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Density Functional Study of the Insertion Step in Olefin Polymerization by Metallocene and Constrained-Geometry Catalysts

T. K. Woo,[†,‡] L. Fan,[†] and T. Ziegler[*,‡]

Novacor Research & Technology Corporation, Calgary, Alberta, Canada T2C 7K4, and Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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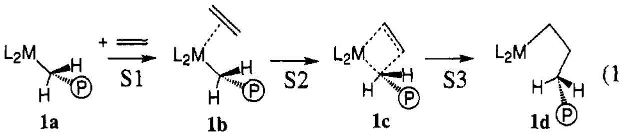
Summary: Nonlocal density functional (DF) calculations have been carried out on the insertion of ethylene into the metal–CH_3 bond of the Kaminsky type metallocenes (KTM) $Cp_2ZrCH_3^+$ (2), $(SiH_2Cp_2)ZrCH_3^+$ (3), $Cp_2ScCH_3^+$ (4), and $(SiH_2(Cp)NH)ZrCH_3^+$ (5).

Kaminsky[1a] type metallocenes (KTM) have recently attracted considerable interest as alternative catalysts to the traditional heterogeneous Ziegler–Natta systems in olefin polymerization. We have carried out density functional (DF)[2] calculations on the insertion of ethylene into the metal–CH_3 bond of the KTM systems $Cp_2ZrCH_3^+$ (**2**), $(SiH_2Cp_2)ZrCH_3^+$ (**3**), Cp_2ScCH_3 (**4**), and the constrained-geometry catalyst (CGC) $(SiH_2(Cp)NH)ZrCH_3^+$ (**5**). The insertion process of eq 1 is the key step in olefin polymerization catalyzed by KTM. The process in eq 1



(1)

1a Active Complex — **1b** π-Complex — **1c** Transition State — **1d** γ-agostic propyl product

involves forming an olefin π-complex, **1b**, in step S1 followed by the formation of the transition state **1c** in step S2 and the alkyl insertion product **1d** in step S3. Our calculations were based on the ADF[3a] program with a triple-ξ STO basis on the metals[3b–d] and a double-ξ STO basis on the ligands.[3b,c,e] Geometries were optimized within the local density approximation[4] (LDA), and energy differences were evaluated by adding nonlocal corrections to exchange[5] and correlation.[6] We are interested in the energy profile for the insertion involving **2** and how it is modified by introducing the SiH_2 bridge in **3**, replacing Cp with NH in **5**, or switching to the neutral system **4**. Previous studies[7] have covered only **3**.

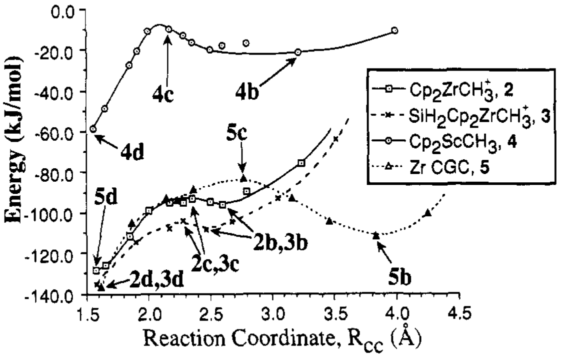


Figure 1. Energy profiles for the insertion of ethylene into the metal–CH_3 bond of **2**–**5**. The labels *n***b** represent the π-complexes for the insertion processes involving species ***n*** = **2**–**5**. Labels *n***c** represent the corresponding transition states and *n***d** the propyl products.

Figure 1 displays the reaction profile for the insertion process described in eq 1. The profiles were generated by varying the R_{CC} distance between the methyl carbon and the approaching ethylene carbon in steps while optimizing all other degrees of freedom. The profiles for **2**–**4** were optimized within a C_s symmetry constraint, while **5** was optimized with no symmetry constraints. For the two bis-Cp zirconium systems with and without a SiH_2 bridge, **2** and **3**, S1 is favorable due to the electrostatic attraction between the positive metal center and the π-electrons on ethylene. S1 is also favorable for the neutral scandium system **4** but is much less exothermic due to the reduced electrostatic attraction. All three bis-Cp systems **2**–**4** exhibit the π-complex **1b**, with a very shallow potential well, and the transition state **1c**, with activation barriers of 3 kJ/mol (**2**), 4 kJ/mol (**3**), and 14 kJ/mol (**4**). Structures **2b** and **2c** correspond to the π-complex and transition state, respectively, for the reaction involving **2**. We note the rotation of the methyl C_3 axis away from the metal toward the olefin carbon and the gradual formation of an α-agostic interaction as well as the stretch of the C–H methyl bond to R_{CH} = 1.15 Å. The importance of α-agostic interactions has been stressed by others.[8] The transition state[9] **2c** with R_{CC} = 2.28 Å already has a close carbon–carbon contact and occurs shortly after the formation of the π-complex **2b** with R_{CC} = 2.60 Å. The transition states and the π-complexes for the reactions involving **3** and **4** exhibit features similar to those in **2b** and **2c**.

[†] Novacor Research & Technology Corp.

[‡] University of Calgary.

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(9) The potential surface around **6b** is too shallow for ordinary transition-state optimization techniques. Thus, the transition state has been determined by a linear transit.

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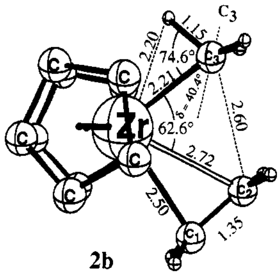
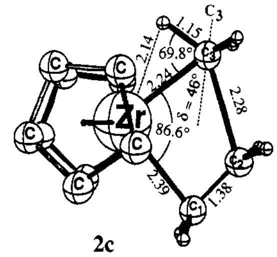
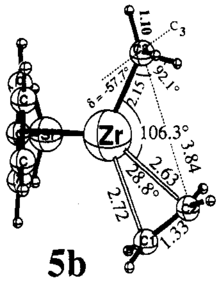


2b

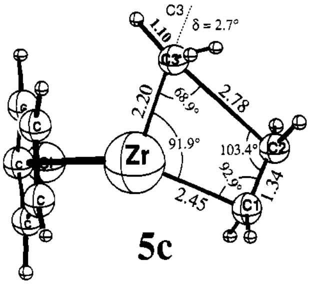


2c

The insertion step S1 involving the zirconium-based constrained-geometry catalyst[1b,c] **5** exhibits a clear minimum for the π-complex **5b** at R_{CC} = 3.84 Å. The corresponding step S2 has a pronounced barrier of 27 kJ/mol with the transition state **5c** at R_{CC} = 2.78 Å. The higher stability of the π-complex **5b** involving **5** compared to **2** and **3** at large R_{CC} distances (~3.75 Å) can be traced to a reduction in the steric interaction between ethylene and the metal fragment as one Cp ring is replaced by a NH group. The higher barrier in the case of **5** is a consequence of the stable π-complex which has to be abandoned in order to proceed to the product **5d** along S2 and S3. The π-complex **5b** has a large R_{CC} distance of 3.84 Å, too large to induce a distortion of the CH_3 group as observed in **2b**. Even at the transition state **5c** the R_{CC} distance of 2.78 Å is too large to allow for a distortion of the CH_3 group.



5b



5c

It is difficult to assess experimental activity data for KTM systems.[10] It seems that **5** and its Ti analogue are versatile copolymerization catalysts, but less active than **2** and **3** for ethylene polymerization.[10] This is in line with the profiles in Figure 1. The scandium system **4** should be quite active, according to Figure 1. However, it is found to be inactive due to dimerization of **4**. The $Cp^*_2Sc-CH_3$ equivalent of **4** with Cp* = $C_5(CH_3)_5$ does not dimerize, and it readily inserts ethylene.[11b] A scandium-based CGC[1d] has also shown activity toward olefin polymerization. The insertion process for **2**, **3**, and **5** is more exothermic than for **4** due to the net positive charge of the zirconium catalysts.

We have shown that the ordinary bis-Cp systems **2**, **3**, and **4** all have a low electronic barrier to insertion irrespective of charge and presence of a SiH_2 bridge. Our findings for **3** are in contrast to previous HF and MP2 results[7] in which the barrier of insertion was calculated to be 58 and 26 kJ/mol, respectively. Here the MP2 value is based on the HF geometry. Investigations have shown[12] that the present DF approach is of the same quality as MP4 calculations, and we expect that the *ab initio* barrier will be reduced at a higher level of *ab initio* theory. The replacement of Cp with NH in **5** results in a substantial increase of the barrier. We attribute that to the stability of the π-complex **5b** at large R_{CC} values. The stability is caused by a reduction in the steric interaction between ethylene and the ligands on the metal center as a Cp ligand is replaced by a NH group. Electronically the metal centers in **2** and **3** are more positive than the metal center on **5** by 0.25e according to a Mulliken population analysis. Thus, electronic factors would favor π-complex formation in **2** and **3** compared to **5**.

Work is now under way to follow the insertion of ethylene into the ethyl and propyl analogues of **2**–**5**. Such a study will not only consider the electronic aspect of the insertion studied here but also deal with the required rearrangement of the polymer chain. It is hoped that such a study will give a more detailed picture of all factors that might contribute to a barrier for the insertion process in olefin polymerization.

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