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# Alternative mechanistic interpretation for unconventional catalytic behaviour of triisobutylaluminium-activated heterocenes in ethylene polymerization

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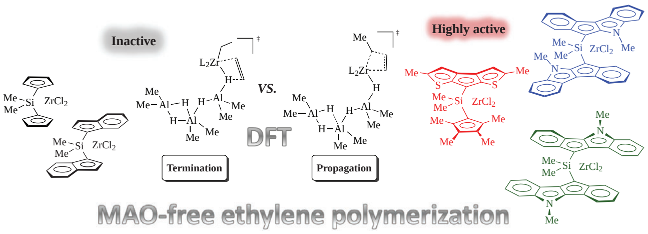
**DFT simulations of ethylene polymerization with the participation of neutral Zr–Al$_3$ hydride species revealed a fundamental difference in catalytic behaviour of triisobutylaluminium-activated heterocenes and conventional *ansa*-zirconocenes.**



*Keywords*: ethylene, polymerization, zirconocenes, single-site catalysts, DFT.

In polyolefin industry, zirconocenes $L_2ZrX_2$ (L = $\eta^5$-ligand, X = Cl, Me) have a special place among single-site polymerization precatalysts due to their high productivity and structural diversity.[1] Generally accepted mechanism of zirconocene-catalyzed polymerization considers the catalytic particle as alkylzirconocene *cation*, formed upon the activation of $L_2ZrX_2$ with methylalumoxane (MAO) or perfluoroaryl borates.[2] Under homogeneous conditions, activation of zirconocenes typically requires $10^3$–$10^4$ equivalents of MAO.[2(*f*),3] Lowering the $Al_{MAO}$/Zr ratio would be highly desirable for polyolefin technology, but conventional $\eta^5$-cyclopentadienyl and $\eta^5$-indenyl zirconium complexes, activated by 1–20 MAO equivalents, also catalyze the slow dimerization or oligomerization of α-olefins.[4] However, recently we showed that *ansa*-zirconocenes containing heterocycle-fused $\eta^5$-cyclopentadienyls (heterocenes), activated by MMAO-12 at Al/Zr ratios of 20 : 1, are highly active in the polymerization of 1-octene.[5]

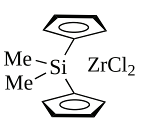
In the absence of MAO, conventional zirconocenes activated by triisobutylaluminium (TIBA) demonstrate negligible activities.[6] Using TIBA as a single activator for bis($\eta^5$-cyclopentadienyl) and bis($\eta^5$-indenyl) *ansa*-zirconocenes **1** and **2**, we tried to conduct polymerization of ethylene and found these complexes to be inactive (Table 1,† entries 1 and 2, respectively). On the contrary, heterocenes **3**–**5** synthesized by known methods[5,7] were active with a formation of high-MW polyethylenes (entries 3–6).

**Table 1** Ethylene polymerization results.

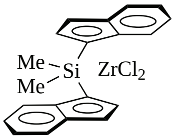
| Entry | Zr complex | PE yield/g | TOF $10^3$/h$^{-1}$ | $M_n \times 10^3$/ SEC$^a$ | $Đ_M$/SEC$^a$ | mp$^b$/°C |
|---|---|---|---|---|---|---|
| 1 | **1** | 0.0 | – | – | – | – |
| 2 | **2** | 0.0 | – | – | – | – |
| 3 | **3** | 2.15 | 3.8 | 456 | 4.2 | 135.9 |
| 4 | **4** | 13.25 | 47.3 | 983 | 2.0 | 137.9 |
| 5$^c$ | **5** | 4.95 | 8.8 | 1436 | 2.1 | 135.9 |

$^a$ In 1,2,4-trichlorobenzene at 135 °C, PS standards. $^b$ DSC data. $^c$ Reaction time 1 h.

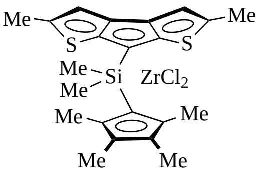
According to the current mechanistic view on α-olefin transformations in the presence of zirconocenes and organoaluminium activators such as TIBA, the reaction of $L_2ZrCl_2$ with $Bu^i_2AlH$ or TIBA leads to the formation of neutral Zr–Al species **A** [Figure 1(*a*)]. Due to the ease of isobutylene elimination in $L_2Zr–Bu^i$ complexes,[8] such species represent Zr–Al hydrides with different Al/Zr ratios.[8(*e*),(*f*),9] Species **A** can



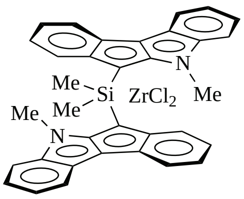
**1**



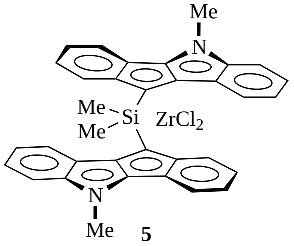
**2**



**3**



**4**



**5**

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† *Polymerization procedure*. *n*-Heptane (200 ml) and TIBA (1 ml of 1 M solution in *n*-heptane, 1 mmol) were placed into an autoclave. A catalyst solution was prepared by the addition of TIBA (1 ml, 1 mmol) to a Zr complex (10 μmol) in *n*-heptane (5 ml) and stirring at 40 °C for 10 min. The catalyst was transferred to the autoclave at 40 °C, the autoclave was pressurized with ethylene. After 2 h, the reactor was cooled to 20 °C and vented. The polymer was collected, washed with 5% HCl and then with MeOH, dried *in vacuo* and weighted.

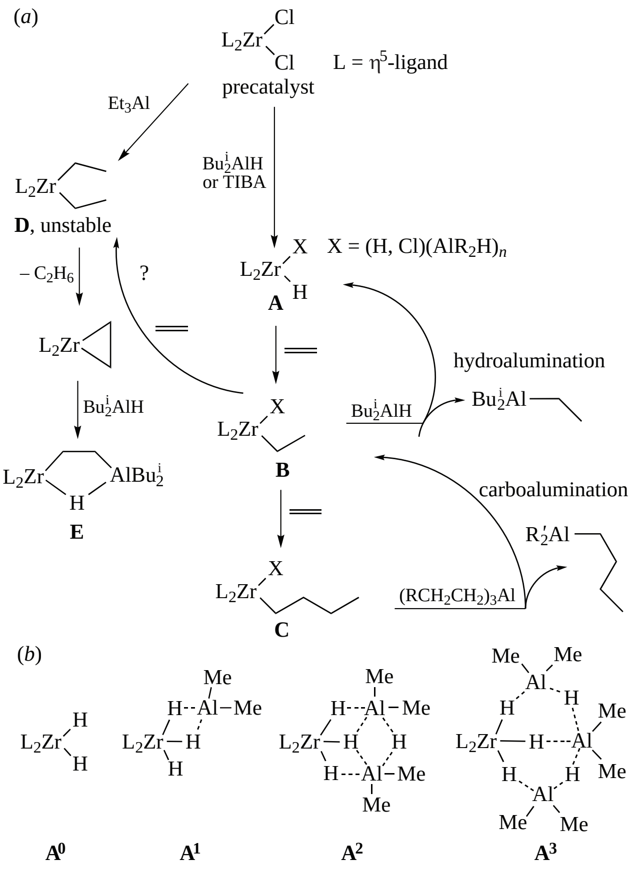

**Figure 1** (*a*) Reactions of neutral zirconocenes with organoaluminium compounds and ethylene and (*b*) model Zr–Al methyl-hydride species.

incorporate a single α-olefin molecule to form monoalkyl complexes **B**.[8(*a*),(*e*),9,10] α-Olefin insertion at the Zr–C bond in these monoalkyl complexes with the formation of carboalumination products **C** has been detected for sterically hindered cyclopentadienyl, indenyl and fluorenyl complexes.[9(*b*),10(*b*),11] A special case is the reaction of $L_2ZrCl_2$ with excess $AlEt_3$, in this process unstable diethyl zirconocenes **D** form zirconacyclopropanes capable of giving Zr–Al species **E**,[9(*b*),12] which are incapable of further α-olefin insertion.

Given that TIBA in our experiments was used in Al/Zr ratio of 200, we proposed alkyl-hydride structure for the type **A** species, and evaluated the relative stability of the model complexes $\mathbf{A^0}$–$\mathbf{A^3}$ [Figure 1(*b*)], derived from zirconocenes **1**–**5**, at the M06-2X/DGDZVP level of the DFT (see Online Supplementary Materials for details)[13] as implemented in Gaussian-09 program package.[14] The results of the calculations are presented in Table 2. For all zirconocenes, type $\mathbf{A^3}$ species were found to be the most stable in *H* scale.

We proposed that type $\mathbf{A^3}$ complexes represent the most adequate model for the starting species that are able to insert olefin with a formation of type $\mathbf{B^3}$ species. This process was found to be exothermic for all complexes and exergonic for **2**–**5** (see Table 2). Note that the activities of zirconocenes under study and relative stability of $\mathbf{B^3}$ species correlate. Considering $\mathbf{B^3}$ as a model species, we optimized the transition states or the insertion of ethylene into the Zr–C bond (chain propagation pathway, Figure 2, left). Calculated $\Delta H^{\neq}$ values varied from 16.1 to 23.1 kcal mol$^{-1}$ (298.15 K), and were substantially lower for *inactive* zirconocenes **1** and **2**! This disappointing result prompted us to consider an alternative pathway for the reaction of $\mathbf{B^3}$ with ethylene, namely, the insertion of the ethylene molecule into Zr–H bond in $\mathbf{B^3}$ complexes. As a result of that

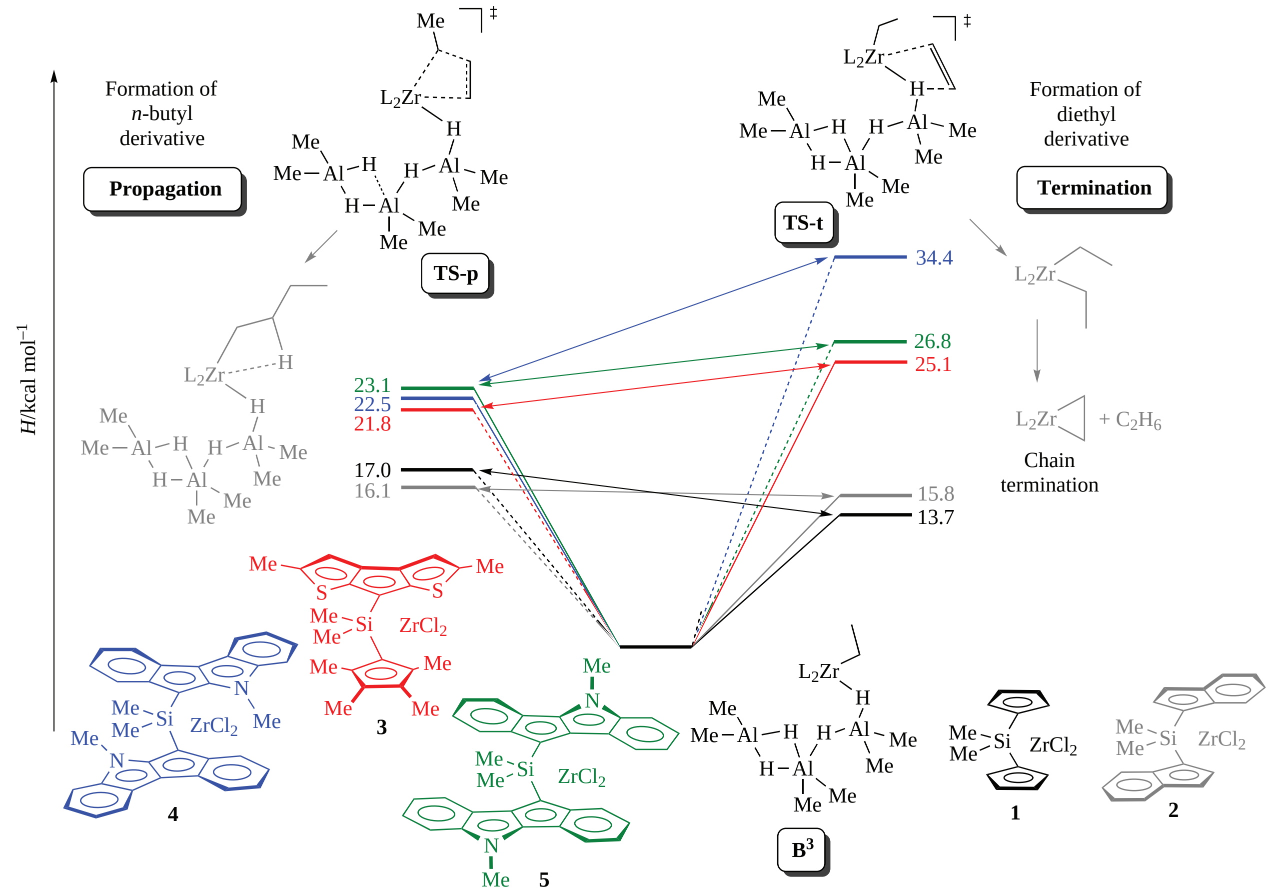

**Figure 2** Calculated free activation enthalpies (kcal mol$^{-1}$, 298.15 K) for ethylene insertion into the Zr–C (left) and Zr–H (right) bonds in $\mathbf{B^3}$ model species for zirconocenes **1**–**5**.

**Table 2** Relative energies of the formation of $\mathbf{A^1}$, $\mathbf{A^2}$ and $\mathbf{A^3}$ complexes (kcal mol$^{-1}$, calculated at 298.15 K).

| Complex | Parameter | Zirconocene | | | | |
|---|---|---|---|---|---|---|
| | | **1** | **2** | **3** | **4** | **5** |
| $\mathbf{A^1}$ | $\Delta G$ | –16.93 | –15.73 | –13.05 | –14.18 | –11.64 |
| | $\Delta H$ | –22.51 | –21.07 | –18.83 | –20.69 | –18.05 |
| $\mathbf{A^2}$ | $\Delta G$ | –16.97 | –11.37 | –8.07 | –12.98 | –4.86 |
| | $\Delta H$ | –26.66 | –23.24 | –18.22 | –25.22 | –18.04 |
| $\mathbf{A^3}$ | $\Delta G$ | –23.54 | –14.68 | –9.54 | –10.50 | –10.57 |
| | $\Delta H$ | –36.54 | –33.26 | –29.26 | –30.87 | –30.89 |
| $\mathbf{B^3}$ | $\Delta G^a$ | 0.33 | –5.02 | –6.19 | –10.36 | –8.93 |
| | $\Delta H^a$ | –12.21 | –14.20 | –14.93 | –21.21 | –17.54 |

[a] Relative to $\mathbf{A^3}$.

examination, we found this reaction with a formation of zirconocene diethyl species **D** to be energetically preferable for **1** and **2**! The details of DFT calculations are presented in Online Supplementary Materials.

Given that these species are unstable and form zirconacyclopropanes and then inert Zr–Al species **E**,[9(*b*),12] or zirconacyclopentanes (see Online Supplementary Materials for details), the results of the modeling allow us to explain the lack in catalytic activity of conventional $\eta^5$-cyclopentadienyl and $\eta^5$-indenyl complexes under MAO- and borate-free conditions by the deactivation of the $\mathbf{B^3}$-type complexes *via* insertion of ethylene molecule into Zr–H bond.

Apparently, the results of our DFT modeling, based on simplified mechanistic concept, do not exhaustively reflect the real processes occurring in the course of zirconocene-catalyzed polymerization of α-olefins under the MAO- and borate-free conditions. These processes may include coordination of organoaluminium fragments on heteroatom, formation of mixed hydride-chloro-alkyl species, and other reactions. However, this model reflects the principal difference in the chemical behaviour between conventional zirconocenes and heterocenes. The further research focused on identification of the catalytic species formed during activation of $L_2ZrCl_2$ by TIBA, would allow for the development of single-site catalysts for polymerization of α-olefins, that are active under low-MAO and MAO-free conditions. We believe that the potential of heterocenes for the use as such catalysts has been substantially undervalued.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.07.029.

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