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Molecular Mechanics and Stereospecificity in Ziegler−Natta 1,2 and *Cis*-1,4 Polymerizations of Conjugated Dienes

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ABSTRACT: In the framework of Porri's mechanism for the 1,2 and *cis*-1,4 diene polymerizations, a geometrical and nonbonded energy analysis on possible catalytic intermediates, which include a cyclopentadienyl group coordinated to the transition metal, is presented. Besides pre-insertion intermediates, post-insertion intermediates presenting a "back-biting" coordination of the growing chain are considered. The post-insertion minimum energy intermediates are structurally very close to the *endo*−*endo* pre-insertion intermediates (presenting *endo* coordinations for both the allyl group of the growing chain and diene monomer), independently of the kind of insertion (1,2 or *cis*-1,4) and of the diene (butadiene, 4-methyl-1,3-pentadiene or (*Z*)-pentadiene). In our hypothesis the energy differences between the considered post-insertion intermediates are close to those present in the transition states, and this assures the isospecificity and the syndiospecificity of the models for the *cis*-1,4 polymerization (of 4-monosubstituted monomers) and for the 1,2 polymerization, respectively. This is in qualitative agreement with the stereoregularities of the polymers obtained with a catalytic system based on cyclopentadienyltitanium trichloride. Support for a 1,2 insertion mechanism for butadiene involving an *endo*−*endo* pre-insertion intermediate is given by comparison between the calculated minimum energy post-insertion intermediate and the crystalline structure of a catalytic cobalt complex.

Introduction

The polymerization of conjugated dienes with transition metal catalytic systems is an insertion polymerization, as is that of monoalkenes with the same systems. However, the polymerization of dienes presents several peculiar aspects mainly related to the nature of the bond between the transition metal of the catalytic system and the growing chain, which is of σ type for the monoalkene polymerizations, while in the diene polymerizations is of the allylic type.[1−9]

Several experimental facts have been rationalized in terms of different mechanisms, depending on the nature of the catalytic systems and of the diene monomer, mainly by the extensive work of Porri and co-workers, as reviewed in refs 8 and 9.

In particular, it has been suggested that 1,2 units and *cis*-1,4 units can derive from a coordination intermediate with an *anti* structure of the butenyl group (allyl terminal of the growing chain) and a *cis*-η^4 coordination of the monomer.[7−9] This kind of arrangement of the ligands would give rise to *cis*-1,4 or to 1,2 units depending on whether the incoming monomer reacts at C_1 or C_3 of the butenyl group, respectively. As described in detail in the previously cited reviews,[8,9] Porri's mechanism is in agreement with experimental observations of the so-called equibinary 1,2/*cis*-1,4 polybutadienes, as well as the type of stereoregularities observed in 1,2 and *cis*-1,4 polydienes.

For the monoalkene stereospecific polymerizations, several studies of molecular mechanics have been reported,[10−17] which have given relevant contributions to the comprehension of the detailed mechanisms. Let us recall, for instance, the finding of a new mechanism of enantioselectivity, involving a "chiral orientation of the growing chain".[12,13,15] A molecular mechanics study has been recently presented, by some of us,[18] also

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relative to the diastereoselectivity in the cyclopolymerization of a nonconjugated diolefin.

In contrast, only a few studies of molecular mechanics have been devoted to the polymerization of conjugated dienes; moreover, they only refer to limited aspects of the mechanisms. In particular, in a old paper of Arlman[19] the coordinations of a diene monomer and of a η^3-allyl terminal of the growing chain, on possible active sites of α or β $TiCl_3$ crystals, were discussed. More recently, a conformational analysis of a growing 1,4-polydiene chain, presenting both *syn*- and *anti*-η^3-allylic coordinations to a catalytic metal atom, has been presented.[20] In that paper, some configurational and conformational requirements for the simultaneous coordination of the η^3-allylic group and of the last double bond of the growing chain ("back-biting") were described.

As for the case of the olefin polymerizations by transition metal catalytic systems, it is nearly generally accepted that, also for the diene stereospecific polymerizations, the insertion reaction occurs in two steps: (i) coordination of the monomer to the metal, where a η^3-allyl bond with the growing chain is present; (ii) monomer insertion into a metal−carbon bond of the allyl group with formation of a new η^3-allyl bond between the new terminal of the growing chain and the metal.[1−9]

In this paper, we apply the molecular mechanics approach to the study of the relative orientations of a *cis*-η^4-coordinated diene monomer and of an *anti*-η^3-coordinated polydiene growing chain, in models for the intermediates corresponding to the coordination step (hereafter referred to as **pre-insertion intermediates**), for the *cis*-1,4 and for the 1,2 polymerizations of dienes.[7−9] Models of possible intermediates corresponding to the completion of the *cis*-1,4 or the 1,2 insertion steps, with a simultaneous *anti*-η^3 coordination of the allyl terminal and a η^2 coordination of the last double bond of the growing chain ("back-biting" coordination), have been also considered (hereafter referred to as **post-insertion intermediates**).

These relative orientations of the two ligands (diene monomer and allyl terminal of the growing chain) in the catalytic intermediates are, of course, determinant in the iso- and syndiotactic isomerism in the coordinated polymerizations of dienes, that is, in particular, for the 1,2 polymerization of generic dienes and for the *cis*-1,4 polymerization of 4-monosubstituted or of 1,4-disubstituted monomers.[7−9]

Models

In this paper, models for the *cis*-1,4 and 1,2 polymerizations of different diene monomers are considered. Our analysis considers models for two possible kinds of minimum energy situations: (i) **pre-insertion intermediates** (preceding the monomer insertion step) which coordinate to the metal atom a polydiene growing chain with *n* monomeric units and a diene monomer molecule; (ii) **post-insertion intermediates** (following the monomer insertion step) which coordinate to the metal atom a polydiene growing chain with $n + 1$ monomeric units. It is assumed that besides the ultimate, also the penultimate monomer unit remains coordinated to the metal atom so that the positions of the atoms should be not far from those possibly present in the transition state of the insertion reaction.

More in detail, the models for the pre-insertion intermediates (Figure 1) include an alkyl-substituted allyl (simulating the portion of a growing chain closest to the catalytic metal atom) and a diene molecule, *anti*-η^3 and *cis*-η^4 coordinated to a metal (titanium) atom, respectively. A cyclopentadienyl ligand (Cp in the following) has been also coordinated to the metal (Figure 1), as proposed for the case of catalytic systems based on $CpTiCl_3$,[21] which are able to promote polymerization of butadiene and several methyl-substituted butadienes,[22−24] as well as styrene and substituted styrenes.[25,26] This choice is mainly due to our desire for a reasonable filling of the coordination sphere of the catalytic models and also presents the advantage of relating the model to a catalytic system whose stereospecific behavior is well established.[22−24] A further advantage of the catalytic models with a Cp coordinated to the metal is the possibility of assuming several geometrical parameters in analogy to the values observed for the crystalline structure of the (η^3-allyl)(η^4-butadiene)(η^5-cyclopentadienyl)zirconium complex,[27] as will be detailed in the next section. Without loss of generality our calculations refer only to models for which the *anti*-η^3-allyl group (which is present in the pre-insertion intermediate) is *re*-coordinated[28] to the metal, that is for the chirality of coordination of the allyl group shown in Figure 1.

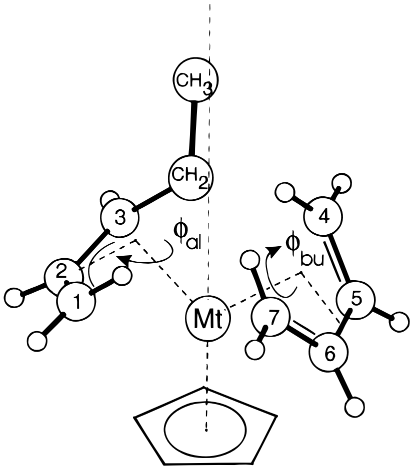


Figure 1. Model for a pre-insertion intermediate including on alkyl-substituted allyl *anti*-η^3 coordinated (simulating the portion of a growing chain closest to the metal catalytic atom), a butadiene molecule *cis*-η^4 coordinated, and a cyclopentadienyl ligand. The chirality of coordination of the allyl group is *re*. The definition of the dihedral angles ϕ_{al} and ϕ_{bu} (assumed equal to 180° for the sketched *endo*−*endo* conformation) and the labeling of the carbon atoms of the allyl group are also indicated. For the sake of simplicity aliphatic hydrogens are omitted.

For the models of the post-insertion intermediates (which are, of course, different for the *cis*-1,4 and the 1,2 insertions), a simultaneous coordination of the η^3-allyl terminal and of the last double bond of the growing chain (that is an intramolecular pentahapto coordination, which has been called "back-biting" coordination[29]) has been assumed. In other words, the *anti*-η^3-coordinated allyl group and the *cis*-η^4-coordinated diene monomer of the pre-insertion intermediate become, in the post-insertion intermediate, an η^2-coordinated double bond and an *anti*-η^3-coordinated allyl group, respectively. The assumption of post-insertion intermediates including a back-biting coordination of the polymeryl group is supported by the analogous structure of several complexes.[30−35]

In the reaction path from the pre-insertion intermediate toward the post-insertion intermediate the transformation of the η^3-allyl bond into a (back-bitten) η^2

bond could involve preliminary formation of a η^1-allyl bond, as observed for the slow insertion of butadiene into a transition metal−allyl bond (by ^{1}H NMR experiments[37,38]). This possible preliminary formation of a η^1-allyl bond, although not explicitly considered, is, however, compatible with the pathway assumed in the present study of molecular mechanics.

Although the relative stabilities of all the considered models certainly depend also on electronic factors,[36] for the sake of simplicity we confine our present analysis to the nonbonded interactions. This simplifying assumption is reasonable since we only compare, for a given kind of insertion (1,4-*cis* or 1,2), situations presenting different relative orientations of the allyl terminal of the growing chain and of the monomer. In particular, for the post-insertion intermediates, different prior relative orientations of the monomer and of the growing chain produce large differences in the nonbonded interaction energies (see the section Results and Discussion), possibly much higher than the differences between the electronic energies.

Method of Calculation

For any geometrical arrangement of atoms the potential energy may be taken as a sum of terms of the kind bond stretching, in-plane and out-of-plane angle bendings, torsional barriers to internal rotations, and electrostatic and nonbonded interactions. Since in the considered ligands only carbon and hydrogen atoms are present, the calculations have been simplified by ignoring possible electrostatic contributions to the potential energy.

The results presented in this paper are obtained within the scheme developed by Bosnich for bent metallocenes.[39] The approach used by Bosnich is a development of the CHARMM force field of Karplus,[40] to include metallocenes of the group 4A. In order to test the dependence of the results on the particular choice of the parameters in the potential functions, some calculations have been also performed by using the valence parameters of the MM2 force field of Allinger[41] with the nonbonded parameters proposed by Scheraga and coworkers.[42] Although with the different sets of parameters the results are numerically different, the overall trends and the locations of the energy minima are nearly the same.

The nonbonded interactions have been calculated with potentials of the Lennard-Jones type. To prevent the effect of long range attractive forces,[43,44] and as discussed in ref 43, for the nonbonded interactions we have assumed pure repulsive potentials according the the following modified Lennard-Jones functional:

$$E_{\mathrm{nb}} = \sum_{m<n}\left[\left(\frac{A_{ij}}{r_{mn}{}^{12}} - \frac{B_{ij}}{r_{mn}{}^{6}}\right) - \left(\frac{A_{ij}}{\bar{r}_{ij}{}^{12}} - \frac{B_{ij}}{\bar{r}_{ij}{}^{6}}\right)\right] \qquad \text{for} \quad r_{mn} < \bar{r}_{ij}$$

$$E_{\mathrm{nb}} = 0 \qquad \text{for} \qquad r_{\mathrm{mn}} \geq \bar{r}_{ij}$$

where A_{ij}, B_{ij}, $\bar{r}_{ij}$ are constants characteristic of the species i and j and $\bar{r}_{ij}$ is the minimum interaction distance. Anyhow, considering that the previous functional form has a discontinuity in the second derivative at $\bar{r}_{ij}$ and that this discontinuity causes an instability of the optimization algorithm, we preferred to fit the modified Lennard-Jones functional with an exponential function and use this exponential function in the optimization processes.

The calculations have been performed by using a package developed at the University of Naples. The energy minimizations have been performed in internal coordinates. The Broyden−Fletcher−Goldfarb−Shanno algorithm[45] has been used, and as convergence criterions we used 10^{-4} kcal/mol on the change of the total energy, and maximum gradients below the threshold of 10^{-3} kcal/(mol·Å) or kcal/(mol·deg) for bond distances and bend and torsional angles, respectively. The same zero of the energy is adopted in the following for a given model complex, irrespective of the coordination chirality of the propene monomer.

For the pre-insertion intermediates the distances between the metal atom and the coordinated carbon atoms of the allylic group and of the diene molecule were derived from the analogous distances observed in the crystal structure of the (η^3-allyl)(η^4-butadiene)(η^5-cyclopentadienyl)zirconium complex described in ref 27 and scaled by 0.16 Å, which is an average value of the difference in the distance of coordination of various ligands to Zr and Ti.[46] The distances Ti−C$_1$ and Ti−C$_2$ of the diene molecule were thus set equal to 2.3 and 2.2 Å, respectively, while the distances Ti−C of the allyl group were set equal to 2.3 Å. For the post-insertion intermediates, the distances between the metal atom and the sp^2 carbon atoms of the product models have been constrained in the range 2.2−2.3 Å, which respectively are the minimum and the maximum values fixed for the five sp^2 carbon atoms to the metal atom in the pre-insertion intermediate model. A further imposed constraint is that all the sp^3 carbon atoms should be at distances from the metal atom larger than 2.2 Å. The distance constraints have been applied by including in the total energy special terms of the type:

$$E_{\mathrm{constr}} = {}^1\!/_2 K_{\mathrm{constr}}(r_{ij}^{\mathrm{min}} - r_{ij})^2 \qquad \text{for} \qquad r_{ij} \leq r_{ij}^{\mathrm{min}}$$

and

$$E_{\mathrm{constr}} = {}^1\!/_2 K_{\mathrm{constr}}(r_{ij}^{\mathrm{max}} - r_{ij})^2 \qquad \text{for} \qquad r_{ij} \geq r_{ij}^{\mathrm{max}}$$

where K_{constr}, which is the constraint constant, was set equal to 100 kcal·mol^{-1}·Å^{-2}, and r_{ij}^{min} and r_{ij}^{max} are the lower and upper bounds of the applied constraint. This contribution was included in the energy minimization, and for all the low-energy structures was null at the end of the minimization procedure.

The numerical values of the energy differences depend on the chosen geometrical parameters and especially on the values assumed for the distances between the metal and the ligands, which can change with the nature and the oxidation state of the metal. However, it seems to us that no reasonable variations of these parameters can significantly modify the conclusions.

Results and Discussion

Pre-Insertion Intermediates. The conformational energy map, for the model of the pre-insertion intermediate, with respect to the torsional angles around the axes passing through the metal atom and the centroids of the allyl moiety and of the butadiene molecule (ϕ_{al} and ϕ_{bu} in Figure 1, respectively), is reported in Figure 2. For the conformation sketched in Figure 1, which presents the allyl group and the butadiene ligand *endo* coordinated,[36] the angles ϕ_{al} and ϕ_{bu} have been assumed equal to 0°. Of course, in our assumption, for the

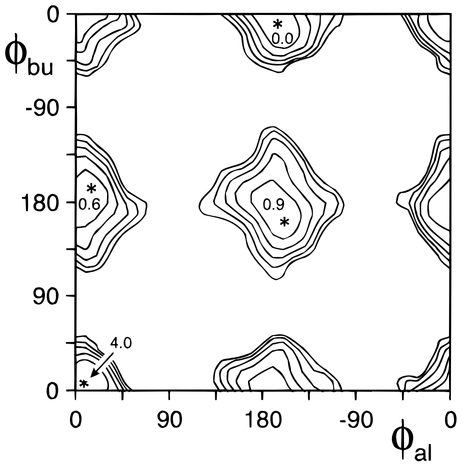


Figure 2. Conformational energy map, for the model of the pre-insertion intermediate of Figure 1, as a function of the torsional angles around the axes passing through the metal atom and the centroids of the allyl moiety and of the butadiene molecule (ϕ_{al} and ϕ_{bu}, respectively). Energy curves are reported each 2 kcal/mol.

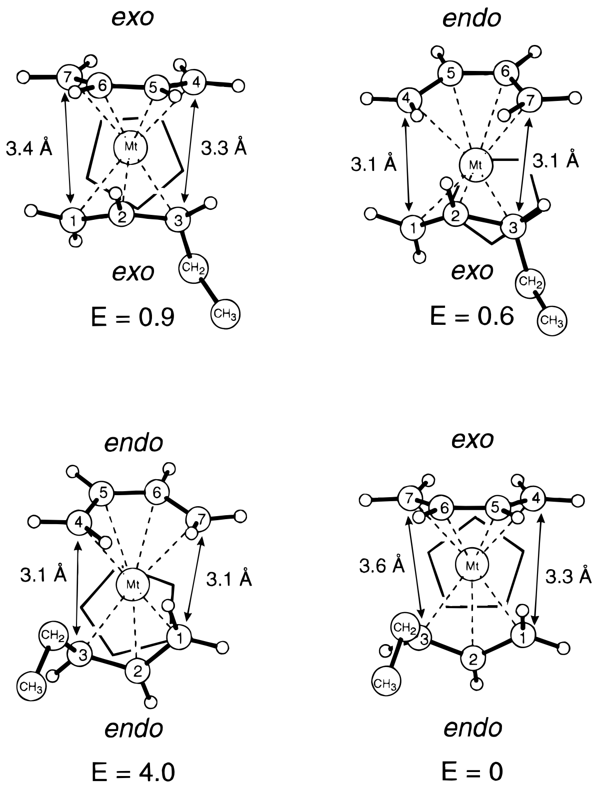


Figure 3. Four minimum energy situations of the map of Figure 2. For the four models, also the distances between the carbon atoms, which should become bonded after *cis*-1,4 or 1,2 insertion reactions, are indicated. *cis*-1,4 and 1,2 polymerizations correspond to the monomer reaction at carbon 1 or 3 of the allyl groups, respectively. For the sake of simplicity aliphatic hydrogens are omitted.

conformation presenting the allyl group and the butadiene ligand *exo* coordinated[36] ϕ_{al} and ϕ_{bu} are equal to 180°.

In the energy map of Figure 2 only four energy minima are present, corresponding to the *endo–endo*, *endo–exo*, *exo–endo*, and *exo–exo* coordinations of the allyl moiety and of the butadiene molecule. In the present paper we assume that the first term refers to the coordination of the allyl group while the second one to the coordination of the diene monomer. The four minimum energy conformations thus located have been subsequently refined by optimizing the geometry as described in the previous section. Similar energy minima correspond to the *exo–exo*, *endo–exo*, and *exo–endo* coordinations, while the energy of the *endo–endo* complex is nearly 4.0 kcal/mol higher. These oversimplified calculations, based only on the nonbonded interactions, are in fair qualitative agreement with some experimental observations on metal complexes presenting general formulas LM(diene)$_2$[38,47] or LM(diene)(allyl),[27,38,48] where the dienes are η^4-*cis*-coordinated and the allyl group η^3 coordinated. In fact in these metal complexes the two ligands generally orient themselves in a parallel *exo–exo* fashion, while in a few cases they orient in the antiparallel *endo–exo* or *exo–endo* fashion (the two coordinations are of course equivalent for the complexes with two diene molecules). Intermediates of higher energy, presenting *endo–endo* coordinations of the two ligands, have been also observed by NMR analysis.[27]

In the models sketched in Figure 3, the distances between the carbon atoms, which in the framework of the present mechanism are assumed as bonded after *cis*-1,4 or 1,2 insertion reactions (for instance, C1 with C7 or C3 with C4 in the *exo–exo* and *endo–endo* models), are indicated. These distances are always in the range 3.1–3.6 Å and are smaller for the models presenting an *endo* diene coordination. Anyhow, with the exception of the *endo–endo* pre-insertion intermediate, short distances between atoms which are not supposed to form a new bond are observed. For instance, the C2–C5 and C2–C6 distances, the C1–C5 and C3–C6 distances, and the C2–C4 and C2–C7 distances are close to 3.1, 3.2, and 3.3 Å for the *exo–exo*, *endo–exo*, and *exo–endo* pre-insertion intermediates, respectively. On the contrary, for the *endo–endo* pre-insertion intermediate the shortest distance between atoms which are not supposed to form a new bond is equal to 3.8 Å. The previous analysis indicates that the most suitable proximity and orientation of the monomer and of the allylic terminal of the growing chain corresponds to the *endo–endo* pre-insertion intermediate. Thus, for the considered model sites, a reaction path starting from the *endo–endo* pre-insertion intermediate should not be hampered by steric interactions between nonreacting atoms.

Post-Insertion Intermediates. The models of the post-insertion intermediates have been derived by the pre-insertion intermediates of Figure 3 by assuming the formation of a bond between two proximal C atoms (whose distances are indicated in Figure 3). In particular, when the new formed bond involves the C1 or C3 carbon atoms of the allyl group, the post-insertion intermediates for the 1,4 or for the 1,2 polymerizations are obtained, respectively. Moreover, for the post-insertion intermediates a simultaneous coordination of the *anti*-η^3 allyl terminal and of the last double bond of the growing chain has been assumed. In this framework local minimum energy situations have been investigated and the minimum energy post-insertion intermediates for the *cis*-1,4 and 1,2 insertions of butadiene are shown in Figures 4 and 5, respectively, with the corresponding pre-insertion intermediates. The calculated energies are also indicated in the Figures 4 and 5. It is apparent that both for the *cis*-1,4 and 1,2 insertions, the post-insertion intermediates of absolute minimum energy are structurally very similar to the *endo–endo* pre-insertion intermediate, while the energy minimization starting from the *exo–exo* pre-insertion intermediate does not lead to any local minimum but,

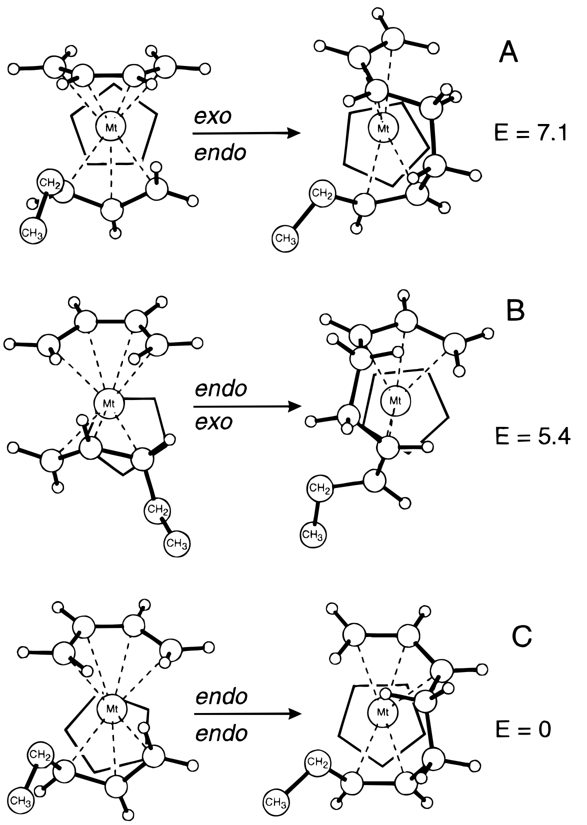


Figure 4. Minimum energy post-insertion intermediates for the *cis*-1,4 insertion of butadiene, with the corresponding pre-insertion intermediates. The coordinated monomer reacts at carbon 1 of the allyl groups. The calculated energies are also indicated. For the sake of simplicity aliphatic hydrogens are omitted.

after large rearrangements, lead to the absolute minimum corresponding to the post-insertion intermediate geometrically close to the *endo*−*endo* pre-insertion intermediate.

It is worth noting that the post-insertion intermediates of absolute minimum energy of Figures 4 and 5 are characterized by nearly *gauche* internal rotation angles relative to the newly formed C−C bond and by nearly tetrahedral adjacent C−C−C bond angles, which result in nonbonded distances of the adjacent carbon atoms always larger than 2.9 Å. Figures 4 and 5 show that, as discussed by Porri and co-workers,[7,9] the chirality of coordination of the new allyl group (in the post-insertion intermediate) depends on the kind of enchainment (*cis*-1,4 or 1,2) as well as on the relative orientations of the allyl group and of the monomer in the pre-insertion intermediate. In particular, starting from an *endo*−*endo* pre-insertion intermediate with the allyl group *re* coordinated, the new *anti*-η^3-allyl group for the post-insertion intermediate is *re* or *si* coordinated for the *cis*-1,4 or the 1,2 polymerizations, respectively. On the contrary, starting from the *endo*−*exo* or the *exo*−*endo* pre-insertion intermediates, again with the allyl group *re* coordinated, the new *anti*-η^3-allyl group is *si* or *re* coordinated for the *cis*-1,4 or the 1,2 polymerizations, respectively.

The chirality of coordination of the allyl groups in successive insertion steps has no relevance (since no tertiary carbon atom is present in the polymer) for the *cis*-1,4 polymerization of butadiene, which is the only one occurring with the considered catalytic system.[21] This would be, instead, determining for the stereoregularity of a possible polybutadiene with 1,2 enchainment.

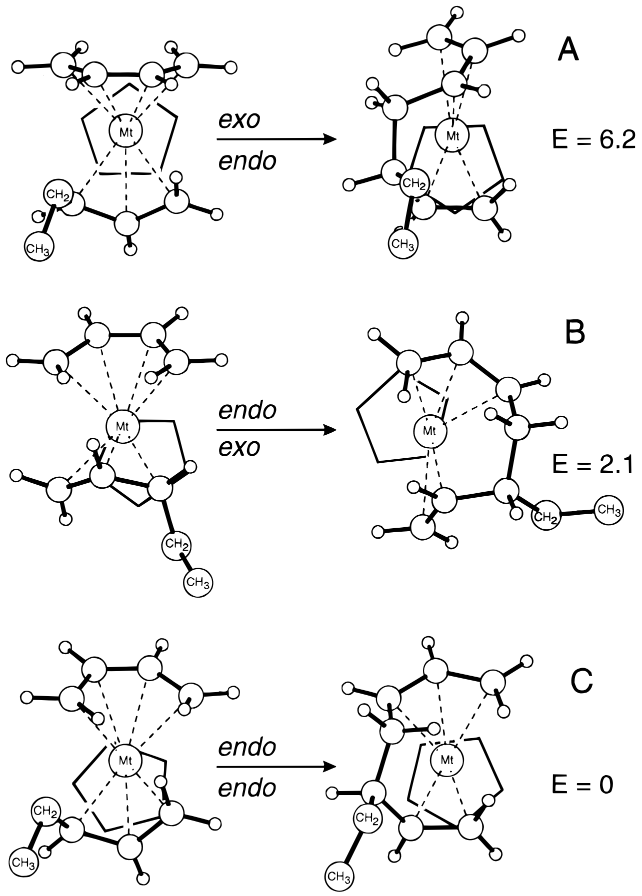


Figure 5. Minimum energy post-insertion intermediates for the 1,2 insertion of butadiene, with the corresponding pre-insertion intermediates. The coordinated monomer reacts at carbon 3 of the allyl groups. The calculated energies are also indicated. For the sake of simplicity aliphatic hydrogens are omitted.

In fact, the models imply that the 1,2 insertions starting from the *endo*−*endo* intermediates would lead to syndiotactic 1,2 polymers, while insertion reactions starting from the *exo*−*endo* intermediates would lead to isotactic 1,2 polymers.

A strong support to a 1,2 insertion mechanism, for butadiene, involving an *endo*−*endo* intermediate is possibly given by the similarity between the intramolecular pentahapto coordination calculated for the minimum energy 1,2 post-insertion intermediate (which originates from the *endo*−*endo* pre-insertion intermediate) (Figure 5C, a different view of this post-insertion intermediate is also shown in Figure 6A) and the intramolecular pentahapto coordination observed in the crystalline structure of the allyl complex (η^3-C_8H_{13})Co-(C_4H_6) (Figure 6B).[48] The latter complex, obtained by reacting $CoCl_2$ with $NaBH_4$ and butadiene at −20 °C, coordinates an allyl group corresponding to a butadiene dimerization through a 1,2 insertion. It is worth noting that this complex has been reported to be able to catalytically polymerize butadiene at low temperatures ($\leq$20 °C), giving syndiotactic 1,2-polybutadiene of high molecular weight and crystallinity.[49]

These kinds of calculations have been extended to analogous catalytic models for the 1,2 and *cis*-1,4 polymerizations of 4-methyl-1,3-pentadiene (4MPD) and of (*Z*)-1,3-pentadiene ((*Z*)-PD).

Though the corresponding models of pre-insertion intermediates, in the *cis*-η^4 coordination of the monomer, have repulsive intramolecular nonbonded interactions

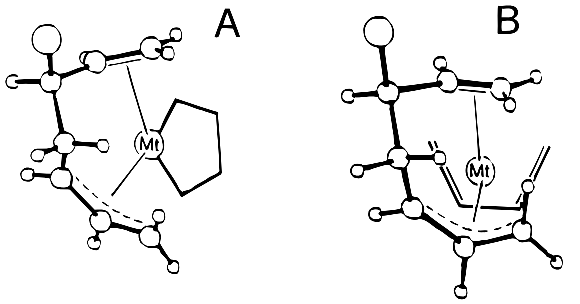


Figure 6. Comparison between the intramolecular pentahapto coordination: (A) calculated for the minimum energy 1,2 post-insertion intermediate (which originates from the *endo–endo* coordination intermediate); (B) observed in the crystalline structure of the catalytic complex (η^3-C_8H_{13})Co-(C_4H_6).[48]

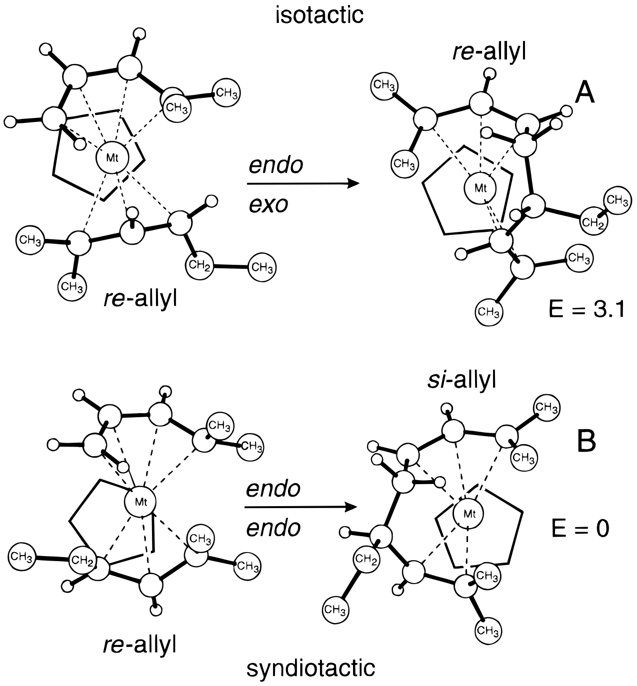


Figure 7. Minimum energy post-insertion intermediates for the 1,2 insertion of 4-methyl-1,3-pentadiene, with the corresponding *endo–endo* and *exo–endo* pre-insertion intermediates. The calculated energies and the chiralities of coordination of the allyl ligands are also indicated. The energy preference for the post-insertion intermediate obtained from the *endo–endo* pre-insertion intermediate accounts for the production of the syndiotactic 1,2 polymer (see text). For the sake of simplicity aliphatic hydrogens are omitted.

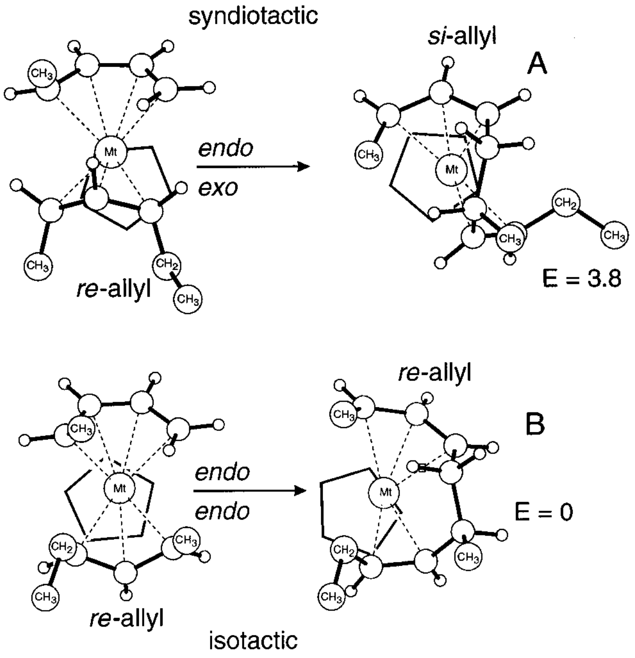


Figure 8. Minimum energy post-insertion intermediates for the cis-1,4 insertion of (*Z*)-1,3-pentadiene, with the corresponding *endo–endo* and *exo–endo* pre-insertion intermediates. The calculated energies and the chiralities of coordination of the allyl ligands are also indicated. The energy preference for the post-insertion intermediate obtained from the *endo–endo* pre-insertion intermediate accounts for the production of a prevailingly isotactic *cis*-1,4 polymer (for high temperatures, see text). For the sake of simplicity aliphatic hydrogens are omitted.

between a methyl group and the terminal methylene group (distance close to 2.8 Å), they are possibly stabilized by the formation of η^4-diene-agostic-yl bonds between a hydrogen atom of that methyl group and the metal, as found for several well-characterized metal complexes (Table V in ref 50).

A comparison of the models for the 1,2 polymerization of 4MPD shows that also in this case the post-insertion intermediate of lowest energy is structurally very similar to the *endo–endo* pre-insertion intermediate. Markedly higher energies correspond to the other post-insertion intermediates, with the ones similar to the *exo–endo* and *endo–exo* pre-insertion intermediates at 3.1 and 3.3 kcal/mol, respectively. The post-insertion intermediates derived from the *endo–endo* and the *exo–endo* pre-insertion intermediates for 4MPD are shown in Figure 7. For the analogous models for the 1,2 polymerization of (*Z*)-PD the post-insertion intermediates derived from the *endo–endo*, *exo–endo*, and *endo–exo* pre-insertion intermediates give relative energies of 0, 3.7, and 6.1 kcal/mol. In the framework of our analysis, this assures the syndiospecificity of the model, for the 1,2 polymerization. These results are in good qualitative agreement with the high syndiospecificity of the catalytic system based on $CpTiCl_3$ in the 1,2 polymerization of 4MPD[22,24] and of (*Z*)-PD (for low polymerization temperatures).[24]

The chirality of coordination of successive allyl groups is also relevant for the iso- and syndiotactic isomerism in the *cis*-1,4 polymerization of 4-monosubstituted or of 1,4-disubstituted monomers.

The extension of these calculations to the *cis*-1,4 polymerization of (*Z*)-PD (Figure 8) indicates again that the minimum energy post-insertion intermediate is very similar to the *endo–endo* pre-insertion intermediate, with the *exo–endo* and *endo–exo* at 3.8 and 6.3 kcal/mol, respectively. The post-insertion intermediates derived from the *endo–endo* and the *exo–endo* pre-intermediates are shown in Figure 8. In the framework of our analysis, this assures the isospecificity of the model, for the *cis*-1,4 polymerization. These results are in good qualitative agreement with the isospecificity of the catalytic system based on $CpTiCl_3$ in the *cis*-1,4 polymerizations of (*E*)-2-methyl-1,3-pentadiene[24] and of (*Z*)-PD (for high polymerization temperatures).[22,24,51]

The present mechanism of stereospecificity hence remains in the framework of the mechanism proposed by Porri and co-workers,[7–9] i.e. the iso- or syndiospecificity is determined by the parallel (*endo–endo* or *exo–exo*) or antiparallel (*endo–exo* or *exo–endo*) placements of the allyl group and of the monomer. However, the molecular mechanics analysis suggests that the pre-insertion intermediates with the *endo–endo* relative orientations of the allyl group and of the diene monomer are more suitable than the other pre-insertion intermediates for the insertion reactions, in the presence of a Cp ring (both for the 1,2 and *cis*-1,4 polymerizations). The post-insertion intermediates with the *exo*−*exo* orientations, if any, are expected to be of very high energy, while the intermediates with the *exo*−*endo* and *endo*−*exo* orientations (of comparable energy, and slightly higher in energy with respect to the *endo*−*endo)* are the other two suitable orientations for the insertion reaction.

The results presented in Figures 4, 5, 7, and 8, are dependent on the bulkiness of the other ligand(s), besides the growing chain and monomer. In particular, the substitution of the Cp with smaller ligands markedly reduces the nonbonded energy differences between the four different intermediates. For instance, the substitution of a Cp group with a Cl atom reduces the energy differences between the *endo*−*endo* and *exo*−*endo* post-insertion intermediates from 3.8 to 1.0 kcal/mol, for the *cis*-1,4 polymerization of (*Z*)-PD, and from 3.1 to 0.9 kcal/mol, for the 1,2 polymerization of 4MPD.

Hence, according to our calculations, restrictions of the conformational space available to the allyl moiety and to the diene molecule, tend to favor post-insertion intermediates from the *endo*−*endo* coordination with respect to the post-insertion intermediates from the *exo*−*endo* or *endo*−*exo* coordinations. This is in qualitative agreement with the experimental information relative to the influence of further ligands (besides the monomer and the growing chain) in the iso−syndio isomerism in the diene polymerization.[9,52] Let us recall, for instance, that the catalytic system $AlEt_2Cl-H_2O-Co(acac)_2$ produces *cis*-1,4-polybutadiene and syndiotactic *cis*-1,4-polypentadiene while after addition of suitable donors (CS_2, THF) produces syndiotactic 1,2-polybutadiene.[9,52]

Conclusions

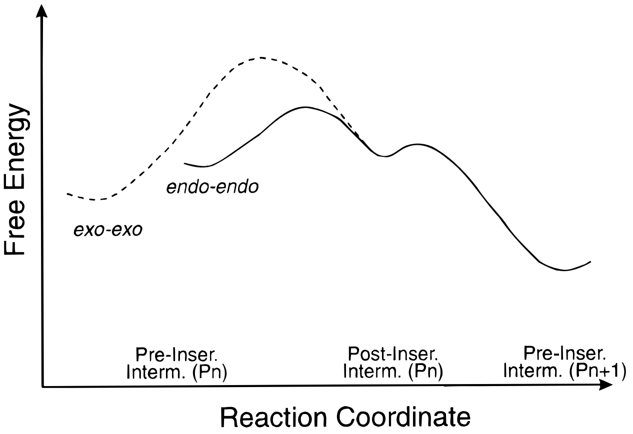
The present molecular mechanics analysis has considered models for possible pre-insertion and post-insertion intermediates, for the 1,2 and *cis*-1,4 polymerizations of dienes, in the framework of the polymerization mechanism proposed by Porri and co-workers.[7−9]

The calculations for the pre-insertion intermediates, which include a Cp coordinated to the metal atom, show the presence of four energy minima, corresponding to the *endo*−*endo*, *endo*−*exo*, *exo*−*endo*, and *exo*−*exo* coordinations of the allyl moiety and of the butadiene molecule. The relative stability of the four minimum energy pre-insertion intermediates is in fair qualitative agreement with some experimental observations on the structure of metal complexes presenting general formulas LM(diene)$_2$[38,47] or LM(diene)(allyl).[27,38,48]

However, these relative stabilities are possibly not relevant for the respective reactivities in the insertion reactions. In fact, possibly closer to the transition states of the (1,2 and *cis*-1,4) insertion reactions could be the supposed post-insertion intermediates, which present a “back-biting” coordination of the growing chain.

The nonbonded energy analysis for post-insertion intermediates, which include a coordinated Cp, indicates that those structurally similar to the *endo*−*endo* pre-insertion intermediates are always of minimum energy, independently of the kind of insertion (*cis*-1,4 or 1,2) and of the diene (butadiene, 4MPD, or (*Z*)-PD). A schematic representation of the possible reaction pathways is shown in Scheme 1.

Scheme 1



In the hypothesis that the energy differences between the post-insertion intermediates are close to those present in the transition states, this assures the isospecificity and the syndiospecificity of the models for the 1,2 and *cis*-1,4 polymerizations, respectively. This is in agreement with the stereoregularities of the polydienes obtained with a catalytic system based on $CpTiCl_3$.[22−24]

A comparison with models where the Cp ring is substituted by a smaller ligand (a chlorine atom) shows that the restrictions of the conformational space available to the pentahapto-coordinated growing chain is determinant on the nonbonded energy preference in favor of the post-insertion intermediates geometrically similar to the *endo*−*endo* pre-insertion intermediates. This is in qualitative agreement with the experimental information relative to the influence of some ligands in the iso−syndio isomerism in the diene polymerization.[9,53]

Strong support for a 1,2 insertion mechanism for butadiene involving an *endo*−*endo* coordination intermediate is possibly given by the similarity between the intramolecular pentahapto coordination calculated for the minimum energy 1,2 insertion intermediate (which originates from the *endo*−*endo* coordination intermediate) (Figure 6A) and that one observed in the crystalline structure of the catalytic complex (η^3-C_8H_{13})Co(C_4H_6)[48] (Figure 6B).

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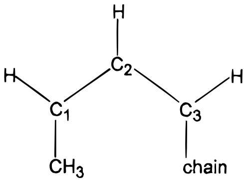

could form, for low temperatures, an agostic bond involving the methyl group (that is an η^3-enyl-agostic-yl) compound like those listed in Table IV of ref 50). This could make more accessible (and probably more reactive) for the insertion reaction the C3 atom of the allyl group and would produce preferably 1,2 units. For high temperatures, due to the weakening of the agostic bond, the C1 atom (less sterically hindered) could become the most accessible and, as a consequence, the insertion reaction could generate preferably 1,4 units.

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