_{\text{centr}}$ plane, respectively, and one of three σ bonds, $\text{C}(13)\text{-C}(1)$, $\text{C}(13)\text{-H}(4)$, or $\text{C}(13)\text{-H}(5)$, is directed toward the vacant metal coordination site. All of these structures have either short $\text{M}\cdots\text{C}(1)\text{H}_3$ distances in the γ -conformers or close $\text{M}\cdots\text{H-C}(13)\text{H}$ contacts in both β -agostic structures. Corresponding elongations of either the $\text{C}(12)\text{-C}(13)$ or $\text{C}(13)\text{-H}$ bonds are observed as a consequence of the agostic interaction, while the $\text{M-C}(12)\text{-C}(13)$ bond angles in the three *n*-propyl conformers differ markedly from that expected for sp^3 hybridization at the $\text{C}(12)$ atom.

The comparative analysis of geometrical parameters (Figure 6) shows that the γ -agostic conformers in $(\text{C}_5\text{H}_5)_2\text{TiCH}_2\text{CH}_2\text{CH}_3^+$ and, to a minor extent, in $(\text{C}_5\text{H}_5)_2\text{-ZrCH}_2\text{CH}_2\text{CH}_3^+$ have longer $\text{M}\cdots\text{C}(1)\text{H}_3$ contacts and

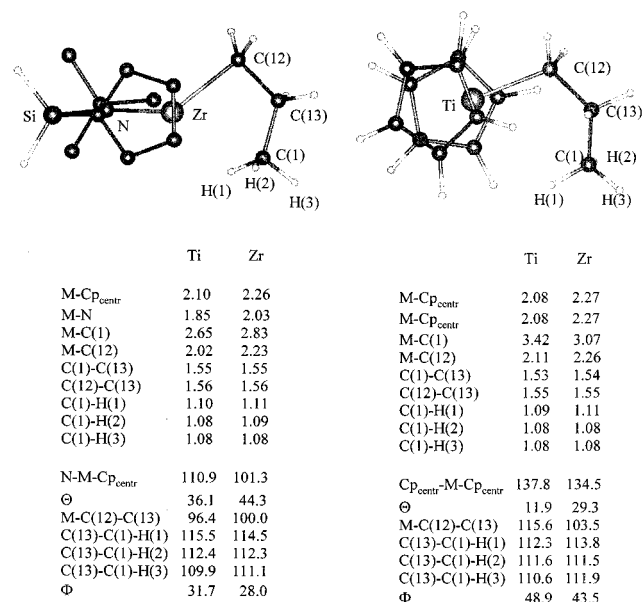


Figure 6. HF optimized structures of $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})\text{ZrC}_3\text{H}_7^+$ and $(\text{C}_5\text{H}_5)_2\text{TiC}_3\text{H}_7^+$ kinetic *n*-propyl products (γ -agostic conformers). Hydrogen atoms on the $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})$ ligand have been omitted for ease of viewing.

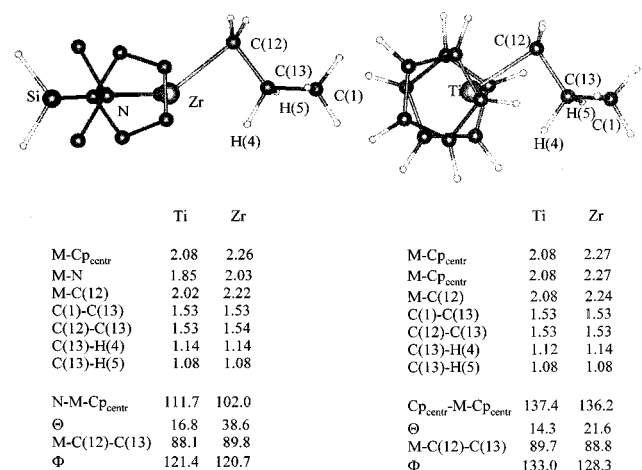


Figure 7. HF optimized structures of $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})\text{ZrC}_3\text{H}_7^+$ and $(\text{C}_5\text{H}_5)_2\text{TiC}_3\text{H}_7^+$ *n*-propyl products (β -agostic conformers) (distances in Å, angles in deg). Hydrogen atoms on the $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})$ ligand have been omitted for ease of viewing. Θ defines the angle between the plane $\text{Cp}_{\text{centr}}\text{-M-N}$ (in CGC systems) or $\text{Cp}_{\text{centr}}\text{-M-Cp}_{\text{centr}}$ (in metallocenes) and the $\text{M-C}(12)$ vector.

greater $\text{M-C}(12)\text{-C}(13)$ bond angles than the corresponding CGC cations, both evidence of reduced agostic interactions because of the more sterically crowded $(\text{C}_5\text{H}_5)_2\text{M}$ coordination sphere. The reduced interaction between the $\text{C}(1)\text{-C}(13)/\text{C}(1)\text{H}_3$ bonds and the vacant metal site in the γ -agostic $(\text{C}_5\text{H}_5)_2\text{MCH}_2\text{CH}_2\text{CH}_3^+$ conformer twists the $\text{M-C}(12)\text{-C}(13)\text{-C}(1)$ ring to an approximately staggered conformation (the $\text{M-C}(12)\text{-C}(13)\text{-C}(1)$ torsional angle is $\sim 50^\circ$), thus relaxing the steric repulsion between the propyl CH_2 and CH_3 groups. These geometries contrast with the data for the $\text{CGCMCH}_2\text{CH}_2\text{CH}_3^+$ analogues, where the small $\text{M-C}(12)\text{-C}(13)\text{-C}(1)$ torsional angle ($\sim 30^\circ$) in the γ -agostic complex indicates a closer coplanarity of the three σ -bonds, hence a more eclipsed conformation of the $\text{CH}_2\text{-CH}_2\text{-CH}_3$ fragment.

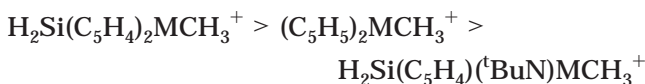
The present structural data agree well with previously reported ab initio results on γ -agostic conformations of $(\text{C}_5\text{H}_5)_2\text{TiCH}_2\text{CH}_2\text{CH}_3^+$ ($\text{Ti-C}(1) = 3.60 \text{ \AA}$, $\text{Ti-C}(12)\text{-C}(13) = 118.1^\circ$)^{6c} and $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{MCH}_2\text{CH}_2\text{CH}_3^+$.^{6b,e} In addition, the β -agostic conformers in $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{MCH}_2\text{CH}_2\text{CH}_3^+$ have been found to be more stable than the γ -agostic counterparts (~ 7 and ~ 2 kcal/mol for $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCH}_2\text{CH}_2\text{CH}_3^+$ and $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCH}_2\text{CH}_2\text{CH}_3^+$, respectively). Comparable results have been obtained at the DFT level for $(\text{C}_5\text{H}_5)_2\text{ZrCH}_2\text{CH}_2\text{CH}_3^+$ with the γ -agostic conformer less stable (5.3 kcal/mol) than the β -agostic structure.^{7k,l} Furthermore, dynamic Car-Parrinello DFT-BP86 studies of $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})\text{TiCH}_2\text{CH}_2\text{CH}_3^+$ indicate that the propyl chain undergoes rapid interconversion between γ - and β -agostic conformations, with essentially equal populations of each.^{7h}

Energetics of Ethylene Insertion at Naked Alkyl Cations. Computed potential energy profile data (HF, MPn, and CCSD) along the ethylene activation/insertion pathway at the metallocene and CGC methyl cations are reported in Table 1 and compared with related literature data. Our results show that the calculated energy values are strongly affected by electron correlation and that this effect is of major consequence for assessing olefin insertion barriers. Inspection of complexation, insertion barrier, and product formation energies for Zr derivatives reveals small fluctuations on passing from MP2 to MP3, MP4, and CCSD wave functions. There is, however, evidence of suitable convergence for the presently adopted basis set. Analogously, energetics for ethylene insertion into $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})\text{TiCH}_3^+$ show modest variation on increasing the level of theory (the greatest energetic deviation is 4.3 kcal/mol). It is seen that the MP2 level of computation represents a practical yet accurate tool for studying the present chemical transformations for the systems discussed above. More marked fluctuations of energies are found for processes involving $(\text{C}_5\text{H}_5)_2\text{TiCH}_3^+$. The formation energy of the overall insertion process yielding the *n*-propyl product $(\text{C}_5\text{H}_5)_2\text{TiCH}_2\text{CH}_2\text{CH}_3^+$ appears to be rather insensitive to the adopted wave function (the greatest energy difference is 3.3 kcal/mol), while in contrast both complexation and insertion energies are very sensitive to the level of theory (the greatest deviations are 8.5 and 10.8 kcal/mol, respectively). Similar observations have been described by Morokuma et al. for $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCH}_3^+$ on passing from MP2 to QCISD energies.^{6b} It therefore emerges that studies involving $(\text{C}_5\text{H}_5)_2\text{TiR}^+$ complexes require the use of highly accurate methodologies.

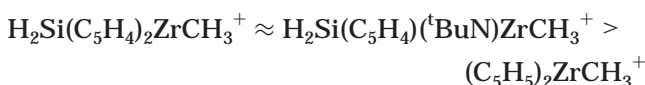
Olefin complexation energies for both CGCMCH_3^+ and $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3^+$ systems are very similar (Table 1), indicating that C_2H_4 binds to the metal centers with similar strength, and hence involve similar electronic and steric interactions. These data are also in accord with the comparable metal-ethylene bond distances ($\text{Zr-C}(12)$ and $\text{Zr-C}(13)$) we find in the $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})\text{ZrCH}_3(\text{C}_2\text{H}_4)^+$ and $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3(\text{C}_2\text{H}_4)^+$ π -complexes as well as with the shorter ($\Delta \approx 0.16 \text{ \AA}$) computed $\text{M}\cdots\text{C}$ distance (due to the smaller Ti ionic radius) for $\text{H}_2\text{Si}(\text{C}_5\text{H}_4)(\text{tBuN})\text{TiCH}_3(\text{C}_2\text{H}_4)^+$. The less exothermic value (~ 8 kcal/mol) obtained for $(\text{C}_5\text{H}_5)_2\text{TiCH}_3(\text{C}_2\text{H}_4)^+$ agrees well with the unusually long $\text{Ti-C}(12)$ and Ti-

C(13) distances, which indicate weaker bonding of ethylene. This is, of course, a consequence of the greater C_5H_5 -based steric congestion about the Ti center (vide supra).^{12e}

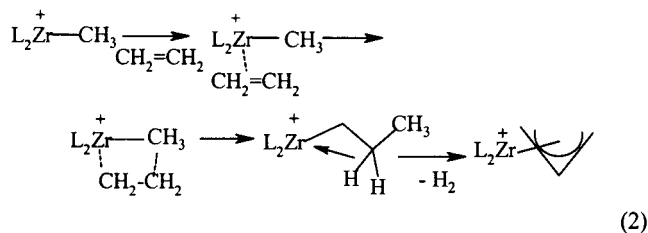
Despite some energetic fluctuations (depending on the level of theory), it is evident (Table 1) that naked metallocene cations invariably have lower ethylene insertion barriers than their CGC counterparts and, in addition, silyl ring-bridging in metallocenes (Table 1) further reduces the barriers. On this basis, the following scale of olefin insertive reactivity can be deduced as a function of ancillary ligation:



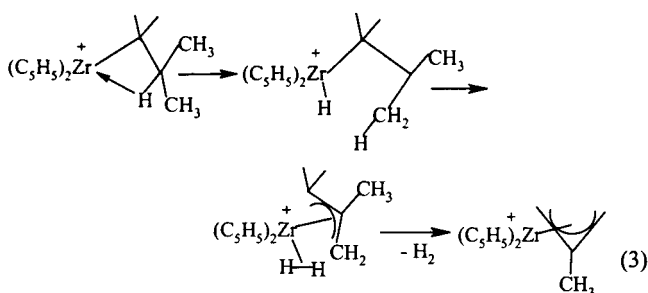
In regard to available experimental data, a slightly different electrophilicity ordering has been proposed on the basis of gas phase mass spectrometry data^{14b} for Zr derivatives:



However, note that the experimental data refer to the result of two consecutive reactions: (i) ethylene insertion and (ii) the subsequent dehydrogenation with formation of a metal η^3 -allyl product. The latter process may play a *major* role in the measured reaction energetics of the two-step process since it requires simultaneous coordination of three atoms to the metal center, which is significantly more congested in the $(C_5H_5)_2MCH_3^+$ cations (eq 2). In this context, the formation of



η^3 -allyl complexes from the $(C_5H_5)_2Zr(isobutyl)^+$ and $H_2Si(C_5H_4)(^tBuN)Ti(n\text{-propyl})^+$ ground state conformations has been investigated theoretically.^{7e,9} It is found that the process proceeds with a high activation barrier (16 kcal/mol in both cases) since it involves initial formation of $(C_5H_5)_2Zr-(H)(isobutene)^+$ and $H_2Si(C_5H_4)(^tBuN)Ti-H(propene)^+$ olefin-hydride complexes, followed by a rearrangement to dihydrogen complexes, and subsequent dihydrogen elimination (eq 3).^{7e,9a}



Several factors contribute to the computed enhanced gas phase reactivities of metallocene versus CGC cations. First, the greater steric congestion around the metal center in the $(C_5H_5)_2MCH_3^+$ ions weakens the M–C(1) bond and lowers the barrier to ethylene insertion. Second, weaker ethylene coordination to $(C_5H_5)_2TiCH_3^+$ in the intermediate π complex renders the olefin more available for insertion (lowers the activation barrier). Finally, there is greater α -agostic “assistance” in $Cp_2MCH_3^+$ cations versus the CGC systems since the energetically greater accessibility of methyl group spatial orientations (vide supra) facilitates the energy-demanding distortion necessary to effect ethylene insertion. Furthermore, it is known that Ti-based complexes are generally more reactive in the gas phase with respect to ethylene insertion than the corresponding Zr cations. In fact, the reacting M–C(1) and C(12)=C(13) bonds of the intermediate π -complexes lie in closer spatial proximity due to the smaller Ti ionic radius, thus lowering the barrier to insertion. In addition, α -agostic assistance appears to be more effective in Ti catalysts, also lowering the insertion barrier. Although the polymerization activity in solution should not necessarily correlate with the gas phase electrophilicity (due to the effects of counteranion and solvent),^{10–12,14} it is instructive to investigate a qualitative correlation. In agreement with the present computational data, the Ti-based catalysts $Me_2Si(C_5Me_4)(^tBuN)TiCH_3CH_3B(C_6F_5)_3$ and $Me_2Si(C_5Me_4)(^tBuN)TiCH_3CH_3B(C_{12}F_9)_3$ display greater ethylene polymerization activities than the Zr homologues.^{4b} In contrast, bis-cyclopentadienyl Zr-based catalysts, independent of cocatalyst (MAO or $C(C_6H_5)_3^+B(C_6F_5)_4^-$)²¹ and cyclopentadienyl ring substitution ($(C_5H_5)_2MCH_3^+$ or $(Me_3SiC_5H_4)_2MCH_3^+$), are more active in solution than the related Ti catalysts. This trend, at variance to present gas phase data may reflect tight ion-pairing effects^{1a} or completing catalyst deactivation (e.g., Ti(IV) \rightarrow Ti(III) reduction under polymerization conditions).²²

The present olefin complexation and insertion product formation energies involving $(C_5H_5)_2MCH_3^+$ cations are less exothermic than those reported by Morokuma et al.^{6b,e} for ring-bridged $H_2Si(C_5H_4)_2MCH_3^+$ cations. This may reflect reduced steric crowding ($Cp_{centr}-M-Cp_{centr} = 135.0^\circ$ and 133.1° in $(C_5H_5)_2TiCH_3^+$ and $(C_5H_5)_2ZrCH_3^+$, respectively, versus 128.2° and 123.6° in the corresponding ring-bridged cations), which stabilizes both olefin π -complexation and the final insertion products. Data obtained using DFT methodologies (Table 1) invariably evidence considerably reduced insertion barriers and therefore should be invoked with caution.^{6b} The diminution may reflect correlation energy overestimations in the transition state which would artificially reduce or annul energetic barriers.²³

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(23) (a) Jensen, F. *Introduction to Modern Computational Chemistry*; Wiley: New York, 1999. (b) Raghavachari, K.; Anderson, J. B. *J. Phys. Chem.* **1996**, *100*, 12960. (c) Head-Gordon, M. *J. Phys. Chem.* **1996**, *100*, 13213. (d) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651, and references therein.

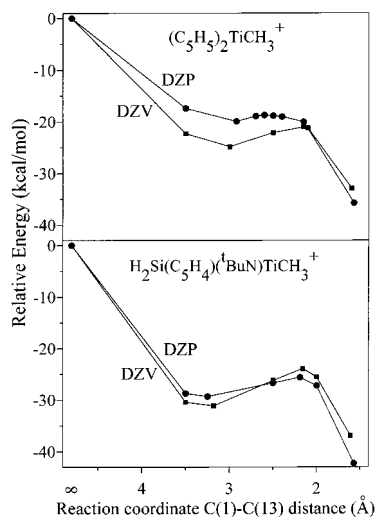


Figure 8. Energy profiles for ethylene insertion into $(C_5H_5)_2TiCH_3^+$ and $H_2Si(C_5H_4)(tBuN)TiCH_3^+$ at the DZV/MP2/MP2 and DZP/MP2/MP2 levels of computation.

Basis Set and Correlation Effects on Ethylene Insertion at $(C_5H_5)_2TiCH_3^+$ and $H_2Si(C_5H_4)(tBuN)TiCH_3^+$ Cations. The results reported here (Table 1) as well as previous results^{6b,c} identify the crucial importance of both electron correlation and basis set effects on the energetics of olefin activation processes involving $(C_5H_5)_2TiCH_3^+$ cations. This is due to known limitations in HF methods for describing first-row transition metals versus those in the second or third row. It is well documented that single-determinant wave functions provide a poorer description of interelectronic repulsion terms in the case of first-row transition metals. Therefore, ethylene insertion processes at metallocene Ti cations have been analyzed here in greater detail at higher levels of theory, and the entire ethylene reaction energy profile for both $(C_5H_5)_2TiCH_3^+$ and $H_2Si(C_5H_4)(tBuN)TiCH_3^+$ cations has been scrutinized by optimizing the relevant structures at the MP2 level using both DZV and DZP basis sets.

$(C_5H_5)_2TiCH_3^+$. The ethylene insertion reaction coordinate (Figure 8) is found to proceed through classical ethylene π -complexation, followed by a four-center transition state insertion step, analogous to results obtained using uncorrelated wave functions for geometry optimization. The present data, however, contrast with previous ab initio MP2 results of Alhrichs et al.,^{6c} which suggest activation and insertion occur without a barrier. This surprising difference is likely caused by the smaller basis set adopted by Alhrichs et al.^{6c} (193 vs the 289 basis functions presently adopted). Additionally, the proper description of the $(C_5H_5)_2TiCH_3^+$ + ethylene electronic system in terms of both primitive Gaussians and polarization functions appears to be critical.^{24,25} Thus, the present results show that the

(24) For example, the present total energy for the γ -agostic $(C_5H_5)_2TiCH_3^+$ product at the MP2 level is -1352.2270 hartrees, while that reported in ref 6c is -1351.2652 hartrees.

(25) Another origin of this discrepancy appears to be the high threshold (10^{-3} hartree/Bohr) used by Alhrichs et al.^{6c} to limit the geometry optimization. Owing to the very flat potential energy surface along the C(1)–C(13) reaction coordinate, high accuracy is necessary to locate minima or maxima. In fact, Alhrichs et al. observed that gradients initially decrease, become very small around 2.45 Å, and subsequently increase until the final product is formed (see Table 3 of ref 6c). It is likely that the very weak π -complex was not detected.

Table 3. π -Complexation, Insertion, and Product Formation Energies (kcal/mol) Computed at Various Levels for Ethylene Insertion into $H_2Si(C_5H_4)(tBuN)TiCH_3^+$ and $(C_5H_5)_2TiCH_3^+$ Complexes

| | π -complex | energy barrier | γ -agostic product |
|-------------------------------|----------------|----------------|---------------------------|
| $H_2Si(C_5H_4)(tBuN)TiCH_3^+$ | | | |
| DZV/MP2/RHF | –29.7 | 7.9 | –33.9 |
| DZV/MP2/MP2 | –31.1 | 7.2 | –36.9 |
| DZP/MP2/MP2 | –29.3 | 3.5 | –42.3 |
| $(C_5H_5)_2TiCH_3^+$ | | | |
| DZV/MP2/RHF | –22.0 | 2.4 | –23.6 |
| DZV/MP2/MP2 | –24.8 | 3.8 | –32.9 |
| DZP/MP2/MP2 | –20.0 | 1.2 | –35.9 |

ethylene complexation and insertion barriers at the DZV/MP2/MP2 level are comparable to the DZV/MP2/HF results (Table 3), with slightly lower values for the energies at the DZP/MP2/MP2 level. In the same context, note that the stability of the γ -agostic insertion product becomes considerably greater under MP2 geometry optimization (Table 3), doubtless due to electron correlation effects on the agostic interaction.²⁶

Figure 9 depicts the geometries of the species involved in the $(C_5H_5)_2TiCH_3^+$ + ethylene insertion process (methyl cation, π -complex, transition state, γ -agostic-propyl cation). Close similarities are evident at both the DZV/MP2/MP2 and DZP/MP2/MP2 levels, with some shortening of the Ti–C_{pcentr} and Ti–C(1) bond lengths observed with DZP basis sets. Differences are also evident upon comparing HF and MP2 geometries. For the $(C_5H_5)_2TiCH_3^+$ cation, the most noticeable effect arising from the MP2 treatment is the enhancement of the α -agostic interaction involving the Ti center and the C(1)–H(1) bond. This induces several structural modifications, namely, (i) bending of the Ti–C(1) bond vector out of the C_{pcentr}–Ti–C_{pcentr} plane, (ii) the elongation of the C(1)–H(1) bond, and (iii) tilting of the C(1)H₃ group relative to the Ti–C(1) vector. In addition, the Cp rings become eclipsed and the Ti–C_{pcentr} bond lengths shorten relative to the HF geometry (0.03 and 0.07 Å at DZV/MP2 and DZP/MP2 levels, respectively). Upon proceeding to the MP2-optimized geometry, the Ti–C_{2H4} distances shorten with ~ 0.3 Å contractions in the Ti–C(12) and Ti–C(13) bond lengths. These geometrical changes doubtless reflect enhanced C_{2H4} dative interactions upon introduction of correlation effects. Similarly, the γ -agostic interactions in the *n*-propyl cation are strengthened at the MP2 level, with the computed Ti \cdots C(1) contact and Ti–C(12)–C(13) bond angle contracting substantially (~ 0.9 Å and $\sim 32^\circ$, respectively) versus that found at the HF level. Computed transition state geometries, once adopting the DZV basis set, are comparable at both the DZV/MP2/HF and DZV/MP2/MP2 levels, with almost identical C(1)–C(13) distances (Figures 5 and 9). However, the transition state occurs somewhat earlier on the adopting the DZP basis set (Figure 9).

(26) Note that increasing the theoretical level of correlation energy evaluation does not necessarily result in increasing the degree of agostic interaction. For example, the DZV/MP3-optimized structure of $(C_5H_5)_2TiCH_3^+$ is closer to the DZV/HF results than that obtained at the DZV/MP2 level: Ti–C(1) = 2.10 Å, C(1)–H(1) = 1.10 Å, C(1)–H(2) = 1.09 Å, C(1)–H(3) = 1.10 Å, Ti–C(1)–H(1) = 104.9°, Ti–C(1)–H(2) = 113.6°, Ti–C(1)–H(3) = 110.7°, and $\theta = 0.7^\circ$. The reduced α -agostic interactions on passing from MP2- to MP3-optimized structures should increase the energetic barrier for ethylene insertion.

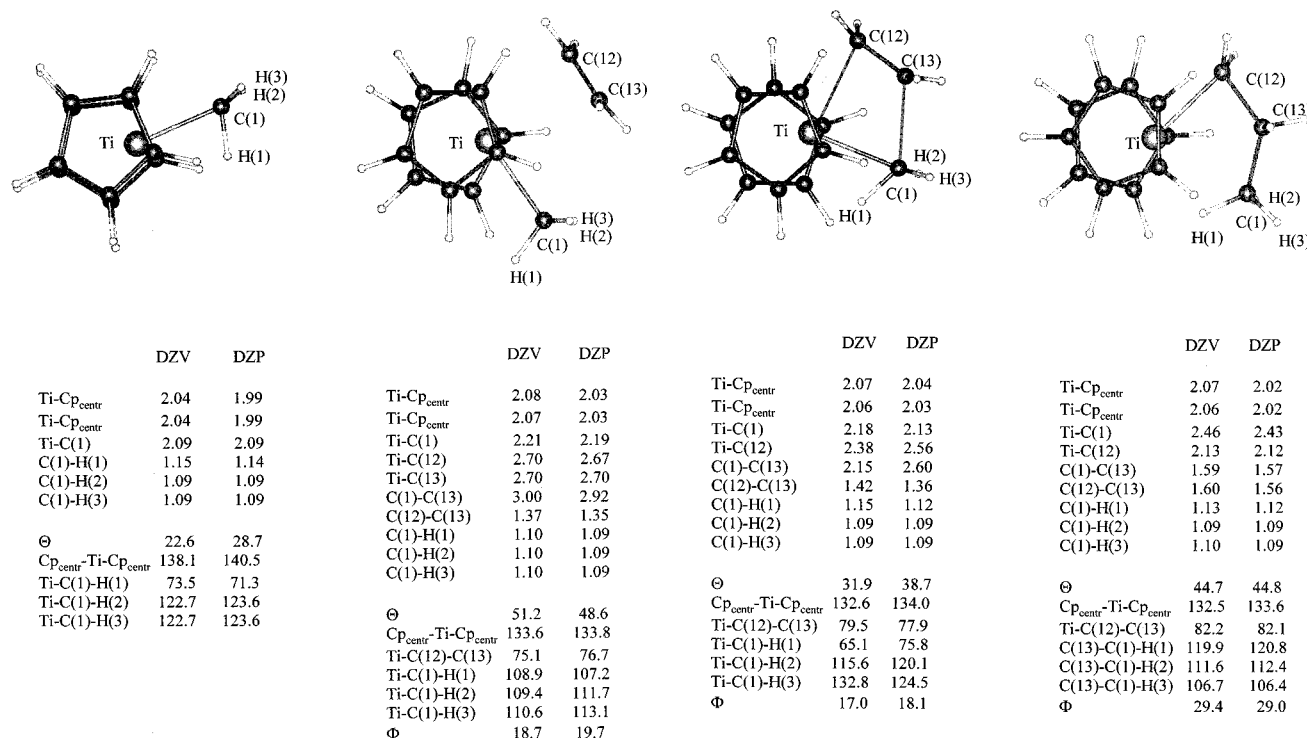


Figure 9. DZV/MP2 and DZP/MP2 optimized structures of species involved in the ethylene activation/insertion into $(C_5H_5)_2-TiCH_3^+$: methyl cation, π -complex, transition state, and γ -agostic final inserted product (distances in Å, angles in deg).

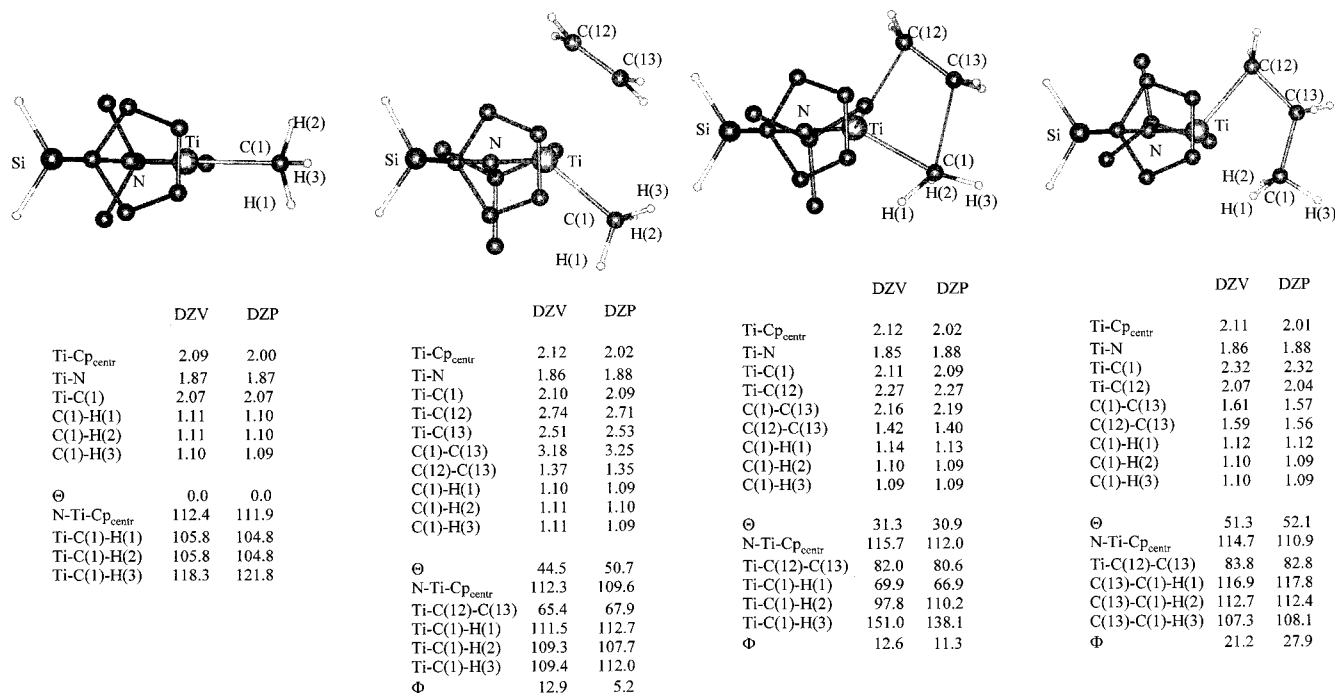
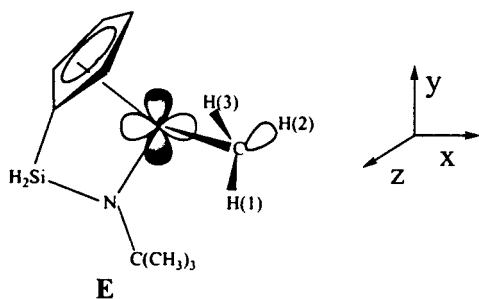


Figure 10. DZV/MP2 and DZP/MP2 optimized structures of species involved in the ethylene activation/insertion into $H_2Si(C_5H_4)(tBuN)TiCH_3^+$: methyl cation, π -complex, transition state, and γ -agostic final inserted product (distances in Å, angles in deg).

$H_2Si(C_5H_4)(tBuN)TiCH_3^+$. The ethylene insertion energetic profiles upon structural optimization at the MP2 level with both DZV and DZP basis sets (Figure 8; Table 3) are very similar to those at the HF level (DZV/MP2/HF). The additional stabilizations of the π -complex and γ -agostic insertion product are indicative of more pronounced dative donation to the metal as the geometry is optimized at the correlated level. The insertion barrier declines (0.7 and 4.4 kcal/mol at the

DZV/MP2/MP2 and DZP/MP2/MP2 levels, respectively) and the transition state does not proceed along the C(1)-C(13) reaction coordinate (C(1)-C(13) = 2.13 vs 2.19 Å at HF and MP2 levels, respectively). The diminished influence of correlation energy and basis set on this pathway is in accord with the moderate variations observed in the cation structures (Figure 10). The structural modifications are similar to those already discussed for the $(C_5H_5)_2TiCH_3^+$ species and, in par-

ticular, involve (i) reduced Ti–C(1)–H(1) and Ti–C(1)–H(2) and increased Ti–C(1)–H(3) bond angles, which are indicative of enhanced α -agostic interactions in the methyl cations; (ii) closer Ti–C₂H₄ contacts in the π -complex responsible for the greater complexation energy; (iii) closer Ti...C(1) contacts and a contracted Ti–(C12)–C(13) bond angle, responsible for the increased γ -agostic interaction in the insertion product. The increased strength of agostic interactions, in geometries optimized at MP2 level, leads to the formation of a stable pyramidal structure ($\theta \approx 58^\circ$) for the H₂Si(C₅H₄)(^tBuN)TiCH₃⁺ cation²⁷ similar to that obtained for H₂Si(C₅H₄)(^tBuN)ZrCH₃⁺ and H₂Si(C₅H₄)(HN)TiCH₃⁺.^{7j} C_s-symmetric and trigonal structures of the H₂Si(C₅H₄)(^tBuN)TiCH₃⁺ cation are almost isoenergetic, and the relative stability (within 1 kcal/mol) depends on the level of theory adopted (MP2, MP3, MP4, and CCSD). In the pyramidal structure, the CH₃ group bonds to the metal center mainly through the d_{xz} orbital, while the d_{x²-y²} acts as an electron acceptor site for α -agostic interaction with the localized C(1)–H(2) bond (**E**; the C(1)–H(2) distance is 0.02 Å longer than the others and the Ti–C(1)–H(2) bond angle is $\sim 20^\circ$ less than the others). All of these results indicate that



although electron correlation and basis set are relevant for the description of the (C₅H₅)₂TiCH₃⁺ system, there is no indication of drastic energetic variations in results along the reaction coordinate, and hence, the computa-

(27) Significant geometrical parameters of the pyramidal structure for the H₂Si(C₅H₄)(^tBuN)TiCH₃⁺ cation: DZV/MP2 Ti–C(1) = 2.11 Å; C(1)–H(1) = 1.10 Å; C(1)–H(2) = 1.12 Å; C(1)–H(3) = 1.10 Å; Ti–C(1)–H(1) = 113.7°; Ti–C(1)–H(2) = 93.7°; Ti–C(1)–H(3) = 121.4°; θ = 57.0°. DZP/MP2 Ti–C(1) = 2.09 Å; C(1)–H(1) = 1.09 Å; C(1)–H(2) = 1.11 Å; C(1)–H(3) = 1.09 Å; Ti–C(1)–H(1) = 112.8°; Ti–C(1)–H(2) = 93.1°; Ti–C(1)–H(3) = 123.6°; θ = 58.8°.

tionally flexible DZV/MP2/HF approach should suffice in terms of cost versus benefit.

Conclusions

The present study provides considerable insight into those factors allowing computation of accurate reaction coordinate profiles for ethylene insertion into the M–CH₃ bonds of catalytically important Cp₂MCH₃⁺ and CGC–MCH₃⁺ cations. In all cases, the reactions proceed via an intermediate π -complex and a subsequent insertion step involving a four-center transition state. The energetics associated with ethylene complexation are similar in both families of complexes. However, less exothermic values are obtained for the (C₅H₅)₂MCH₃⁺ complexes due to greater steric congestion at the metal center. However, the Cp₂MCH₃⁺ complexes invariably have lower olefin insertion barriers than the CGCMCH₃⁺ analogues. Two factors account for the lower insertion barrier in metallocenes: (i) a longer/weaker M–CH₃ bond and (ii) greater α -agostic assistance during the ethylene insertion. Ti-based complexes are generally more insertion-reactive than the analogous Zr cations because the smaller Ti radius favors closer approach of the relevant M–C(1) and C(12)=C(13) bonds in the π -complexes preceding the insertive transition state. This induces greater activation of the M–C(1) bond, hence, a lower barrier to insertion. As far as the methodological approach is concerned, the general trend found indicates that (i) geometry optimization at the HF level, followed by MP2 (or MP3, MP4, and CCSD when practicable) calculations for energetics, and (ii) DZV-quality basis sets adopting ECPs on the metal center represent the best compromise to reliably study elaborate “real-world” catalytic systems or realistic models thereof.

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Supporting Information Available: A complete list of Cartesian coordinates of all structures presently analyzed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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