

# Theoretical Investigation of the Mechanism of Cis–Trans Regulation for the Allylnickel(II)-Catalyzed 1,4 Polymerization of Butadiene<sup>†</sup>

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Received January 3, 2001

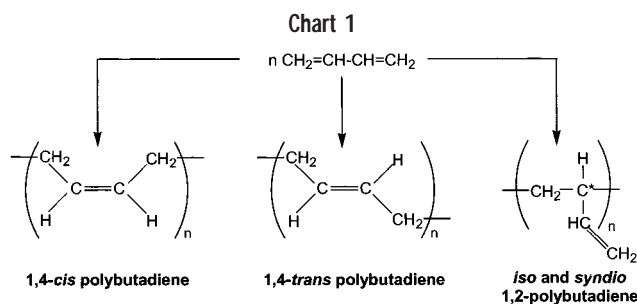
## ABSTRACT

In this Account we summarize the recent progress in the computational modeling of the transition-metal-catalyzed 1,3-diene polymerization. We present a comprehensive and theoretically well-founded view of the cis–trans regulation mechanism of the intriguing C–C coupling for the allylnickel(II)-catalyzed 1,4 polymerization of butadiene. The crucial elementary reactions of the entire polymerization process were theoretically explored for typical trans-1,4- and cis-1,4-regulating catalysts. As a result, the catalytic structure–activity relationships are deduced, which are responsible for opening that reaction channel which yields trans-1,4 and cis-1,4 polymer units.

## 1. Introduction

The transition-metal-catalyzed polymerization of butadiene is a very important process in the chemical industry,<sup>1</sup> and from a mechanistic point of view it represents one of the most fascinating and challenging subjects in the field of transition-metal-assisted C–C bond formation reactions.<sup>2</sup> This process is characterized by (I) a high regioselectivity (i.e., it yields a polybutadiene consisting nearly exclusively of one type of the monomer, 1,4 or 1,2) and (II) a high degree of stereoselectivity achieved in the C–C coupling reaction.<sup>3</sup> Depending on the chosen catalyst complex, four highly stereoregular polybutadienes were obtained, with a trans-1,4, a cis-1,4, a 1,2 isotactic, and a 1,2 syndiotactic polymer structure, respectively (cf. Chart 1).<sup>4</sup>

The discovery of those factors, which are responsible for the generation of highly stereoregular polybutadienes, is a prerequisite for a tailored catalyst design, allowing the production of polybutadienes with desired properties. In the mid-1960s, the groups of Wilke,<sup>5a</sup> Dolgoplosk,<sup>5b</sup> and Porri<sup>5c</sup> showed that allyl transition metal complexes are able to catalyze the butadiene polymerization stereoselectively and that those complexes very likely represent the real catalysts. A substantial amount of research has been directed toward elucidating the catalytic reaction mechanism.<sup>3,6</sup> Allylnickel(II) complexes, in particular, were



applied in kinetic and NMR investigations.<sup>7</sup> This leads to some understanding of individual mechanistic aspects. However, with the two-channel reaction model suggested by Taube et al.,<sup>8</sup> for the first time an experimentally well-founded catalytic model was proposed that allows a convincing explanation of the cis–trans regulation in the case of allylnickel(II)-catalyzed butadiene polymerization. Although many mechanistic details are fairly well established, a careful theoretical exploration of the catalytic cycle is highly desirable for a deep, fundamental understanding of kinetic and thermodynamic aspects of the polymerization process.

With the refinement of density functional theory (DFT) during the past decade, a quantum chemical method is now available that, especially for organometallic compounds, can provide quantitative information of high accuracy about structural and energetic properties of educts and products as well as reactive intermediates and transition states of elementary processes and is capable of treating large systems.<sup>9</sup> Computational modeling allows the exploration of individual elementary steps of the catalytic cycle at an atomic level. This provides a fundamental understanding how the catalysts operate.

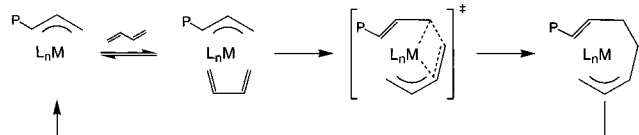
Despite the great importance of the transition-metal-catalyzed 1,3-diene polymerization, theoretical mechanistic studies are scarce.<sup>10,11</sup> In most cases these studies focused on a single reaction step and were mainly concerned with thermodynamic aspects. The goal of this Account is to summarize the progress in the theoretical foundation of the cis–trans regulation in the allylnickel(II)-catalyzed butadiene polymerization<sup>12</sup> and to give a demonstrated example of how computational modeling can substantially contribute to the elucidation of the reaction mechanism.

This Account is organized as follows. In section II, we briefly describe general aspects of butadiene polymerization that are necessary for the understanding of mechanistic details, followed by an outline of the two-channel reaction model in section III. In section IV, we describe the computational approach and present the results for crucial elementary steps of the catalytic cycles together with mechanistic conclusions. In section V, the conclusions, we briefly summarize the results and discuss future directions for improving the mechanistic insight.

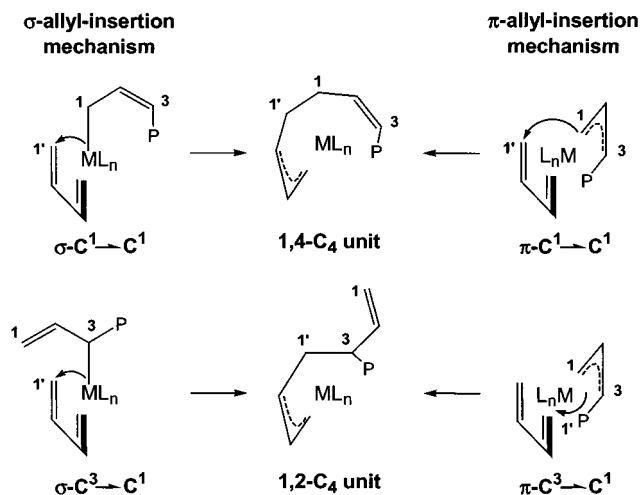
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<sup>†</sup> Dedicated to Professor Rudolf Taube on the occasion of his 70th birthday.

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**Scheme 1. Allyl Insertion Mechanism as the Catalytic Principle of Chain Growth for the Metal-Catalyzed Butadiene Polymerization<sup>a</sup>**


<sup>a</sup> P denotes the growing polybutadienyl chain. (Adapted from ref 8c. Copyright 1996 Wiley-VCH.)



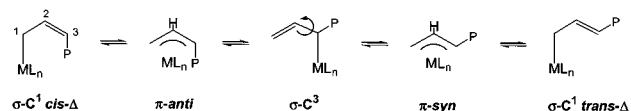
**FIGURE 1.** C–C bond formation between butadiene and the butenyl group achieved as C<sup>1</sup>–C<sup>1</sup> or C<sup>3</sup>–C<sup>1</sup> linking according to the  $\sigma$ -allyl and the  $\pi$ -allyl insertion mechanism (P denotes the growing polybutadienyl chain). (Adapted from ref 8c. Copyright 1996 Wiley-VCH.)

## II. General Aspects of Butadiene Polymerization

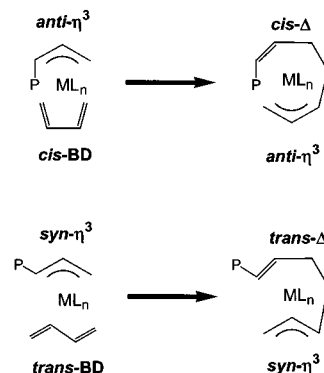
Transition-metal-catalyzed butadiene polymerization is an insertion polymerization.<sup>13</sup> It is generally agreed that chain propagation proceeds in two steps, first by coordination of free monomer to an empty site of the metal which gives rise to ( $\eta^3$ -butenyl)butadiene  $\pi$ -complexes, and then by subsequent insertion into the  $\eta^3$ - $\pi$ -allylic transition metal–carbon bond of the terminal group on the reactive growing chain (cf. Scheme 1). The allyl insertion mechanism was proven by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy for both trans-regulating, i.e., [Ni(C<sub>4</sub>H<sub>7</sub>)I]<sub>2</sub>,<sup>14</sup> and cis-regulating, i.e., [Ni(C<sub>3</sub>H<sub>5</sub>)O<sub>2</sub>CCF<sub>3</sub>]<sub>2</sub>,<sup>15</sup> butadiene polymerization catalysts.

Two general mechanistic proposals for the nature of the monomer insertion step have emerged. They differ with regard to the suggested insertion mode of the butenyl group, which can be either  $\eta^1$ - $\sigma$  or  $\eta^3$ - $\pi$ . On one hand there is the  $\sigma$ -allyl insertion mechanism of Cossee and Arlman,<sup>16</sup> which was generally believed to be operative in the literature,<sup>3,6</sup> where the butenyl group in  $\eta^1$ - $\sigma$ -coordination reacts like an alkyl group. In contrast, Taube et al.<sup>8</sup> suggested that the C–C bond formation can also proceed through a nucleophilic attack of the  $\eta^3$ - $\pi$ -butenyl group on the diene (cf. Figure 1).

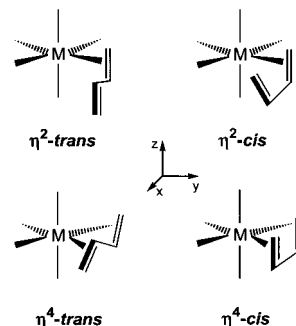
The  $\eta^3$ -butenyl–transition metal bond can exist in two isomeric forms, namely anti and syn, which are in equilibrium. The interconversion of these forms (anti–syn isomerization) very likely proceeds through an  $\eta^1$ - $\sigma$ -



**FIGURE 2.** Different configurations and coordination modes of the butenyl anion together with their interconversion (anti–syn isomerization) via a  $\sigma$ -C<sup>3</sup> intermediate (P denotes the growing polybutadienyl chain). (Adapted from ref 8c. Copyright 1996 Wiley-VCH.)



**FIGURE 3.** Anti–cis and syn–trans correlation of the 1,4 polymerization of butadiene (P denotes the growing polybutadienyl chain).



**FIGURE 4.** Structurally different modes of butadiene coordination at the metal M in butadiene  $\pi$ -complexes.

butenyl intermediate<sup>17</sup> accompanied by rotation of the vinyl group around the C<sup>2</sup>–C<sup>3</sup> single bond (cf. Figure 2). According to the principle of least structure variation, which is verified theoretically by following the reaction path, butadiene insertion gives rise to a cis or trans double bond in the newly formed C<sub>4</sub> unit of the growing polymer chain, when starting from an anti or syn butenyl group (anti–cis and syn–trans correlation, cf. Figure 3).

Another characteristic of the transition metal–butenyl bond is that it has two reactive sites, C<sup>1</sup> and C<sup>3</sup>, which for example may give rise to 1,4 and 1,2 polymers (cf. Figure 1).

Butadiene coordination can occur in two different modes: monodentate ( $\eta^2$ ) or bidentate ( $\eta^4$ ), either from the s-trans or the s-cis configuration (cf. Figure 4). An anti or syn butenyl terminal group is formed under kinetic control by diene insertion to occur from the s-cis (anti insertion) or s-trans (syn insertion) configuration, respectively (cf. Figure 3).

For the butenyl–metal coordination as well as the butadiene–metal one, different arrangements must be taken into account, since those bonds are chiral and prochiral, respectively. In the case of  $\eta^3$ -butenyl and

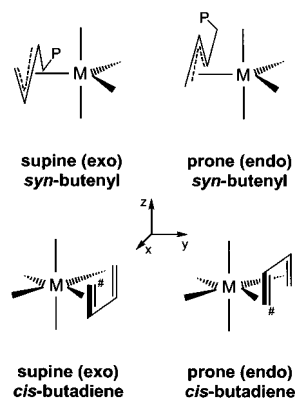
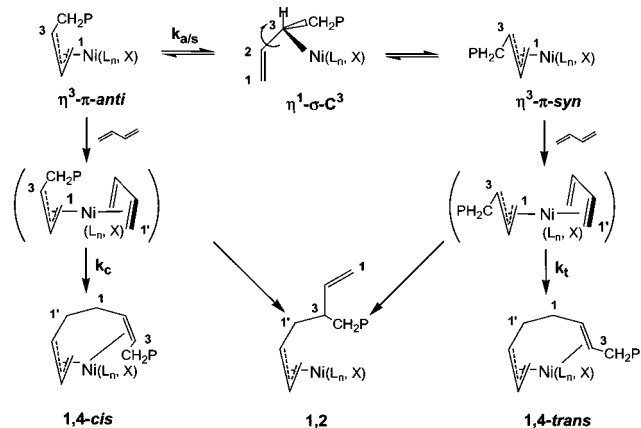


FIGURE 5. Two enantiomeric forms of the  $\eta^3$ -butenyl-metal (syn form exemplified) and the  $\eta^4$ -*cis*-butadiene-metal coordination.

Scheme 2. Formation of *Trans*-1,4, *Cis*-1,4 ( $C^1-C^1$  Linking), and 1,2 ( $C^3-C^1$  Linking) Polymer Units via *cis*-Butadiene Insertion into the Butenyl-Metal Bond in Allylnickel(II) Complexes<sup>a</sup>



<sup>a</sup> L, neutral ligand; X, monovalent anion; P, growing polybutadienyl chain. The alternative *trans*-butadiene insertion is omitted for the sake of clarity.

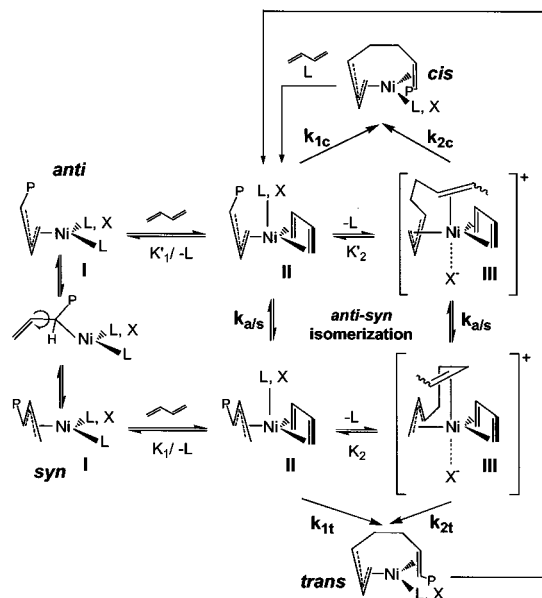
$\eta^4$ -*cis* butadiene coordination, they are denoted as supine (exo) and prone (endo),<sup>18</sup> which represents the binding of the metal to the two enantiofaces of the butenyl group and of butadiene (cf. Figure 5).

To elucidate the mechanism of *cis*-*trans* regulation, at least two different elementary steps are thought to be crucial, and their relative rates must be interrelated. These are the monomer insertion step (cf.  $k_t$  and  $k_c$  for butadiene insertion into the syn and anti butenyl-metal bond, which gives via  $C^1-C^1$  linking *trans*-1,4 and *cis*-1,4 polymer units, respectively, cf. Scheme 2) and the anti-syn isomerization (cf.  $k_{a/s}$  in Scheme 2).

### III. The Two-Channel Reaction Model for the Allylnickel(II)-Catalyzed *Trans*-1,4 and *Cis*-1,4 Polymerization of Butadiene

Historically, allylnickel(II) compounds were discovered as the first one-component butadiene polymerization catalysts.<sup>5</sup> Four different types of structurally well-defined ( $\eta^3$ -allyl)nickel(II) complexes are experimentally proven to be "single-site" catalysts for butadiene polymerization: (a) neutral dimeric allylnickel(II) compounds  $[\text{Ni}(\text{C}_3\text{H}_5)\text{X}]_2$  ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-,^{19a} \text{RCO}_2^-,^{19b}$ ); (b) cationic allylbis(ligand)-

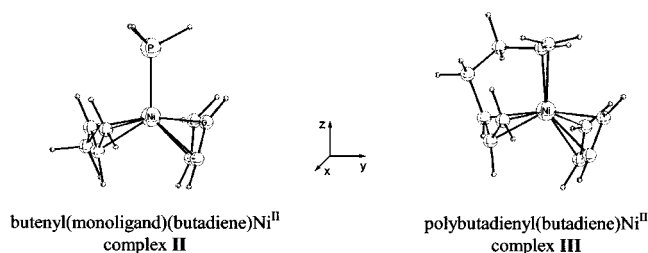
Scheme 3. General Reaction Model of the Allylnickel(II)-Catalyzed *Trans*-1,4 and *Cis*-1,4 Polymerization of Butadiene with Chain Propagation That Occurred via *s-cis*-Butadiene Insertion<sup>a</sup>



<sup>a</sup> L, neutral ligand; X, anion; P, growing polybutadienyl chain.  $\eta^2$ -Butadiene  $\pi$ -complexes are not included for sake of clarity. (Adapted from ref 8c. Copyright 1996 Wiley-VCH.)

nickel(II) complexes  $[\text{Ni}(\text{C}_3\text{H}_5)_2\text{L}_2]\text{PF}_6$  ( $\text{L} = \text{P}(\text{OR})_3$  and other ligands<sup>19c</sup>); (c) cationic  $\text{C}_8$ -allyl(monoligand)nickel(II) complexes  $[\text{Ni}(\text{C}_8\text{H}_{13})\text{L}]\text{PF}_6$  ( $\text{L} = \text{PPh}_3$  and other ligands<sup>19d</sup>); and (d) cationic "ligand-free"  $\text{C}_{12}$ -allylnickel(II) complexes  $[\text{Ni}(\text{C}_{12}\text{H}_{19})\text{X}]$  ( $\text{X}^- = \text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4^-, \text{PF}_6^-, \text{SbF}_6^-, \text{BF}_4^-$ , and other anions<sup>19e</sup>). All of these complexes catalyze nearly exclusively the formation of 1,4-polybutadienes with 1,2-polybutadienes as minor products. The catalytic activity (under comparable conditions) and the composition of the polymer product, with predominance of either a *trans*-1,4 or a *cis*-1,4 structure, or a statistical *cis/trans* equibinary polybutadiene consisting of approximately 50% *cis* and 50% *trans* polymer units, however, strongly depends on the molecular structure of the active catalyst complex. The formation of an anti butenyl group in the kinetic insertion product was convincingly established in the case of the allylnickel(II)-catalyzed butadiene polymerization for both *trans*-1,4- and *cis*-1,4-regulating catalysts.<sup>7e,20</sup> Therefore, the C-C bond formation very likely proceeds via *cis*-butadiene insertion into the butenylnickel(II) bond.

The two-channel reaction model of the allylnickel(II)-catalyzed polymerization of butadiene proposed by Taube et al.<sup>8</sup> is outlined in Scheme 3. Starting from the butenyl-bis(ligand)nickel(II) complex I, which is the precatalyst and exists predominantly in the thermodynamically more stable syn form, two structurally different ( $\eta^3$ -butenyl)-butadiene  $\pi$ -complexes are formed by successive ligand or anion substitution via equilibria  $K_1$ ,  $K_2$  and  $K'_1$ ,  $K'_2$  for the syn and anti butenyl forms, respectively. For all the substitution equilibria involving butadiene, it is reasonable to suppose that they are rapid and do not undergo any significant kinetic barrier (in accordance with the common experience in  $\text{Ni}^{\text{II}}$  coordination chemistry, with  $\text{Ni}^{\text{II}}$  in a spin-paired  $d^8$  configuration).<sup>21</sup> Both the butenyl(mono-



**FIGURE 6.** Square pyramidal supine  $\eta^4$ -*cis*-butadiene model complexes  $[\text{Ni}(\eta^3\text{-C}_4\text{H}_7)(\text{C}_4\text{H}_6)\text{L}]^+$  ( $\text{L} = \text{P}(\text{OMe})_3$ ) and  $[\text{Ni}(\eta^3, \eta^2\text{-C}_7\text{H}_{11})(\text{C}_4\text{H}_6)]^+$  of the real catalysts **II** and **III** (most stable isomers), respectively (for **II**,  $\text{L} = \text{PH}_3$  is adopted to simplify the drawing).

ligand)(butadiene)nickel(II)  $\pi$ -complex **II** and the “ligand-free” polybutadienyl(butadiene)nickel(II)  $\pi$ -complex **III** represent the active catalyst complexes for polymerization proceeding along the two alternative reaction channels  $k_1$  and  $k_2$ , respectively. For each of the different channels there are two competing pathways for chain propagation by *cis*-butadiene insertion into the syn and anti butenyl–nickel bond. These give rise to *trans*-1,4 and *cis*-1,4 units in the growing polybutadienyl chain, via  $k_{1t}/k_{2t}$  and  $k_{1c}/k_{2c}$ , respectively. For all the complexes an anti–syn equilibrium must be supposed (for **I** exemplified in Scheme 3), whose rate and position were proven to be strongly dependent on structure.

#### IV. Theoretical Examination of Crucial Elementary Steps of the Entire Polymerization Process—Mechanistic Consequences

**Models.** The entire catalytic cycle for polymerization is theoretically explored by employing a gradient-corrected density functional (DFT) method for suitable and computationally practicable models of the catalyst complexes **II** and **III**.<sup>12b,c,22</sup> The inevitable simplifications inherent in a computational model for reasons of computational convenience are critical to the model’s reliability and to the mechanistic conclusions drawn. These include the reductions in the theoretical method applied and the truncation of the real catalyst system. In the present study, the cationic  $[\text{Ni}(\eta^3\text{-C}_4\text{H}_7)(\text{C}_4\text{H}_6)\text{P}(\text{OMe})_3]^+$  complex and the cationic  $[\text{Ni}(\eta^3, \eta^2\text{-C}_7\text{H}_{11})(\text{C}_4\text{H}_6)]^+$  complex (cf. Figure 6) are adopted for **II** and **III**, respectively, which are closely related to the real catalyst complexes proposed for the experimentally well-characterized *trans*-1,4-regulating  $[\text{Ni}(\eta^3\text{-C}_3\text{H}_5)(\text{P}(\text{OPh})_3)_2]\text{PF}_6$ <sup>7e</sup> and *cis*-1,4-regulating ( $\text{C}_{12}$ -allyl)-nickel(II)  $[\text{Ni}(\text{C}_{12}\text{H}_{19})]\text{X}$ <sup>7f</sup> precatalysts. The effect of the solvent or the counterion upon the catalytic cycle, however, was neglected. The mechanistic conclusions drawn in the present study, therefore, are valid for polymerization occurring in noncoordinating solvents with weakly coordinating counterions involved. Experiment verified that neither the catalytic activity nor the *cis*–*trans* selectivity is significantly influenced by the solvent and/or the counterion for these reaction conditions.<sup>23</sup>

**Method.** Currently, the DFT method has become the method of choice for studying of reaction mechanism with transition metals involved. For all atoms a standard all-electron basis set of triple- $\zeta$  quality for the valence

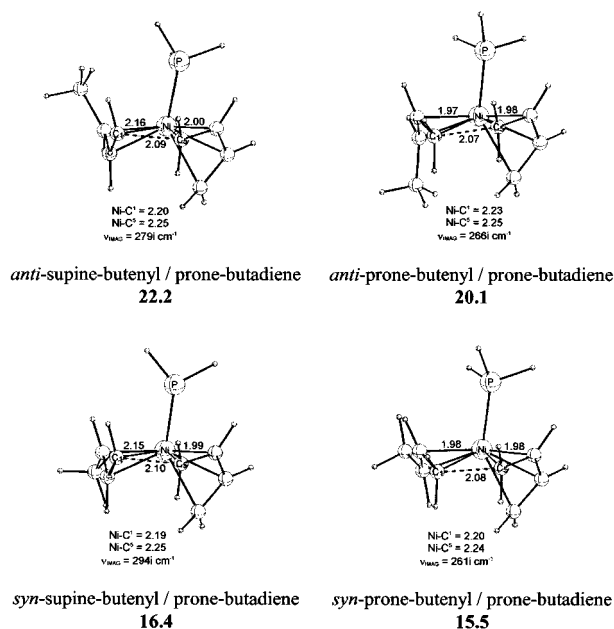
electrons augmented with polarization functions was used in the calculations.<sup>22</sup> The local exchange–correlation potential by Vosko et al.<sup>24a</sup> was augmented with gradient-corrected functionals for electron exchange according to Becke<sup>24b</sup> and correlation according to Perdew<sup>24c</sup> in a self-consistent fashion. This gradient-corrected density functional is usually termed BP86 in the literature. In recent benchmark computational studies, it was shown that the BP86 functional gives results in excellent agreement with the best wave-function-based method available today for the class of reactions investigated here.<sup>25</sup> Activation barriers for monomer insertion and monomer uptake energies are reproduced with an accuracy of  $\sim 2$  kcal/mol when compared with sophisticated wave-function-based methods. Due to the similar structure of key species for competing insertion and isomerization steps of the polymerization cycle investigated in this study, a higher accuracy could be expected for the relative barriers calculated.

**A. Thermodynamic Stability of the Butadiene  $\pi$ -Complexes.** Butadiene  $\pi$ -complexes are formed via the substitution equilibria  $K_1$  and  $K_2$  (cf. section F). At the end of each successful chain propagation step, they are regenerated in an exothermic process by expulsion of the coordinated last double bond of the growing polybutadienyl chain with free monomer. Four- and five-coordinate  $\pi$ -complexes are formed as possible starting complexes for subsequent monomer insertion, with butadiene either monodentate or bidentate coordinated, respectively.

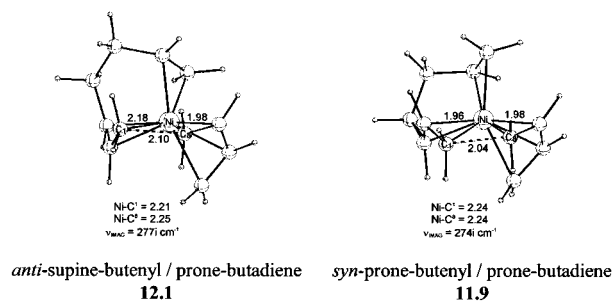
Bidentate butadiene coordination is found to be energetically preferred relative to monodentate coordination. The thermodynamic stability of  $\eta^4$ -butadiene complexes is essentially determined by the butadiene orientation, with bidentate supine coordination giving the most stable  $\pi$ -complexes. The  $\eta^4$ -butadiene  $\pi$ -complexes represent the active catalyst complexes, since they are confirmed to be the direct precursors of the transition states for C–C bond formation.

The thermodynamic stability of anti and syn butenyl forms differs for the butenyl(monoligand)(butadiene) complex **II** and the polybutadienyl(butadiene) complex **III**. For **II**, the syn butenyl forms are found to be thermodynamically more stable than the anti forms. This order of anti–syn stability, however, is turned around for **III** due to the coordinated chelating polybutadienyl chain. For **III**, the anti forms become thermodynamically preferred relative to the syn forms.

**B. Reactivity of the Butadiene  $\pi$ -Complexes—Kinetic Barrier for C–C Bond Formation.** The C–C bond formation always proceeds via *cis*-butadiene insertion into the ( $\eta^3$ -butenyl)nickel(II) bond with regeneration of an anti  $\eta^3$ -butenyl group as the reactive end of the growing polybutadienyl chain. The alternative insertion of *trans*-butadiene, however, is found to be kinetically disabled due to a distinctly higher activation barrier.<sup>12b</sup> The butadiene insertion from the *s-cis* form, therefore, is convincingly established for the allylnickel(II)-catalyzed butadiene polymerization by both experimental<sup>7e,20</sup> and theoretical<sup>12</sup> evidence.



**FIGURE 7.** Selected geometric parameters of the optimized structures (Å) of transition states for *cis*-butadiene insertion into the *anti*- and *syn*-( $\eta^3$ -butenyl)nickel(II) bond in the butenyl(monoligand)(butadiene)nickel(II) complex **II**, together with free activation energies ( $\Delta G^\ddagger$  in kcal/mol) relative to the most stable isomer of the  $\eta^4$ -butadiene  $\pi$ -complex (L = PH<sub>3</sub> is adopted to simplify the drawing).



**FIGURE 8.** Selected geometric parameters of the optimized structures (Å) of transition states for *cis*-butadiene insertion into the *anti*- and *syn*-( $\eta^3$ -butenyl)nickel(II) bond in the polybutadienyl-(butadiene)nickel(II) complex **III**, together with free activation energies ( $\Delta G^\ddagger$  in kcal/mol) relative to the most stable isomer of the  $\eta^4$ -butadiene  $\pi$ -complex.

For *cis*-butadiene insertion to occur along the most feasible pathway, a quasi planar four-membered transition-state structure is passed through, composed of the butenyl group's terminal carbon, one of butadiene's olefinic subunits (double bond), and the nickel atom. The  $\pi$ -coordination of the butenyl group and of butadiene is essentially preserved in the transition states (cf. Figures 7 and 8), thus indicating that C–C bond formation is energetically feasible within the  $\pi$ -coordination of the reacting moieties. This confirms the  $\pi$ -allyl insertion mechanism as the energetically favored mechanistic alternative for the monomer insertion step in the case of the allylnickel(II)-catalyzed polymerization.

The reactivity of the butadiene  $\pi$ -complexes is found to be essentially determined by butadiene's orientation. The quasi planar four-membered transition-state structure

can best be realized by butadiene in a prone orientation (cf. Figures 7 and 8). This gives rise to a distinctly higher reactivity of prone butadiene forms relative to supine butadiene forms, with a difference in the free activation energy for insertion ( $\Delta\Delta G_{\text{INS}}^\ddagger$ ) of  $\sim 15$  kcal/mol in favor of the prone forms.<sup>12b,c</sup> Thus, the thermodynamically more stable supine butadiene  $\pi$ -complexes are less reactive than the prone butadiene counterparts. It was concluded from stereochemical consideration that insertion very likely proceeds from butadiene in a prone orientation.<sup>26</sup> This is conclusively supported by our research.

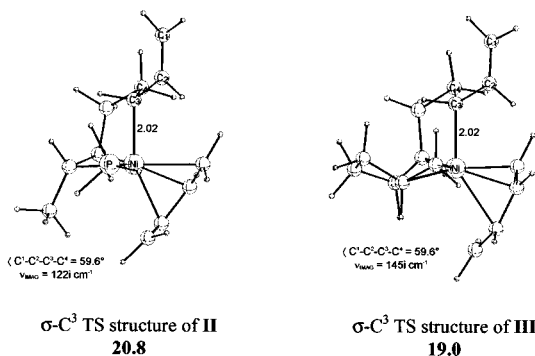
A nearly identical reactivity of both *anti* and *syn* butenyl  $\sigma$ -forms can naturally be supposed. In contrast, the  $\pi$ -butenyl forms could differ in their reactivity. For the butenyl(monoligand)(butadiene) complex **II**, the thermodynamically more stable *syn* butenyl form must be regarded as distinctly more reactive than the *anti* form, since  $\Delta\Delta G_{\text{INS}}^\ddagger$  amounts to  $\sim 5$  kcal/mol in favor of the *syn* form (cf. Figure 7). Therefore, for polymerization to occur along the  $k_{1t}$  channel, the *trans*-1,4 production cycle via  $k_{1t}$  is likely passed through, with the competing *cis*-1,4 cycle via  $k_{1c}$  being disabled by a higher kinetic barrier. Whereas a prone butadiene orientation is crucial in the transition states, the orientation of the  $\pi$ -butenyl group is found to have a minor effect on the activation barrier. Very similar insertion barriers result for the  $k_{1t}$  pathway from either a supine or a prone butenyl orientation.

Nearly identical activation barriers must be overcome for the polybutadienyl(butadiene) complex **III** along the competing  $k_{2t}$  and  $k_{2c}$  pathways (cf. Figure 8), indicating a very similar reactivity of *anti* and *syn* butenyl forms. This is due to the coordinated chelating polybutadienyl chain, which additionally restricts the *anti* butenyl group to a supine orientation and the *syn* butenyl group to a prone orientation.

The free activation barrier for insertion ( $\Delta G_{\text{INS}}^\ddagger$ ) that must be overcome for **II** and **III** commencing from the most stable supine butadiene  $\pi$ -complexes is lower by  $\sim 4$  kcal/mol for the latter, which therefore indicates a distinctly higher intrinsic reactivity of the polybutadienyl-(butadiene) complex **III** when compared with the butenyl(monoligand)(butadiene) complex **II**.<sup>27</sup>

**C. Anti–Syn Isomerization—Kinetic Barrier for Butenyl Group's Conversion.** In accord with experimental indication,<sup>17</sup> *anti*–*syn* isomerization is found to take place most likely via  $\eta^3$ - $\pi$ -  $\rightarrow$   $\eta^1$ - $\sigma$ -C<sup>3</sup>-butenyl group conversion, followed by internal rotation of the vinyl group around the C<sup>2</sup>–C<sup>3</sup> single bond (cf. Figure 2).<sup>28</sup> A trigonal bipyramidal transition state is passed through during isomerization, with the  $\sigma$ -C<sup>3</sup>-butenyl group occupying an axial position (cf. Figure 9).

Two aspects are found to be important in order to stabilize the rotational transition-state structure, making the isomerization energetically practicable. First, butadiene must participate in this process, and second, the coordination number of nickel must always be kept at five. Thus, for the single vacant site arising during the  $\pi \rightarrow \sigma$  butenyl conversion, an occupation by the next double bond of the polybutadienyl chain is reasonable.



**FIGURE 9.** Selected geometric parameters of the optimized structures (Å) of transition states for anti-syn isomerization in the butenyl(butadiene)nickel(II) complexes **II** and **III**, respectively, together with free activation energies ( $\Delta G^\ddagger$  in kcal/mol) relative to the most stable anti isomer of the  $\eta^4$ -butadiene  $\pi$ -complexes (for **II**,  $L = \text{PH}_3$  is adopted to simplify the drawing).

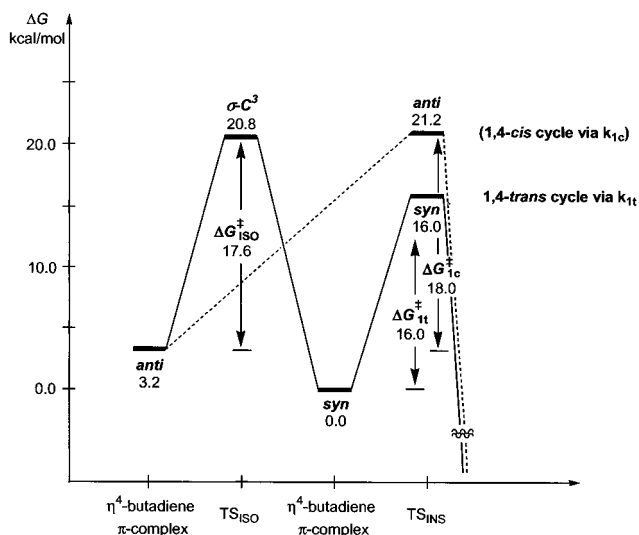
The interconversion of the butenylnickel(II) forms, therefore, most probably happens when commencing from anti butenyl butadiene  $\pi$ -complexes, which are formed from the kinetic anti insertion product with subsequent coordination of free monomer. The conversion proceeds through a  $\sigma$ - $\text{C}^3$  transition-state structure that is stabilized by the coordinated next double bond of the polybutadiene chain and yields the syn butenyl isomers.

**D. Interrelation of Butadiene Insertion and Anti-Syn Isomerization—Consequences for the Mechanism of Cis-Trans Regulation.** An anti butenyl group is always formed as the kinetic insertion product of the monomer insertion step. For that reason, anti-syn isomerization is a necessary step in the catalytic cycle in order to generate trans-1,4 polymer units. From a kinetic point of view, the cis-trans selectivity is therefore determined by the reactivity of anti and syn butenyl forms in relation to the isomerization rate and the position of the associated equilibrium.

The subtle energetic balance between isomerization and insertion is found to be strongly dependent on the structure of the catalyst complex. The condensed Gibbs free energy profile, consisting of competitive pathways for the generation of trans-1,4 and cis-1,4 polymer units and of anti-syn isomerization, is presented for the  $k_1$  and  $k_2$  channels in Schemes 4 and 5, respectively.

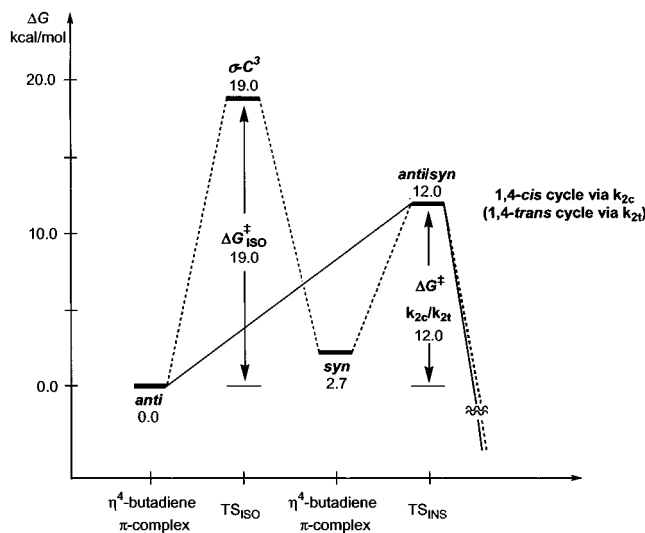
For the  $k_1$  channel, the isomerization barrier is higher relative to the insertion barrier that must be overcome along the trans-1,4-generating cycle  $k_{1t}$ ; however, it is lower than the insertion barrier associated with the cis-1,4-generating cycle  $k_{1c}$  (cf. Scheme 4). It is therefore reasonable to suppose the isomerization is rapid enough that C-C bond formation can occur along the  $k_{1t}$  pathway. As a consequence, in the presence of free butadiene, the less reactive anti butenyl form should be enriched in the reaction solution, while the thermodynamically more stable syn butenyl form practically does not exist in a detectable amount due to its higher reactivity, in accord with experimental observation.<sup>7e</sup> The cis-1,4-generating cycle  $k_{1c}$ , however, is suppressed nearly completely by

**Scheme 4.** Condensed Gibbs Free Energy Profile for the Trans-1,4 (—) and the Cis-1,4 (---) Production Cycle of the  $k_1$  Channel with the Cationic Butenyl(monoligand)(butadiene)nickel(II) Complex **II**  $[\text{RC}_3\text{H}_4\text{Ni}(\text{C}_4\text{H}_6)\text{L}]^+$  as the Catalyst<sup>a</sup>



<sup>a</sup>  $L = \text{P}(\text{OMe})_3$ . Free energies  $\Delta G$ ,  $\Delta G^\ddagger$  in kcal/mol. See ref 12b for the energetic profile of the entire catalytic cycle.

**Scheme 5.** Condensed Gibbs Free-Energy Profile for the Trans-1,4 (—) and the Cis-1,4 (---) Production Cycle of the  $k_2$  Channel with the Cationic Polybutadienyl(butadiene)nickel(II) Complex **III**  $[\text{RC}_3\text{H}_4\text{Ni}(\text{C}_4\text{H}_6)]^+$  as the Catalyst<sup>a</sup>



<sup>a</sup> Free energies  $\Delta G$ ,  $\Delta G^\ddagger$  in kcal/mol. See ref 12c for the energetic profile of the entire catalytic cycle.

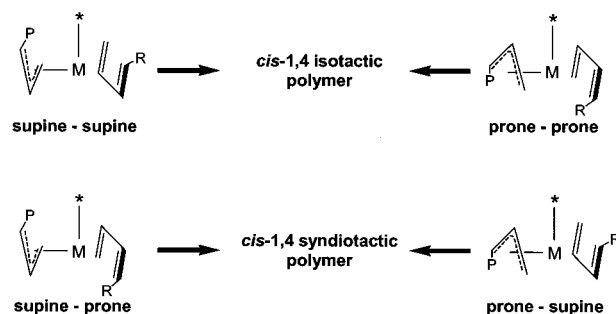
kinetic considerations, due to a distinct lesser reactivity of the anti butenyl complex relative to that of the syn butenyl complex. The anti-syn isomerization appears as the rate-determining step of the entire  $k_1$  catalytic cycle, in agreement with experiment.<sup>7e</sup> For polymerization to occur along the  $k_1$  channel, which will be opened via formation of the butenyl(monoligand)(butadiene) complex **II**, the formation of a polybutadiene of predominantly trans-1,4 structure is catalyzed (via  $k_{1t}$ ), in accord with experimental observation.<sup>7e</sup> The decisive factors for the high trans-1,4 selectivity are the higher reactivity of the syn butenyl form together with a sufficiently facile anti-

syn isomerization, regardless of the fact that isomerization is rate-determining.

For the  $k_2$  channel the situation is different. The activation barrier for isomerization is significantly higher than that for *cis*-butadiene insertion, with a nearly identical insertion barrier that must be overcome through the competitive *trans*-1,4 (via  $k_{2t}$ ) and *cis*-1,4 (via  $k_{2c}$ ) branches (cf. Scheme 5). Therefore, one can conclude that the isomerization rate should be distinctly slower compared with the rate of insertion. The anti–syn isomerization must be regarded as the discriminating factor between the *cis*-1,4 and *trans*-1,4 generation cycles, since the anti butenyl  $\pi$ -complex is formed exclusively (on account of *cis*-butadiene insertion), and the syn butenyl  $\pi$ -complex is negligibly populated. The  $k_{2t}$  pathway, therefore, is suppressed by a slow anti–syn isomerization. The *cis*-butadiene insertion into the *anti*-( $\eta^3$ -butenyl)nickel(II) bond is the rate-determining step of the entire  $k_2$  channel. The *cis*–*trans* selectivity is determined by the formation of anti butenyl complexes (due to the preferred *cis*-butadiene insertion), their high reactivity, and the much slower isomerization. In agreement with experiment,<sup>7f</sup> the polybutadienyl(butadiene) complex **III** nearly exclusively catalyzes the formation of a *cis*-1,4 polybutadiene along the  $k_{2c}$  cycle, although with an almost identical reactivity of anti and syn butenyl forms.

**E. Reactivity of Butadiene  $\pi$ -Complexes Dependent on the Orientation of the Reactive Parts—Consequences for the Formation of Tactic 1,4 Polymers of Substituted Butadienes.** The 1,4 polymerization of a butadiene with an unsymmetrically substituted methylene group (which leads to a chiral center) gives rise to a tactic 1,4 polymer. If the chiral centers possess the same configuration, then an isotactic polymer is formed, while for a syndiotactic polymer the chiral centers possess alternating configurations. For allylnickel(II) catalysts, the configurational regularity within the methylene groups of the polymers was investigated for the *cis,cis*-1,4-dideuterio-1,3-butadiene monomer.<sup>29,30</sup> *Cis* catalysts give a highly stereoregular *cis*-1,4 syndiotactic polymer, and *trans* catalysts give a *trans*-1,4 polybutadiene that lacks any stereoregularity within the deuterated methylene groups.<sup>29</sup> It was suggested<sup>2b</sup> that the formation of tactic 1,4 polymers is determined by the chirality of the active center. Thus, the mutual orientation of the butenyl and butadiene part should be the critical factor, which is exemplified in Figure 10 for production of *cis*-1,4 iso- and syndiotactic polymers that arise from a terminally, unsymmetrically substituted butadiene.

As discussed in detail in section B, C–C bond formation take place via a quasi planar four-membered transition state, thus restricting the *cis*-butadiene always to a prone orientation. Therefore, the orientation of the butenyl group must be regarded as the crucial factor that determines the stereoregularity within the deuterated methylene groups. The reactivity of prone *cis*-butadiene complexes of **II** and **III**, respectively, depending on the butenyl group's enantioface involved, provides the key to elucidating the stereoregulation. The missing stereoregularity in



**FIGURE 10.** Formation of *cis*-1,4 iso- and syndiotactic polymer units via insertion of a terminally, unsymmetrically substituted butadiene into the *anti*-( $\pi$ -butenyl)metal bond.

the case of the *trans*-1,4 deuterated polybutadiene formed along the  $k_1$  channel is due to the nearly identical reactivity of the prone and supine syn butenyl isomers of **II**. On the other hand, the chelating polybutadienyl chain restricts the anti butenyl group to a supine orientation in **III** (cf. section B), which explains the production of *cis*-1,4 syndiotactic deuterated polybutadiene along the  $k_2$  channel.

**F. Thermodynamic Control of the *Cis*–*Trans* Regulation.** The production of a *trans*-1,4 polybutadiene is catalyzed by the butenyl(monoligand) complex **II** along the  $k_1$  channel, while for the production of a *cis*-1,4 polybutadiene, the  $k_2$  channel must be accessible by formation of the polybutadienyl(butadiene) complex **III**. The catalyst complexes **II** and **III**, however, are formed via the pre-established substitution equilibria  $K_1$  and  $K_2$  (cf. Scheme 3). Therefore, in addition to the kinetic control (given by the preferred  $k_{1t}$  and  $k_{2c}$  pathways, respectively) discussed so far, the activity as well as the *cis*–*trans* selectivity are also regulated thermodynamically by the concentration of **II** and **III**. The catalyst's activity is thermodynamically determined by the concentration of **II** and **III**, given by  $K_1$  and  $K_2$ , respectively. Depending on the electronic and steric properties of the ligand L or the anion X, butadiene and/or the polybutadienyl chain are able to compete with them for coordination to the nickel center, which leads to either **II** or **III** as the active catalyst. This controls thermodynamically the generation of a stereoregular polybutadiene of either *trans*-1,4 or *cis*-1,4 structure, respectively.

Starting from the butenyl(bisligand) precatalyst **I** with sterically less demanding phosphite ligands, the  $K_1$  equilibrium is found to lie essentially in the direction of **I**, which confirms experiment.<sup>7e</sup> In contrast to very similar intrinsic activation barriers for insertion and isomerization that can reasonably be assumed for alkylphosphite ( $P(OR)_3$ ) and arylphosphite ( $P(OAr)_3$ ) butenyl(monoligand) complexes **II**, experiment determined arylphosphites to be moderately active catalysts, while alkylphosphites are almost catalytically inactive.<sup>19c</sup> Thus, the concentration of the active catalyst **II**, which is negligible for alkylphosphites and somewhat higher for arylphosphites due to their lower basicity, must be regarded as being decisive for the catalytic activity.

## V. Conclusion

We have presented, for the first time, a consistent and theoretically well-founded comprehensive mechanistic view of the allylnickel(II)-catalyzed 1,4 polymerization of butadiene including both kinetic and thermodynamic aspects, that has been derived from a computational exploration of crucial elementary steps of the entire polymer-generating cycles by means of an accurate quantum-chemical method for experimentally well-characterized trans-1,4- and cis-1,4-regulating allylnickel(II) catalysts. The reaction model by Taube et al.<sup>8</sup> has been verified in all important details. The computational modeling at the atomic level, however, provided insights that would have otherwise been inaccessible, resulting in a substantial contribution in elucidating the mechanism of cis–trans regulation of the allylnickel(II)-catalyzed 1,4 polymerization of butadiene. The most important results can be summarized as follows:

(1) We have verified that chain propagation takes place by *cis*-butadiene insertion into the  $\pi$ -butenylnickel(II) bond ( $\pi$ -allyl insertion mechanism) via a quasi-planar four-membered transition state. The insertion most likely occurs from a prone orientation of *cis*-butadiene.

(2) We have shown that the two isomeric butenylnickel(II) forms of the active catalyst complex, the anti and syn forms, can differ in their reactivity. Which one of the two forms is more reactive depends on the catalyst's structure.

(3) We have confirmed that the interconversion of the anti and syn forms most likely proceeds via an  $\eta^1$ - $\sigma$ -C<sup>3</sup> transition state. To make the insertion and isomerization energetically feasible, the coordination number of nickel must always be kept at five. This can be achieved, e.g., by coordination of either a new monomer or the polybutadienyl chain on nickel.

(4) We have demonstrated that the possible different reactivity of *anti*- and *syn*-butenylnickel(II) forms of the active catalyst complex in relation to their interconversion and together with the associated anti–syn equilibrium provides the definite key for understanding the cis–trans regulation.

(5) We have deduced the catalytic structure–activity relationships, which are decisive for the production of a stereoregular trans-1,4 and cis-1,4 polybutadiene.

For a deeper understanding of the polymerization process, however, the exploration of the catalytic structure–activity relationship needs further refinement along the following lines. First, the effect of the coordinating counterion and of the solvent should be taken into account in order to clarify their influence on the cis–trans selectivity as well as on the catalytic activity. Second, the role of the ligand's steric and electronic properties for the kinetic and thermodynamic control of the polymerization process needs further clarification.

*The author is deeply indebted to Prof. Dr. Rudolf Taube for valuable and stimulating discussions and for his ongoing interest in this research. Excellent service by the computer centers ZIB Berlin and URZ Halle is gratefully acknowledged.*

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