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A Second Transition State for Chain Transfer to Monomer in Olefin Polymerization Promoted by Group 4 Metal Catalysts

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In olefin polymerization catalyzed by transition metals, polymer chain length is limited by the occurrence of various chain termination mechanisms. Thus, detailed knowledge of chain transfer mechanisms is crucial for the design of improved catalysts. Even in the absence of external chain transfer agents (hydrogen, aluminum alkyls), chain termination still occurs. The "standard" chain termination mechanisms are (see Scheme 1):[1,2]

• β-Hydrogen transfer to monomer, which involves a transition state (TS_A) as shown in path A ("associative displacement").

• β-Hydrogen elimination, followed by loss, replacement, and reinsertion of the olefin, as in path B ("dissociative displacement").

Chain transfer to monomer according to path A is generally accepted to be the dominant chain termination pathway for olefin polymerization promoted by group 4 metal catalysts.[1] It has been supported by extensive theoretical studies,[3] which have shown it to be preferred to β-hydrogen elimination for most catalysts. Theoretical studies have also provided detailed knowledge of the TS_A geometry.[3,4] In particular, they find that it requires much more space around the metal than monomer insertion.[1] This has led to the "design principle" of using sterically congested systems to obtain high molecular weights, as in 2,2′-substituted *rac*-bis(1-indenyl) *ansa*-zirconocenes[5] or the square-planar Brookhart-type Ni and Pd catalysts.[6] Recent theoretical results[7,8] suggest that this principle might also apply to octahedral amine phenolate[9] and bis(phenoxy-imine) catalysts.[10]

The geometry around the transition metal in TS_A, characterized by a strong metal−hydrogen interaction, differs substantially from the one we discussed earlier for chain transfer at the main-group metal aluminum.[11] For Al, the TS corresponds to direct hydrogen transfer from alkyl to alkene, without significant metal−hydrogen interaction (Scheme 1, path C).[11] This intriguing difference led us to wonder whether such an alternative mechanism could also be relevant for group 4 transition-metal catalysts. In the present theoretical study, we show that it not only can occur, but can even become a strongly preferred path in cases where steric constraints block the "classical" path A.

Table 1 shows a systematic comparison of the two types of chain transfer to propene for various prototypical ligands (**1**−**6**, Scheme 2) and the metals Ti, Zr, and Hf as calculated at the B3LYP/SVP level[12,13] (for calculation details, see the Supporting Information). Separate transition states for path C (TS_C) could be located for all systems except for the very open constrained-geometry systems **4** and **5** in combination with Zr.[14]

Examination of the data reported in Table 1 reveals clear trends:

Scheme 1. Standard (A,B) and New (C) Paths for Chain Transfer to Monomer in Olefin Polymerization

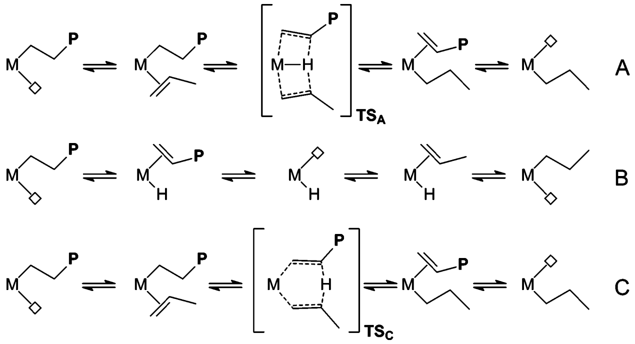
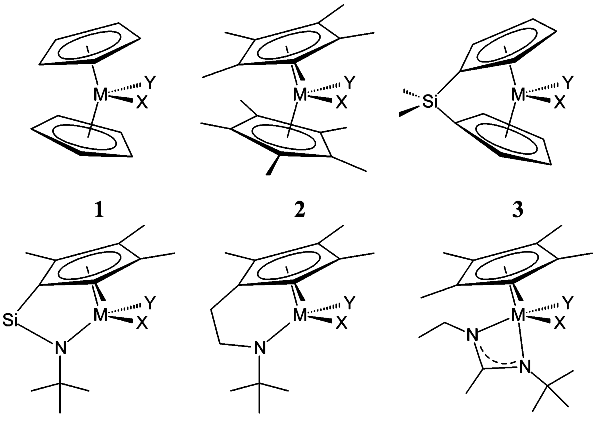


Table 1. Energy (Free Energy)[a] Differences in kcal/mol between β-H-Transfer Transition States for Paths A and C, from ^{i}Bu to Propene[b]

ligand	$\Delta\Delta E^\ddagger$ ($\Delta\Delta G^\ddagger$)		
	Ti	Zr	Hf
1	−0.8 (+0.6)	−8.7 (−6.9)	−1.1 (+0.4)
2	+8.0 (+10.4)	+0.1 (+2.2)	+7.0 (+8.1)
3	−3.9 (−2.7)	−11.3 (−10.3)	−3.5 (−1.9)
4	−5.3 (−2.4)	n.d.	−3.4 (−1.6)
5	−3.6 (−2.0)	n.d.	−2.3 (−0.9)
6[15]	+9.1 (+10.6)[16]	+7.6 (+11.6)	+16.8 (+18.6)

[a] Free energies (273 K, 1 bar) calculated for gas-phase cations. [b] Positive numbers indicate path C is favored.

Scheme 2. Systems Considered in This Study (M = Ti, Zr, Hf; X = ^{i}Bu, Y = Propene)



1 **2** **3** **4** **5** **6**

(1) Ligand variation has a dramatic effect on the relative energies of the two paths, covering a range of ca. 14 (Ti) or 18−20 (Zr, Hf) kcal/mol. In particular, steric hindrance around the metal favors path C (compare Cp and Cp* systems, **1** and **2** in Table 1). The relatively open bridged systems **3**−**5** all favor path A, while the extremely crowded Cp*-amidinate system **6**[15] has the largest preference for the new path C.

(2) For each ligand, Ti and Hf display a higher tendency than Zr (by about 6 kcal/mol) to follow path C.[16]

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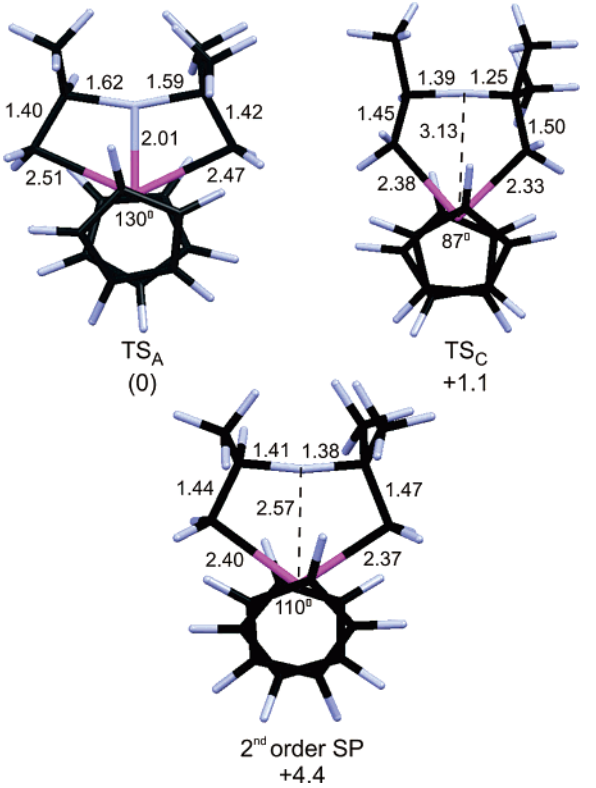

Figure 1. Geometries (Å, deg) and relative energies (kcal/mol) for the two chain transfer to monomer transition states of the **1**-Hf system and (bottom) the second-order saddle point connecting them.

(3) For each system, thermal corrections (ZPE and entropy) increase the preference for path C, typically by 1−2 kcal/mol.

The geometries we calculate for TS$_C$ (see, for example, Figure 1 for **1**-Hf) strongly resemble those reported earlier for Al.[11] They have a CMC angle of less than 90° (cf. 120−130° for TS$_A$), which explains why this alternative path is preferred for more hindered systems.

In a further analysis, we identified the second-order saddle points of system **1** which connect TS$_A$ and TS$_C$ (see, for example, Figure 1, bottom).[17] These were found to be only slightly above the higher of the two regular transition states (by 1−6 kcal/mol) for all systems, suggesting that the potential-energy surface (PES) between the two paths is extremely flat. The flatness explains why we do not find a separate TS$_C$ for Zr in the more open systems **4** and **5**, where the preference for path A is strongest.[14]

The existence of two distinct reaction paths, both involving only a single elementary step, leading from the same reactant to the same product is a rare event. Its occurrence here demonstrates how delicate and complicated the seemingly simple process of olefin polymerization can be.[18] It is difficult to distinguish between paths A and C on the basis of experiments alone, because they lead to identical rate equations and similar isotope effects. The existence of the alternative path C helps to explain observed trends in molecular weight dependence on metal and ligand structure. This path should be particularly relevant for Ti and Hf and for bulky ligands.[19] It not only requires less space around the metal than path A does, but even less than the chain propagation step of olefin insertion. Thus, the "design principle" of using ligand steric bulk to increase molecular weights needs some qualification, because when taken to extremes it would lead to catalysts preferring path C to chain growth.

Acknowledgment. This article is dedicated to the memory of Professor Paolo Corradini for his fundamental contributions to polymer science. We thank the CIMCF of the Università di Napoli "Federico II" for technical assistance. This work was supported by PRIN 2004 grants and a contribution from SABIC Petrochemicals.

Supporting Information Available: Details of the calculation methods, total energies and thermal corrections for transition states and second-order saddle points, calculated with different functionals and basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) See, for example: Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253 and references therein.

(2) Various alternative mechanisms of chain transfer reactions in olefin polymerization with homogeneous single-site catalysts have been proposed (see: Resconi, L.; Camurati, I.; Sudmeijer, O. *Top. Catal.* **1999**, *7*, 145); here we will only discuss the two main ones.[1]

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(10) Leading references: (a) Makio, H.; Kashiwa, N.; Fujita, T. *Adv. Synth. Catal.* **2002**, *344*, 477. (b) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236.

(11) See, for example: Budzelaar, P. H. M.; Talarico, G. In *Group 13 Chemistry III: Industrial Applications*; Roesky, H. W., Atwood, D. A., Eds.; Structure and Bonding; Springer-Verlag: Berlin, 2003; Vol. 105, and references therein.

(12) Calculations carried out with *Gaussian03*, *Gaussian98*, and *Turbomole* programs. For further details, see the Supporting Information.

(13) Separate TS$_A$ and TS$_C$ stationary points and second-order saddle points were also located for Et to ethene and ^{n}Pr to ethene transfer in the Cp$_2$M systems; see the Supporting Information for energies.

(14) For the **4**-Zr and **5**-Zr systems, no separate path C seems to exist; the energy increases monotonically on increasing the Zr−H separation from 2.8 to 3.6 Å.

(15) This C_1 symmetric system (see: Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958) shows two TSs for both paths A and C, differing in the monomer and chain positions. Values in Table 1 refer to the lowest-energy TSs.

(16) In TS$_A$ for the extremely crowded system **6**-Ti, one of the amidinate nitrogens has dissociated from the metal. This disturbs the otherwise consistent trend in metal effect somewhat.

(17) The second-order saddle points were located using a development version of our own external optimizer (see Supporting Information).

(18) Recently, the possibility of a path C-like TS has even been suggested for *β-methyl* transfer to monomer: Yang, P.; Baird, M. C. *Organometallics* **2005**, *24*, 6013.

(19) The stronger preference of Ti (compared to Zr) for path C might be due to steric factors. For Hf vs Zr, the explanation is probably more complicated (Budzelaar, P. H. M.; Talarico, G. Manuscript in preparation). In ref 3, Ziegler et al. calculated a weakening of the M−H bond (relative to the M−C bond) on going from lighter to heavier metals, which agrees with our Zr → Hf trend.

JA0586034