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Inverse Isotope Effects of a Late Transition Metal Olefin Polymerization Catalyst: A DFT Study

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An unusual inverse KIE of 0.48 was observed for the catalyst $[C_5Me_5(P(OCH_3)_3)CoCH_2CH_2\text{-}\mu\text{-}H]^+$ in the polymerization of ethylene, which prompted the investigation of one full catalytic cycle by density functional theory calculations at the B3LYP/6-311+G(d,p) level of theory. In agreement with results from previous NMR investigations, the alkyl complex exhibiting a strong β-agostic interaction in the ground state could be identified as the catalyst resting state. This interaction leads to a smaller zero-point energy difference in the ground state and to the quantum mechanically calculated free activation energy difference of 0.6 kcal/mol between the hydrogen and the deuterium isotopomer. The migratory insertion step corresponds to the rate-determining transition state with a total activation barrier of 28.6 kcal/mol. The overall reaction profile is exergonic by −7.0 kcal/mol. The calculated inverse kinetic isotope effect ($k_H/k_D = 0.37$) is consistent with the experimental value of 0.48. Additionally the equilibrium isotope effect for a competition experiment, the opening of the β-agostic interaction with 2-fluoropyridine, was calculated as 0.71, a little higher than the experimentally determined value of 0.59.

Introduction

The polymerization activity of Ni(II) and Pd(II) diimine complexes was discovered in 1995, and since then much attention has been paid to the polymerization of α-olefins by late transition metal catalysts.[1] Compared to early transition metal complexes, they exhibit a greater tolerance toward polar reagents, which is useful for the copolymerization of ethylene with new types of functionalized monomers and simplifies the purification of educts. They also provide the possibility to make polymers with novel branching structures and thereby new material properties.[2−4]

The polymerization mechanism of late transition metal catalysts has been studied, both experimentally[5−7] and theoretically.[8−11] It is widely accepted that the catalytic cycle of the polymerization follows the Cossee−Arlmann mechanism, starting with the coordination of an olefin at the metal followed by the insertion of the olefin into the metal−carbon bond of the polymer chain.[12−14] Kinetic isotope effects (KIEs) have been determined, as they reflect the changes in the structure between the resting state, the energetically lowest ground state of the catalytic cycle, and the rate-determining transition state. Usually, KIEs for early transition metal catalysts in the polymerization of ethylene range from $k_H/k_D = 1.2$ to 1.3, which is evidence for the presence of an α-agostic interaction in the transition state of the olefin insertion, while in some other cases no kinetic isotope effect ($k_H/k_D = 1$) could be determined.[15−19] Generally, inverse KIEs are rare. One of these examples is the observation by Brookhart et al. of $k_H/k_D = 0.48$ in the polymerization of ethylene by the Co(III) catalyst **1** (Figure 1).[20] This result is contrary to those of previous studies and indicates major differences during the catalytic cycle.

We report DFT calculations on the reaction profile, a theoretical prediction of the related KIEs for the polymerization reaction in order to investigate the origin of the inverse KIE, and the equilibrium isotope effect of a competition experiment to compare the mechanism of this catalyst to that of early transition metals. The

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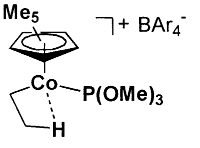


Ar = 3,5-$(CF_3)_2C_6H_3$

1

Figure 1. Active catalyst.

results will also be compared to earlier experimental investigations by NMR spectroscopy.[20,21]

The DFT calculations are carried out on different theoretical levels to study the dependency of the results from the basis sets used. All structures of the catalytic cycle of the polymerization are contemplated, including the transition state of the coordination of ethylene, a structure up to now unknown for most polymerization reactions of late transition metal catalysts.

Computational Details

The density functional/Hartree−Fock hybrid model Becke3LYP[22−25] as implemented in GAUSSIAN 98[26] has been used throughout this study together with either the valence double-ζ basis set 6-31G(d) or the valence triple-ζ basis set 6-311+G(d,p). All geometries have been fully optimized, and frequency calculations ensured that they correspond to either minima or transition states on the potential energy surface. All energies listed include zero-point and entropy corrections at 298.15 K and 1 atm, unless otherwise noted, and are given in kcal/mol relative to the reactants. Frequencies were scaled with 0.9806 (6-31G(d)) or 0.989 (6-311+G(d,p)).[27,28]

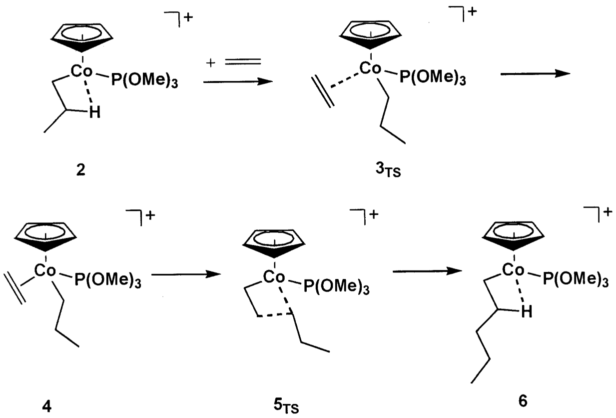
Kinetic isotope effects were calculated from statistical mechanics using harmonic vibrational frequencies obtained from frequency calculations.

$$\mathrm{KIE} = \frac{k_\mathrm{H}}{k_\mathrm{D}} = \mathrm{e}^{(\Delta G_\mathrm{D} - \Delta G_\mathrm{H})/RT} \qquad (1)$$

$$\Delta G_\mathrm{X} = G_\mathrm{X}^{\ddagger} - G_\mathrm{X}^{Educts} \quad \mathrm{X} = \mathrm{H\ or\ D} \qquad (2)$$

Results and Discussion

Scheme 1. Intermediates of the Polymerization Cycle



We refrained from using a model system and calculated the full catalyst (only the Cp* ligand of **1** was replaced by Cp) as shown in Scheme 1. Any influence of the counteranion was neglected as fluorinated tetraphenylborates are known as weakly interacting ligands.[29]

To model the influence of the polymer chain properly, the propyl complex **2** was chosen as the starting complex. From there one full cycle of the polymerization was investigated. All structures have been optimized with B3LYP/6-311+G(d,p) and are shown in Figure 2. They are treated as closed shell singlet state molecules, as calculations with higher spin states give much higher energies, and the NMR investigations showed no contribution of paramagnetic species.[20,21] Important geometrical parameters are given in Table 1.

Structures **2** and **6** show a characteristic C−H−Co three-center two-electron β-agostic interaction. The C9−H16 bond in **2** (C12−H16 in **6**, respectively) is elongated to 1.21 Å, while the Co−H16 contact is shortened to 1.66 and 1.65 Å, respectively. The distance between the Co-center and the β carbon atom C9 is only 2.18 Å. This shows the stabilization of the coordinatively unsaturated 16-e$^-$ center by the agostic interaction. On the other hand the C8−C9 bond in **2** and C11−C12 bond in **6** are shortened compared to a C−C single bond and show partial C−C double bond character. In previously published calculations on a lower theoretical level of the related complexes $[C_5H_5Co(PH_3)CH_2CH_2R]^+$ (R = H, CH_3) the elongation of the C−H bond is somewhat stronger, with a bond distance of 1.294 Å.[30]

In the first transition state $\mathbf{3_{TS}}$ the agostic bond has opened. The Co−C9 distance increased to 2.73 Å, and the C−H bond distance of 1.10 Å shows that the agostic interaction is nearly completely released. Ethylene is coordinated to the metal center with slightly asymmetric Co−C bond distances of 3.58 and 3.77 Å. The C11−C12 bond length of 1.33 Å represents a regular double bond. This indicates clearly that the main contribution to the energy barrier of this transition state mostly results from the opening of the agostic interaction. The ethylene-propyl complex **4** shows that the C11−C12 bond length of the coordinated ethylene increases to 1.37 Å, and the Co−C distances are 2.18 (C11) and 2.21 Å (C12). In $\mathbf{5_{TS}}$ the olefin inserts into the Co−alkyl bond. This elongates the Co6−C8 bond by approximately 0.2 Å, and the distance for the forming

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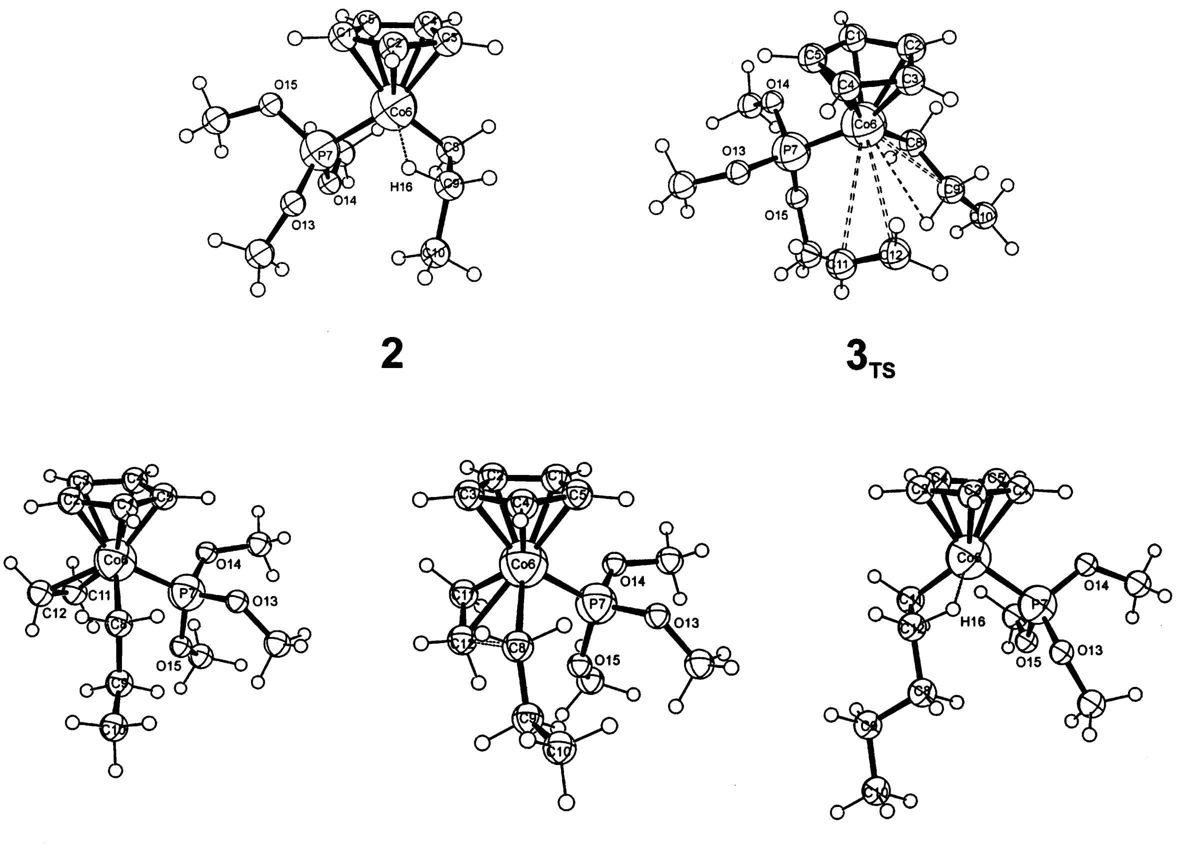

2 **3_{TS}** **4** **5_{TS}** **6**

Figure 2. Optimized structures (B3LYP/6-311+G(d,p)).

Table 1. Selected Calculated Bond Length in Å (B3LYP/6-311+G(d,p))

	2	3_{TS}	4	5_{TS}	6
Co6−C8	1.97	1.97	2.06	2.27	3.42
Co6−C9	2.18	2.73	3.14	3.58	4.63
Co6−C11		3.58	2.18	1.99	1.97
Co6−C12		3.77	2.21	2.20	2.18
Co6−H16	1.66	2.76	3.42	3.71	1.65
C8−C9	1.48	1.53	1.53	1.53	1.54
C9−H16	1.21	1.10	1.09	1.09	1.21 (C12−H16)
C8−C12		4.68	2.91	2.08	1.54
C11−C12		1.33	1.37	1.43	1.48

bond C12−C8 becomes 2.08 Å. An α-agostic interaction, which has been observed in the transition state of early transition metal complexes,[17,31] could not be identified. The insertion results in a new β-agostic alkyl complex, and the polymerization continues by coordination of another ethylene molecule. It should be noted that for steric reasons in the four-coordinated structures **4** and **5_{TS}** the phosphite ligand is in a conformation where all three methoxy arms point away from the metal center. In the three-coordinated structures **2**, **3_{TS}**, and **6** one methoxy group is turned toward the inside of the complexes. The dependency of the conformation of the phosphite ligand on the metal−ligand environment was also reported in a recent study of X-ray structures in the CSD.[32] Our calculations predict that this conformational change can happen during a catalytic reaction.

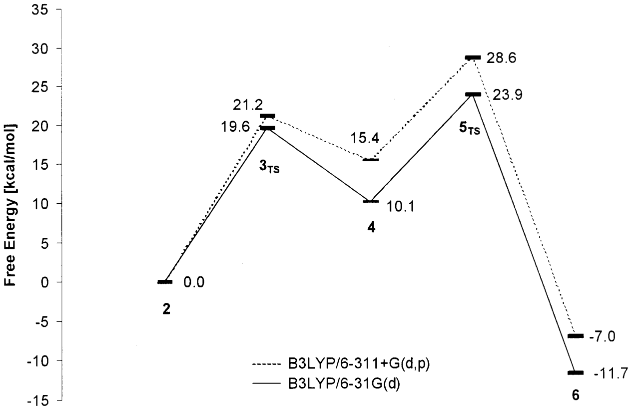

Figure 3. Energy profile of the polymerization cycle.

The relative free energies of the structures for both basis sets are given in Figure 3, and the results of the more accurate basis set 6-311+G(d,p) are discussed in the following. The barrier of the first transition state **3_{TS}** is 21.2 kcal/mol, and the resulting ground state **4** is endergonic by 15.4 kcal/mol. In **3_{TS}** ethylene is attacking the cobalt center from the front of the agostic interaction, as can be seen in Figure 2. The transition state where ethylene is coordinating from the back was also calculated, and the resulting energy barrier is 2.3 kcal/mol higher (B3LYP/6-31G(d)). The relative energy of **4** is in agreement with the experimental observations.[21] It was shown in NMR investigations of the polymerization reaction that the β-agostic complex is the resting state of the catalyst, and only low concentrations of **4** are present. The discrepancy in the calculated energies

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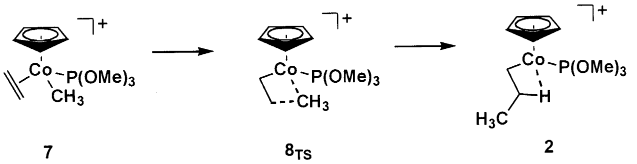
Scheme 2. Ethylene Insertion in the Methyl Complex 7



between the two basis sets is small, but there is a remarkable shift in the ethylene binding energy, i.e., from **2** to **4**, of about 5 kcal/mol. It points out the necessity of high-quality basis sets to describe this system accurately. We also looked at two basis sets that have frequently been used for calculations on first-row transition metals, 3-21G and LANL2DZ. The results are disappointing, as they calculate **4** to be at +6.3 kcal/mol (LANL2DZ) or even exergonic by −5.5 kcal/mol (3-21G). As mentioned before, one methoxy group of the phosphite ligand has to turn during the coordination of ethylene, so all three methoxy arms point to the outside. A calculation on complex **6** where all methoxy substituents are forced to point to the outside is unfavorable, with an energy difference of about 3.5 kcal/mol for this process. The activation energy of the migratory insertion from **4** to $\mathbf{5_{TS}}$ is 13.3 kcal/mol, which is in good agreement with the experimental value of 14.3 ± 0.2 kcal/mol.[21] Thus, the second transition state is the rate-determining step, a finding also reported by Brookhart.[20] The overall energy balance of the reaction is − 7.0 kcal/mol.

Ziegler had previously calculated the barrier of the migratory insertion to be 15.2 for the related complex $[C_5H_5Co(PH_3)(CH_2{=}CH_2)CH_3]^+$ and the total energy of the migratory insertion as − 12.7 kcal/mol.[30] The difference from the − 22.4 kcal/mol computed here (i.e., from **4** to **6**) results from the fact that the insertion of ethylene into the methyl complex is much less exergonic than into the propyl complex. This could be shown by a recalculation of the migratory insertion in the methyl-ethylene complex **7**, where the activation barrier is 17.1 kcal/mol and the total reaction energy only −15.2 kcal/mol (B3LYP/6-31G(d); Scheme 2). The latter energy includes the released energy for the turning of the phosphite ligand, so the greater total energy in our case is a result of the substituents at the phosphorus atom. The difference of more than 7 kcal/mol in the total energy of the insertion between the methyl complex **7** and the propyl complex **2** results from the larger bond strength of the methyl−cobalt bond. For the related complex $[(\eta^1,\eta^5\text{-}H_2N\text{-}CH_2\text{-}CH_2\text{-}C_5H_4)Co(CH_3)]^+$ a barrier of 14.4. kcal/mol was calculated for the migratory insertion.[33]

To exclude the possibility of other agostic interactions which might stabilize the complex, we studied structures with different agostic C−H bonds, namely, the α- and γ-agostic pentyl complexes **9** and **10** (B3LYP/6-31G*).

The calculated free energies predict that both are more than 10 kcal/mol higher in energy compared to **6** (**9**, 10.2 kcal/mol; **10**, 10.9 kcal/mol). Earlier calculations proposed that the γ-agostic interaction should be lower in energy compared to the α-agostic interaction.[30] This is true for the electronic energies, but not for the entropy-corrected values, where the α-agostic complex is slightly more stable by 0.7 kcal/mol. One reason for the stability of the β-agostic interaction is the geometry, which allows an empty d orbital of the metal to interact best with the occupied σ orbital of the C−H bond.

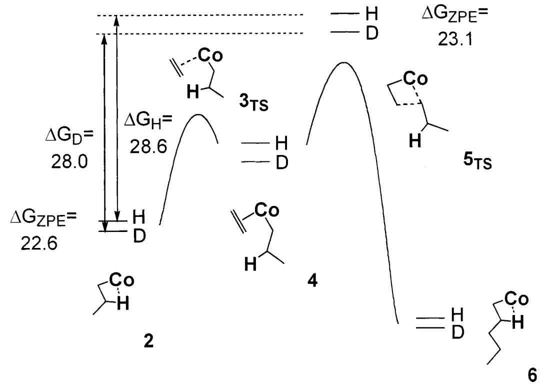
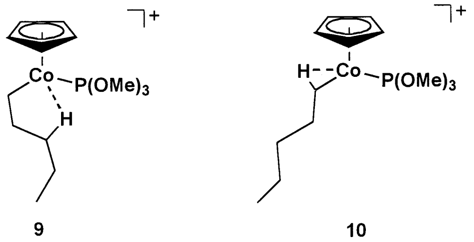


Figure 4. Free energy differences for the isotopomers.

Scheme 3. α- and γ-agostic Structures



To predict the KIE from the theoretical calculations, we used the β-agostic complex **2**, which is the lowest ground state in energy, and the rate-determining transition state of the migratory insertion $\mathbf{5_{TS}}$ (Figure 4).

These results are in agreement with the experimental findings of Brookhart.[20,21] Frequency calculations were repeated after replacing the hydrogen atoms of the alkyl group and the ethylene molecule to determine the free activation energy for the reaction with perdeuterated ethylene. The difference in the zero-point energy (22.6 kcal/mol for the reactants compared to 23.1 kcal/mol in the transition state) is a result of the conversion of the agostic interaction in the ground state to a terminal C−H bond in the transition state, as proposed by Brookhart earlier.[20] The lower vibrational frequency in the Co−C−H(D) agostic bond compared to the C−H(D) bond in the transition state causes the smaller difference of the zero-point energy in the ground state for the deuterium complex. The calculated free activation energy of the reaction is 28.6 kcal/mol for the hydrogen isotopomers and 28.0 kcal/mol in the deuterium case. According to eq 1 the KIE can be calculated as 0.37. This is consistent with the observed inverse kinetic isotope effect of 0.48, a result of the lower activation enthalpy of the deuterium isotopomer.[20]

To confirm the role of the β-agostic interaction in the inverse KIE, Brookhart et al. have also reported an NMR competition experiment.[20] An excess of 2-fluoropyridine was added to a solution of the catalyst **1**, and the resulting equilibrium with adduct **12** was studied by ^{1}H NMR spectroscopy (Scheme 4) for $[C_5Me_5Co(P(OMe)_3)C_2H_5]^+$, $\mathbf{1_H}$, and $[C_5Me_5Co(P(OMe)_3)C_2D_5]^+$, $\mathbf{1_D}$.

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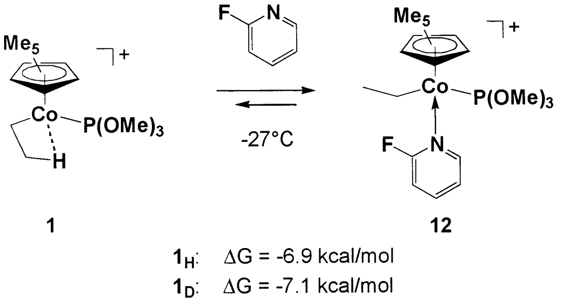
Scheme 4. Competition Experiment



The calculated structures confirm that the complex **12** is favored and that the fluoropyrdine occupies the open coordination site. Consequently the agostic interaction is converted to a terminal bond. The experiment was repeated with $\mathbf{1_D}$, and an equilibrium isotope effect K_H/K_D of 0.59 was reported.[20] For the calculations on the B3LYP/6-31G(d) level the experimentally used Cp* was replaced by Cp. K_H/K_D could be determined from the frequency computations as 0.71 at − 27 °C. The calculated free energies at this temperature are −6.9 kcal/mol for $\mathbf{1_H}$ and −7.1 kcal/mol for $\mathbf{1_D}$. The agreement of the isotope effects predicted by DFT calculations and those measured by NMR is very good keeping in mind that no experimental errors are given for the latter.

Conclusions

For the Co(III) catalyst under investigation a full catalytic cycle was computed and the alkyl complex was identified as the resting state. This structure exhibits a strong β-agostic interaction, which is responsible for the observed inverse kinetic isotope effect. We could confirm that significant differences in the mechanism compared to other late transition metal catalysts based on Fe or Ni/Pd exist, where the resting state is the alkyl-ethylene complex.[5−11] In those cases a significantly higher kinetic isotope effect should be expected, although they also exhibit strong β-agostic interactions in the alkyl complex.

Moreover we could show that it is necessary to use basis sets of valence triple-ξ quality to accurately describe the system by DFT calculations and sufficient to predict the isotope effects. Basis sets of double-ξ quality (3-21G, LANL2DZ, 6-31G(d)) give results that are not in agreement with the experimental findings.

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