

Catalytic Linear Oligomerization of Ethylene to Higher  $\alpha$ -Olefins Promoted  
by the Cationic Group-4  $[(\eta^5\text{-Cp}-(\text{CMe}_2\text{-bridge})\text{-Ph})\text{M}^{\text{II}}(\text{ethylene})_2]^+$   
(M = Ti, Zr, Hf) Catalysts: A Density Functional Investigation of the Influence  
of the Metal on the Catalytic Activity and Selectivity

Tobisch, Sven<sup>‡</sup> and Ziegler, Tom<sup>§</sup>

Institut für Anorganische Chemie der Martin-Luther-Universität Halle-Wittenberg,  
Fachbereich Chemie, Kurt-Mothes-Straße 2, D-06120 Halle, Germany,<sup>‡</sup> and

Department of Chemistry, University of Calgary, University Drive 2500,  
Calgary, Alberta, Canada T2N 1N4<sup>§</sup>

E-mail: tobisch@chemie.uni-halle.de, ziegler@ucalgary.ca

Mono(cyclopentadienyl)titanium systems with a hemilabile ancillary arene functionality have been reported recently as generators for a class of highly active catalysts for the selective ethylene trimerization.<sup>1</sup> The cationic  $[(\eta^5\text{-Cp}-(\text{CMe}_2\text{-bridge})\text{-Ph})\text{Ti}^{\text{IV}}(\text{alkyl})_2]^+$  species has been demonstrated as one of the most active precatalysts. We have recently reported a comprehensive theoretical-mechanistic study for this precatalyst exploring all crucial elementary steps of a tentative catalytic cycle that involves metallacycle intermediates.<sup>2</sup> The original suggested mechanism by *Hessen* and coworkers (which is based on prior work of *Briggs* and *Jolly*)<sup>3</sup> could be verified in important details but supplemented and extended by novel insights into how the linear oligomerization proceeds.

We report here a comprehensive theoretical investigation of crucial elementary steps of both the oligomerization reaction cycle and the initial precatalyst activation process for the corresponding Zr and Hf catalysts. It is the objective of the present study to evaluate the catalytic abilities of the heavier group 4 congeners for ethylene oligomerization. The following questions will be addressed: (1) How is the energy profile for the growth of metallacycle intermediates and for their decomposition into  $\alpha$ -olefins affected with the variation of the metal? (2) Are the rates for these two processes quite similar or do they exhibit a non-uniform behavior as a function of the metallacycle size? (3) What is the largest possible size of metallacycle intermediates occurring in the reaction course? (4) Which step is rate-determining? (5) Which factors control the  $\alpha$ -olefin distribution on the oligomerization process? The clarification of these points provides deeper insights into the catalytic structure-reactivity relationships for the linear ethylene oligomerization supported by the title class of catalysts. Furthermore, it may lead us to suggest promising catalyst modifications aimed at (1) enhancing the catalytic ability for ethylene trimerization and/or (2) proposing a possible route for generation of 1-octene or a higher linear  $\alpha$ -olefin as the predominant product.

(1) Deckers, P. J. W., Hessen, B., Teuben, J. H. *Organometallics*, **2002**, *21*, 5122.

(2) Tobisch, S., Ziegler, T. *Organometallics* **2003**, *22*, 5392.

(3)(a) Briggs, J. R. *Chem. Soc. Chem. Commun.* **1989**, 674. (b) Jolly, P. W. *Acc. Chem. Res.* **1996**, *29*, 544.