



Olefin Metathesis in the bis-Dicyclopentadienyl Titanium(IV) System

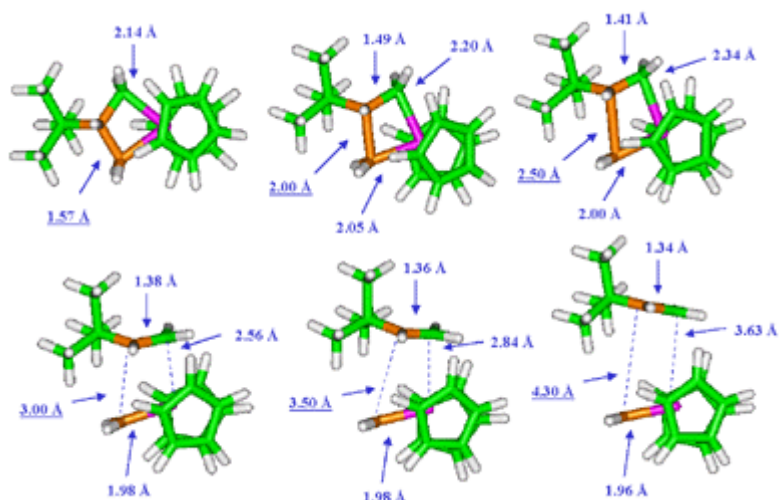
Scientists at Accelrys have performed DMol³ calculations on the nature of the olefin metathesis in the $\text{TiCp}_2\text{C}_3\text{H}_4(\text{R}_1, \text{R}_2)$ system.

The predicted bond lengths, bond angles, and dihedral angles for the metallocyclobutane species were found to be in excellent agreement with experimental data. The relative stability of the metallocyclobutanes and the experimental free energy values for the corresponding reactions were also accurately reproduced.

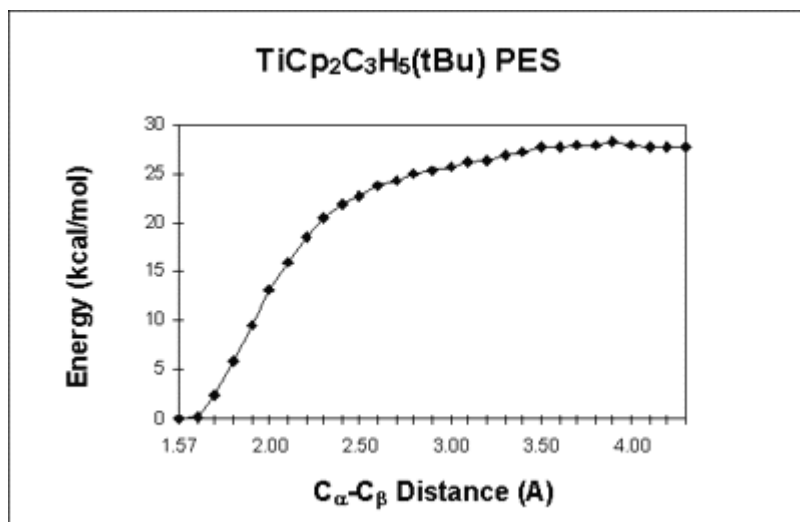
Olefin metathesis is an important organometallic transformation capable of the isomerization and polymerization of olefins and its mechanism is closely related to Ziegler-Natta polymerization catalysis. The actual metathesis reaction proceeds via a metallocyclobutane intermediate. If certain cyclic olefins are used, the metathesis reaction can be used to perform ring-opening metathesis polymerization (ROMP), which is a synthetic route to speciality polymers.

Bis-dicyclopentadienyltitanium (IV) metallocyclobutane system, $\text{TiCp}_2\text{C}_3\text{H}_4(\text{R}_1, \text{R}_2)$, is one of the most comprehensively studied metathesis systems with respect to geometries of the metallocyclobutane and the thermodynamics of olefin exchange, the mechanism of metathesis, the barrier to metathesis and the ring-opening polymerization of olefins.

Scientists at Accelrys have performed DMol³ calculations on the nature of the olefin metathesis in the $\text{TiCp}_2\text{C}_3\text{H}_4(\text{R}_1, \text{R}_2)$ system. The mechanism of olefin metathesis, and the olefin elimination from the metallocyclobutane, $\text{TiCp}_2\text{C}_3\text{H}_5(\text{tBu})$ was as well studied. In addition, the thermochemistry for the olefin exchange processes has been calculated. The calculated potential energy surface for olefin elimination in $\text{TiCp}_2\text{C}_3\text{H}_5(\text{tBu})$ is shown below for key structures along the reaction pathway. Click on the figure or the graph for larger images.

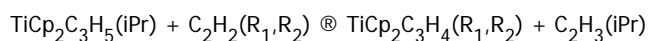


The key structures along the reaction pathway for olefin elimination in $\text{TiCp}_2\text{C}_3\text{H}_5(\text{tBu})$ (above), and the calculated potential energy surface for olefin elimination in $\text{TiCp}_2\text{C}_3\text{H}_5(\text{tBu})$ (below).



The predicted bond lengths, bond angles, and dihedral angles for the metallocyclobutane species were found to be in excellent agreement with experimental data. The relative stability of the metallocyclobutanes and the experimental free energy values for the corresponding reactions were also accurately reproduced. The following table shows a comparison of energies in the olefin exchange process where a very good agreement between the experimental results and the DMol³ predicted values is observed.

Table - Calculated and Experimental Relative Olefin Exchange Energies^a



| Compound | DE _{VWN} ^b | DE _{BP} ^b | DG _{BP} ^c | DZPE ^d | DG _{Expt.} ^e | T _c ^f |
|--|--------------------------------|-------------------------------|-------------------------------|-------------------|----------------------------------|-----------------------------|
| TiCp ₂ C ₃ H ₅ (iPr) | 0.0 | 0.0 | 0.0 | 0.000 | 0.0 | ---- |
| TiCp ₂ C ₃ H ₅ (tBu) | 0.2 | 1.6 | 1.2 | -0.392 | 0.8 | 55 |
| TiCp ₂ C ₃ H ₄ (Cyc) | 0.9 | 1.8 | 1.4 | 0.012 | 1.0 | 45 |
| TiCp ₂ C ₃ H ₄ (Me ₂) | 6.3 | 6.3 | 4.5 | -0.911 | 3.7 | 5 |
| TiCp ₂ C ₃ H ₄ (Me, Et) | 6.1 | 7.2 | 5.3 | -1.324 | 5.2 | 0 |
| TiCp ₂ C ₃ H ₄ (Me, iPr) | 6.7 | 9.3 | 6.3 | -1.981 | 6.0 | -5 |
| TiCp ₂ C ₃ H ₅ (Ph) | 3.8 | 2.9 | | | ---- | ---- |
| TiCp ₂ C ₃ H ₄ (Nor) | -2.7 | -1.1 | | | ---- | 65 |

a) All values in kcal/mol

b) Calculated with DMol Version 2.6

c) Calculated with DMol³ Version 1.0, DE_{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

e) Ref. 4

f) Cleavage temperature (°C) Ref. 5

Finally the reaction mechanism of this polymerization reaction has also been studied. For ROMP, the calculations predict that the

polymerization is always favored over free olefin production. It was also predicted that norbornene polymerization is more favourable than the polymerization of cyclopentene.

Reference

F. U. Axe and J. W. Andzelm, "Theoretical Characterization of Olefin Metathesis in the Bis-dicyclopentadienyltitanium (IV) System by Density Functional Theory", *J. Am. Chem. Soc.*, **121** (1999) 5396-5402.

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