Zirconium−Alkyl Isomerizations in Zirconocene-Catalyzed Olefin Polymerization: A Density Functional Study

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The migration of a Zr center between adjacent carbon atoms of a Zr-bound alkyl group is investigated by a density functional study of alternative reaction paths available to a $(C_5H_5)_2Zr$−alkyl cation. This migration is found to occur by the classical reaction route, i.e. by β-H transfer, olefin rotation, and reinsertion into the Zr−H bond without loss of the olefin ligand, rather than by a concerted Zr/H exchange. The activation barrier is determined to decrease from 75 kJ/mol for the degenerate isomerization of a zirconocene ethyl cation to 49 kJ/mol for the isomerization of a primary to a secondary zirconocene propyl cation and 41 kJ/mol for its back-reaction. It is further reduced to 40 kJ/mol for the isomerization of a primary to a tertiary zirconocene isobutyl cation and 31 kJ/mol for its reverse, which model the isomerization process competing with stereoregular chain growth in zirconocene-based catalysts. The facility with which the zirconocene isobutyl cation transfers its β-H atom is connected with a particularly soft stretching vibration of the agostic β-C−H bond. Substantial stabilization of positive charge at the β-carbon atom by two alkyl substituents appears to be the cause. Reaction paths by which an olefin ligand in an intervening isomerization intermediate can change its coordination from one enantioface to the other have also been identified.

Introduction

Stereoregular homogeneous olefin polymerizations with chiral zirconocene catalysts[1] have recently been shown to be seriously affected by Zr−alkyl isomerizations, which participate in stereoerror formation,[2−4] regioerror transformation,[5] cycloolefin concatenation[13] and chain-growth termination.[3] Common to all these phenomena is the ability of the catalytically active Zr center to migrate along the metal-bound polymer chain. Zr-migration reactions of this type appear to be related to the “chain running” processes recently observed also for Ni- and Pd-based polymerization catalysts.[6,7]

Observations of this kind raise the question as to the reaction sequences and relevant intermediates responsible for these isomerizations. Previous studies on the isomerization of olefin hydrozirconation products[8] have led to the generally accepted view that these isomerizations proceed via β-H transfer to the metal center, rotation of the ensuing olefin around the metal−olefin bond, and its reinsertion into the Zr−hydride bond. Some of these elementary reaction steps have been analyzed with regard to the essential factors affecting their activation energies,[9−11] but overall sequences of this type still require further clarification: especially, a rotation of an unsaturated polymer chain end around the Zr−olefin bond within the sterically restricted coordination gap[12] of a zirconocene catalyst is difficult to imagine. Loss of an olefinic polymer end from the Zr center, on the other hand, would hardly be reversible in the presence of the huge excess of monomer present in these reaction systems. An unresolved question concerns also the stereochemistry of these isomerizations: in at least two instances, isomerizations have been found to occur with an apparent interchange of the Zr center from one enantioface of the coordinated olefin to the other.[3,13]

In order to analyze conceivable reaction paths for Zr-alkyl isomerizations, we have undertaken model calculations by the density functional method,[14] to study several types of intramolecular Zr shifts between neigh-

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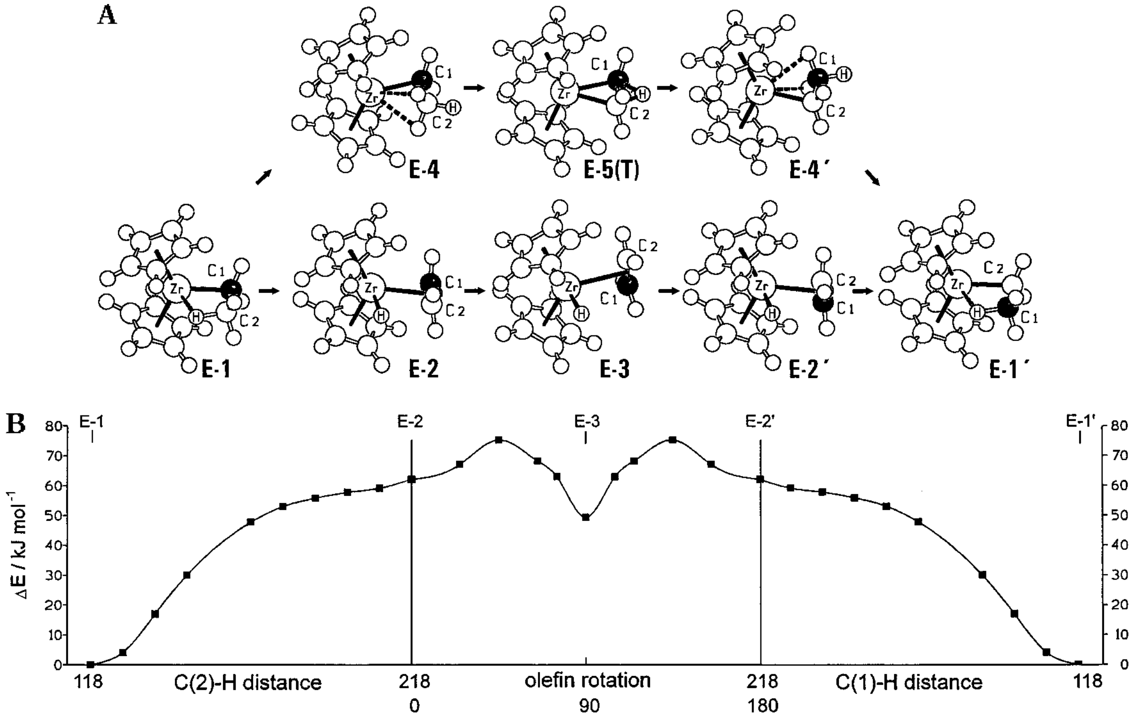

Figure 1. (A) Reaction paths for the degenerate isomerization of the cation $(C_5H_5)_2ZrC_2H_5^+$, by the classical reaction route (bottom) and by an alternative, concerted Zr/H exchange (top). (B) Energy profile for the isomerization of the cation $(C_5H_5)_2ZrC_2H_5^+$ according to the reaction sequence E-1, E-3, E-1′.

boring carbon centers of linear and branched hydrocarbon chains in cationic zirconocene complexes of the general type $(C_5H_5)_2Zr{-}alkyl^+$.[15] This method has recently been successfully employed for investigations of related organometallic reaction paths[16] and reaction dynamics.[17]

Computational Methods

For geometry optimizations of the complexes studied, we used the functional of Vosko, Wilk, and Nusair.[18] After the final SCF procedure, energy differences were corrected for nonlocal exchange and correlation using the gradient-corrected functional according to Becke[19] and Perdew.[20] For all calculations the program DGAUSS (2.3.1)[21] with the medium integration grid option was used on a Cray J916/6-1024. The DZVP[21] valence basis set was used for all Zr, C, and H atoms; for the J_{ij} Coulombic term[22] the A1[21] auxiliary basis was used for all atoms. All stationary points were checked by frequency calculations for the absence of negative eigenvalues and the presence of only one for each transition state.

Table 1. Geometry Parameters of the Zirconocene Ethyl Cation $(C_5H_5)_2ZrC_2H_5^+$ along the Isomerization Path Represented in Figure 1 (Distances in pm, Angles in deg)

	E-1	E-2	E-3	E-4	E-5
Zr−H	209	186	184	250/254	
C(β)−H(β)	118	218	330	112/112	131
ν(C−H$_b$)/cm^{-1}	2296				-892
Zr−C(1)−C(2)	84	70		80	69
C(1)−C(2)−H(β)	115	131			53
(C_5H_5)−Zr−(C_5H_5)	138	132		135	139
Zr−C	223	246/275	276/276	225	228/228
Θ^a	0	0	90	180	180
E/(kJ mol^{-1})	0	62	49	26	130

[a] Dihedral angle H−Zr−C(1)−C(2).

Results and Discussion

To probe alternative mechanisms for the isomerization of Zr−alkyl units, we consider first the simplest possible model system, the degenerate isomerization of the ethylzirconocene cation $(C_5H_5)_2ZrC_2H_5^+$ (E) represented in Figure 1A. For the initial state of this cation, E-1, we obtain the bonding parameters listed in Table 1. A short Zr−H contact of 209 pm, an elongated C(2)−H(2) distance (118 pm), a decreased Zr−C(1)−C(2) angle (84°), and a reduced C(2)−H(2) stretching frequency of 2296 cm^{-1} are indicative of the β-agostic interaction in such a species, in accord with experimental and theoretical data previously reported for related complexes.[23]

For this isomerization one might consider, in addition to the classical reaction sequence (β-H transfer, olefin rotation, reinsertion) also concerted reaction modes, in which the Zr center at C(1) and one of the hydrogen atoms at C(2) exchange their positions simultaneously. Related interchange reactions of a Zr center with an H atom in a δ or ϵ position have been proposed as

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(15) Not considered here are intermolecular processes involving e.g. two Zr centers or H^+ transfer between a zirconocene−alkyl cation and some other species.

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Table 2. Geometry Parameters of the Zirconocene Propyl Cation $(C_5H_5)_2ZrC_3H_7^+$ along the Isomerization Path Represented in Figure 2 (Distances in pm, Angles in deg)

	P-1	P-2	P-3	P-4	P-5	P-6	P-7
Zr−H	205	186	185	184	185	187	207
C(β)−H(β)	120	198	258		218	178	115
ν(C−H$_b$)/cm^{-1}	2121	−153					2263
Zr−C(1)−C(2)	84	89	90	90	81	79	83
C(1)−C(2)−H(β)	112	104	100		107	111	115
(C_5H_5)−Zr−(C_5H_5)	136	134	133	133	131	132	136
Zr−C	225	240	251/286	253/286	247/262	240	226
Θ^a	−1	4	−7	75	151	151	180
E/(kJ mol^{-1})	0	45	39	49	35	37	8

[a] Dihedral angle H−Zr−C(1)−C(2).

elementary steps in the "back-biting" isomerization[2,24] of branched Zr−alkyl groups in sterically hindered zirconocene complexes.

One conceivable transition state for such a "direct" reaction mode (E-5) is represented in Figure 1A. The C_{2v}-symmetric transition state E-5 is reached from a doubly β-agostic geometry, E-4, if the outside hydrogen atom at C(2) is moved toward C(1), while the Zr center is displaced in the opposite sense. The resulting transition state can be considered as a protonated zirconocene ethene complex, with the H^+ embedded in the π-electron cloud opposite to the Zr center. The geometry of this transition state, which is minimized with respect to all interatomic distances, has only one negative frequency (−892 cm^{-1}) for a combined H-atom displacement and C_2H_4 rocking mode, which carries one olefin terminus toward the Zr center, the other one toward the migrating H atom.[25,26] The energy of species E-5 is found to be 130 kJ/mol above that of the initial state E-1, however, which makes it rather unlikely that this reaction mode contributes to the isomerization to any significant degree. An alternative geometry, in which one of the C(2)-bound hydrogen atoms of E-1 migrates toward C(1) via the inside of the coordinated olefin, is found to be associated with a much higher energy of 286 kJ/mol; it is thus even less likely to represent a viable reaction path.

We return, therefore, to the classical reaction sequence for metal alkyl isomerization in an attempt to locate plausible transition states and intermediates. In a first approach, we elongate the β-H−C bond while relaxing all other interatomic bonds, retaining, however, an overall C_s symmetry for the reaction complex. In accord with previous studies,[16a] we cannot locate a distinct energy minimum for a putative zirconocene hydride complex containing the ethylene molecule in the equatorial ligand plane. From an energy plateau found at C(2)−H(2) distances of ca. 200 pm, we estimate an energy of 62 kJ/mol for such a complex (E-2), relative to the initial state E-1 (Figure 1B). Such a species contains its olefin ligand in an unsymmetrical geometry,[27] with significantly different Zr−C(1) and Zr−C(2) distances of 246 and 275 pm. Complex E-2 would revert to the initial state E-1 without any significant activation energy.

The energy profile of a another C(2)−H(2) elongation mode, in which all interatomic distances are optimized without retention of C_s symmetry, yields an energy minimum at a C(2)−H(2) distance of 330 pm. This minimum is associated with a species in which the C_2H_4 molecule is coordinated to the Zr center with the C═C axis perpendicular to the equatorial ligand plane. Surprisingly, this nearly C_s symmetrical intermediate E-3, with Zr−C(1) and Zr−C(2) distances of 274 pm, is found to be more stable, by approximately 13 kJ/mol, than the previously described species E-2 with in-plane C_2H_4 coordination.[28]

This geometry thus appears to represent the most favorable intermediate for the isomerization process given in Figure 1. The overall activation energy of $\Delta E_A \approx 75$ kJ/mol, represented by the maximum at $\theta = 45°$ in Figure 1B, appears rather high, compared to an activation energy of 29 kJ/mol, calculated for chain termination by β-H transfer to a coordinated olefin.[16b,c] In this case, β-H transfer to the metal is thus unlikely to compete with β-H transfer to a coordinated olefin.

To approach the situation in actual polymerization systems, we will now consider Zr−alkyl isomerizations with more highly substituted alkyl residues. For the isomerization of a $(C_5H_5)_2$Zr−*n*-propyl to a $(C_5H_5)_2$Zr−isopropyl cation (P, Figure 2A), we obtain, along a totally relaxed reaction path, the energy profile represented in Figure 2B.

For the initial state P-1, we find a geometry similar to that described above for E-1, with a β-agostic bond characterized by a Zr−H(2)−C(2) distance of 205 pm, an H(2)−C(2) distance of 120 pm, Zr−C(1)−C(2) and C(1)−C(2)−H(2) angles of 84 and 112°, and a C(2)−H(2) stretching frequency of 2121 cm^{-1}. By all these criteria, the β-agostic interaction appears to be stronger here than in the ethyl complex E-1.

Upon elongation of the C(2)−H(2) distance, the reaction complex proceeds, over an activation barrier of $\Delta E_A \approx 45$ kJ/mol (P-2), to the intermediate P-3, located in a very shallow energy minimum at 39 kJ/mol above P-1. This intermediate contains a propene ligand with its C═C axis inclined by −7° with respect to the $(C_5H_5)_2$Zr

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(26) The migrating H atom is placed at a distance of 131 pm from C(1) and C(2), in accord with a distance of 131 pm calculated for a C_{2v}-symmetric $C_2H_5^+$ cation. Ajith Perera, S. A.; Bartlett, R. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 8476.

(27) Similarly unequal Zr−C distances of 268 and 289 pm have been observed for olefin coordination in the cation $(C_5H_5)_2Zr^+H_2C{=}CH{-}(CH_2)_3C(CH_3)_2O$: Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867.

(28) The olefin in complex E-4 has a bonding energy of 98 kJ/mol relative to the dissociated species.

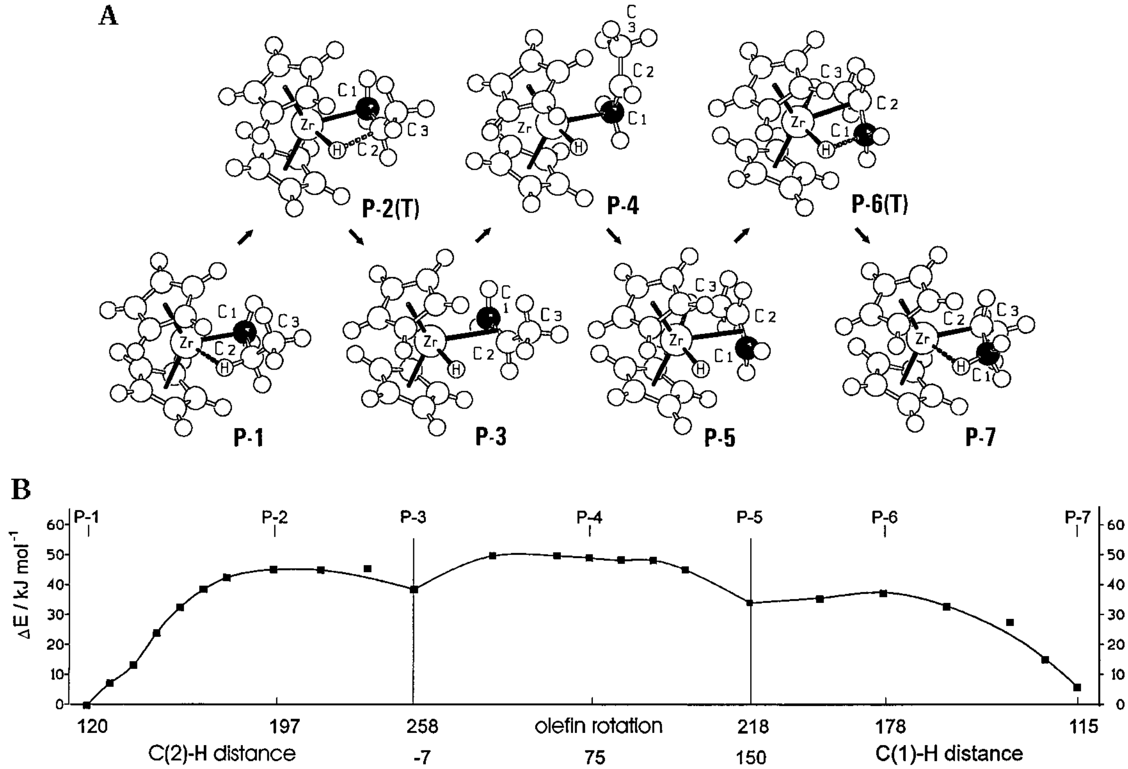

Figure 2. (A) Reaction path for the isomerization of the cation $(C_5H_5)_2ZrC_3H_7{}^+$. (B) Energy profile for the isomerization of the cation $(C_5H_5)_2ZrC_3H_7{}^+$ according to the reaction sequence P-1, P-4, P-7.

bisector plane. The Zr−C(1) and Zr−C(2) distances (251 and 286 pm) are slightly more unequal than in E-2.[29] A rotation of the propene ligand, i.e. an increase of the dihedral angle θ (H−Zr−C(1)−C(2)) from the minimum at $\theta = -7°$, leads over a flat activation barrier of only 10 kJ/mol (P-4) to another energy minimum P-5 at $\theta \approx 150°$, with the C(1) terminus close to the hydride ligand. During this rotation, the olefin remains strongly bonded to the zirconium center, with a dissociation energy of 85 kJ/mol. In this intermediate, P-5, an additional agostic interaction (d(Zr−H) = 220 pm) is apparent between the methyl substituent of the propene ligand and the Zr center.

Migration of the hydride to C(1) proceeds, over a very small activation barrier of 2 kJ/mol (P-6), to the isopropyl product P-7. For the latter, we find a β-agostic geometry at an energy of 8 kJ/mol above that of the initial $(C_5H_5)_2Zr$−*n*-propyl species P-1. The overall activation energy for this isomerization would thus amount to 49 kJ/mol, while the reverse reaction requires only 41 kJ/mol. These activation energies are now in the same range as those calculated e.g. for chain growth termination processes.[30] This would indicate that the two types of processes are competitive with each other, as suggested by experimental data concerning the rearrangement of 2,1- to 3,1-misinsertions.[5,31]

The decrease in activation energy for the $(C_5H_5)_2Zr$−propyl cation relative to that for the $(C_5H_5)_2Zr$−ethyl cation is most likely due to a stabilization of positive charge at the β-carbon atom in the transition state by hyperconjugation of the CH_3 substituent.[32] Even lower activation energies are thus to be expected for the isomerization of $(C_5H_5)_2Zr$−isobutyl$^+$ to $(C_5H_5)_2Zr$−*tert*-butyl$^+$, which models the isomerization of a growing polypropene chain (B, Figure 3A). For the initial state B-1, we find a nearly C_s-symmetric geometry with a β-agostic bond, the characteristics of which (Table 3) indicate an even stronger agostic stabilization than for the $(C_5H_5)_2Zr$−ethyl and $(C_5H_5)_2Zr$−propyl systems analyzed above.

Elongation of the C(2)−H(2) distance leads, over an activation barrier of 40 kJ/mol (B-2), to the zirconocene hydride−isobutene complex B-3, with a C_s symmetric geometry and an energy of 24 kJ/mol above the initial state B-1. The isobutene ligand is coordinated in a strongly asymmetric manner, with Zr−C(1) and Zr−C(2) distances differing by ca. 40 pm (Table 3).

Rotation of the olefin is modeled by increasing the dihedral angle θ, H−Zr−C(1)−C(2). It leads over an additional activation barrier of ca. 9 kJ/mol to another intermediate B-4, which contains the isobutene ligand coordinated perpendicularly to the $(C_5H_5)_2Zr$ bisector plane. This intermediate is about equally stable as the in-plane geometry B-3. In intermediate B-4, the Zr−C(2) distance (311 pm) is much longer than Zr−C(1) (245 pm) and can hardly be considered as bonding any more. This indicates that the isobutene ligand is coordinated in an η^1 fashion, approaching the situation of a Zr-bound β-carbenium ion. This view is also supported by a Mulliken charge analysis, which yields a positive charge of 0.27 units at C(2), apparently stabilized by hyperconjugative delocalization involving the CH_3 groups at C(2). Dissociation of the olefin from this intermediate requires 95 kJ/mol.

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[29] The differences between E-2 and P-3 are presumably caused by steric interactions between the CH_3 substituent and the H atoms of the C_5H_5 ring ligands.

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[32] Bercaw and co-workers[9] have observed activation energies of $\Delta G^\ddagger = 90$ kJ/mol for β-H elimination from $(C_5Me_5)_2Sc$−ethyl and $\Delta G^\ddagger = 86$ kJ/mol from $(C_5Me_5)_2Sc$−propyl.

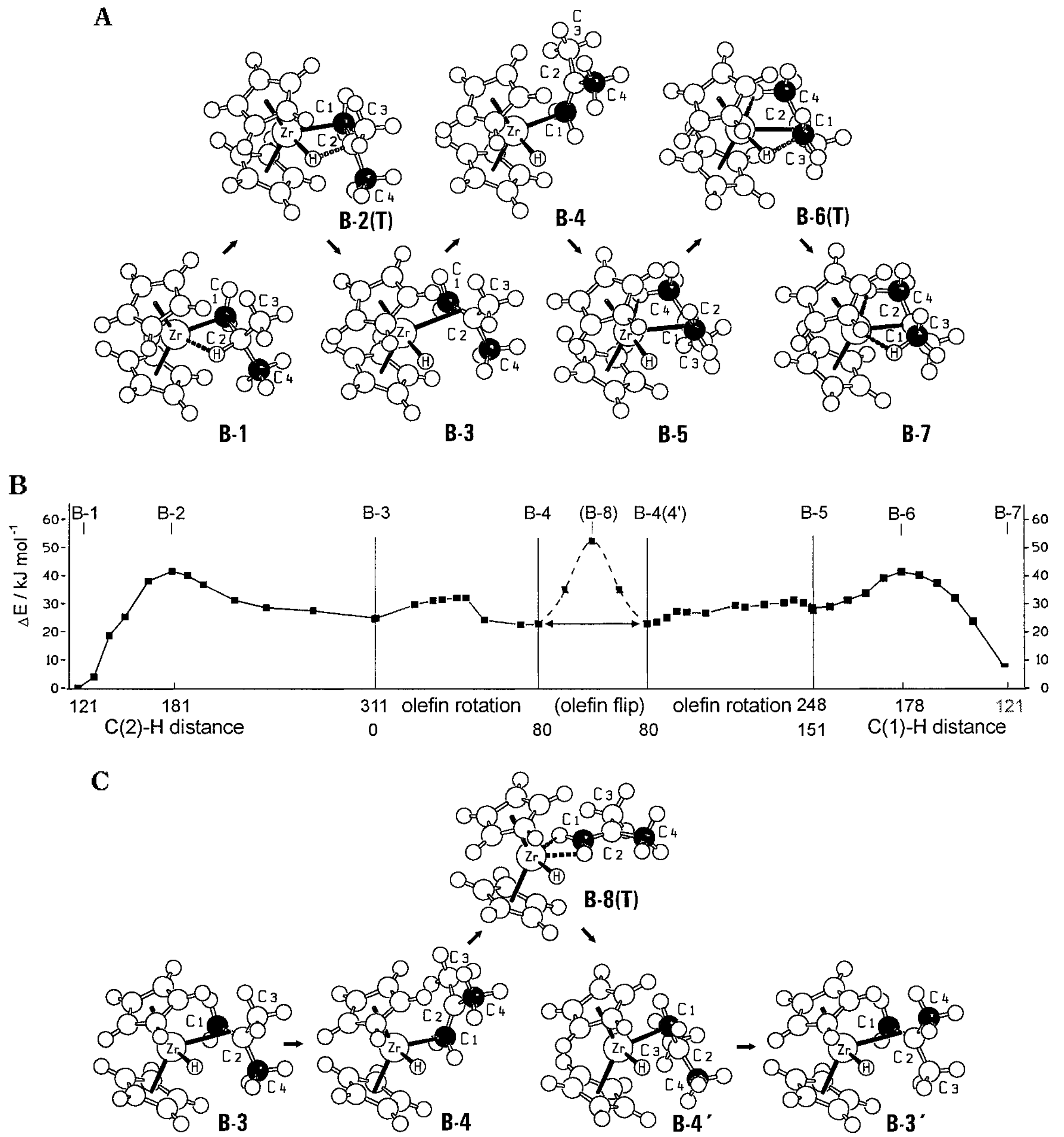

Figure 3. (A) Reaction path for the isomerization of the cation $(C_5H_5)_2ZrC_4H_9{}^+$. (B) Energy profile for the isomerization of the cation $(C_5H_5)_2ZrC_4H_9{}^+$ according to the reaction sequence B-1, B-4, B-7. (C) Reaction path for the enantiofacial interchange of a Zr-bound isobutene ligand.

Table 3. Geometry Parameters of the Zirconocene Isobutyl Cation $(C_5H_5)_2ZrC_4H_9{}^+$ along the Isomerization Path Represented in Figure 3 (Distances in pm, Angles in deg)

	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8
Zr−H	205	186	185	184	184	187	206/205	184
C(β)−H(β)	121	181	311		248	178	121/121	
ν(C−H$_b$)/cm^{-1}	2038						2249/2194	
Zr−C(1)−C(2)	86	89	95	106	75	75	79	180
C(1)−C(2)−H(β)	110	103	93		111	114	115/114	
(C_5H_5)−Zr−(C_5H_5)	133	133	134	133	131	131	130	139
Zr−C	224	235	255/301	245/313	264/265	252	235	242
Θ[a]	0	4	0	80	146	151	150	−3
E/(kJ mol^{-1})	0	40	24	22	27	37	9	55

[a] Dihedral angle H−Zr−C(1)−C(2).

Further rotation to $\theta = 151°$ leads, over an activation barrier of 5 kJ/mol, to the roughly equally stable, alternative isobutene complex B-5 with a slightly tilted C(1)−C(4) olefin plane and an agostic interaction of one of the methyl groups of the isobutene ligand (d(Zr−H) = 216 pm). This geometry appears to avoid some of the steric repulsions between the CH_3 groups of the olefin and the cyclopentadienyl H atoms.

The final insertion leads, with an additional activation barrier of only 10 kJ/mol (B-6), to the $(C_5H_5)_2Zr$−*tert*-butyl cation B-7, which is 9 kJ/mol less stable than the initial isobutyl cation B-1. The *tert*-butyl complex has a slightly elongated Zr−C(2) bond (235 pm) and an agostic interaction of two of the CH_3 groups with the Zr center (Table 3).[33] The inclination of two CH_3 groups toward the Zr center moves the third CH_3 group away from the adjacent C_5H_5 ring. An increased sum of the three C−C−C angles at C(2) (358°) indicates a planarization, i.e. a hybridization at C(2) approaching a *tert*-butyl cation.

For chain growth termination, β-H transfer to the metal and to a coordinated olefin are to be discussed as alternative mechanisms.[16bc,34] For the cation $(C_5H_5)_2$-Zr−ethyl, β-H transfer to the metal ($\Delta E_A = 75$ kJ/mol) appears improbable compared to β-H transfer to a coordinated olefin ($\Delta E_A = 29$ kJ/mol). For the $(C_5H_5)_2$-Zr−*n*-propyl and $(C_5H_5)_2$Zr−isobutyl cations, however, we derive substantially reduced activation energies of 45 and 40 kJ/mol for β-H transfer to the metal. To assess the viability of this reaction step in comparison to β-H transfer to a coordinated olefin, we have determined the activation barriers for the latter process in the cations $(C_5H_5)_2$Zr−*n*-propyl(propene)$^+$ and $(C_5H_5)_2$-Zr−fisobutyl(propene)$^+$, for which we find values of ΔE_A = 40 and 52 kJ/mol, respectively.[30]

For the isomerization of a Zr−*n*-propyl unit, a reaction path would thus appear debatable, which differs from that represented in Figure 2 by replacement of the hydride ligand by an *n*-propyl group. For the Zr−isobutyl system, however, β-H transfer to the metal with $\Delta E_A = 40$ kJ/mol appears to be significantly favored over β-H transfer to a propene ligand ($\Delta E_A = 52$ kJ/mol). The reaction sequences described by parts A and C of Figure 3 thus represent the most favorable isomerization paths.

The results discussed so far provide reasonable explanations for the isomerization reactions involved in the rearrangement of 2,1- to 3,1-misinsertions[4] as well as for those leading to the generation of stereoerrors by epimerization of the last-inserted CH_2CHCH_3 unit in isotactic polypropene formation,[2,3,24] which results when the reaction path B-1 to B-7 is followed by a reaction in the reverse direction, with a hydrogen atom being transfered from C(4).

A still unsolved puzzle concerns the stereochemistry of these isomerization reactions. As indicated by deuterium labeling experiments, the coordinated olefin appears to change from one enantioface to the other in isomerization intermediates such as B-3.[3] We assume that such an olefin flip occurs within the coordination sphere, i.e. without prior dissociation of the olefin. For such an olefin flip, several reaction pathways appear possible.[35] Of these, a rotation of the olefin ligand in intermediate B-4, with the C═C bond axis remaining in a plane perpendicular to the $(C_5H_5)_2$Zr bisector plane and with the CH_2 protons fixed to the Zr center (Figure 4) yields the lowest activation energy of 34 kJ/mol (+55 kJ/mol above B-1). In this transition state, the olefin ligand remains bound to the Zr center by an energy increment of 61 kJ/mol relative to a dissociated species. The activation energy for enantioface interchange via transition state B-8 exceeds that for a subsequent isomerization by only 15 kJ/mol; this interchange would thus appear to be within reasonable reach for such an intermediate. For *ansa*-zirconocene complexes, in which alkyl substituents or annelated benzene rings are attached to the β-position of the C_5H_5 ligands, formation of a transition state of the type B-8 with its olefin ligand in the $(C_5H_5)_2$Zr bisector plane would most probably require an even smaller energy increment, due to an increased repulsion of the olefin substituents in B-4; in these cases, enantioface interchange and isomerization according to Figure 3 might occur with comparable rates, as observed by deuterium labeling experiments.[3,36]

Conclusions

For Zr−alkyl isomerizations in cationic zirconocene complexes, the classical reaction sequence (β-H transfer, olefin rotation, reinsertion) is found to be the energetically most easily accessible reaction path. The overall activation energies obtained are within reasonable ranges, especially for branched alkyl ligands. The olefin fragment appears to remain coordinated to the Zr center in all reasonably accessible transition states and intermediates.

To analyze how the activation energies for Zr−alkyl isomerizations vary for different Zr−alkyl species, we have to consider the effects of increasing substitution at the β-carbon atom on the relative energies of the individual initial and transition states. In the series E-1, P-1, B-1, the angle Zr−C(1)−C(2) increases from 84 to 86° and the Zr−C(2) distance increases accordingly from 254 to 257 and 260 pm. Remarkably, however, the Zr−H(2) distances decrease from 209 pm in E-1 to 205, in P-1 and B-1, while the agostic C(2)−H(2) bonds elongate from 118 to 120 and 121 pm. This increase in β-agostic interaction is also reflected in decreasing frequencies of the agostic C(2)−H(2) stretching vibrations, for which vibrational analyses yield 2296 cm^{-1} in E-1, 2121 cm^{-1} in P-1, and 2038 cm^{-1} in B-1. The softening of the agostic C(2)−H(2) bond by increasing substitution at C(2), which is presumably caused by hyperconjugative stabilization of positive charge arising at this atom, must facilitate the transfer of the β-H atom to the Zr center along the C(2)−H(2) stretching coordinate. The same conclusion is reached when the stabilizing effects of CH_3 substituents at C(2) on the positive charge accumulating at this atom in the transition states E-2, P-2, and B-2 is considered.[9,37]

A possible reaction route, which explains the loss of stereoselectivity associated with isomerizations of this type, appears to involve coordination of the olefin ligand via its CH_2 terminus in the mid-plane of a zirconocene hydride cation (B-8).

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(33) The energy of the doubly β-agostic cation B-5 is calculated to be 5 kJ/mol lower than that of a singly β-agostic cation analogous to P-5.

(34) Stehling, U.; Diebold, J.; Kirsten, R.; Röll, W.; Brintzinger, H. H.; Jüngling, S.; Mülhaupt, R.; Langhauser, F. *Organometallics* **1994**, *13*, 964.

(35) Not considered here is a rotation of the two olefin termini of the isobutene ligand relative to each other.

(36) A related stereochemical problem concerns the isomerization of 1,2-inserted cyclopentene units to a 1,3-concatenation, which has been found by Collins and co-workers to occur with almost complete loss of cis selectivity when en(th-ind)$_2$ZrCl$_2$−MAO is used as a catalyst.[13] We have modeled such an enantioface interchange using *cis*-2-butene instead of an alkylcyclopentene bound to a $(C_5H_5)_2ZrH^+$ fragment. The transition state for the olefin flip is found to have a nearly C_s-symmetric geometry with the H atoms at C(2) and C(3) in contact with the Zr center and the C(1)−C(4) olefin plane in the zirconocene bisector plane. For the activation energy of this rearrangement we find a value of 80 kJ/mol.

(37) In comparison to this electronic effect, steric effects appear to be of less importance, as indicated by practically identical distances of C(3) and C(4) from adjacent C_5-ring centroids in B-1 and B-2.