Theoretical Characterization of Olefin Metathesis in the Bis-dicyclopentadienyltitanium(IV) System by Density Functional Theory

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Abstract: Local and nonlocal density functional theory (DFT) was used to study olefin metathesis in the $TiCp_2C_3H_4(R_1,R_2)$ system, in which the alkyl substituents (R_1,R_2) are at the β-position of the metallocyclobutane ring. The structures and stabilities of the metallocyclobutanes were calculated, and the mechanism of olefin insertion and the process of ring-opening metathesis polymerization were investigated. The predicted geometries of the metallocyclobutanes agree well with experimental structures, especially those predicted by nonlocal DFT. The relative stabilities of the metallocyclobutanes were studied by calculating the energy change for the following olefin exchange reaction: $TiCp_2C_3H_4(R_1,R_2) + C_2H_2(R_3,R_4) \rightarrow TiCp_2C_3H_4(R_3,R_4) + C_2H_2(R_1,R_2)$. The relative stabilities of the metallocyclobutanes are also strongly dependent upon the number and steric size of the alkyl group(s) (R_1,R_2) at the β-position in the metallocyclobutane ring. In general, nonlocal DFT predicts olefin exchange energies that are in better agreement with the experimentally observed free energies of olefin exchange than local DFT. The quantitative agreement between the experimental and calculated ΔG's for olefin exchange are within 0.8 kcal/mol. The mechanism of metathesis was investigated by calculating the potential energy surface for olefin elimination from $TiCp_2C_3H_5(tBu)$. No compelling evidence was found for a local minimum corresponding to a titanium−alkylidene−olefin complex, which is inconsistent with conclusions drawn from experimental mechanistic studies but is consistent with all prior theoretical calculations on metal assisted 2 + 2 insertions. The mechanism of cyclopentene and norbornene ring-opening polymerization was also studied.

Introduction

Olefin metathesis is an important organometallic transformation capable of the isomerization and polymerization of olefins,[1,2] and its basic mechanism is considered to be closely related to Ziegler−Natta (ZN) polymerization catalysis.[1,2] The mechanism of olefin metathesis is shown schematically in Figure 1. In this mechanism, a vacant coordination site in a transition metal−alkylidine complex bonds an incoming olefin to form a metal−alkylidine−olefin complex. The next step in the mechanism involves a 2 + 2 insertion of the olefin into the metal−alkylidine multiple bond, forming a metallocyclobutane, which is a stable intermediate observed in many systems.[1,2] At this point in the reaction mechanism, the metallocyclobutane can eliminate an olefin from either side of the ring, leading to the retro reaction or isomerization of the olefin. When certain cyclical olefins are used, the metathesis reaction may be used to perform ring-opening metathesis polymerization[2] (ROMP), which is a synthetic route to specialized polymers. The mechanism of ROMP is illustrated in Figure 2.

One of the most comprehensively studied metathesis systems is the bis-dicyclopentadienyltitanium(IV) metallocyclobutane system, $TiCp_2C_3H_4(R_1,R_2)$ (Figure 3), by Grubbs and co-workers.[3−7] This system has been studied extensively with respect to the geometries of the metallocyclobutane,[3] the
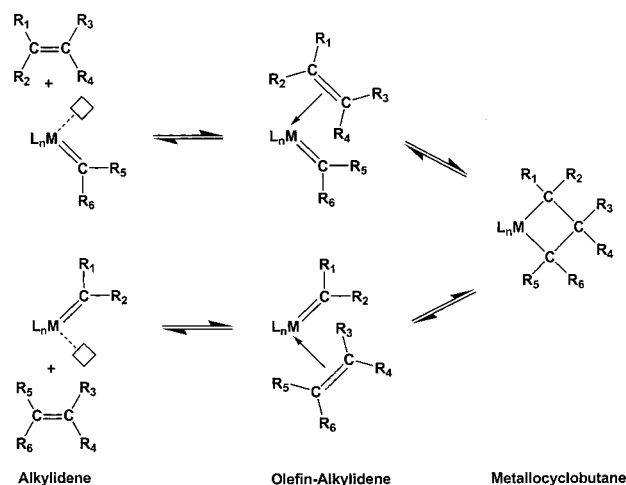
Figure 1. Schematic representation of the olefin metathesis mechanism.

thermodynamics of olefin exchange,[4] the mechanism of metathesis,[5] the barrier to metathesis,[5,6] and the ring-opening polymerization of olefins.[7] In addition, many of the newer homogeneous ZN catalysts are metallocenes, containing early transition metals, much like the $TiCp_2C_3H_4(R_1,R_2)$ system.[1,2] In fact, the only difference between the $TiCp_2C_3H_4(R_1,R_2)$ system and a ZN catalyst system is a proton. The close similarity

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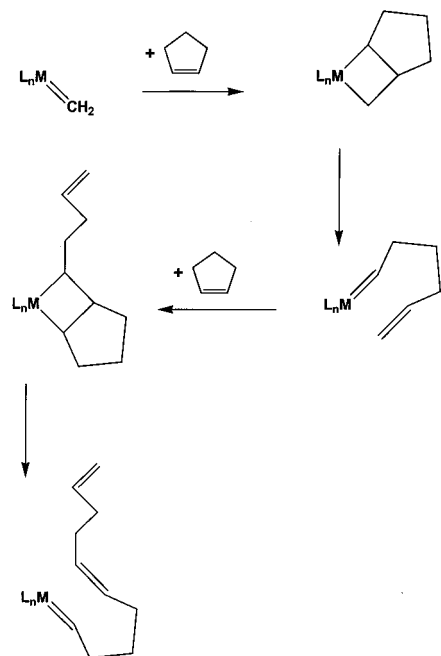
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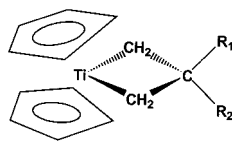(4) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

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Figure 2. Schematic representation of the ring-opening metathesis polymerization (ROMP) mechanism.

Figure 3. Bis-dicyclopentadienyltitanium(IV) system.

of the metallocenes involved in these two mechanisms strongly suggests that the nature of their $2 + 2$ additions is also similar.

Quantum mechanical methods can provide important qualitative and quantitative insights into the mechanisms of chemical reactions, including homogeneous catalytic cycles.[8] Density functional theory (DFT) is a first principles quantum mechanical method which has been used to study the ground-state properties of molecules and the mechanism of chemical reactions.[9-12] DFT explicitly includes electron correlation effects and has been shown to be of comparable accuracy to conventional pos-Hartree−Fock methods.[11,12] The importance of electron correlation in the treatment of transition metal systems has been demonstrated by many previous studies reported in the literature.[11-13] In the past, DFT calculations were always performed with local density functionals (LDFs)[11] for exchange and correlation; however, more recently, DFT calculations are being performed with nonlocal density functionals (NLDFs), which are considered to be more accurate than LDF theory for predicting the geometries and energetics of molecules.[11,12]

The theoretical nature of olefin metathesis has been investigated by several groups.[14,15] Hoffman and co-workers[14] studied olefin metathesis by the extended Hückel method, and their calculations predict the metal−alkylidiene−olefin complex to be more stable than the metallocyclobutane by ∼20 kcal/mol.

In a different study, Rappé and Upton used $TiCl_2CH_2(C_2H_4)$ as a model for $TiCp_2CH_2(C_2H_4)$.[15] In that paper,[15] Hartree−Fock (HF) and generalized valence bond (GVB) calculations were used to study the olefin insertion process. A metal−alkylidiene−olefin complex was found, and an extremely small barrier to insertion of the olefin into the metal−alkylidine bond was predicted at the HF level of theory, but when the barrier was reevaluated at the GVB level with zero-point energies included, the transition state and the metal−alkyidine−olefin complex were found to be nearly degenerate in energy.[15] Effectively, no barrier for olefin insertion was found at either level of theory.[15] In addition, olefin insertions in the related $TiCp_2CH_3(C_2H_4)^+$ and $ZrCp_2CH_3(C_2H_4)^+$ ZN catalyst systems have been studied by MP2[16] and NLDF[17] theories, respectively, which are the highest levels of theory applied heretofore to the study of ZN catalysts. In both of these studies,[16,17] little or no barrier to olefin insertion was found, in contrast to the experimental estimates of 7−12 kcal/mol.[18]

In this paper, we present a theoretical study of olefin metathesis in the $TiCp_2C_3H_4(R_1,R_2)$ system using LDF and NLDF theories. We are in a unique position to assess the accuracy of DFT calculations on these systems due to the enormous wealth of experimental information on the geometries[3] and thermodynamic stabilities[4] of the metallocyclobutanes and the mechanisms of olefin metathesis[5] and ROMP.[6] The structures and relative stabilities of the metallocyclobutanes were calculated and will be compared to experimental values. Also, the mechanism and the calculated barrier to olefin insertion was studied and will be compared to experimental information. In addition, the role of the $TiCp_2C_3H_4(R_1,R_2)$ system as a ROMP catalyst will be discussed. The $TiCp_2C_3H_4(R_1,R_2)$ system also provides an excellent opportunity to study the ability of DFT to predict the geometries, energetics, and barriers of a system that is similar to ZN catalysts, for which there is a paucity of experimental data regarding the structures and energetics of intermediates along a reaction pathway.

Calculations

All DFT calculations were performed with the DMol program.[19-21] DMol utilizes a basis set of numerical atomic functions which are exact solutions to the Kohn−Sham equations for the atom.[19-21] To obtain additional basis functions to extend this basis set, excited states and cation states of the atom are calculated.[19-21] These basis sets are generally more complete than a comparable set of linearly independent Gaussian functions and have been demonstrated to have small basis set superposition errors.[19] In the present study, a polarized split valence basis set, termed double numerical polarized (DNP), was used. The following two density functionals for exchange and correlation were used in this study: (1) the local functional of Vosko, Wilk, and Nussair[22]

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Table 1.   Calculated and Experimental Geometries of the Metallocyclobutanes[a]

compound/ functional	Ti–C$_1$	Ti–C$_2$	Ti–C$_{Cp}$[b]	Ti–Cp[c]	C$_1$–C$_3$	C$_2$–C$_3$	C$_3$–R$_1$	C$_3$–R$_2$	C$_1$–Ti–C$_2$	Ti–C$_1$–C$_3$	Ti–C$_2$–C$_3$	C$_1$–C$_3$–C$_2$	Ti–C$_1$–C$_2$–C$_3$
TiCp$_2$C$_3$H$_5$(iPr)/ VWN	2.098	2.098	2.342– 2.379	2.021, 2.028	1.548	1.548	1.536		75.995	82.978	82.978	113.121	154.352
TiCp$_2$C$_3$H$_5$(iPr)/ BP	2.137	2.137	2.414– 2.451	2.111, 2.118	1.567	1.567	1.565		74.380	84.914	84.914	111.044	155.274
TiCp$_2$C$_3$H$_4$(Cyc)/ VWN	2.092	2.104	2.337– 2.372	2.019, 2.037	1.607	1.538	1.528		80.300	79.700	80.800	118.600	171.700
TiCp$_2$C$_3$H$_4$(Cyc)/ BP	2.127	2.140	2.404– 2.436	2.096, 2.112	1.631	1.556	1.549		79.400	80.800	82.000	117.800	172.000
TiCp$_2$C$_3$H$_5$(tBu)/ VWN	2.098	2.098	2.340– 2.372	2.022, 2.029	1.545	1.545	1.558		76.245	83.002	83.002	113.096	157.227
TiCp$_2$C$_3$H$_5$(tBu)/ BP	2.136	2.136	2.418– 2.460	2.119, 2.119	1.568	1.568	1.584		74.793	85.135	85.135	111.714	159.570
TiCp$_2$C3H$_5$(tBu)/ expt[d]	2.15	2.15	2.07– 2.51		1.54	1.54	1.52		75.00	84.50	84.50	116.00	
TiCp$_2$C$_3$H$_4$(Me$_2$)/ VWN	2.101	2.101	2.349– 2.369	2.037	1.565	1.565	1.522	1.522	77.000	84.900	84.900	113.300	180.000
TiCp$_2$C$_3$H$_4$(Me$_2$)/ BP	2.144	2.144	2.431– 2.446	2.121	1.584	1.584	1.545	1.545	74.900	87.200	87.200	110.700	180.000
TiCp$_2$C$_3$H$_4$(Me$_2$)/ expt[d]	2.14	2.15	2.38– 2.44		1.59	1.59	1.53	1.53	74.80	87.10	87.10	110.90	
TiCp$_2$C$_3$H$_4$(Me,Et)/ VWN	2.101	2.107	2.347– 2.375	2.038, 2.040	1.563	1.560	1.535	1.522	76.200	85.700	85.500	112.600	178.300
TiCp$_2$C$_3$H$_4$(Me,Et)/ BP	2.148	2.144	2.425– 2.448	2.122, 2.120	1.585	1.583	1.561	1.545	74.500	87.600	87.800	110.100	178.600
TiCp$_2$C$_3$H$_4$(Me,iPr)/ VWN	2.094	2.101	2.342– 2.385	2.047, 2.041	1.564	1.564	1.555	1.522	76.300	85.900	85.800	112.000	176.800
TiCp$_2$C$_3$H$_4$(Me,iPr)/ BP	2.146	2.151	2.427– 2.454	2.123, 2.125	1.585	1.582	1.582	1.546	73.600	88.800	88.700	108.800	177.900
TiCp$_2$C$_3$H$_5$(Ph)/ VWN	2.088	2.097	2.346– 2.363	2.024, 2.028	1.578	1.546	1.503		78.700	81.800	82.300	116.200	168.100
TiCp$_2$C$_3$H$_5$(Ph)/ BP	2.123	2.134	2.412– 2.440	2.101, 2.103	1.600	1.569	1.525		77.300	83.600	84.000	114.200	168.900
TiCp$_2$C$_3$H$_5$(Ph)/ expt[d]	2.11	2.13	2.36– 2.40		1.58	1.55	1.52		75.30	85.70	86.00	112.00	
TiCp$_2$C$_3$H$_4$(Nor)/ VWN	2.099	2.094	2.337– 2.396	2.046, 2.053	1.594	1.539	1.537		78.500	80.500	81.900	115.700	158.400
TiCp$_2$C$_3$H$_4$(Nor)/ BP	2.148	2.141	2.400– 2.473	2.120, 2.144	1.609	1.557	1.558		76.100	82.300	83.700	113.200	155.200

[a] Bond lengths are given in angstroms and bond angles in degrees. [b] Cp carbons. [c] Centroid of Cp ring. first distance is cis to R$_1$ at the β-position in the metallocyclobutane ring. [d] Reference 3.

(VWN) and (2) the nonlocal functional consisting of Becke's nonlocal exchange functional[23] and Perdew's nonlocal correlation functional[24] (BP). Atom-centered grids were used for the numerical integrations. This particular grid corresponds to the "fine" option in DMol.[20] DMol has been used in the past to study the geometries and energetics of transition metal complexes.[19,25]

All SCF calculations were converged to a root-mean-square change in the charge density of less than 1×10^{-4}. Geometries were optimized using analytic gradients and the optimization methods of Baker.[26] Geometries were optimized such that the value of the gradient was less than 1×10^{-3} hartrees/bohr. All geometry optimizations were performed with C_1 symmetry except where noted.

The potential energy surface (PES) for olefin metathesis in TiCp$_2$C$_3$H$_5$-(tBu) was calculated by energy-optimizing the structure of TiCp$_2$C$_3$H$_5$-(tBu) using the BP functional with one of the C_α–C_β bond lengths fixed at values between 1.57 and 4.30 Å.

Vibrational frequencies and zero-point energies were calculated with a brand new version of the DMol program, called DMol^3.[21] This was accomplished by finite difference calculations using the first derivatives. The translational, rotational, and vibrational contributions were evalu-

ated by standard statistical mechanical formulas at 298.15 K and 1 atm pressure.[27]

Results and Discussion

Several metallocyclobutanes were studied in the present work which differ by the types of alkyl substituents (R$_1$,R$_2$) at the β-position. They are shown in Figure 4. The following naming conventions were used to abbreviate the alkyl groups at the β-position for compounds **1–8** respectively in Figure 4: (iPr), (Cyc), (tBu), (Me$_2$), (Me,Et), (Me,iPr), (Ph), and (Nor).

I. Geometries of the Metallocyclobutanes. The optimized geometries of the metallocyclobutanes **1–8** using the VWN and BP functionals are presented in Table 1, along with the corresponding experimental values when available. The structures of the three metallocyclobutanes with experimentally determined geometries[3] (TiCp$_2$C$_3$H$_5$(Ph), TiCp$_2$C$_3$H$_5$(tBu), and TiCp$_2$C$_3$H$_5$(Me$_2$)) are shown in Figure 5. Each of these molecules was found to have a distinct minimum energy orientation of the Cp rings, either eclipsed, staggered, or partially staggered. In TiCp$_2$C$_3$H$_5$(Ph), the Cp rings are eclipsed. The staggered structure for this compound was predicted to be less stable than the eclipsed form by 0.4 kcal/mol at the BP level. In TiCp$_2$C$_3$H$_5$(tBu), the Cp rings are staggered. The eclipsed structure for this compound was predicted to be less stable than

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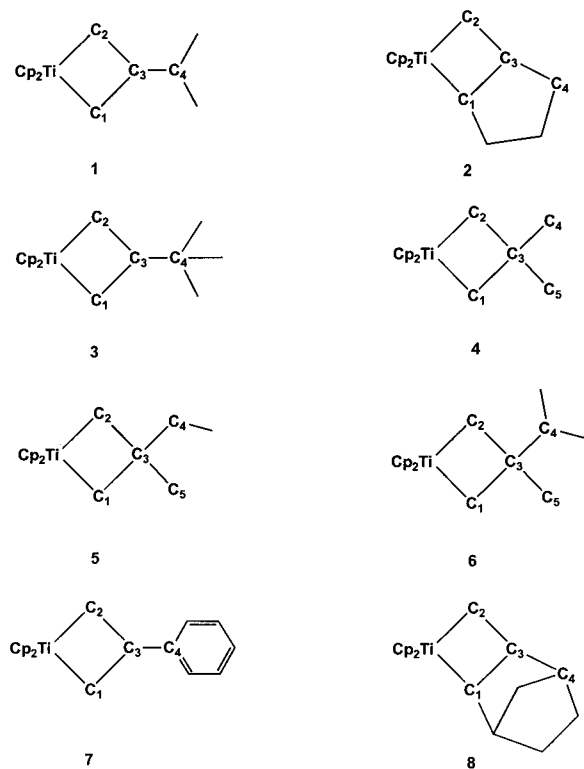
Figure 4. Metallocyclobutane molecules studied in this paper. **1**, TiCp$_2$C$_3$H$_5$(iPr); **2**, TiCp$_2$C$_3$H$_4$(Cyc); **3**, TiCp$_2$C$_3$H$_5$(tBu); **4**, TiCp$_2$C$_3$H$_4$-(Me$_2$); **5**, TiCp$_2$C$_3$H$_4$(Me,Et); **6**, TiCp$_2$C$_3$H$_4$(Me,iPr); **7**, TiCp$_2$C$_3$H$_5$(Ph); and **8**, TiCp$_2$C$_3$H$_4$(Nor).
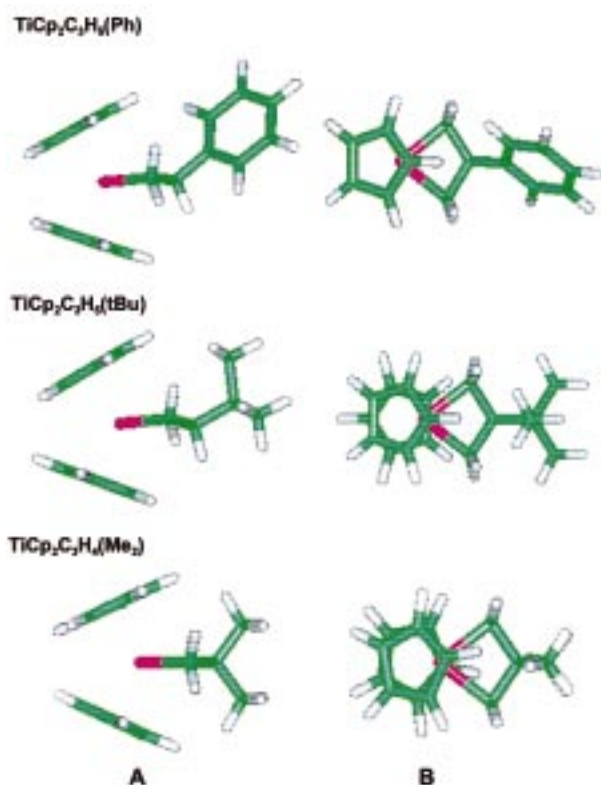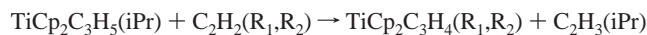

Figure 5. Optimized geometries of metallocyclobutanes TiCp$_2$C$_3$H$_5$-(Ph), TiCp$_2$C$_3$H$_5$(tBu), and TiCp$_2$C$_3$H$_4$(Me$_2$): (a) side view and (b) top view.

the staggered form by 0.6 kcal/mol at the BP level. The driving force for staggering appears to be the steric presence of the *tert*-butyl group at the β-position. In TiCp$_2$C$_3$H$_4$(Me$_2$), the Cp rings

are partially staggered, lying somewhere between eclipsed and fully staggered. The driving force for the partial staggering of the Cp rings in this compound is the methyl groups at the β-position. The eclipsed form of this compound does not appear to be a minimum for this compound. The Cp rings are staggered in TiCp$_2$C$_3$H$_5$(iPr), partially staggered in TiCp$_2$C$_3$H$_4$(Me,Et) and TiCp$_2$C$_3$H$_4$(Me,iPr), and partially staggered in TiCp$_2$C$_3$H$_5$(Cyc) and TiCp$_2$C$_3$H$_5$(Nor) due to interactions with the ring system of the olefin.

(a) Bond Lengths. The interatomic distances corresponding to metal—ligand interactions in Table 1 are the Ti—C$_1$, Ti—C$_2$, Ti—C$_{cp}$, and Ti—Cp parameters, which are the two metallo-cyclobutane titanium—carbon distances, the range of metal cyclopentadiene carbon distances, and the titanium cyclopen-tadiene centroid distances, respectively. For the three molecules with experimentally determined structures[3] (TiCp$_2$C$_3$H$_5$(tBu), TiCp$_2$C$_3$H$_4$(Me$_2$), and TiCp$_2$C$_3$H$_5$(Ph)), the Ti—C$_1$ and Ti—C$_2$ distances calculated by the BP functional are in good agreement with experiment and are in better agreement than the distances calculated by the VWN functional (Table 1). The range of Ti—C$_{cp}$ distances calculated by the VWN functional is slightly shorter than the experimental ranges reported for TiCp$_2$C$_3$H$_4$-(Me$_2$) and TiCp$_2$C$_3$H$_5$(Ph), by as much as 0.03 Å, while the same distances calculated by the BP functional are longer than the experimental ranges by as much as 0.04 Å. The anomolously short experimental Ti—C$_{cp}$ distance of 2.07 Å in TiCp$_2$C$_3$H$_5$-(tBu) falls well outside of our calculated range for this compound. A structure in which one of the Cp rings was bonded in a σ fashion to the titanium atom, which had a Ti—C$_{cp}$ distance of 2.07 Å, was studied. It was predicted to be significantly higher in energy than structures in which the two Cp rings were bonded penta-hapto. Also, the σ-bonded structure minimizes to the penta-hapto structure. The short experimental Ti—C$_{Cp}$ distance range may be the result of the poor resolution of the structure, which was noted as being significantly disordered.[3] The Ti—Cp distances, which correspond to the distance between the titanium atom and the centroid of the cyclopentadiene ring, follow a trend that is similar to that observed for the Ti—C$_{cp}$ distances for both functionals studied. The C$_1$—C$_3$ and C$_2$—C$_3$ distances in the metallocyclobutane predicted by both functionals are in good agreement with the corresponding experimental values in TiCp$_2$C$_3$H$_5$(tBu), TiCp$_2$C$_3$H$_4$(Me$_2$), and TiCp$_2$C$_3$H$_5$-(Ph). It is interesting to note that the predicted and experimental C$_1$—C$_3$ and C$_2$—C$_3$ distances in TiCp$_2$C$_3$H$_5$(Ph) differ by ~0.04 Å, which may be indicative of the π system of the phenyl ring interacting with one of the C$_\beta$—C$_\gamma$ bonds. Also, the C$_1$—C$_3$ distance is longer than the C$_2$—C$_3$ distance in TiCp$_2$C$_3$H$_4$(Cyc) and TiCp$_2$C$_3$H$_4$(Nor) by ~0.07 and ~0.05 Å, respectively, at the BP level, which is indicative of the internal ring strain present in this metallocyclobutane. The calculated C$_3$—R$_1$ and C$_3$—R$_2$ distances agree very well with the corresponding experimental values for TiCp$_2$C$_3$H$_5$(tBu), TiCp$_2$C$_3$H$_4$(Me$_2$), and TiCp$_2$C$_3$H$_5$(Ph) for both functionals.

(b) Bond Angles. The C$_1$—Ti—C$_2$, Ti—C$_1$—C$_3$, and Ti—C$_2$—C$_3$ angles predicted by the BP functional are in good agreement with the experimental values for TiCp$_2$C$_3$H$_5$(tBu), TiCp$_2$C$_3$H$_4$-(Me$_2$), and TiCp$_2$C$_3$H$_5$(Ph) and are in better agreement than those predicted by the VWN functional. The C$_1$—C$_3$—C$_2$ angles predicted by the BP functional for TiCp$_2$C$_3$H$_4$(Me$_2$) and TiCp$_2$C$_3$H$_5$(Ph) agree better with the experimental values for these compounds, while the C$_1$—C$_3$—C$_2$ angle calculated by the VWN functional for TiCp$_2$C$_3$H$_5$(tBu) is in better agreement with the experimental value for this compound than the BP functional.

Table 2. Calculated and Experimental Relative Olefin Exchange Energies[a]

$$TiCp_2C_3H_5(iPr) + C_2H_2(R_1,R_2) \rightarrow TiCp_2C_3H_4(R_1,R_2) + C_2H_3(iPr)$$

compound	ΔE_{VWN}[b]	ΔE_{BP}[b]	ΔG_{BP}[c]	ΔZPE[d]	ΔG_{expt}[e]	T_c[f]
$TiCp_2C_3H_5(iPr)$	0.0	0.0	0.0	0.000	0.0	
$TiCp_2C_3H_5(tBu)$	0.2	1.6	1.2	−0.392	0.8	55
$TiCp_2C_3H_4(Cyc)$	0.9	1.8	1.4	0.012	1.0	45
$TiCp_2C_3H_4(Me_2)$	6.3	6.3	4.5	−0.911	3.7	5
$TiCp_2C_3H_4(Me,Et)$	6.1	7.2	5.3	−1.324	5.2	0
$TiCp_2C_3H_4(Me,iPr)$	6.7	9.3	6.3	−1.981	6.0	−5
$TiCp_2C_3H_5(Ph)$	3.8	2.9				
$TiCp_2C_3H_4(Nor)$	−2.7	−1.1				65

[a] All values are given in kcal/mol. [b] Calculated with DMol Version 2.6. [c] Calculated with DMol³ Version 1.0; ΔE_{BP} calculated by DMol³ Version 1.0 differs from values calculated by DMol Version 2.6 by <|0.4| kcal/mol. [d] Zero-point energy difference; calculated with DMol³ Version 1.0. [e] Reference 4. [f] Cleavage temperature (°C), ref 5.

(c) Dihedral Angles. The significant dihedral angle in the metallocyclobutanes is the $Ti-C_1-C_2-C_3$ dihedral angle. This dihedral angle is a measure of how much the metallocyclobutane ring deviates from planarity. The metallocyclobutanes with one β-substituent exhibit $Ti-C_1-C_2-C_3$ dihedral angles ranging from 154 to 172°, which is consistent with the substituent at the β-position minimizing its steric interactions with the Cp rings. This is particularly true for molecules such as $TiCp_2C_3H_5$-(iPr) and $TiCp_2C_3H_5(tBu)$, which have the largest predicted $Ti-C_1-C_2-C_3$ dihedral angles. The metallocyclobutanes with two substituents at the β-position have $Ti-C_1-C_2-C_3$ dihedral angles close to 180°, which is indicative of a crowded environment in the coordination sphere of the titanium atom. The profile of the structures in Figure 5 illustrates the range of variation in the $Ti-C_1-C_2-C_3$ angle in the molecules for which the structure has been experimentally determined.

II. Olefin Exchange Energies. The ability of an olefin to react with a coordinately unsaturated metal−alkylidene complex and form a stable metallocyclobutane is determined largely by the types of substituents on the olefin. In particular, the steric size and shape of the substituents on a particular olefin play a role in determining the overall stability of the metallocyclobutane formed from it. In a study by Grubbs and co-workers, the relative free energy of stability of various metallocyclobutanes with different β-substituents was reported.[4] In this study,[4] the following olefin exchange free energies were measured experimentally for a series of olefins in which $TiCp_2C_3H_5(iPr)$ was the reference metallocyclobutane in all reactions:

$$TiCp_2C_3H_5(iPr) + C_2H_2(R_1,R_2) \rightarrow$$
$$TiCp_2C_3H_4(R_1,R_2) + C_2H_3(iPr) \quad (1)$$
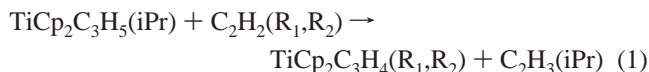
The relative stabilities of the series of metallocyclobutanes (**1**−**8**) were studied by calculating the energy change for the reaction shown in eq 1. The calculated olefin exchange energies (ΔE) using the VWN and BP functionals are presented in Table 2, along with the corresponding experimental ΔG values[4] and cleavage temperatures[5] when available. The ΔE's calculated by the local VWN functional for the two olefins that have a single alkyl group ($C_2H_3(tBu)$ and $C_2H_2(Cyc)$) are in reasonable agreement with experiment, while the ΔE's calculated for olefins that have two alkyl groups are in less satisfactory agreement with experiment for this functional. The VWN functional does not correctly differentiate between the steric size of the olefins that have two alkyl groups ($C_2H_2(Me_2)$, $C_2H_2(Me,Et)$, and C_2H_2-(Me,iPr)). In particular, the calculated olefin exchange energy

of $C_2H_2(Me,Et)$ is more favorable than that of $C_2H_2(Me_2)$, which is qualitatively inconsistent with experiment. The ΔE's calculated by the nonlocal BP functional are in much better overall agreement with experiment than those calculated using the VWN functional. This is particularly true for olefins that have two alkyl groups, for which the qualitative agreement with experiment is greatly improved over the VWN functional, although the absolute values are more disparate. Both the VWN and BP functionals appear to overestimate the relative stabilities of metallocyclobutanes with a single β-substituent versus those with two β-substituents. Although there is no experimental ΔG for $TiCp_2C_3H_4(Nor)$, there is strong evidence based on the experimental olefin cleavage temperature measured for this compound to suggest that $TiCp_2C_3H_4(Nor)$ is thermodynamically more stable toward olefin elimination than $TiCp_2C_3H_5(iPr)$, which is in agreement with our calculations.[5] The underestimation of the steric repulsions by the VWN functional leads to overbinding and a poor representation of the metallocyclobutane ligand exchange energies. The nonlocal BP functional, which appears to describe steric repulsions better, predicts metallocyclobutane ligand exchange energies in much better agreement with the experimental olefin exchange free energies. In particular, the BP functional is able to qualitatively account for the steric encumbrance of the various alkyl groups at the β-position correctly, whereas the VWN functional does not.

To assess the effects of zero-point energy and thermal contributions on the olefin exchange energetics, we calculated ΔG's for the reactions which have experimental ΔG's (Table 2). The agreement between the calculated ΔG's using the BP functional and the experimental ΔG's are now within 0.8 kcal/mol or less (Table 2). The zero-point energy differences (Table 2) are the largest for the olefins with two substituents at the β-position, which are the olefins that have the greatest difference between ΔE_{BP} and ΔG_{expt}. Thus, vibrational zero-point effects appear to be largely responsible for the discrepancies between ΔE_{BP} and ΔG_{expt}. Based on our calculated results, the qualitative trends predicted by ΔE_{BP} are reliable.

III. Mechanism. The mechanism of olefin metathesis was investigated by calculating the potential energy surface (PES) for olefin elimination from the metallocyclobutane. The calculated PES for olefin elimination in $TiCp_2C_3H_5(tBu)$ is shown graphically in Figure 6, along with key structures along the reaction pathway. As one of the $C_\alpha-C_\beta$ bond lengths in the metallocyclobutane is increased, the total energy of the system increases until it reaches a plateau value of ∼28 kcal/mol at 3.9 Å. At very long distances (>4.3 Å), the total energy decreases slightly from the plateau value by ∼1 kcal/mol. In this regime of the PES, the reaction coordinate varies rapidly with no change in energy. Our calculated PES effectively predicts no barrier to olefin insertion nor the existence of a metal−alkyidene−olefin complex, which are both inconsistent with the conclusions of experimental mechanistic studies.[5] Remarkably, the calculated energy of the olefin elimination is very similar to the experimental estimates[5,6] of the barrier to olefin metathesis for $TiCp_2C_3H_5(tBu)$, which is 27 kcal/mol. The geometry of the Cp rings changes during the course of the reaction by rotating from the starting staggered orientation to a nearly eclipsed orientation upon olefin elimination (Figure 6). At a reaction coordinate of 3.50 Å, the C−C double bond of the olefin is essentially fully formed (Figure 6), indicating the reaction is complete, which is consistent with the plateau value of the energy at this point in the reaction.

Our DFT calculations predict no stable structure corresponding to a titanium−alkylidene−olefin complex and no barrier to
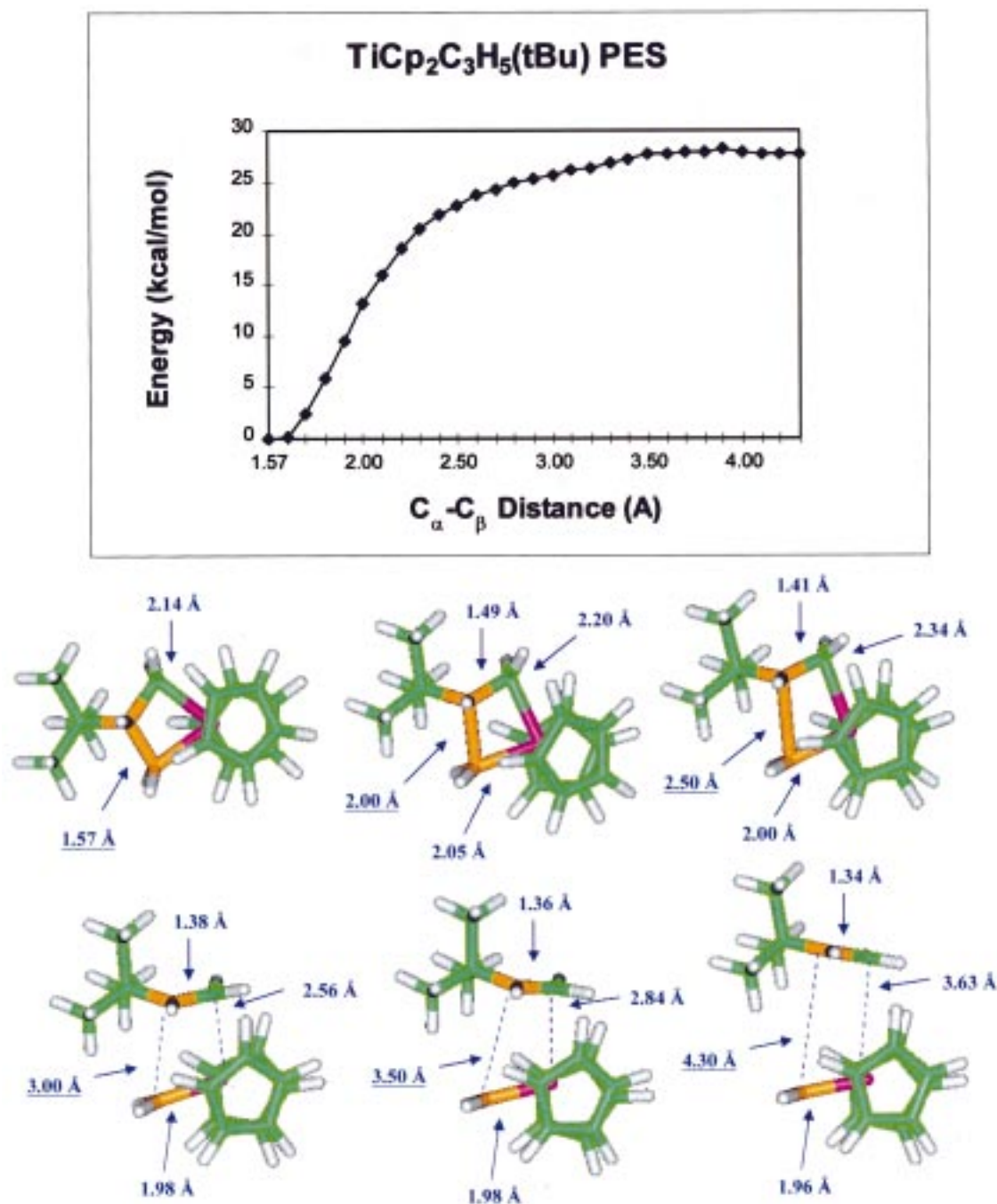
Figure 6. Calculated potential energy surface of olefin elimination from TiCp$_2$C$_3$H$_5$(tBu). The reaction coordinate is defined as one of the C$_\alpha$—C$_\beta$ bond lengths which was constrained along the reaction coordinate (the two carbon atoms used to define the reaction coordinate are shown in orange). Structures along the reaction coordinate include C$_\alpha$—C$_\beta$ values of 1.57, 2.00, 2.50, 3.00, 3.50, and 4.3 Å and are underlined.

olefin insertion. This result is consistent with the calculations of Rappé and Upton[15] for the model TiCl$_2$CH$_2$(C$_2$H$_4$) system, in which essentially no barrier to insertion was predicted; however, they did not calculate the entire PES for olefin insertion. Our calculated energy difference on going from the metallocyclobutane to a metal—alkylidene complex and C$_2$H$_3$-(tBu) (∼28 kcal/mol) is in reasonable agreement with the value of ∼22 kcal/mol calculated by Rappé and Upton for their model system. DFT calculations[17] on the ZrCp$_2$CH$_3$(C$_2$H$_4$)$^+$ ZN catalyst system predict essentially no barrier to olefin insertion, and MP2 calculations[16] on the related TiCp$_2$CH$_3$(C$_2$H$_4$)$^+$ ZN system also predict no barrier to olefin insertion. Standard density functionals, like BP, have been shown to underestimate and even fail to predict the barriers of chemical reactions,[28] which may be the reason no barrier is predicted by our calcu-

lations. However, density functionals that include exact exchange are found to improve this situation.[28] Preliminary calculations using one of these hybrid functionals indicate no qualitative difference from a standard BP functional for the metathesis reaction.[29] The general consensus is that all theories (DFT, MP2, and GVB), except HF, predict metal-assisted 2 + 2 reactions to be barrierless.[15–17]

The possibility of a bimolecular metathesis mechanism was investigated using two approaches. First, we studied whether

(28) (a) Baker, J.; Muir, M.; Andzelm, J. *J. Chem. Phys.* **1995**, *102*, 2063. (b) Johnson, B. G.; Gonzalez, C. A.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1994**, *221*, 100.

(29) We have calculated the potential energy surface for olefin elimination from TiCp$_2$C$_3$H$_6$ using Becke's adiabatic connection method at geometries optimized using a Becke—Perdew functional. We find no qualitative difference with the Becke—Perdew functional.
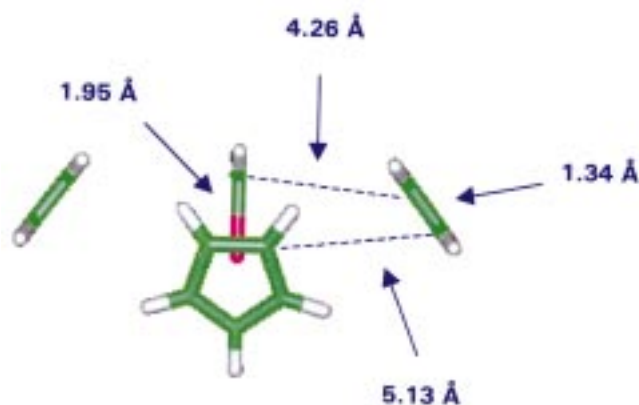
Figure 7. Hypothetical bimolecular transition state with C_{2v} symmetry involving TiCp$_2$CH$_2$ and two C$_2$H$_4$ molecules.
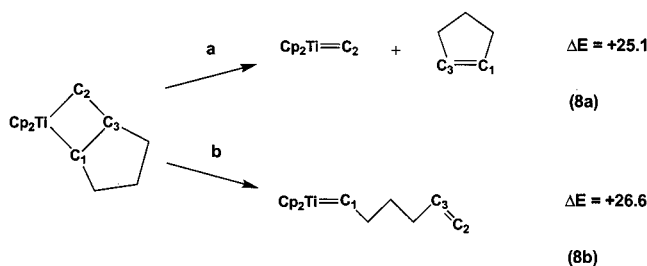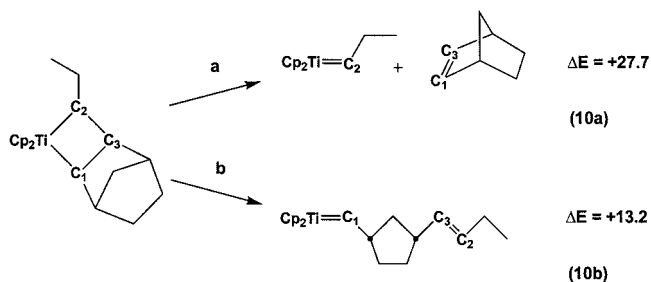

Figure 8. Energetic results of the two possible olefin eliminations from TiCp$_2$C$_3$H$_4$(Cyc).

C$_2$H$_4$ could form a stable complex with TiCp$_2$C$_3$H$_6$ by placing it in close proximity of TiCp$_2$C$_3$H$_6$ and optimizing. We were unsuccessful in locating any stable complexes of TiCp$_2$C$_3$H$_6$ and C$_2$H$_4$. Second, we calculated the energy of a C_{2v} structure involving TiCp$_2$CH$_2$ and two C$_2$H$_4$ molecules (Figure 7), which would correspond to a symmetrical transition state. Although this structure does not necessarily correspond to a transition state, it does provide an important "benchmark" of the upper limit for a bimolecular process. The energy of this structure is comparable to the sum of the energies of TiCp$_2$CH$_2$ and two C$_2$H$_4$ molecules. The geometry of the C_{2v} structure (Figure 7) does not suggest that any interaction between the olefin(s) and the titanium exist. Thus, our calculations provide no compelling support for a bimolecular metathesis mechanism.

IV. Ring-Opening Metathesis Polymerization. Details of the ROMP mechanism were investigated by calculating the energetics of the two possible olefin elimination reactions from TiCp$_2$C$_3$H$_4$(Cyc) and TiCp$_2$C$_3$H$_4$(Nor). In Figure 8, the energetics of the two possible olefin eliminations from TiCp$_2$C$_3$H$_4$-(Cyc) are shown. For TiCp$_2$C$_3$H$_4$(Cyc), the elimination of the olefin leading to cyclopentene (Figure 8a) is 1.5 kcal/mol more favorable than elimination of the olefin that leads to polymer (Figure 8b), which is most likely due to the fact that the alkylidiene formed in Figure 8a is less sterically crowded than the alkylidene formed in Figure 8b. If the effect of the growing polymer chain is modeled by an ethyl group on the C$_2$ carbon of TiCp$_2$C$_3$H$_4$(Cyc) (Figure 9), then the elimination of the olefin leading to polymer (Figure 9b) is more favorable than elimination of cyclopentene (Figure 9a) by 4.7 kcal/mol. This result supports our argument for the reaction shown in Figure 8a being more favorable than that shown in Figure 8b. In Figure 10, the energetics of the olefin eliminations from TiCp$_2$C$_3$H$_4$(Nor) are shown. In this example, we included the ethyl group on the C$_2$ carbon to model the effects of the growing polymer chain. The elimination of the olefin leading to polymerization (Figure 10b) is 14.5 kcal/mol more favorable than elimination of norbornene
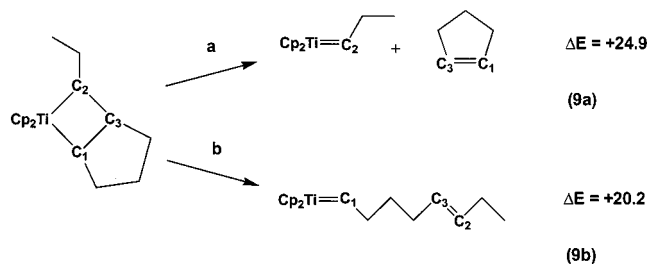
Figure 9. Energetic results of the two possible olefin eliminations from TiCp$_2$C$_5$H$_8$(Cyc).

Figure 10. Energetic results of the two possible olefin eliminations from TiCp$_2$C$_5$H$_8$(Nor).

(Figure 10a). In conclusion, the polymerizations of cyclopentene and norbornene by a metathesis mechanism are reasonable. Norbornene polymerization is predicted to be energetically more favorable than polymerization of cyclopentene, which is most likely due to the greater strain present in norbornene relative to cyclopentene. We have only considered the thermochemistry of ROMP reactions in the present work. The barriers of these reactions undoubtedly play an important role in determining the products formed.

Conclusions

We have studied the nature of olefin metathesis in the TiCp$_2$C$_3$H$_4$(R$_1$,R$_2$) system. The structures of the metallocyclobutane intermediates studied in this work are predicted to be in good accord with experiment, with NLDF theory performing better than LDF theory. The olefin exchange energies calculated by NLDF theory agree qualitatively well with the experimental free energies of olefin exchange, while the quantitative agreement dramatically improves when zero-point energy and thermal contributions are added. The mechanism of olefin metathesis was studied by calculating the potential energy surface of olefin elimination from TiCp$_2$C$_3$H$_5$(tBu). No compelling evidence for a titanium–olefin–alkylidiene complex was found, which is in disagreement with the conclusions of experimental mechanistic studies. However, the lack of any predicted barrier in the TiCp$_2$C$_3$H$_5$(tBu) system is consistent with all prior theoretical studies of 2 + 2 transition metal-mediated olefin insertion reactions involving early metals. Calculations on olefins capable of ROMP indicate that olefin eliminations leading to polymer are more favorable than olefin eliminations leading to free olefin only if the growing polymer chain is present. Norbornene is predicted to be a more favorable ROMP substrate than cyclopentene, which is most likely due to the greater strain present in norbornene relative to cyclopentene. Our calculations suggest that NLDF theory is capable of describing the interactions that govern structure and relative stability of the metallocyclobutane in the bis-dicyclopentadienyltitanium(IV) system; however, it does not appear to be capable of describing their reactions.