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DFT Studies on the Copolymerization of α-Olefins with Polar Monomers: Ethylene−Methyl Acrylate Copolymerization Catalyzed by a Pd-Based Diimine Catalyst

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Abstract: Gradient-corrected density functional theory has been used to study the elementary reactions for the copolymerization of ethylene with methyl acrylate catalyzed by Pd-based diimine catalysts, modeled by the generic complex N∧N-Pd(n-C_3H_7)$^+$, with N∧N = −NHCHCHNH−. The steric effects in the real systems are discussed on the basis of the calculations for the catalyst with N∧N = −NArCRCRNAr−, R = CH_3, and Ar = C_6H_3(i-Pr_2) and the previous calculations on ethylene/propylene polymerization. Considerations have been given to the different possible acrylate complexes, as well as the transition states and the products (agostic complexes and the alternative chelates) for two acrylate insertion paths (1,2 and 2,1). The chelate-opening reactions have also been studied. The results revealed a strong electronic preference for the 2,1-insertion paths, with a barrier that is 4.5 kcal/mol lower than any other studied insertion pathway. In the real systems the 2,1-insertion of acrylate is preferred by 0.5 kcal/mol. The 2,1-insertion barrier calculated for the real system of 12.4 kcal/mol is in very good agreement with the experimental value of 12.1 kcal/mol. The six-member chelate is the most stable insertion product with an energy that is 21 kcal/mol lower than the kinetic insertion product. The reactions of the chelate opening by ethylene that start from the lowest energy complexes have the lowest barrier for the four-member ring (23 kcal/mol) and the highest for the six-member structure (30.4 kcal/mol). The high barrier for the opening of the six-member chelate suggests the possibility of a two-step chelate-opening mechanism. The internal barriers for the chelate-opening reactions starting from the higher energy complexes are lower then the one-step reaction that starts from the preferred complex and comparable to those of the ethylene insertion into the Pd−alkyl bond. While the chelate opening by a subsequent acrylate insertion seems to be facile for the generic catalyst, steric effects in the real catalyst are likely to decrease the acrylate π-complexation energies and increase the insertion barriers to the extent where such a reaction becomes unfeasible.

Introduction

The development of homogeneous catalysts for olefin polymerization has revolutionized the olefin polymerization field.[1−4] Since the structures of the single-site catalysts are well defined, they offer more control over the polymer properties than the heterogeneous Ziegler−Natta catalyst.[5−8] Presently, a large number of organometallic olefin polymerization catalysts are known, involving almost all transition metals, some lanthanides, and a few main-group elements, as well as a great variety of ligands.[9−20]

A new emerging frontier in olefin polymerization is the controlled copolymerization of α-olefins with monomers bearing a polar functional group.[21,22] Of particular interest are the monomers with oxygen-containing polar groups, such as vinyl

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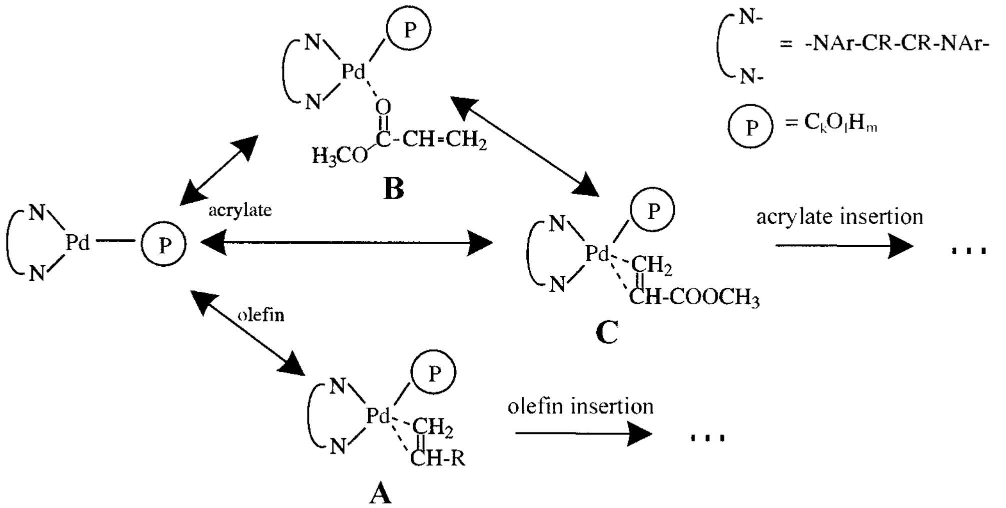
Scheme 1. Initial Steps in the Copopymerization of α-Olefins with Polar Monomers[a]



alcohols, acids, and esters. Presently, available polar copolymers are produced in radical polymerization processes under high-temperature and high-pressure conditions.[23] The design of a single-site copolymerization catalyst would open new, less expensive routes to commercially available copolymers. Also, it could lead to the synthesis of novel materials, since even small amounts of polar monomers dramatically modify the polymer properties compared to regular polyolefins.

The heterogeneous Ziegler−Natta system and the homogeneous catalysts based on early-transition metals are highly oxophilic and inactive in random copolymerization processes. A few known polar homopolymerization[20,24−29] and block copolymerization[29−32] processes based on group 4 metals, are known but they involve mechanisms[20,24,25] different from that of the Ziegler−Natta-type polymerization of ethylene/α-olefins.[33,34] Hence, the attempts to incorporating polar groups into a polyolefin chain must employ alternative approaches, such as functional group protection and use of special monomers[22,35−49] or chemical modifications of the polymer.[50−54]

However, the use of less oxophilic, late-transition-metal complexes has shown some promise in the design of a direct copolymerization catalyst, as demonstrated by some recent pioneering studies.[55−57] The Brookhart Pd-based diimine catalyst[58−61] has been shown to copolymerize[55,56] ethylene and higher α-olefins with acrylates and vinyl ketones. Other late-transition-metal-based complexes are also known to tolerate the presence of polar functional groups[62,63]

An incorporation of polar monomers into a polymer chain by coordination copolymerization is only possible if the polar monomer insertion follows the same reaction mechanism as that of α-olefin Ziegler−Natta polymerization.[33,34] Thus, before insertion, the polar monomer must be bound to the metal center by its double $C{=}C$ bond rather than by the oxygen atom of the polar group. Initially, the mechanism of copolymerization involves a competition between olefin and the polar monomer (Scheme 1). Further steps in the copolymerization mechanism are shown in Scheme 2, with the methyl acrylate used as an

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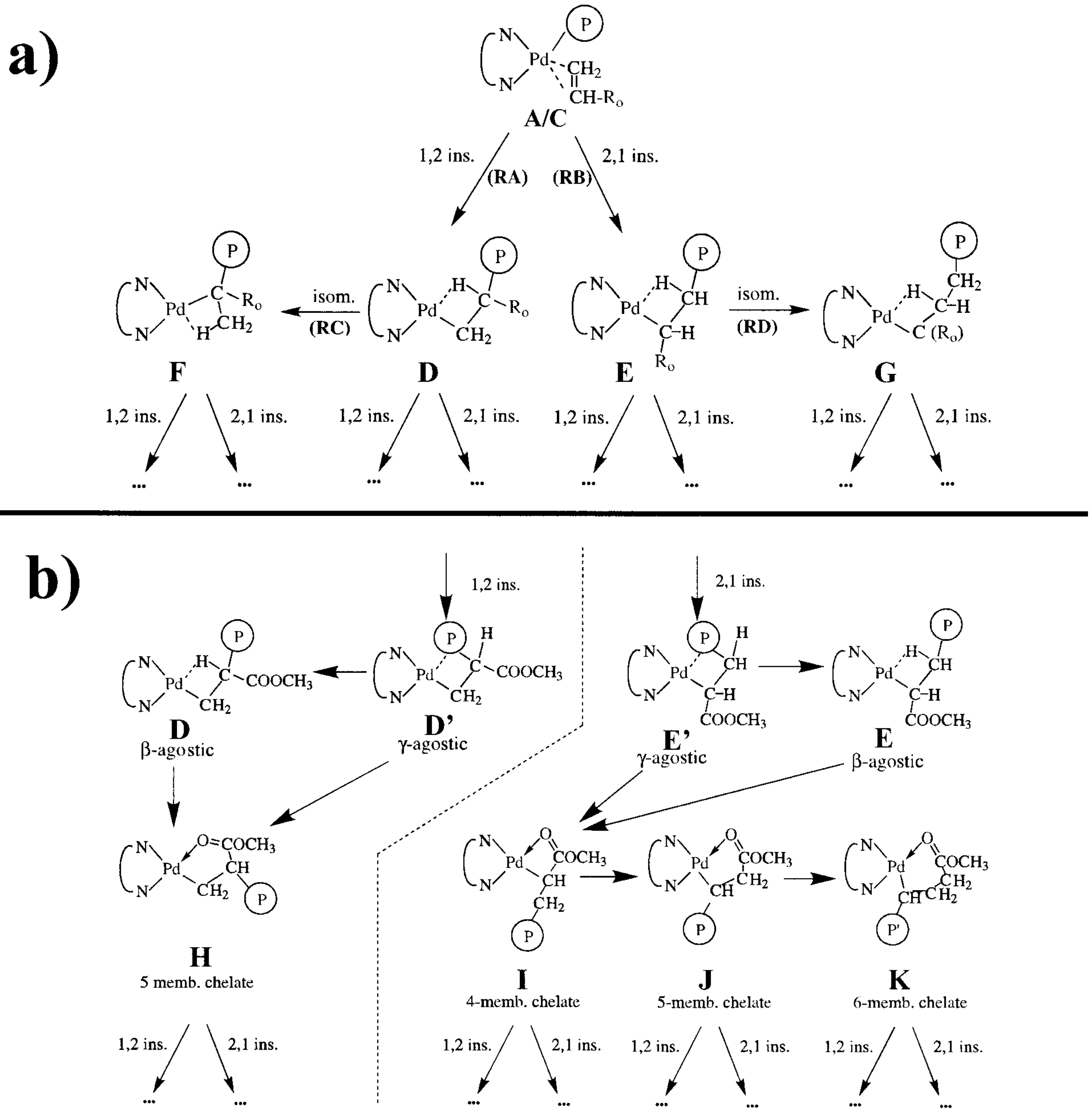
Scheme 2. Monomer Insertion in the Polar Copolymerization Processes[a]



example for the monomer. For both the olefin and polar monomer, two alternative insertion routes are possible: 1,2-insertion (RA in Scheme 2) in which the unsubstituted carbon atom forms the bond with the metal, and the 2,1- insertion (RB), in which the substituted carbon is linked to the metal. In the olefin case, the stable insertion products are β-agostic complexes, **D** and **E**; they can capture the next olefin/polar monomer molecule or isomerize to other agostic complexes, **F** or **G**. In the case of a polar monomer, the insertion mechanism is more complicated because of the formation of the chelate structures. Thus, after the 1,2-insertion of acrylate the agostic complexes, **D** and **D′,** may isomerize to a five-member chelate **H**. Similarly, the 2,1-insertion may be followed by the formation of a four-member chelate, **I**, that may further isomerize to the five- and six-member structures, **J** and **K**. The latter has been found to be a stable resting state for the Brookhart Pd-based catalyst.[55,56] A next step involves an opening of one of the chelates by another monomer molecule, after which the catalytic cycle can repeat itself. Thus, an understanding of the copolymerization processes requires knowledge of the relative stabilities of all the reaction intermediates, as well as the activation barriers for all the elementary reaction steps.

In the present studies, we have computationally investigated the elementary reactions in the copolymerization of ethylene with methyl acrylate catalyzed by the Pd-based diimine catalyst. Despite the fact that the systems developed by Brookhart et al. were the first successful examples of active catalysts in polar copolymerization,[55,56] there have not been any computational studies of these processes yet. The main goal of the present investigation was to understand the details of the copolymerization mechanism. We believe that a comparison of the results presented here with similar studies for other systems may be helpful for the design of an even more active copolymerization catalyst with a larger tolerance for polar monomers. Theoretical calculations has previously been very useful in studies of many aspects of polymerization chemistry.[64,65]

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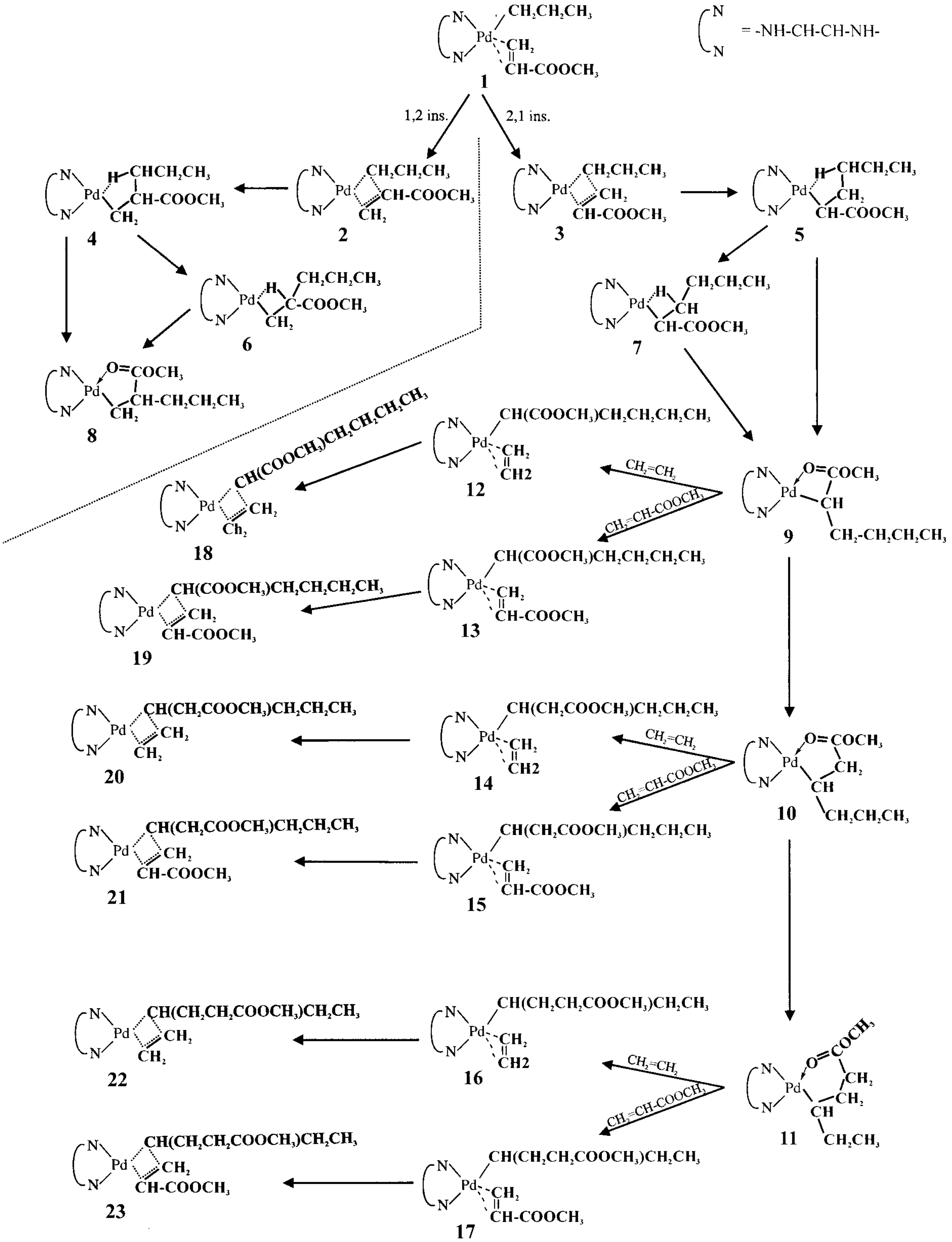
Scheme 3. Complexes Studied in the Present Work



In the following, we will discuss the stability of the acrylate complexes, the transition states, and the products for two acrylate insertion paths (1,2 vs 2,1), as well as the chelate opening by a subsequent ethylene/acrylate insertion.

We point out that in most of the calculations presented here a generic model for the catalyst has been used; the results of such calculations reflect the electronic effects only. However, for the acrylate π-complexes and the alternative insertion TS, calculations have been performed for the real catalyst as well. Thus, the role of the steric effects will be discussed on the basis of these calculations and previous studies.[66–74]

Computational Details and the Model Systems

The molecular systems studied in the present work are shown in Scheme 3. In most of the calculations, the Pd-based diimine catalyst was modeled by a generic N∧N-Pd$^+$ complex, with N∧N =

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−NHCHCHNH−, in which the bulky substituents of the real catalysts were replaced by hydrogen atoms. The polymer chain initially attached to the catalyst was modeled by a *n*-propyl group. Starting from the acrylate complex **1**, both, 1,2- and 2,1-insertion paths have been considered. Thus, calculations have been performed on the 1,2- and 2,1-insertion transition states (**2** and **3**, respectively), as well as the γ- (**4** and **5**) and β-agostic insertion products (**6** and **7**), corresponding to the structures present in the α-olefin homopolymerization processes. Further, the following chelate structures have been considered: the five-member ring (**8**) formed after 1,2-insertion and the 4-, 5-, and six-membered rings (**9**−**11**) present in the 2,1-acrylate insertion path. As the next step, the chelate opening by both, ethylene and acrylate, has been investigated. Calculations have been carried out for the ethylene (**12**, **14**, **16**) and acrylate (**13**, **15**, **17**) π-complexes (formed from four-, five-, and six-membered chelates, respectively), as well as for the corresponding insertion transition states (**18**/**19**, **20**/**21**, and **22**/**23** for ethylene/acrylate, respectively). Here, in the acrylate case, only the 2,1-insertion has been taken into account, as the preferred insertion path.

In addition, for the 1,2- and 2,1-acrylate insertion transition states, the calculations have been performed for the real catalyst, with R = CH_3 and Ar = $C_6H_3(i\text{-}Pr)_2$, in order to investigate the influence of steric bulk on the insertion barriers and its regioselectivity preference.

For agostic complexes, the chelates, and especially for the structures resulting from the chelate opening, various isomeric structures are possible. Numerous alternative structures have been considered in the calculations. In the following, we discuss mainly the most stable minimums on the potential energy surface. However, in the case of the six-member chelate opening, we also discuss the possibility of a two-step mechanism, in which there is an isomerization to a higher energy complex prior to the monomer insertion.

All the results were obtained from a DFT calculations based on the Becke−Perdew exchange correlation functional,[76−78] using the Amsterdam density functional (ADF) program.[79−84] The standard double-ζ STO basis with one set of polarization functions was applied for H, C, N, and O atoms, while the standard triple-ζ basis sets were employed for the Pd atom.[85] The 1s electrons of C, N, and O as well as the 1s−3d electrons of Pd were treated as frozen core. Auxiliary s, p, d, f, and g STO functions,[79,80] centered on all nuclei, were used to fit the electron density and obtain accurate Coulomb and exchange potentials in each SCF cycle. The reported energy differences include first-order scalar relativistic correction,[86−88] since it has been shown that such an relativistic approach is sufficient for 4d transition metal atoms.[89]

Results and Discussion

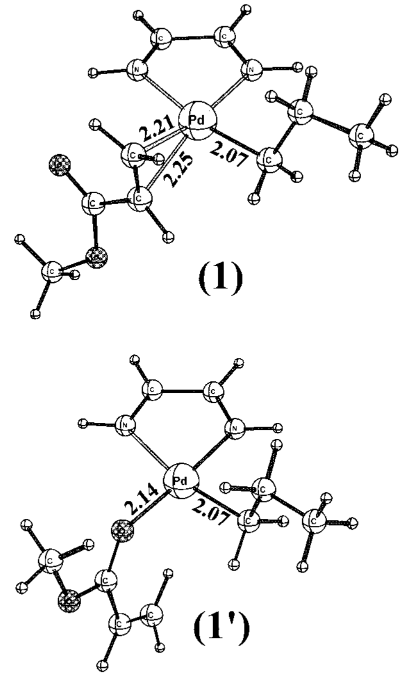

Figure 1. Geometries of the methyl acrylate π- (**1**) and O-complexes (**1′**) with the Pd-based Brookhart catalysts. The key interatomic distances are indicated.

Relative energies of the stationary points for the methyl acrylate 1,2- and 2,1-insertion reactions are presented in Figure 2 and listed in Table 1. The relative energies for the reaction intermediates in the chelate-opening reactions (ethylene and acrylate π-complexes and the insertion transition states) are summarized in Figure 5 and Table 2. The most important structures of the present work are shown in Figures 1, 3, 4, and 6. In the following, we will first discuss the stability of methyl acrylate complexes and then 1,2- and 2,1-insertion paths, the stability of alternative chelate structures, and finally, the chelate-opening reactions.

Acrylate Complexes. For the Pd-based Brookhart catalyst, the most stable methyl acrylate complex is a structure in which the polar monomer is bound to the metal by its olefinic functionality (see Figure 1, left side). Such a π-complex is energetically preferred by 3.4 kcal/mol over the alternative O-complex, in which the acrylate molecule is bound to the metal by the carbonyl oxygen atom (see Figure 1, right side). The relative stability of alternative π- and O-complexes for different monomers and catalysts was discussed in detail in a recent paper.[75] Here, we point out only that the preference for the π-complex over the O-bound structure, or at least an easy interconversion between the O- and π-complexes, is a necessary condition for a random copolymerization to occur. To follow an insertion mechanism similar to that of etylene/α-olefins homopolymerization, the polar monomer π-complex must be formed. Thus, the computational result presented here shows that for Pd-based diimine catalyst this condition is fulfilled, unlike for the analogous Ni-based catalyst (inactive in copolymerization) for which the O-complex is more stable by 4 kcal/mol.[75]

Similarly to α-olefins, in the case of the acrylate π-complexes, a polar monomer adapts an orientation in which the C=C bond is roughly perpendicular to the plane of the catalyst; the "planar"

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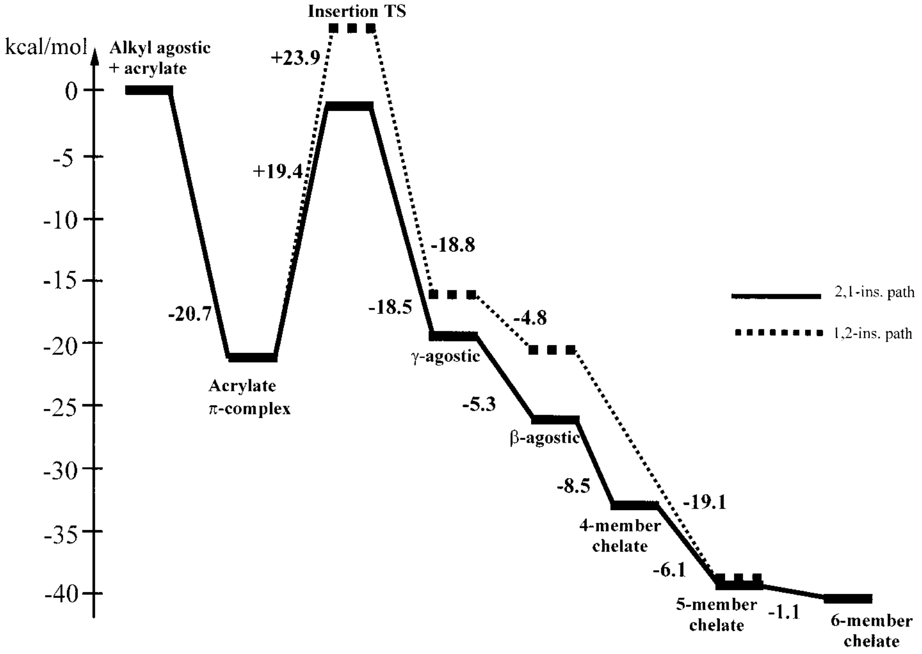

Figure 2. Energy profile for the two acrylate insertion paths. The energy differences (in kcal/mol) between two subsequent species in the reaction path are indicated.

acrylate complexes do not form a stable minimum on the potential energy surface. There exist four minimums corresponding to four different "perpendicular" orientations of acrylate, with the most stable geometry shown in Figure 1. As in the case of propylene, in the most stable complex, the distance between the $COOCH_3$ group of acrylate and the alkyl chain attached to the catalyst is maximized, to minimize the steric repulsion between these groups.

In all acrylate π-complexes, the two Pd−C bonds are inequivalent (2.21 and 2.25 Å); the bond involving unsubstituted acrylate carbon is shorter, as indicated in Figure 1. A similar effect has been observed for propylene,[66] as well as other polar monomer complexes,[75] and comes from the polarization of the monomer π/π^*-orbitals toward the CH_2 group.

The calculated methyl acrylate bonding energy for the π-complex with a generic catalyst is −20.7 kcal/mol. Compared to the corresponding α-olefin complexes, the acrylate π-complex stabilization energy lies between those for ethylene (−18.82 kcal/mol) and propylene (−20.85 kcal/mol). As we discussed in a recent paper,[67] for a generic catalyst, this energetic order of the monomers is determined by the electronic factors that are overridden by steric factors in the complexes involving real catalysts with bulky substituents; for the real Brookhart complex [R = CH_3, Ar = $C_6H_3(i\text{Pr})_2$], the acrylate bonding energy is decreased to −13.6 kcal/mol. Thus, the calculations for the real Brookhart Pd-based systems indicate the largest bonding energies for ethylene (−16.4 kcal/mol),[67] followed by propylene (−16.3 kcal/mol)[67] and acrylate (−13.6 kcal/mol), in agreement with known experimental relative binding constants.[56]

1,2- versus 2,1-Insertion of Methyl Acrylate. The calculated barriers for the 1,2- and 2,1-insertion of methyl acrylate into the Pd−carbon bond are listed in Table 1. The energy profile of the copolymerization process following two insertion paths is shown in Figure 2. The results clearly show that for the generic catalyst (R = H, Ar = H) the 2,1-insertion is strongly preferred: the transition state for the 2,1-insertion has a lower energy by 4.5 kcal/mol than the corresponding 1,2-transition-state structure. For the real system, the 2,1-insertion has a lower barrier by ~0.5 kcal/mol than the 1,2-insertion. For a generic system, a similar preference of the 2,1-insertion path has been found for propylene, with a much smaller energy difference (2.05 kcal/mol) between the two transition states; in the real systems, this preference has been inverted: the 1,2-propylene insertion barrier is lower by ~0.5 kcal/mol that that of the 2,1-insertion.[66]

Table 1. Relative Energies[a] for the Stationary Points in the 1,2- and 2,1-Acrylate Insertion Reactions into the Pd−Alkyl Bond (see Scheme 3)

	relative energy[a]			
structure	1,2-insertion path		2,1-insertion path	
π-complex	**1**	−20.70 (0.00) [−13.60 (0.00)]		
insertion TS	**2**	+3.24 (+23.93) [−0.65 (+12.95)]	**3**	−1.31 (+19.39) [−1.16 (+12.44)]
γ-agostic	**4**	−15.52 (+5.18)	**5**	−19.77 (+0.93)
β-agostic	**6**	−20.28 (+0.42)	**7**	−25.39 (−4.69)
4-member chelate			**9**	−33.64 (−12.95)
5-member chelate	**8**	−39.38 (−18.70)	**10**	−39.68 (−18.98)
6-member chelate			**11**	−40.77 (−20.07)

[a] With respect to the isolated reactants (methyl acrylate + β-agostic alkyl complex), and to the acrylate π-complex (in parentheses); in kcal/mol. The numbers in brackets refer to the real catalyst [R = CH_3, Ar = $C_6H_3(i\text{-Pr})_2$].

Let us now discuss the origin of the 2,1-insertion preference. We point out here that this preference is not intuitive: one could expect the opposite trend from the asymmetry of the C−Pd bonds in the acrylate π-complexes (see previous section) that reflects a stronger interaction between the metal and the unsubstituted carbon. Definitely, such an asymmetry would determine the transition-state preference in the reactions with early-transition states (i.e., in which the transition state is reactant-like).

However, in the case of late-transition-metal complexes, for which the geometries of the insertion transition states are closer to the product (see distances in Figure 3), the factor of importance[66] for the barrier is the energy required to distort the olefin from the geometry of the free monomer. For Pd-based diimine catalyst, the propylene distortion energy accounts already for ~76% of the insertion barriers, and the difference

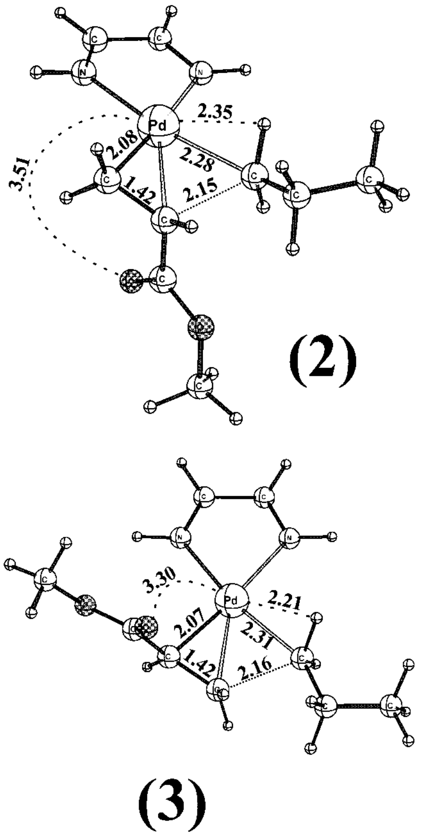

Figure 3. Structures of two alternative transition states (1,2 and 2,1) for methyl acrylate insertion. The key interatomic distances are indicated. Structure numbering as in Scheme 3.

between the two propylene distortion energies is very close to the difference between the energies of the two transition states.[66]

For methyl acrylate, the distortion energies in 1,2- and 2,1-transition states are 16.3 and 13.6 kcal/mol, respectively. Thus, the difference between these two values (2.7 kcal/mol) is substantially smaller than the difference between the energies of the alternative insertion transition states (4.5 kcal/mol). This is because yet another factor, almost negligible for propylene, influences the relative stability of the two transition states: the steric repulsion between the olefin substituent (CH_3 in propylene and $COOCH_3$ here) and the polymer (alkyl) chain destabilizes the 1,2-TS and does not affect the 2,1-TS. Thus, compared to propylene, in the case of methyl acrylate, the preference for the 2,1-insertion is strengthened for a generic catalyst.

As in the case of propylene, in the real systems, the 2,1-acrylate insertion TS is destabilized due to the steric repulsion between the bulky substituents of the catalyst and the olefin substituent. The 1,2-insertion TS is practically not affected by the steric effects. As a result, the energy difference between the two TS is decreased. In propylene, this effect leads to the inversion of the regioselectivity: the 2,1-TS is preferred by ~2 kcal/mol for the generic system, and the 1,2-, by 0.5 kcal/mol, for a real catalyst; thus, the steric effects destabilize the 2,1-TS by ~2.5 kcal/mol compared to the 1,2-TS. In the acrylate case, it is understandable that this steric destabilization of the 2,1-TS must be larger than for propylene, due to the size of the substituents on both monomers ($COOCH_3$ vs CH_3). Indeed, our calculations indicate a steric destabilization of the 2,1-TS by ~4.0 kcal/mol, compared to the 1,2-TS (corresponding to a decrease in the TS energy difference from 4.5 to 0.5 kcal/mol). However, unlike for propylene, this steric effect is not large enough to invert a strong electronic preference of the insertion regioselectivity observed in the generic systems, and the 2,1-insertion pathway remains preferred for the real catalyst. The calculated preference of 0.5 kcal/mol is slightly smaller than the experimental value of ~1 kcal/mol (corresponding to ~95% selectivity at −100 °C).[56]

It comes as no surprise that the insertion barriers calculated for a generic catalyst are incomparably larger than those for the real catalyst. As we have already discussed, the steric effects strongly destabilize the π-complex (relative to the mother alkyl complex + free olefin) and thus decrease the *internal* insertion barrier (relative to the π-complex). The 2,1-insertion barrier of 12.4 kcal/mol calculated for the real catalyst is in excellent agreement with the experimental value of $\Delta H^{\ddagger} = 12.1 \pm 1.4$ kcal/mol.[56]

An important conclusion from the experimental results[56] and the above consideration is that in the real systems the acrylate insertion barriers are substantially lower than those for ethylene. Thus, a low incorporation of the polar comonomer does not come from a difficult insertion, but comes from a low population of the acrylate π-complexes, compared to the ethylene π-complexes, as reflected by their respective π-complexation energies.

From the above and the π-complexation enegies of ethylene and acrylate obtained for the generic and real catalysts [$R = CH_3$; $Ar = C_6H_3(i\text{-}Pr_2)$], it is easy to explain the experimental observation that an incorporation of acrylate increases for the catalysts with less bulky substituents. Both, ethylene and acrylate π-complexes are destabilized in the real complexes. Since the effect is larger for acrylate than for ethylene, for the catalysts with less bulky substituents, the complexation energy difference between the two monomers must be then smaller than that observed for the catalyst with $R = CH_3$ and $Ar = C_6H_3i\text{-}Pr_2$ (see Figure 4). As a result, the population of the acrylate π-complexes is increased for the less bulky catalysts and so is the comonomer incorporation.

Finally, we point out that in all the insertion transition states there is no extra stabilization coming from the metal−oxygen interaction; in the transition-state geometries, the Pd−O distances are 3.51 and 3.30 Å, for the 1,2- and 2,1 insertion, respectively. (see Figure 3). Instead, as in the mechanism of α-olefin homopolymerization, the acrylate insertion TS is stabilized by a γ-agostic interaction. The agostic H−Pd bond lengths are 2.35 and 2.21 Å, for the 1,2- and 2,1-insertion transition states, respectively. Therefore, the γ-agostic complex can be considered as a kinetic insertion product which may further isomerize to more stable compounds.

Stability of Insertion Products: Agostic Complexes versus Chelates. As has already been mentioned, the kinetic product from the methyl acrylate insertion into the metal−alkyl bond is a structure involving γ-agostic interaction between the alkyl hydrogen and the metal atom (**4**, **6**; see Figure 5). The results of our calculations show that both the γ- and β-agostic structures form a stable minimum on the potential energy surface. This is true for both, 1,2- and 2,1-insertion paths. The results presented in Table 1 show that the agostic complexes formed after 2,1-insertion are more stable (by 4−5 kcal/mol) than the corresponding structures resulting from the 1,2-insertion. Kinetic products of both acrylate insertions are less stable than the starting acrylate π-complex (by 0.9 and 5.2 kcal/mol, for 2,1- and 1,2-insertions, respectively). The energies of β-agostic products (**5**, **7**) are lower by 4.5−5.5 kcal/mol than those of γ-agostic complexes (**4**, **6**). All these results are very similar to those from homopolymerization of propylene.[66]

The structures of the agostic complexes formed after acrylate insertion are qualitatively similar to those formed in the

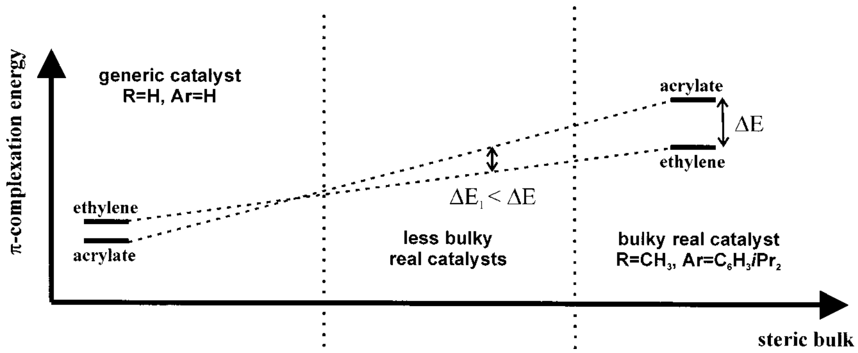

Figure 4. Influence of the catalyst substituents on the π-complexation energies of ethylene and acrylate.

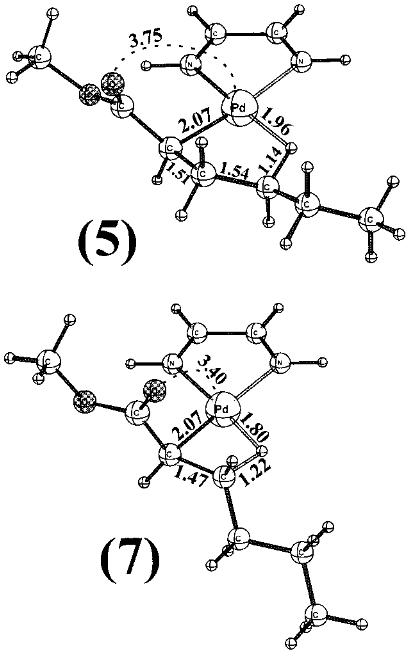

Figure 5. Structures of the γ- and β-agostic complexes resulting from the 2,1-acrylate insertion. The key interatomic distances are indicated. Structure numbering as in Scheme 3.

homopolymerizations of regular α-olefins.[66] Here, we point out that in these structures no chelating O−Pd bond is present. Except for the olefin substituent, there is no qualitative difference compared to the agostic complexes present in propylene homopolymerization. As an example, in Figure 5, γ- and β-agostic interactions are presented in the structures resulting from the 2,1-insertion.

Unlike the α-olefin homopolymerization, the agostic complexes following acrylate insertion may easily isomerize to chelate structures, which are substantially lower in energy. In the case of the 1,2-insertion, the five-member ring (**8**), and in the case of the 2,1-insertion, the four-member ring (**9**) can be formed immediately from both, γ- and β-agostic complexes, by a simple rotation around the Pd−C bond, accompanied by breaking the agostic bond. The five-member chelate **8** is 19.1 kcal/mol lower in energy than the β-agostic structure **6**, and the four-member chelate **9** is 8.26 kcal/mol lower than the β-agostic complex **7**.

Further, the four-member chelate **9** resulting from the 2,1-insertion can isomerize to a five-member ring **10**, lower in energy by another 6 kcal/mol (by 14.3 kcal/mol with respect to the β−agostic complex **7**), and to the most stable structure **11**, comprising the six-member chelate ring. Compared to the initial acrylate π-complex, the six-member chelate **11** is lower in energy by 20.1 kcal/mol. Compared to the isolated reactants (alkyl β-agostic complex + free acrylate), it is lower in energy by 40.8 kcal/mol.

The structures of the four chelates **8**−**11** are shown in Figure 6. It should be noticed that in all these structures the chelating Pd−O bond is very short (2.12−2.15 Å), comparable to the Pd−O bond in the η_1-O-bound complex **1′** of methyl acrylate (2.14 Å, see Figure 1); this reflects a relatively strong Pd−O bond in this structures.

The results presented here are in good qualitative agreement with experimental observations. All the chelate structures discussed here have been observed experimentally. The six-member chelate has been found to be a stable resting state of the catalyst in acrylate/olefin copolymerization catalyzed by Pd−diimine complexes.[55,56]

Finally, we point out that we have not studied mechanistic details of the isomerization reactions leading from the four- to six-member chelate. Although these reactions involve a hydrogen transfer between two carbon neighbors, like the chain isomerization reactions in the α-olefin homopolymerization, the mechanism can be slightly different. The chain isomerization reactions involve hydrogen transfer to the metal with the formation of the olefin−hydride complex. Here, the presence of a strong chelating bond can influence formation of such intermediates. Without detailed studies of the chelate isomerization reactions, it is hard to speculate about the barriers of such reactions. However, the barriers for the chain isomerization in the homopolymerization processes catalyzed by Pd-based diimine has been experimentally[90] determined to be $\Delta G^{\ddagger} = 7.2$ kcal/mol ($\Delta H^{\ddagger} = 6.1$ kcal/mol); i.e., they are much lower than the olefin insertion barriers. Moreover, since the experimental values are very close to the theoretical results[66] ($\Delta H^{\ddagger} = 5.8$ kcal/mol; $\Delta G^{\ddagger} = 6.8$ kcal/mol) obtained for the generic catalyst, it seems that the isomerization barriers are practically not affected by the steric bulk. Thus, even if the barriers for the chelate isomerization were higher in comparison to regular chain isomerization reactions, it seems reasonable to assume that they are negligible, compared to the insertion. In what follows, we have assumed that there exists an equilibrium between the alternative chelate structures, with a very low population of the four-membered species.

Chelate Opening by Ethylene. (1) Ethylene π-Complexes. The relative energies of the structures involved in chelate-opening reactions are listed in Table 2 and schematically presented in Figure 7. The results show that formation of ethylene π-complexes is exotermic by 7.8−10.1 kcal/mol. The most stable is the complex **12** formed from a four-member chelate, and the least stable is structure **14** derived from a five-member chelate.

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[90] Shultz, L. H.; Brookhart, M. *Organometallics* **2001**, *20*, 3975.

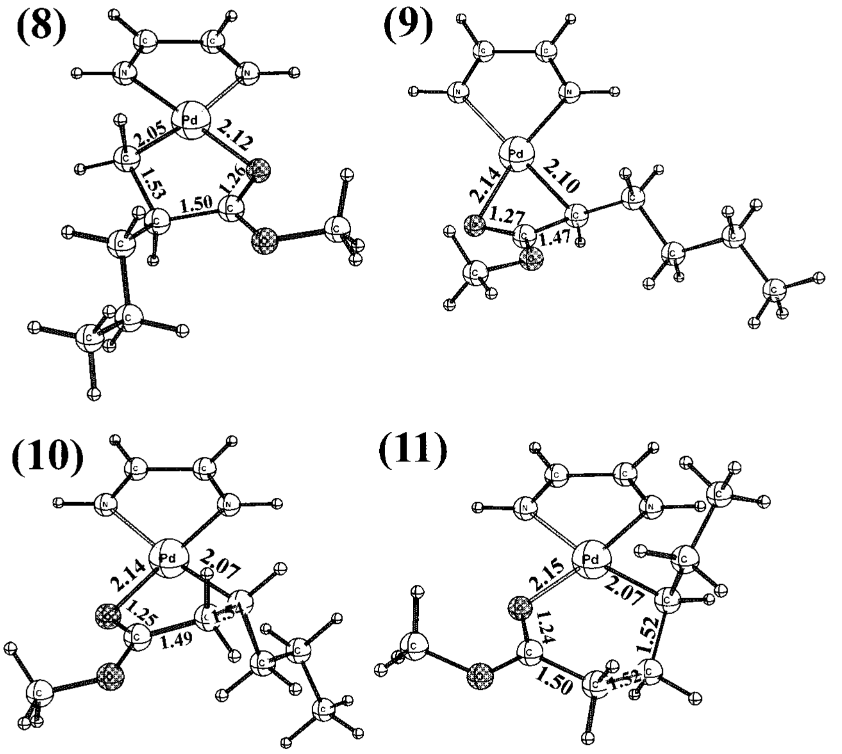


Figure 6. Geometries of alternative chelates. The key interatomic distances are indicated. Structure numbering as in Scheme 3.

Table 2. Relative Energies[a] for the Stationary Points in the Chelate-Opening Reactions (see Scheme 3)

	relative energy[a]			
structure		π-complex		insertion TS
4-member chelate				
ethylene	**12**	−10.14 (0.00)	**18**	+12.83 (+22.97)
acrylate	**13**	−13.00 (0.00)	**19**	+13.22 (+26.22)
5-member chelate				
ethylene	**14**	−7.79 (0.00)	**20**	+17.25 (+25.04)
acrylate	**15**	−9.5 (0.00)	**21**	+15.43 (+25.93)
6-member chelate				
ethylene	**16**	−9.09 (0.00)	**22**	+21.35 (+30.44)
acrylate	**17**	−11.0 (0.00)	**23**	+20.65 (+30.65)

[a] With respetct to the isolated reactants (free ethylene + corresponding chelate), and to the corresponding π-complexes (in parentheses); in kcal/mol.

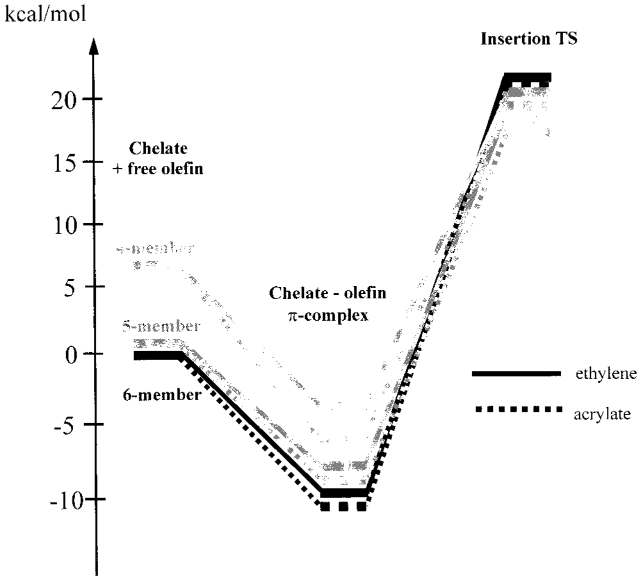


Figure 7. Energy profile for the chelate opening by ethylene and methyl acrylate.

A comparison of the π-complex stabilization energies of Table 2 with the corresponding results for ethylene π-complexes formed from alkyl agostic complexes with the same catalyst (−18.8 kcal/mol) shows that the acrylate π-complexes are substantially less stable. We have performed frequency calculations on the systems **11** and **16** to evaluate the entropic contribution to the free energy of the reaction **11** + C_2H_4 $\leftrightarrow$ **16**. The calculated $-T\Delta S$ value of +10.1 kcal/mol (at 300 K) is in a very good agreement with the experimental values[36] varying between 9 and 10.2 kcal/mol for the catalysts with different substituents. Taking into account this entropic contribution, it may be concluded that the equilibrium of the π-complex formation reaction is shifted toward the chelates. The complexation free energy of $\Delta G = +1.0$ kcal/mol calculated for the generic catalyst compares well with the experimental free energies[36] obtained for six-member chelates with the real catalysts, $\Delta G = +2.0$ to $+3.6$ kcal/mol. The difference comes mainly from the enthalpic part (calculated $\Delta E = -9.1$ kcal/mol, experimental $\Delta H = -5.7$ to -8.1 kcal/mol, for the systems with different substituent), due to a steric destabilization of the olefin complex in the real systems. A comparison between our results for the generic catalyst and the experimental results for the real systems indicates that the steric destabilization of the ethylene π-complexes derived from the chelates (free energy difference up to 2.6 kcal/mol) is similar in magnitude for ethylene π-complexes derived from alkyl complexes, discussed in the previous paper[67] (destabilization by 2.4 kcal/mol in the most bulky system).

Let us now examine the structures of the most stable ehylene π-complexes resulting from the chelates, presented in Figure 8. It is clearly seen that the chelating Pd−O bond has been moved from an equatorial to an axial position, but it is still present in all the structures of the π-complexes. Thus, formation of the ethylene complexes from the chelates is not yet, formally, the chelate-opening reaction. The bond lengths of Figure 8 show

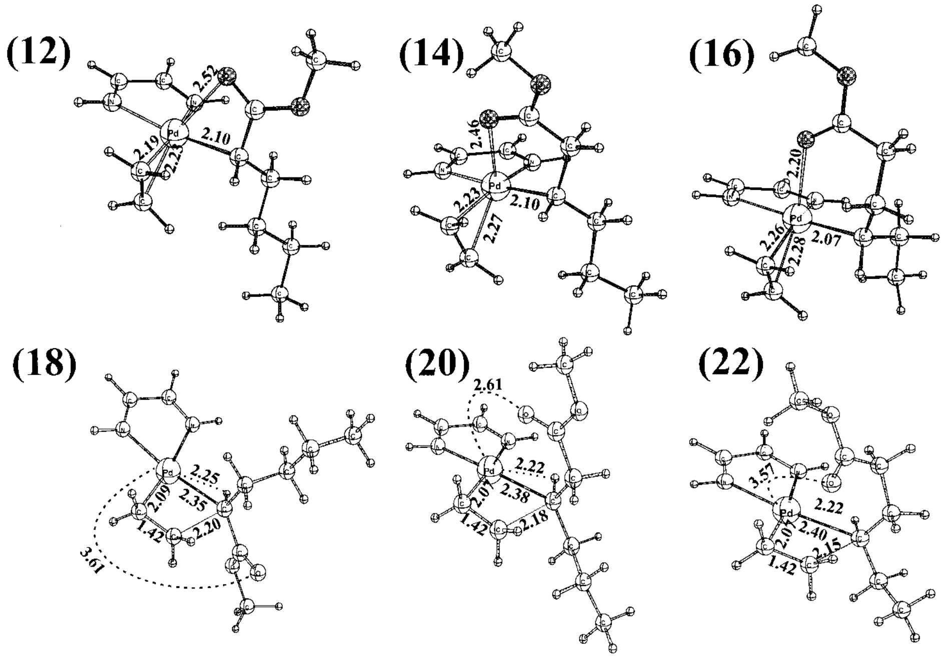


Figure 8. Structures of the ethylene π-complexes and the insertion TS for opening of the chelates. The key interatomic distances are indicated. Structure numbering as in Scheme 3.

that the chelating bond is shortest (and in what follows, the strongest) in a six-member structure (2.20 Å) and substantially extended for five- (2.46 Å) and four-member chelates (2.52 Å). This trend is understandable from the fact that the flexibility of a six-member ring easily allows for the Pd−O coordination in **16**, while in the five- and four-member structures, the strain in the ring results in extended (weakened) Pd−O bonds. The extent of the Pd−O chelating bond strength is also reflected in the Pd−C bond length. Thus, the shorter the Pd−O distance, the longer the Pd−C bond.

It should also be observed that the stronger (shorter) the Pd−O bond, the weaker (longer) is ethylene coordination. In structure **16**, the Pd−C bond lengths are 2.26 and 2.28 Å, while in **12** they are shortened to 2.19 and 2.23 Å. Also, in all the structures, ethylene is slightly shifted from an equatorial toward an axial position; this results in an asymmetry in the two Pd−C bond lengths.

Finally, we point out that, except for the structures discussed here with the chelating bond present in an axial position, there exist numerous isomers of the ethylene complexes resulting from the chelates, in which the chelating Pd−O bond is completely broken. Although these complexes are higher in energy, their presence in the copolymerization cycle can be very important. We will discuss this point later.

(2) Ethylene Insertion. The results of Table 2 and Figure 8 show that the barriers of ethylene insertion are substantially different for various chelates. The opening of the four-member chelate is the easiest, with a internal barrier of 22.9 kcal/mol. For the five-member chelate, the insertion barrier increases to 25.0 kcal/mol, and for the six-membered ring, it goes up to 30.4 kcal/mol. Thus, the barriers for opening of all the chelates are much larger than the corresponding barriers for ethylene and acrylate insertion into a regular Pd−C(alkyl) bond. As also suggested by experimental results,[56] the opening of the chelate structures seems to be the rate-determining step in the polar copolymerization processes.

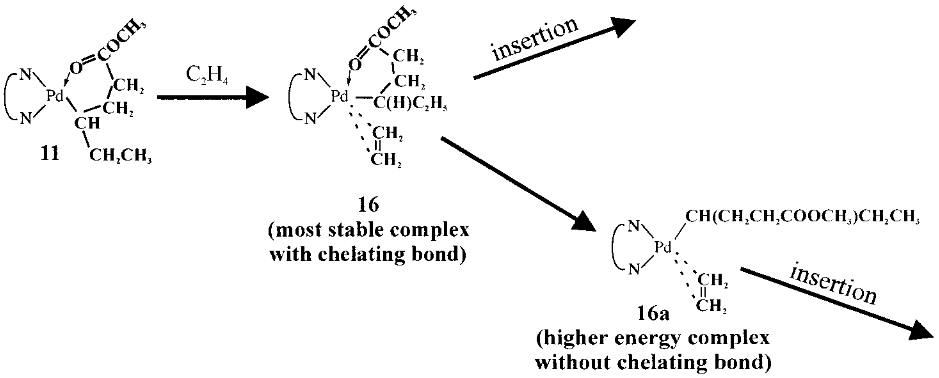
Let us now examine the structures of the ethylene insertion transition states presented in Figure 8. The transition-state geometries resemble the structures of the transition states for olefin insertion into a regular Pd−C(alkyl) bond; this is true for the general orientation of the four atoms forming/breaking the bonds, as well as for the bond lengths (cf. Figure 3 and refs 66 and 67). It can be observed that in all the structures the chelating bond has been broken. Instead, all the structures contain a stabilizing agostic interaction between the γ-hydrogen and the metal (2.22−2.25 Å). In **18** and **22**, the carbonyl oxygen is located far away from the Pd atom (3.6 Å). In **20**, it is directed toward the metal. However, in this structure as well, the Pd−O distance (2.61 Å) is much larger than other Pd−O coordination bonds discussed here.

Finally, we discuss the relative importance of the insertion barriers into three alternative chelates for the whole copolymerization process. Our results suggest that the opening of the four-member chelate is much easier than that of five- and six-member structures. However, it should be emphasized that the opening of the six-member structure is anyway inevitable in the copolymerization process. This is because even if ethylene is inserted into the four-member structure (before it isomerizes to larger chelates), such an insertion will add two carbon atoms to the ring. Thus, the kinetic product of such an insertion (γ-agostic complex) can easily isomerize to another six-member chelate, an analogue of structure **11.** Although we have not studied the products of ethylene insertion into the chelate structures, from the results for acrylate insertion (Table 1 and Figures 2, 5, and 6), it seems obvious that such an analogous six-member chelate must be more stable than both alternative agostic complexes. Also, opening of such a chelate will be equally difficult. Thus, the barrier for the six-member chelate opening seems to be a crucial parameter for characterizing the polar copolymerization processes.

The very high barrier for opening the six-member chelate of 30.4 kcal/mol suggests that the entire copolymerization process looks unfeasible, in disagreement with the experimental data.[55,56] In the last section, we will discuss an alternative mechanism for the chelate opening.

Chelate Opening by Acrylate. Finally, we briefly discuss the possibility of chelate opening by a subsequent insertion of an acrylate molecule. In Table 2, the π-complexation energies

Scheme 4. Alternative Chelate-Opening Mechanisms



are listed, together with the barriers for the 2,1-insertion. We point out that all the structures involved in the chelate opening by acrylate are qualitatively similar to those presented for ethylene and can be easily imagined by combining the plots of Figures 1 and 3 with those of Figure 8. Therefore, we do not present these structures here (see Supporting Information).

(1) Acrylate π-Complexes. A comparison of the π-complex stabilization energies for ethylene and acrylate indicates that for the generic catalyst the acrylate complexes formed from the chelates are more stable by ~2 kcal/mol. This is not surprising in view of a the previous comparison between the acrylate complex **1** and the respective ethylene complexes. Also, it can be expected that the acrylate complexes analogous to **13**, **15**, and **17** but formed with the real catalysts will be strongly destabilized, due to steric effects. As we have already discussed, the steric effects are comparable for the ethylene complexes resulting from the chelates and from the alkyl complexes. We will recall here that the analogue of complex **1** with the real catalyst is destabilized by ~7 kcal/mol,[75] while the corresponding ethylene complex with a real catalyst is destabilized only by 2.4 kcal/mol,[67] compared to a generic catalyst. Thus, a similar effect must occur in the case of complexes **13**, **15**, and **17** compared to **12**, **14**, and **16**. Therefore, it can be expected that for the real catalysts the acrylate π-complexes derived from the chelates will be less stable than those of ethylene by at least 5 kcal/mol. Thus, it seems very unlikely that in the case of the real catalysts the formation of the next acrylate π-complex would immediately follow an acrylate insertion. Therefore, already from this, and regardless of the acrylate insertion barriers, two subsequent acrylate insertions seem to be very unlikely.

The experimental results do not give definitive answers about the probablity of two subsequent acrylate insertions.[55,56] However, if in this *random copolymerization* the resting state of the catalyst is the six-member chelate, and if the polar monomer incorporation is relatively low (1−12%),[55,56] it can be concluded that the acrylate insertion must be preceded and succeeded by a series of ethylene insertions. Otherwise, an incorporation of the polar monomer would have to be much larger, or the mechanisms for the chelate opening by ethylene and acrylate would have to be different.

(2) Acrylate Insertion Barriers. Although the discussion above suggests that, in the case of the real systems, the formation of acrylate complexes derived from the chelates seems to be unlikely, we have still determined the acrylate 2,1-insertion barriers for the sake of completeness. A comparison with the corresponding results for ethylene insertion (Table 2) indicates that, already for a generic catalyst, the acrylate insertion is slightly less favorable than ethylene insertion for all the chelates. For six- and five-member chelates, the barriers for ethylene and acrylate insertion are comparable, while for the four-member ring, the barrier for acrylate insertion is substantially higher (by 3.3 kcal/mol). Again, it may be expected that the steric repulsion in the real systems will affect the acrylate insertion barriers more than the barriers for the ethylene insertion. However, even if this steric effect was negligible, two subsequent acrylate insertions seem to be quite unlikely, due to a very low population of the acrylate π-complexes derived from the chelates, compared to the population of the corresponding ethylene complexes.

Two-Step Chelate Opening. The high ethylene/acrylate insertion barriers after formation of the chelates suggest the possibility of an alternative two-step mechanism of chelate opening: first, the chelating bond is broken at the π-complex stage, and then olefin is inserted, starting from the higher energy π-complex without a Me−O bond (see Scheme 4). It can be expected that, if the chelating bond is broken and the polar group is situated far from the metal center, the ethylene insertion barriers (relative to the starting complexes) should not be much larger than the barriers for ethylene insertion into the M−C bond involving the secondary carbon atom (18.8 kcal/mol).[66]

To check whether such a mechanism is feasible, we performed calculations on the ethylene/acrylate π-complexes without a chelating bond resulting from the six-member chelate. We further determined the insertion TS starting from such a complex. Due to the complexity of the system, there are likely to exist hundreds of isomeric π-complex structures (resulting from the rotations around all the C−C bonds) and, thus, many alternative insertion paths. Besides chelated structures, there exist three groups of π-complexes: with the carbonyl oxygen situated either far from the catalyst and all the chain atoms, interacting with the hydrogens of the chain, or interacting with the hydrogen of the N−H group of catalyst. We optimized geometries for 30 structures, in which we have the examples from all the three groups. All the structures without a chelating bond are higher in energy compared to **16** of Figure 7 (with chelating bond) by 1.7−13.1 kcal/mol. For further studies, we selected the lowest energy complex **16a** (higher in energy than **16** by 1.7 kcal/mol), with the O−H−N hydrogen bond and complex **16b** (higher in energy than **16** by 11.8 kcal/mol)**,** which has the lowest energy among the structures from the first group (see Figure 9).

The transition-state optimizations have been performed for the ethylene and the acrylate insertions starting from the two example structures **16a** and **16b** and their acrylate analogues; the TS structures for ethylene insertion are shown in Figure 9 (**22a**, **22b**). They have energies of 20.7 and 18.1 kcal/mol, relative to the mother complexes **16a** and **16b** (i.e., they are higher in energy than **16** by 22.5 and 29.9 kcal/mol, respectively). Thus, **22a** is substantially lower in energy than the

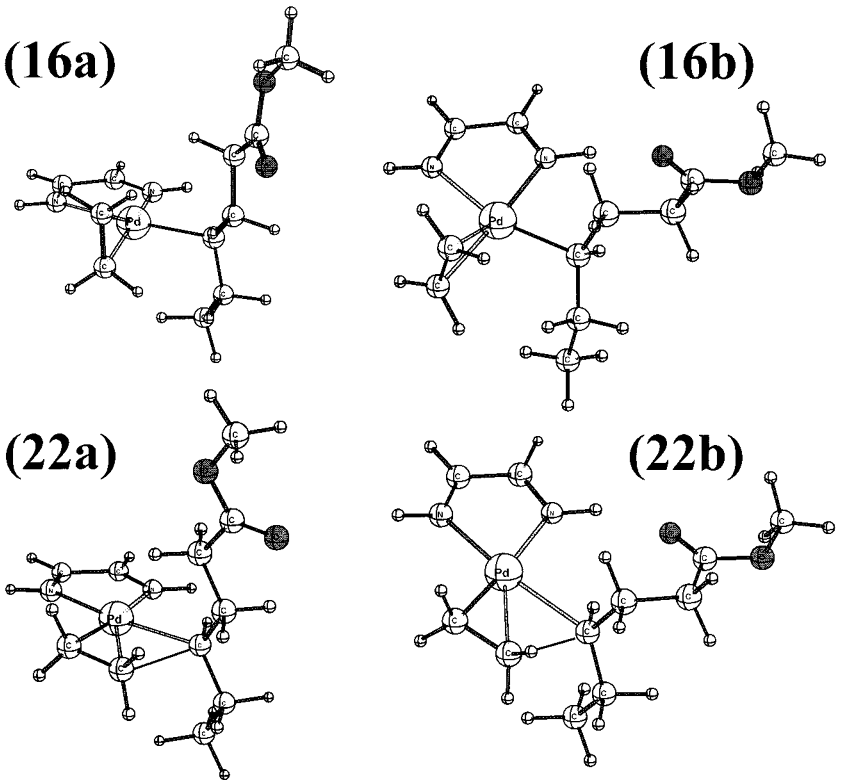


Figure 9. Examples of the alternative structures of the ethylene π-complexes (without the chelating Pd−O bond) and the corresponding insertion TS.

previously discussed TS **22** (by 7.9 kcal/mol), and **22b** is of similar energy (lower by 0.5 kcal/mol). Similarly, for acrylate insertion, the corresponding barriers are 21.3 and 18.3 kcal/mol, relative to the mother complexes (without chelating bond), and 22.3 and 29.5 relative to the most stable complex **17** (with chelating bond).

The results presented here support the two-step chelate-opening mechanism. It can be expected that in the real copolymerization cycle at finite temperatures there exists a dynamic equilibrium between the complexes with and without a chelating bond. Moreover, since the number of possible ethylene complexes without the chelating bond is very large, the population of the species without a chelating bond will substantially exceed the population of the species with a Pd−O bond. As a consequence, the meaningful insertion barriers cannot be calculated relative to the single, lowest energy complex **16**.

From the practical point of view, it is not possible to perform the calculations for all the possible isomers of **16** and all the possible insertion TS for the reaction paths starting from them, especially because the evaluation of the entropic contributions would be required to adequately describe the dynamic equilibrium at finite temperatures. Here, the molecular dynamic approach seems to be more suitable, as it can model the equilibrium at the free energy surfaces in a natural way. However, such a study is certainly beyond the scope of the present investigation and will be the subject of a future study. It should be pointed here, however, that from the preliminary MD simulation we have found that the barrier for the opening of the six-member chelate at the π-complex stage (i.e., for the reaction **16** → **16a**) is as low as 9 kcal/mol. Also, frequency calculations have been done for the complexes **16**, **16a**, and **16b**. It is found that the entropic contributions $-T\Delta S$ to the free energy at 300 K of the chelate-opening reactions **16** → **16a** and **16** → **16b** are only slightly destabilizing, by 0.8 and 1.0 kcal/mol, respectively.

Concluding Remarks

We have carried out DFT studies on the mechanism for copolymerization of methyl acrylate catalyzed by a generic Pd-based diimine compounds. The formation of the acrylate complexes, regioselectivity of the acrylate insertion, stability of the insertion products (agostic complexes vs alternative chelate structures), and chelate opening by a subsequent ethylene/acrylate insertion were studied. The results show that the acrylate π-complexes are stable with a complexation energy of −20.7 kcal/mol and preferred over the O-bound complexes. The acrylate insertion follows the 2,1-regioselectivity, with a barrier of 19.4 kcal/mol, lower by 4.5 kcal/mol than the 1,2-insertion barrier. Similarly to the olefin insertion, a kinetic product of this reaction is a γ-agostic complex that may isomerize to the more stable β-agostic complex, but also to the energetically preferred oxygen chelates. The most stable chelate structure is a six-member ring, with an energy that is 21.0 kcal/mol lower than that of the isomeric γ-agostic complex.

The chelate-opening reactions involve formation of ethylene complexes followed by insertion. The ethylene π-complexes are characterized by relatively low complexation energies (7.8−10.1 kcal/mol). In the most stable π-complex structures, the chelating bond is still present (in the axial position), and it is broken in the insertion TS geometries. Starting from the most stable complexes, the ethylene insertion barriers are lowest for the opening of the four-member chelate (23.0 kcal/mol) and highest for the six-member ring opening (+30.65 kcal/mol). However, the four-member chelate opening may be followed by the formation of another six-member chelate. Therefore, the barrier for opening of the six-member chelate may be considered as the crucial parameter that characterizes the copolymerization process. The high barrier for the six-member chelate opening suggests the possibility for a two-step chelate-opening mechanism, in which the chelating bond is broken at the π-complex stage, and insertion starts from the higher energy π-complexes. The barriers for such insertions are in the range of 18−21 kcal/mol, relative to the starting π-complexes. Due to the large number of isomers for such complexes, a dynamic approach seems to be required to describe the equilibrium between the isomeric species and the alternative insertion paths, at the finite-temperature free energy surface; it will be a subject of a future study.

Calculations on the real catalyst [with R = CH_3, Ar = C_6H_3-(i-Pr)$_2$] indicate that the presence of the steric bulk decreases the acrylate π-complexation energy by ∼7 kcal/mol. As a results, both insertion barriers are decreased as well. Since the steric bulk on the catalyst strongly affects the 2,1-insertion TS, its preference is decreased in the real systems. The 2,1-insertion barrier of 12.4 kcal/mol is in excellent agreement with the experimental value of 12.1 kcal/mol. Also, the energy difference between the two insertion TS of 0.5 kcal/mol is in a reasonable agreement with experiment (∼1.0 kcal/mol). A comparison of the present results obtained for the generic system with the experimental data[36] and our previous calculations[67] indicates that steric effects are similar in the ethylene π-complexes derived from the chelates and those derived from the alkyl complexes.

For a generic catalyst, the acrylate π-complexes derived from the chelates are more stable than the corresponding ethylene complexes, while the acrylate insertion barriers are higher for the four-member chelate opening and comparable for five- and six-member chelates. However, it can be expected that in the real systems both the acrylate π-complexation energies and the internal insertion barriers will be strongly affected by steric effects. Thus, two subsequent acrylate insertions in the real copolymerization systems seems to be very unlikely.

The present studies have focused on the Pd-based catalyst only. It would be interesting to perform similar mechanistic studies on the analogous Ni-based catalyst (inactive in copolymerization) as well as on other late-transition-metal-based systems. We believe that computational studies of this kind can be helpful in understanding the factors inhibiting polar copolymerizations and, thus, in the development of highly active catalysts for such processes.

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Supporting Information Available: The optimized geometries of the structures discussed (Cartesian coordinates, in Å). This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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