Articles

Mechanistic Studies of the 1,4-Polymerization of Butadiene According to the π-Allyl-Insertion Mechanism. 3. Density Functional Study of the C−C Bond Formation Reaction in Cationic “Ligand-Free” (η^3:η^2-Heptadienyl)(η^2-/η^4-butadiene)nickel(II) Complexes $[Ni(C_7H_{11})(C_4H_6)]^+$

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According to the π-allyl-insertion mechanism the entire catalytic cycle of 1,4-polymerization of butadiene has been theoretically studied by employing a gradient-corrected density functional method with the polybutadienylnickel(II) cation $[Ni(\eta^3:\eta^2:\eta^2\text{-}RC_{12}H_{18}]^+$ as the precatalyst. We have investigated competitive chain propagation cycles for generation of a cis-1,4- and trans-1,4-polymer, and also anti−syn isomerization. The calculations provide a clear insight into the stereoregulation mechanism of cis-1,4-polymerization. Chain propagation proceeds via educt-like trigonal-bipyramidal transition states with an almost identical free activation energy of 12.0 kcal/mol for both the cis-1,4- and the trans-1,4-pathway. The free activation barrier for anti−syn isomerization is 19.0 kcal/mol, which takes place via π → σ conversion of the butenyl group followed by rotation of the vinyl group around the C^2−C^3 single bond through a trigonal-bipyramidal transition state. Accordingly, the trans-1,4-generating cycle is suppressed by a slow anti−syn isomerization. The cis−trans selectivity is determined by the formation of an *anti*-butenyl structure in the catalyst complexes which together with a slow isomerization yields nearly exclusively a cis-1,4-polymer, although of an almost identical reactivity of *anti*- and *syn*-butenyl forms. The calculations confirmed the formation of a stereoregular, highly selective cis-1,4-polymer quite in accord with experimental observations.

Introduction

The transition-metal-catalyzed polymerization of conjugated dienes is of considerable interest from both the scientific and the industrial point of view.[1,2] From a mechanistic point of view, the diene polymerization, as a chemo-, regio-, and stereoselective C−C bond formation reaction, is of fundamental importance. The polymerization of 1,3-dienes and of monoalkenes is an insertion polymerization.[3] Chain propagation proceeds by coordination of free monomer and insertion into the metal−carbon bond. The important difference is that the metal−carbon bond is of σ-type for monoalkenes and of the allylic π-type for 1,3-dienes, which can exist in two isomeric forms, anti and syn. Furthermore, there is a much greater variety of structurally different stereoregular polydienes than of polyolefins. The mechanism of stereoregulation of 1,3-diene polymerization, which has not yet been completely understood to date, therefore, is much more complicated than that of monoalkene polymerization.

To elucidate the mechanism of cis−trans regulation, two different processes must be interrelated. Those are the diene insertion and the interconversion of the two isomeric forms of the metal−butenyl bond, the anti−

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(1) (a) *Applied Homogeneous Catalysis with Organometallic Complexes*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996. (b) Porri, L.; Giarrusso, A. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, B., Eds.; Pergamon: Oxford, U.K., 1989; Vol. 4, Part II, pp 53−108.

(2) La Flair, R. T.; Wolf, U. U. In *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; Verlag Chemie: Weinheim, Germany, 1993; Vol. A23, pp 273−282.

(3) Pino, P.; Giannini, U.; Porri, L. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1987; Vol. 8, pp 147−220.

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syn isomerization. For the insertion reaction two commonly accepted mechanisms were proposed. They differ in the suggested butenyl group's mode being capable of achieving the insertion. The butenyl group may react either from the η^1-σ-coordination, as first suggested by Cossee and Arlman,[4] or from the η^3-π-coordination, as introduced by Taube et al.[5] This has consequences for the reactivity of *anti*- and *syn*-butenyl forms. A nearly identical reactivity of the σ-butenyl forms can naturally be supposed, whereas the π-butenyl forms may differ in their reactivity. Furthermore, the insertion of either the *s-cis*- or the *s-trans*-butadiene isomer, the position of the anti−syn equilibrium, and the relative rates for insertion and isomerization are important factors in understanding the mechanism of stereoregulation.

In a series of papers we have applied a gradient-corrected density functional method to shed light on the mechanistic aspects of the stereospecific polymerization of butadiene. We have focused on the π-allyl-insertion mechanism, which has been explored on experimentally well characterized catalysts for the nickel-catalyzed stereospecific butadiene polymerization, as an example. At the beginning we have shown that the butadiene insertion into the butenylnickel(II) bond is energetically feasible within the π-coordination of the reacting parts.[6a] By examining theoretically the entire polymerization cycle for typical trans-regulating nickel catalysts, we were able to deduce the structure−activity relationships which are responsible for opening the trans-1,4-polymer generation cycle.[6b]

In the present study we will explore the entire catalytic reaction course for typical cis-regulating nickel catalysts. By examining competitive reaction pathways, we aim to make a contribution to elucidate the mechanistic details of the stereospecific cis-1,4-polymerization of butadiene. Although the essential mechanistic details of the process are well-established, to our knowledge no theoretical investigation has been performed yet.

Taube et al.[7] have shown that the cationic (C_{12}-allyl)nickel(II) complex $[Ni(C_{12}H_{19})]X$ (with the bulky, probably extremely weakly coordinating tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[8]as the counteranion) is a highly active precatalyst for the *cis*-1,4-butadiene polymerization. The cationic polybutadienyl(butadiene)nickel(II) complex $[RC_3H_4Ni(C_4H_6)]^+$ must be regarded as the real catalyst for the *cis*-1,4-butadiene polymerization. The formation of butadiene π-complexes was supported by the preparation of (η^3-1,3-dimethallyl)(η^4-*cis*-hexa-2(*E*),4(*E*)-diene)nickel(II) tetrafluoroborate, $[(CH_3)_2C_3H_3Ni(CH_3C_4H_4CH_3)]BF_4$, from $[(CH_3)_2C_3H_3NiBr]_2$, hexadiene, and $AgBF_4$ in CD_2Cl_2 at −70 °C.[9]

The proposed catalytic reaction mechanism for the *cis*-1,4-polymerization of butadiene (according to k_{2c}) is depicted in Scheme 1, with the cationic polybutadienylnickel(II) $[Ni(\eta^3{:}\eta^2{:}\eta^2\text{-}RC_{12}H_{18})]^+$ complex as the precatalyst. The mechanism is based on the anti-cis and syn-trans correlation;[1b] i.e., the butadiene insertion gives rise to a cisoid (k_{2c}) or transoid (k_{2t}) double bond in the growing polymer chain which is extended by a newly formed C_4 unit when starting from an *anti*- or *syn*-butenyl group, respectively.

The chain propagation is envisioned as follows: Commencing with the cationic $[Ni(C_{12}H_{19})]^+$ precatalyst **1** stable polybutadienyl complexes **2** (always with an *anti*-butenyl group, due to the preferred anti insertion) are rapidly formed by butadiene insertion during a very short initialization period. They represent stable store complexes within the polymerization cycle. Subsequently, with butadiene two kinds of polybutadienyl(butadiene) complexes are formed. They differ in the mode of butadiene coordination, i.e., η^2 (monodentate) **3**, or η^4 (bidentate) **4**, where the η^4-butadiene π-complexes should represent the actual catalyst complexes. The formation of butadiene π-complexes is verified by the dependence of the overall polymerization rate on nickel and butadiene concentrations according to the rate law[10] $r_p = k_p[Ni][C_4H_6]$. *cis*-Butadiene insertion takes place through transition states **5**, which leads in every case to the insertion products **2a** (anti insertion); in turn, the polymer chain is elongated by a new C_4 unit containing one new cisoid or transoid double bond, depending on whether the insertion proceeds via k_{2c} or k_{2t}, respectively. Simultaneously, an η^3-coordinated butenyl group in the anti configuration is regenerated as the chain end from the former butadiene moiety, thus allowing the polymerization to proceed. 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 Ni^{II} coordination chemistry, with Ni^{II} in a spin-paired d^8 configuration).[12] With regard to the anti−syn isomerization, two different cases must be distinguished. The isomerization occurs in the starting material **1** (indicated by $K_{a/s}{}^{s}$) and also under polymerization conditions in the presence of butadiene via **6** (indicated by $K_{a/s}{}^{p}$).

We model the real catalyst, the polybutadienyl(butadiene)nickel(II) complex $[RC_3H_4Ni(C_4H_6)]^+$, by the cationic $[Ni(C_7H_{11})(C_4H_6)]^+$ complex. This choice was motivated by the experimental observation on the $[Ni(\eta^3{:}\eta^2{:}\eta^2\text{-}C_{12}H_{19})]B(C_6H_3(CF_3)_2)_4$ complex[7] and also by theoretical results[6] of (i) the coordinative participation of the first double bond of the polybutadienyl chain in order to stabilize the transition states for butadiene

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(4) (a) Cossee, P. In *Stereochemistry of Macromolecules*; Ketley, A. D., Ed.; Marcel Dekker: New York, 1967; Vol. 1, p 145. (b) Arlman, E. J. *J. Catal.* **1966**, *5*, 178.

(5) (a) Taube, R.; Gehrke, J.-P.; Radeglia, R. *J. Organomet. Chem.* **1985**, *291*, 101. (b) Taube, R.; Gehrke, J.-P.; Böhme, P. *Wiss. Z. Tech. Hochsch. Leuna-Merseburg* **1987**, *39*, 310. (c) Sieler, J.; Kempe, R.; Wache, S.; Taube, R. *J. Organomet. Chem.* **1993**, *455*, 241. (d) Taube, R.; Wache, S.; Sieler, J.; Kempe, R. *J. Organomet. Chem.* **1993**, *456*, 131. (e) Taube, R.; Schmidt, U.; Gehrke, J.-P.; Böhme, P.; Langlotz, J.; Wache, S. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 245. (f) Taube, R.; Windisch, H.; Maiwald, S. *Makromol. Chem., Macromol. Symp.* **1995**, *89*, 393. (g) Taube, R.; Sylvester, G. In *Applied Homogeneous Catalysis with Organometallic Complexes*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996; pp 280−317.

(6) (a) Tobisch, S.; Bögel, H.; Taube, R. *Organometallics* **1996**, *15*, 3563. (b) Tobisch, S.; Bögel, H.; Taube, R. *Organometallics* **1998**, *17*, 1177.

(7) (a) Taube, R.; Wache, S. *J. Organomet. Chem.* **1992**, *428*, 431. (b) Wache, S.; Taube, R. *J. Organomet. Chem.* **1993**, *456*, 137.

(8) Kobayashi, H.; Sonoda, T.; Iwamoto, H.; Yoshimura, M. *Chem. Lett.* **1981**, 579.

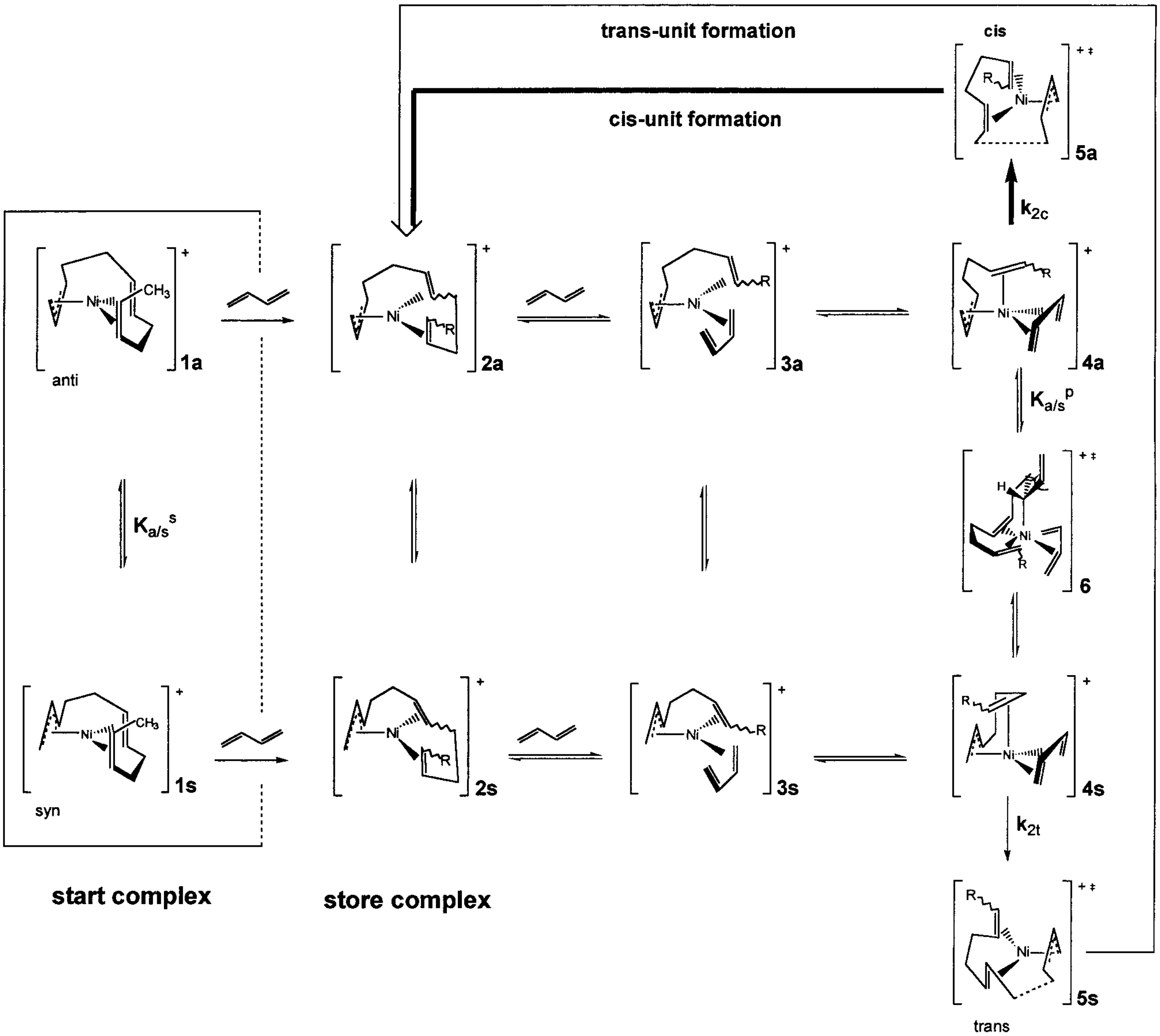
(9) Wache, S. Ph.D. Thesis, Reihe Chemie, Verlag Shaker, Aachen, Germany, 1993.

(10) Taube, R.; Langlotz, J. *Makromol. Chem.* **1993**, *194*, 705.

(11) (a) *Mechanisms in Inorganic Chemistry*; Basolo, F., Pearson, R. G., Eds.; Thieme Verlag: Stuttgart, Germany, 1973. (b) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. I, pp 281−384. (c) Cross, R. J. *Chem. Soc. Rev.* **1985**, *14*, 197. (d) Cross, R. J. *Adv. Inorg. Chem.* **1989**, *34*, 219.

(12) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

Scheme 1. Catalytic Cycle of the 1,4-Polymerization of Butadiene with the Cationic Polybutadienylnickel(II) Complex $[Ni(\eta^3:\eta^2:\eta^2\text{-}RC_{12}H_{18})]^+$ as the Precatalyst in a Noncoordinating Solvent or without Solvent in Liquid Butadiene[a]



[a] The influence of the counteranion is neglected.

insertion (in compliance with Tolman's 18−16-electron rule)[12] and (ii) the evidence of the existence of a contact ion pair with an anion which can be regarded as essentially noncoordinated, which thus allows us in a first attempt to leave the influence of the counteranion out of consideration. The investigations we present are focused on the polymerization cycle; i.e., the initialization step of forming stable polybutadienyl complexes **2** from the starting material **1** will not be considered. We restrict our examination solely to the *cis*-butadiene insertion, thus not taking the alternative insertion of butadiene from its s-trans configuration into consideration. This can be justified in the case of nickel by both experimental[5a,13] and theoretical evidence,[6b] which convincingly establishes the anti insertion. The course of anti−syn isomerization will be explored concerning $K_{a/s}{}^{p}$. However, any alternative competing mechanism, for instance the σ-allyl-insertion mechanism, will not be examined. The effect of the solvent upon the catalytic cycle was neglected since the polymerization reaction occurs in aromatic hydrocarbons such as toluene, benzene, and chlorohydrocarbons, which all can be regarded as noncoordinating under polymerization conditions. Experiments provided evidence for this assumption, since the catalytic activity and also the cis−trans selectivity is nearly unchanged upon variation of the solvent, as long as noncoordinating solvents such as toluene, benzene, chlorobenzene, dichloroethane, and dichloromethylene are used.[10,14a] The effect of the counteranion is briefly examined with regard to the starting complex **1**.

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(13) (a) Lehmkuhl, H.; Keil, T.; Benn, R.; Rufinska, A.; Krüger, C.; Poplawska, J.; Bellenbaum, M. *Chem. Ber.* **1988**, *121*, 1931. (b) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 6777.

(14) (a) Taube, R.; Wache, S.; Sieler, J. *J. Organomet. Chem.* **1993**, *459*, 335. (b) Taube, R.; Langlotz, J.; Sieler, J.; Gelbrich, Th.; Tittes, K. *J. Organomet. Chem.*, submitted for publication.

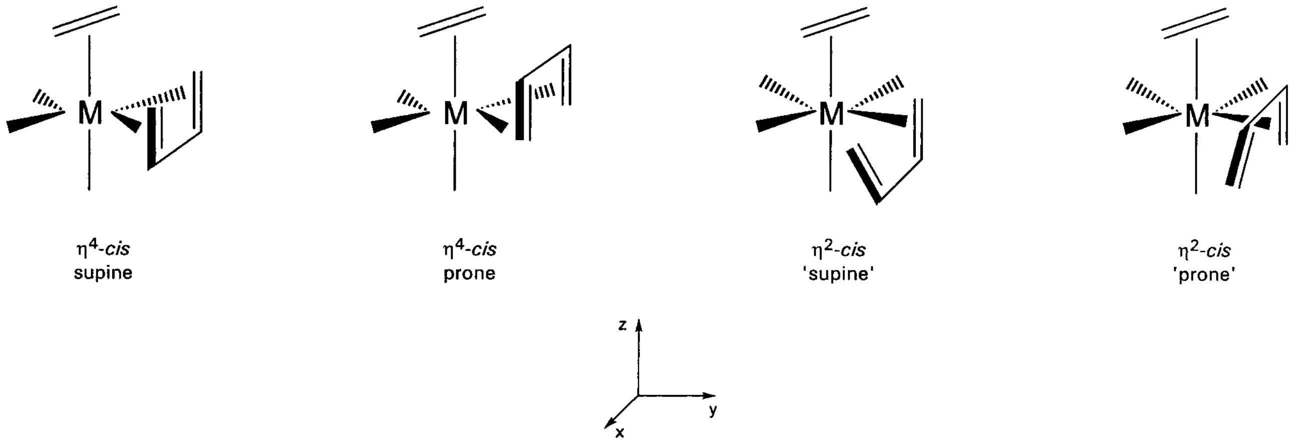

Figure 1. Structurally different modes of *cis*-butadiene coordination at the metal M in the butadiene π-complexes.

Computational Details

The approximate density functional (DFT) calculations reported here were performed by using the DGauss program within the UniChem software environment[15] and the program package TURBOMOLE,[17] developed by Ahlrichs et al. at the University of Karlsruhe.

All calculations were carried out using the LDA with Slater's exchange functional[17a,b] and Vosko–Wilk–Nusair parametrization on the homogeneous electron gas for correlation,[17c] augmented by gradient corrections to the exchange-correlation potential. Gradient corrections for exchange based on the functional of Becke[17d] and for correlation based on that of Perdew[17e] were added variationally within the SCF procedure (LDA/BP-NLSCF).

All-electron Gaussian orbital basis sets were used for all atoms. The geometry optimization and the saddle-point search were done by using a standard DZVP basis which consists of a 15s/9p/5d set contracted to (63321/531/41) for nickel,[18a] a 9s/5p/1d set contracted to (621/41/1) for carbon,[18b] and a 5s set contracted to (41) for hydrogen.[18b] The energy was evaluated for the optimized structures using the Wachters 14s/9p/5d set[18c] supplemented by two diffuse p[18c] and one diffuse d function[18d] contracted to (62111111/5111111/3111) for nickel and a TZVP basis for carbon[18b] (a 10s/6p/1d set contracted to (7111/411/1)) and for hydrogen[18b] (a 5s/1p set contracted to (311/1)). The corresponding auxiliary basis sets were used for fitting the charge density.[18b] This is the standard computational methodology used throughout this paper.

The geometry optimization and the saddle-point search were carried out at the LDA/BP-NLSCF level of approximation by utilizing analytical gradients/Hessians according to standard algorithms. No symmetry constraints were imposed in any case. The stationary points were identified exactly by the curvature of the potential-energy surface at these points corresponding to the eigenvalues of the analytically calculated Hessian. The zero-point energy corrections (ZPC) and Gibbs free energy calculations (at 298 K and 1 atm) were performed for reactants, intermediates, transition states, and products which describe the full catalytic cycle for the cationic polybutadienyl(butadiene)nickel(II) complexes we investigate. Geometries of all relevant structures are given in the Supporting Information.

The intrinsic energy of inserting *s-cis*-butadiene into a C–C bond, thus forming a cis-1,4 polymer chain (the energy gain from breaking one C–C double bond and forming a C–C single bond during the insertion), without a catalytically active Ni^{II} center was estimated as the average value of the exothermicities which were obtained for the general reaction $C_4H_7–(C_4H_6)_n–C_4H_7 + C_4H_6 \rightarrow C_4H_7–(C_4H_6)_{n+1}–C_4H_7$ ($n = 0–2$). It amounts to 20.3 and 16.8 kcal/mol (without and with ZPC, respectively), which is in good agreement with the experimental value of 18.7 kcal/mol (determined if the polymerization proceeds in the gas phase[19]).

For **2**–**5** a number of isomers are possible for each compound, which were carefully explored. They originate from the anti and syn configurations of the butenyl group, which will be labeled as **a** and **s**, respectively, throughout this paper. Additionally, four different mutual arrangements of the reacting butenyl and butadiene moieties are taken into account, which originate from the prone and the opposite supine[20] orientations of both parts (thus giving rise to supine/supine (SS), supine/prone (SP), prone/supine (PS), and prone/prone (PP), where in XY, X and Y are related to butenyl and butadiene, respectively). In the case of the quasi-planar 16-electron complexes **2** and **3**, however, the SS and PP and the SP and PS orientations are identical with regard to the coordination pattern.

To distinguish the different isomers in a consistent manner, the following arrangement is made throughout the paper. The first double bond from the growing polymer chain is assumed to occupy the axial position in the $+z$ direction above the tetragonal coordination plane in the 18-electron complexes **4**. The orientations of the butenyl and butadiene moieties with the terminal atoms pointing toward or away from the axial double bond are denoted as supine and prone, respectively. This is schematically outlined in Figure 1 for the mono- and bidentate coordination of *cis*-butadiene.

Regarding the orientation of the coordinated polybutadienyl chain, two cases can be distinguished; for **4**, the coordinated double bond points in front (labeled with an additional **f**) and in back (labeled with an additional **b**) (cf. Figure 2). In the quasi-planar complexes **2** and **3** the coordinated double bond (from the penultimate and ultimate C_4 units in **2** and **3**, respectively) is aligned upward in the first case (**f**) and downward in the second case (**b**), relative to the quasi-planar coordination plane.

In the 16-electron complexes **2** the orientation of the two coordinated double bonds from the growing chain are denoted

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(15) (a) Andzelm, J.; Wimmer, E. *Physica B* **1991**, *172*, 307. (b) Andzelm, J. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer: Berlin, 1991. DGauss and UniChem are software packages available from Molecular Simulations Inc.

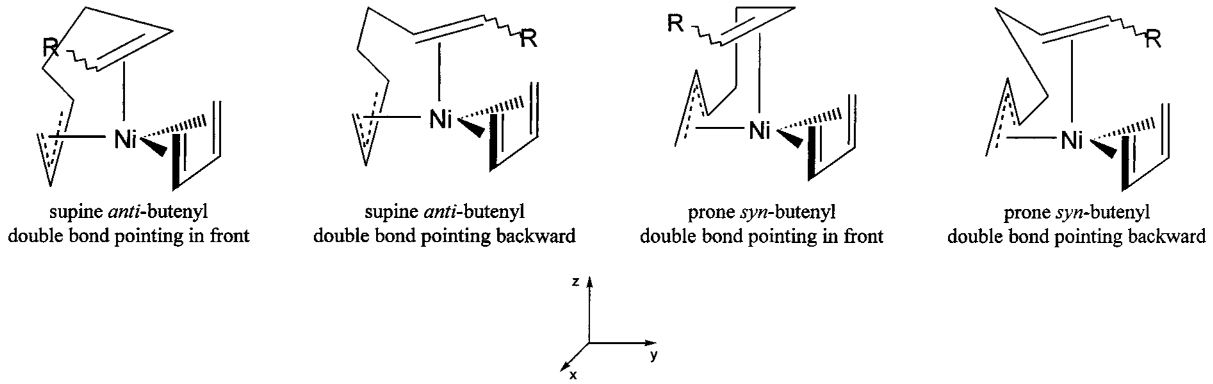
(16) (a) Häser, M.; Ahlrichs, R. *J. Comput. Chem.* **1989**, *10*, 104. (b) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(17) (a) Dirac, P. A. M. *Proc. Cambridge Philos. Soc.* **1930**, *26*, 376. (b) Slater, J. C. *Phys. Rev.* **1951**, *81*, 385. (c) Vosko, S. H.; Wilk, L.; Nussiar, M. *Can. J. Phys.* **1980**, *58*, 1200. (d) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (e) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822.

(18) (a) DGauss basis set library. (b) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560. (c) Wachters, A. H. J. *J. Chem. Phys.* **1970**, *52*, 1033. (d) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

(19) Robert, D. E. *J. Res. Natl. Bur. Stand.* **1950**, *44*, 221.

(20) Yasuda, H.; Nakamura, A. *Angew. Chem.* **1987**, *99*, 745.



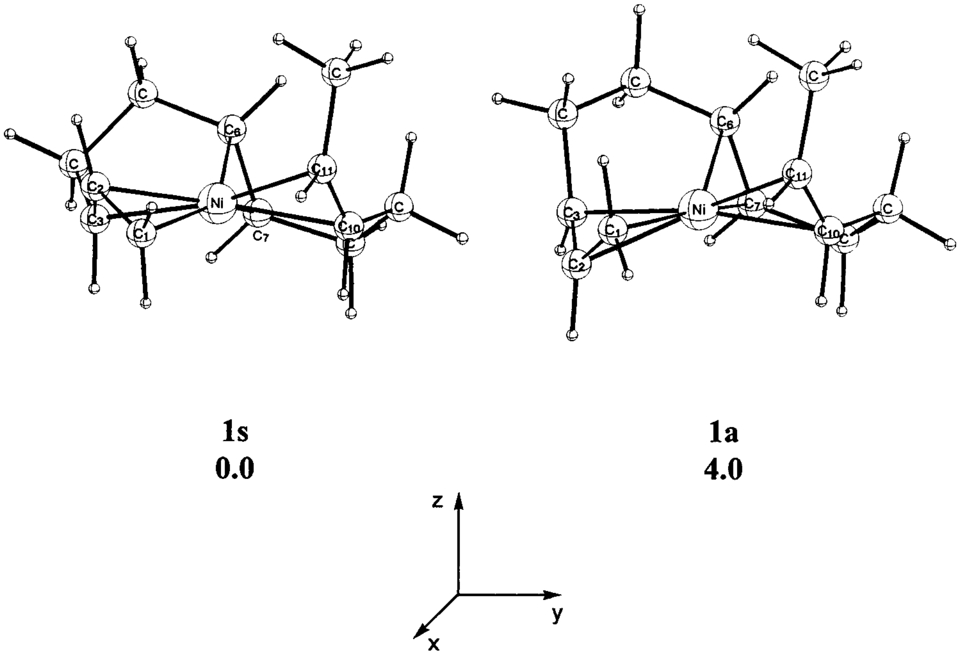
supine *anti*-butenyl double bond pointing in front

supine *anti*-butenyl double bond pointing backward

prone *syn*-butenyl double bond pointing in front

prone *syn*-butenyl double bond pointing backward

Figure 2. Different alignments of the coordinated polybutadienyl chain in bidentate *cis*-butadiene π-complexes.



1s
0.0

1a
4.0

Figure 3. Optimized structures of the $[Ni(C_{12}H_{19})]^+$ cation **1s** and **1a**, together with relative energies (ΔE in kcal/mol). Selected geometric parameters are given in Table 1.

according to the labeling of the corresponding transition states **5**. To distinguish between insertion products which stem from passing through the cis-1,4- or the trans-1,4-cycle an additional **c** and **t** are added, which are related to the cisoid and transoid configurations of the polymer chain's first double bond (from the ultimate C_4 unit).

Results and Discussion

A. Geometric Structure of the Precatalyst. Cationic (C_{12}-allyl)nickel(II) complexes of the type $[Ni(\eta^3:\eta^2:\eta^2\text{-}C_{12}H_{19})]X$ with weakly or essentially noncoordinating anions X^- such as PF_6^-,[21] SbF_6^-,[10,21] $B(C_6H_3(CF_3)_2)_4^-$,[7a] and other anions[22] can be prepared from the (C_{12}-bis(allyl))nickel(II) complex $[Ni(\eta^3:\eta^3\text{-}C_{12}H_{18})]$[23] by partial protolysis with the respective Brønsted acid HX. X-ray data were available for $X^- = PF_6^-$ (**I**),[5d] BF_4^- (**II**),[14b] $FB(C_6F_5)_3^-$ (**III**),[14a] and $CF_3SO_3^-$ (**IV**).[14b] The precatalyst is characterized by a quasi planar coordination of the Ni^{II} center with a π-*syn*-butenyl group and two olefinic C_4 units. The first and second double bonds from the polybutadienyl chain are in trans and cis configurations, respectively, which gives a (η^3:η^2:η^2-dodeca-2(*E*),6(*E*),10(*Z*)-trien-1-yl)nickel(II).

As shown in Figure 3, **1s** is calculated to be a true minimum with a quasi planar structure, in great agreement with the X-ray data. Selected structural parameters resulting from the geometry optimizations are collected in Table 1 and compared to the experimental values. The calculated geometries for the $[NiC_{12}H_{19}]^+$ cation and also for **I** and **II** match the X-ray crystal structures of **I** and **II** with satisfactory agreement, except for the shorter Ni–F distances, which arise due to the neglect of packing effects. The dodecatrienyl chain coordination with Ni^{II} is not substantially affected by the anion, although the cation–anion interaction should increase in the order **I** < **II** $\sim$ **III** < **IV**, along with decreasing metal–anion distance (cf. X-ray data in Table 1).

Experiment determined that the syn form was thermodynamically more stable than the anti form.[21] This is confirmed by our calculations. **1s** (cf. Figure 3) is calculated to be 4.0 kcal/mol (ΔE) below **1a** for the cation and 5.4 and 6.0 kcal/mol (ΔE) for **I** and **II**, respectively.

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[21] Taube, R.; Böhme, P.; Gehrke, J.-P. *J. Organomet. Chem.* **1990**, *399*, 327.

[22] Taube, R.; Gehrke, J.-P.; Böhme, P.; Scherzer, K. *J. Organomet. Chem.* **1991**, *410*, 403.

[23] Bogdanovic, B.; Heimbach, P.; Kröner, M.; Wilke, G.; Hoffmann, E. G.; Brandt, J. *Justus Liebigs Ann. Chem.* **1969**, *727*, 143.

Table 1. Optimized and X-ray Structural Parameters[a] of [Ni(η^3:η^2:η^2-$C_{12}H_{19}$)]X Complexes 1s

	DFT/DFT[b] cation	DFT/X-ray			
		$X^- = PF_6^-$ [5d] (**I**)	$X^- = BF_4^-$ [14b] (**II**)	$X^- = FB(C_6F_5)_3^-$ [14a] (**III**)	$X^- = CF_3SO_3^-$ [14b] (**IV**)
Ni−C^1	2.075/2.063	2.125/2.067	2.144/2.079	−/2.095	−/2.131
Ni−C^2	2.054/2.056	2.051/2.016	2.049/2.021	−/2.028	−/2.021
Ni−C^3	2.053/2.085	2.044/2.018	2.037/2.031	−/2.028	−/2.011
Ni−C^6	2.121/2.102	2.103/2.109	2.105/2.111	−/2.110	−/2.121
Ni−C^7	2.135/2.175	2.109/2.126	2.097/2.119	−/2.139	−/2.111
Ni−C^{10}	2.122/2.121	2.167/2.133	2.179/2.145	−/2.134	−/2.211
Ni−C^{11}	2.255/2.250	2.239/2.211	2.259/2.227	−/2.206	−/2.251
C^1−C^2	1.411/1.414	1.405/1.387	1.404/1.367	−/1.387	−/1.382
C^2−C^3	1.420/1.415	1.425/1.406	1.427/1.395	−/1.406	−/1.412
C^6−C^7	1.392/1.391	1.395/1.365	1.397/1.343	−/1.365	−/1.392
C^{10}−C^{11}	1.388/1.387	1.384/1.361	1.382/1.334	−/1.361	−/1.382
Ni−X[c]	−/−	2.357/2.914	2.245/2.679	−/2.678	−/2.274

[a] Bond distances are in Å. For atom labeling see Figure 3. [b] Anti counterpart **1a**. [c] Metal−anion distance; i.e., Ni−F distance for **I**−**III** and Ni−O distance for **IV**.

Applying Maxwell−Boltzmann statistics (298 K) yields a ratio of about 1:860 for both cationic forms, with **1s** being favored. The calculations may indicate an increasing anti−syn gap under the influence of weakly coordinating anions. ^{13}C NMR measurements,[7b] however, revealed no significant cation−anion interaction for the very active precatalysts **I** and **III** and also with $X^- = SbF_6^-$, $B(C_6H_3)(CF_3)_2)_4^-$. All of them highly selectively yield a cis-1,4-polymer product.[5e,7a,10,21] On the basis of this observation, together with the restricted reliability of gas-phase calculations to properly take this type of interaction into account, we do not take the influence of the counteranion into consideration in further computations. On the other hand, however, experiments have shown a strongly decreasing catalytic activity and cis selectivity already for the BF_4^- anion,[22] which is much more pronounced for oxygen-containing ligands such as $CF_3SO_3^-$ and $B(O_2C_6H_4)_2^-$.[22] This can be attributed to an increasing tendency of anion coordination.

NMR investigation suggested identical configurations and conformations of the dodecatrienyl chain both in the crystal lattice and in solution.[7b] Therefore, the quasi planar η^3:η^2:η^2-coordination of the butenyl group and the polybutadienyl chain's first and second double bond can in a straightforward manner be proposed for the polybutadienyl complexes **2**.

B. Chain Propagation. 1. Stable Store Complexes. Commencing from the precatalyst **1s**, polybutadienyl complexes **2a** are generated after a short initialization period by insertion of a few diene units. They are formed at the end of each propagation cycle if the diene insertion into the Ni−butenyl bond takes place successfully. The bonding situations around the Ni^{II} in **1** and **2** are identical with a η^3:η^2:η^2-coordination of the π-butenyl group and of the first two double bonds from the polybutadienyl chain, which arise from the ultimate and penultimate inserted C_4 unit. Therefore, we focus exclusively on the energetics, which are decisive in the thermodynamic control of the overall polymerization cycle.

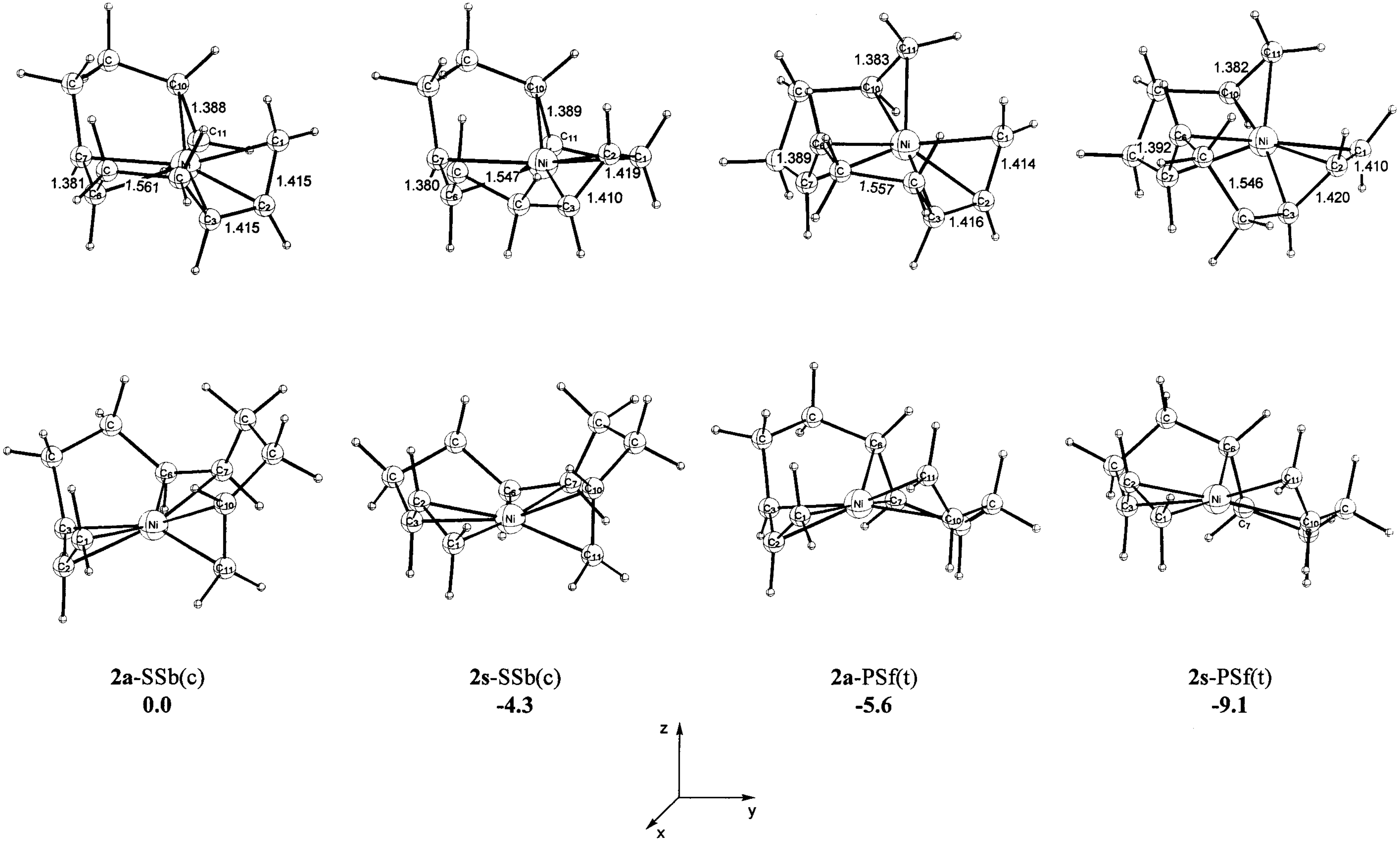
We will start with the examination of relative stabilities of the kinetic insertion products **2a** of the cis-1,4- (via k_{2c}) and the trans-1,4-cycle (via k_{2t}). These are always *anti*-butenyl species either with an all-cis or with an all-trans configuration of the polybutadienyl chain's double bonds. Several conformations for each of the isomers of **2a** were optimized; the most stable all-cis/all-trans species are displayed in Figure 4, together with the syn counterparts, **2s**. Two different views are shown in Figure 4, to make it easier to interrelate the uniform notation of different isomers of the complexes used throughout this paper. The energetics of different conformations of possible isomers of **2** are summarized in Table 2. The discussion, however, is restricted to the most stable species (cf. Figure 4).

2a-SSb(c) is the most stable kinetic insertion product of the cis-1,4-cycle. It lies 5.6 kcal/mol (ΔE) above **2a**-PSf(t), which is the most stable kinetic insertion product that is formed during the trans-1,4-cycle.

The *syn*-butenyl complexes, **2s**, are in all cases thermodynamically more stable than the corresponding anti counterparts, **2a** (cf. Table 2). **2s**-SSb(c) and **2s**-PSf(t), therefore, represent the most stable polybutadienyl complexes, i.e., the thermodynamic insertion products, when the cis-1,4- and trans-1,4-generating cycles, respectively, are passed through. For the most stable all-cis (**2a**/**2s**-SSb(c)) and all-trans (**2a**/**2s**-PSf(t)) isomers the anti−syn gap amounts to about 4 kcal/mol (ΔE). Using Maxwell−Boltzmann statistics (298 K) for this energy difference yields a ratio of approximately 1:860 between anti and syn isomers. It is worth noting that **2s**-PSf(t) exactly resembles the geometric structure of the precatalyst **1s**, except for the last methyl group.

The most stable all-trans species are about 5 kcal/mol (ΔE) below the most stable all-cis species, irrespective of whether kinetic insertion products (**2a**-PSf(t) and **2a**-SSb(c)) or thermodynamic insertion products (**2s**-PSf(t) and **2s**-SSb(c)) are concerned. Therefore, the polymerization cycle via k_{2t} likely would be passed through in the the limit of thermodynamic control. That would give rise to a predominantly trans-1,4-polymer, in sharp contrast to experiment, which verifies that the cationic (C_{12}-allyl)nickel(II) complex serves as a highly active precatalyst for the cis-1,4-polymerization.[5e,7a,10,21] We conclude that the generation of cis or trans polymer units must be essentially determined by kinetic considerations.

2. Formation of Butadiene π-Complexes. Formation of butadiene π-complexes commencing from **2** is envisioned to proceed in a practically barrierless fashion by expulsion of the last coordinated double bond from the polybutadienyl chain by the diene in an exothermic process. Four- and five-coordinate π-complexes, which are capable of performing the insertion step, are formed, which depends on the diene's coordination mode. In the first case, butadiene is coordinated in a monodentate



2a-SSb(c) **0.0**

2s-SSb(c) **-4.3**

2a-PSf(t) **-5.6**

2s-PSf(t) **-9.1**

Figure 4. Most stable *anti*- and *syn*-butenyl store complexes with all-cis and all-trans double bonds within the polybutadienyl chain together with relative energies (ΔE in kcal/mol), with the most stable all-cis kinetic insertion product (**2a**-SSb(c)) chosen as energetic reference (for abbrevations see text). Two different views are shown: (top) the former butenyl group in the $-y$ and the former butadiene in the $+y$ direction; (bottom) the same species with the regenerated butenyl group in the $-y$ direction, similar to Figure 3.

Table 2. Calculated Potential Energy (with and without ZPC) and Gibbs Free Energy Profile for the *cis*-Butadiene Insertion into the Cationic $[Ni(C_7H_{11})(C_4H_6)]^+$ Complexes (kcal/mol)[a]

2a^b	**2s**^{b}	**3**	**4**	**5**
		Cis-1,4-Cycle		
SSf(c)^c −4.6 (−2.6) *−3.3*	SSf(c)^c −8.7 (−6.9) *−8.0*	*anti*-SSf^c 11.5 (10.6) *8.6*	*anti*-SSf^c **0.0 (0.0)** ***0.0***	*anti*-SSf^c **26.0 (26.1)** ***25.9***
SSb(c)^d **−8.8 (−7.0)** ***−7.1***	SSb(c)^d **−13.1 (−11.4)** ***−11.2***	*anti*-SSb^d **9.1 (8.1)** ***6.0***	*anti*-SSb^d 0.8 (1.3) *1.5*	*anti*-SSb^d 27.3 (27.4) *27.2*
SPf(c)^c −2.1 (−0.7) *−0.7*	SPf(c)^c −9.3 (−7.5) *−7.8*	*anti*-SPf^c 12.7 (11.9) *10.3*	*anti*-SPf^c **4.2 (4.0)** ***3.6***	*anti*-SPf^c 14.2 (14.6) *15.3*
SPb(c)^d **−3.1 (−1.8)** ***−1.6***	SPb(c)^d **−12.3 (−10.7)** ***−10.7***	*anti*-SPb^d **8.7 (7.9)** ***6.2***	*anti*-SPb^d 5.3 (5.5) *5.4*	*anti*-SPb^d **10.8 (11.5)** ***12.1***
		Trans-1,4-Cycle		
PSf(t)^c **−14.4 (−12.6)** ***−12.3***	PSf(t)^c **−17.9 (−16.5)** ***−16.2***	*syn*-PSf^c **2.7 (2.2)** ***0.9***	*syn*-PSf^c **2.6 (2.7)** ***2.7***	*syn*-PSf^c **25.4 (25.2)** ***26.0***
PSb(t)^d −13.1 (−12.1) *−11.3*	PSb(t)^d −17.7 (−16.2) *−15.9*	*syn*-PSb^d 3.8 (3.3) *2.2*	*syn*-PSb^d	*syn*-PSb^d 29.4 (27.9) *28.0*
PPf(t)^c −8.7 (−7.2) *−7.1*	PPf(t)^c −13.4 (−12.0) *−12.1*	*syn*-PPf^c 7.6 (6.7) *5.5*	*syn*-PPf^c **4.1 (4.1)** ***4.0***	*syn*-PPf^c **10.8 (11.2)** ***11.9***
PPb(t)^d **−9.0 (−7.2)** ***−7.1***	PPb(t)^d **−14.0 (−12.6)** ***−12.7***	*syn*-PPb^d **4.5 (3.7)** ***2.3***	*syn*-PPb^d	*syn*-PPb^d 15.2 (15.4) *15.8*
SSf(t)^c −9.0 (−7.2) *−7.0*	SSf(t)^c −14.0 (−12.6) *−12.7*	*syn*-SSf^c 4.5 (3.7) *2.3*	*syn*-SSf^c	*syn*-SSf^c **39.8 (39.1)** ***38.8***
SSb(t)^d −8.7 (−7.2) *−7.1*	SSb(t)^d −13.4 (−12.0) *−12.1*	*syn*-SSb^d 7.6 (6.7) *5.5*	*syn*-SSb^d	*syn*-SSb^d
SPf(t)^c −13.1 (−12.1) *−11.3*	SPf(t)^c −17.7 (−16.2) *−15.9*	*syn*-SPf^c 3.8 (3.3) *2.2*	*syn*-SPf^c	*syn*-SPf^c **16.9 (16.9)** ***17.0***
SPb(t)^d −14.4 (−12.6) *−12.3*	SPb(t)^d −17.9 (−16.5) *−16.2*	*syn*-SPb^d 2.7 (2.2) *0.9*	*syn*-SPb^d	*syn*-SPb^d

[a] **4a**-SSf was chosen as reference; numbers in parentheses include the zero-point correction, while those in italics are the Gibbs free energies. For the labeling that essentially concerns **3**−**5**, see the text. For the different isomers the most stable of f and b forms are marked in boldface type. Please note the anti-cis and syn-trans correlation; i.e., anti/syn butenyl in **3**−**5** corresponds to **2a**-cis/trans for the kinetic insertion products and after anti-syn isomerization to **2s**-cis/trans for the syn counterparts. [b] Cis and trans configurations of the first double bond are denoted by c and t, respectively. [c] The first (**3**−**5**)/second (**2**) double bond within the polybutadienyl chain is pointing in front (axial position in **4**,**5**) or upward (relative to the *xy* plane in **2**,**3**), respectively. [d] The first (**3**−**5**)/second (**2**) double bond within the polybutadienyl chain is pointing backward (axial position in **4**,**5**) or downward (relative to *xy* plane in **2**,**3**), respectively.

(or η^2) fashion, which yields the 16-electron complexes **3** with a quadratic planar configuration.[6] Additionally, the diene can act as a bidentate ligand (η^4-mode), which gives the 18-electron tetragonal-pyramidal complexes **4** (cf. Figure 5).[6]

Figure 5 shows the geometries of the optimized isomers of **4** together with relevant structural data. They exhibit geometric characteristics very similar to those found for the related cationic $[Ni(C_4H_7)(C_4H_6)(C_2H_4)]^+$ complex, which has been previously discussed in detail.[6b]

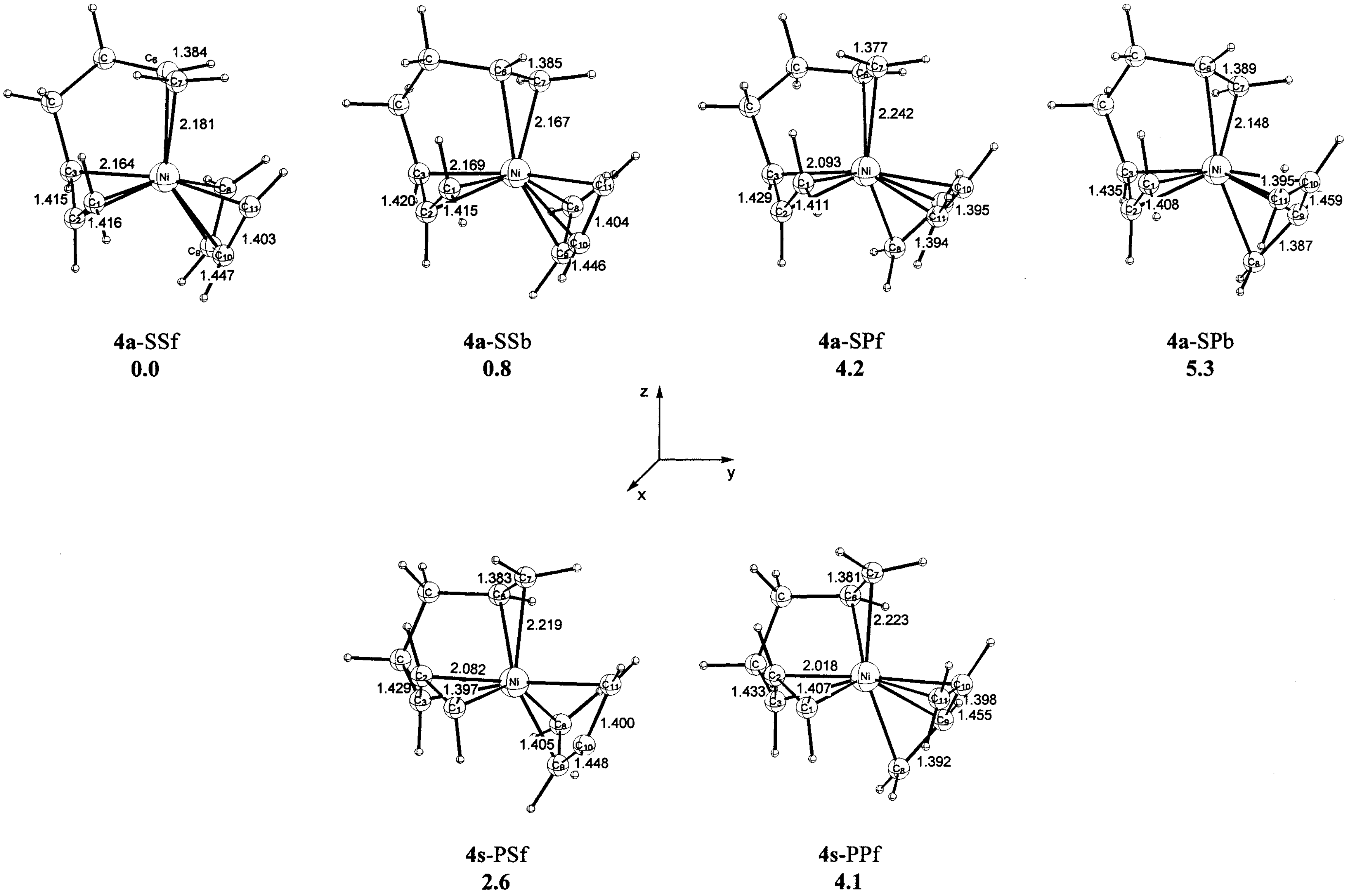
For several isomers we could find no stable minima for bidentate π-complexes, neither for the supine *syn*-butenyl isomers with the polybutadienyl chain coordinated in front or back nor for the prone *syn*-butenyl isomers with a backward-pointing chain. Geometry optimization starting from the tentative bidentate butadiene complexes inevitably leads to the corresponding monodentate butadiene complexes **3**. This can be rationalized in terms of restricted adaptability of the polybutadienyl chain to make an axial coordination possible, since its coordination was found to be a prerequisite to form stable η^4-butadiene complexes.[6] The chain orientation prevents axial double bond coordination in all the isomers, where no stable minima for a bidentate butadiene coordination could be determined.

Bidentate supine butadiene coordination is found to give the most stable π-complexes; the most stable anti isomer, **4a**-SSf, lies 2.6 kcal/mol (ΔE) below the most stable syn species, **4s**-PSf (cf. Table 2). The most stable prone butadiene isomers are calculated to be higher in energy than the supine counterparts by 4.2 kcal/mol (ΔE) for anti (**4a**-SPf, **4a**-SSf) and less pronounced by 1.5 kcal/mol (ΔE) for syn (**4s**-PPf, **4s**-PSf). Concerning **4a**, the different orientations of the coordinated double bond affect the stability to a minor extent by about 1 kcal/mol (ΔE), with the alignment in front being favored.

A large energetic gap between monodentate and bidentate butadiene coordination is calculated, if the axial coordination of the polybutadienyl chain is not hindered by the chain orientation. This can best be discerned for anti isomers. For the most stable anti complexes, **4a**-SSf is well separated from **3a**-SPb by 8.7 kcal/mol (ΔE), which is reduced to 7.9 kcal/mol (with ZPC) and to 6.2 kcal/mol using the Gibbs free energy. In the opposite case, which is found for the most stable syn complexes, **3s**-PSf and **4s**-PSf are almost identical in potential energy. The η^2-complex becomes energetically favored by 0.5 and 1.8 kcal/mol with inclusion of ZPC and in Gibbs free energy, respectively.

Though the thermodynamic driving forces to form both kinds of butadiene complexes are very similar during the generation of trans-1,4-polymer units, only the η^4-butadiene species are of primary concern, since they represent the direct precursors of the transition states for insertion according to the minimum energy path (see next section). The η^2-butadiene complexes, however, can be regarded as possible starting, but transient π-complexes during the process of forming the η^4-butadiene complexes.

Comparison with Cationic $[Ni(C_4H_7)(C_4H_6)(C_2H_4)]^+$ Complexes.[6b] For both model complexes the bidentate butadiene coordination is energetically preferred, in general, to the monodentate mode. The most stable isomers of **4** are characterized by a supine butadiene coordination. The distinguishing feature of



4a-SSf
0.0

4a-SSb
0.8

4a-SPf
4.2

4a-SPb
5.3

4s-PSf
2.6

4s-PPf
4.1

Figure 5. Selected geometric parameters of the optimized structures (Å) of bidentate *cis*-butadiene π-complexes together with relative energies (ΔE in kcal/mol), with the most stable **4a**-SSf isomer chosen as energetic reference (for abbrevations see text).

both models is the reverse order of anti−syn stability of **4**. For $[Ni(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)(C_2H_4)]^+$ the syn forms are always thermodynamically more stable than the anti counterparts by about 4 kcal/mol (ΔE). This is different from the results obtained for $[Ni(\eta^3{:}\eta^2\text{-}C_7H_{11})(\eta^4\text{-}C_4H_6)]^+$, where the most stable anti isomer is 2.6 kcal/mol (ΔE) below the most stable syn isomer. The stability of related anti and syn forms of **4**, i.e., with identical butadiene orientations, is largely influenced by the ability of the ligand or the polybutadienyl chain to occupy the axial site. Therefore, upon going from an additional monodentate-coordinated monomer (modeled by $[Ni(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)(C_2H_4)]^+$) to a coordinated chelating polybutadienyl chain, the order of anti−syn stability, due to a lesser stability of the syn forms, is turned around, with the anti form becoming thermodynamically more stable than the syn counterparts. If this order of anti−syn stability is preserved in the insertion transition states, than the *cis*-1,4-selectivity naturally can be elucidated by the higher reactivity of the anti complexes, relative to the syn complexes.

3. Insertion. After forming stable butadiene π-complexes the subsequent insertion proceeds through two different transition state configurations: tetragonal-pyramidal supine butadiene and trigonal-bipyramidal prone butadiene (cf. Figure 6). The optimized structure of the butadiene moiety displays a nearly completely preformed π-butenyl group for supine butadiene isomers, which is indicated by C−C distances of about 141−142 pm for the C^8−C^9 and C^9−C^{10} bonds, and an essentially retained butadiene moiety, at least the C^8−C^9 and C^9−C^{10} bonds, for prone butadiene forms. Thus, the **5-**SS and **5-**PS isomers are quite late and appear product-like, whereas the **5-**SP and **5-**PP isomers are quite early and can be characterized as educt-like.

The transition states, which occur at C^1(butenyl)−C^{11}(butadiene) distances of the newly formed σ-C−C bond of about 200−230 pm, are characterized by a nearly complete change in hybridization of the affected carbons from sp^2 to sp^3. In **5** the polybutadienyl chain occupies a position halfway between the axial (as in **4**) and the in-plane position (as in **2**). Therefore, the stability of related isomers of **5a** and **5s** should be less influenced by the polybutadienyl chain than in the case of **4**. This is underlined by the fact that we could find PSb, PPb, SSf, and SPf **5s** isomers, in addition to PSf and PPf, which already were determined for **4s** (cf. Figure 6). For the supine *syn*-polybutadienyl chain with a backward-pointing first double bond, which therefore is unable to occupy any other than an in-plane site, no structures that describe the *cis*-butadiene insertion into the Ni−butenyl bond could be determined.

The energetics of the insertion process are included in Figure 6 and summarized in Table 2. Starting from the most stable supine butadiene isomers of **4**, the insertion is strongly disabled by large activation barriers of about 25−30 kcal/mol (ΔE). The extraordinary amount of 39.8 kcal/mol (ΔE) required to come across **5s**-SSf presumably results from the limited flexibility of the polybutadienyl chain to occupy the favorable coordination site. On the other hand, however, the insertion barrier decreases significantly for the prone butadiene coordination by about 15 kcal/mol (ΔE). This can be attributed to an effective interaction of prone butadiene with the d_{zz} nickel AO in such a way that makes it easier to reach the transition state, which therefore yields a significantly reduced activation barrier. This was discussed previously in detail.[6] The energy needed for butadiene conversion from the thermodynamically stable supine to the reactive prone orientation amounts to about 5.3 and 1.5 kcal/mol (ΔE) for **4a** and **4s**, respectively, provided that this process takes place in a barrierless fashion, which is suitable to assume.

Due to a similar kind of butadiene coordination, the bidentate π-complexes must be regarded as the direct precursors of the transition states for insertion. This was confirmed by optimization of relaxed transition state structures after a small perturbation, which ensures that they are connected to corresponding reactants and products. Although the insertion via **5s**-SS and **5s**-SP most likely takes place in a direct way from the corresponding monodentate π-complexes **3**, this is not of any concern for the determination of the minimum energy pathway by which the chain propagation preferentially proceeds, since the routes through these transition states are ruled out by energy.

The most stable anti and syn transition states are **5a**-SPb and **5s**-PPf, where the double bond is aligned in back and in front, respectively. They represent the most reactive intermediates, which were passed through along the minimum energy pathway of the cis-1,4- and trans-1,4-production cycle. The corresponding species with an inverse double bond coordination are 3.4 kcal/mol (**5a**-SPf) and 4.4 kcal/mol (**5s**-PPb) higher in energy (ΔE). The barriers across the energetically preferred anti and syn species are calculated to be almost identical. ZPC and entropy contributions, although they slightly enlarge the insertion barrier, do not noticeably influence the anti−syn gap. The activation energies amount to 10.8 and 11.3 kcal/mol (without and with ZPC) and to about 12.0 kcal/mol in the Gibbs free energy, respectively, relative to the most stable butadiene π-complex, **4a**-SSf.

If we suppose a very mobile preestablished anti−syn equilibrium, such that a typical Curtin−Hammett situation[24] exists with isomerization being more rapid than insertion ($k_{a/s}{}^p \gg k_{2c}$, k_{2t}), then, due to the calculated almost identical reactivities of anti and syn forms, a statistical cis/trans equibinary polybutadiene consisting of about 50% cis and 50% trans units should be generated. Experiment, however, showed that cationic (C_{12}-allyl)nickel(II) complexes $[Ni(C_{12}H_{19})]^+$ (with weakly coordinating anions) yield nearly exclusively *cis*-1,4-polymers.[5e,7a,10,21] Therefore, the calculations suggest the anti−syn isomerization to be the discriminating factor between the competing cis-1,4- and trans-1,4-polymer generation cycles.

Experiment determined a high stereoregularity within the methylene groups of the *cis*-1,4-polymer.[1] This is confirmed by the calculations, since the counterparts of the preferred prone butadiene transition states with an inverse butenyl orientation,[25] with **5s**-SPf as the most stable one, are at least 6.1 kcal/mol (ΔE) higher. Porri

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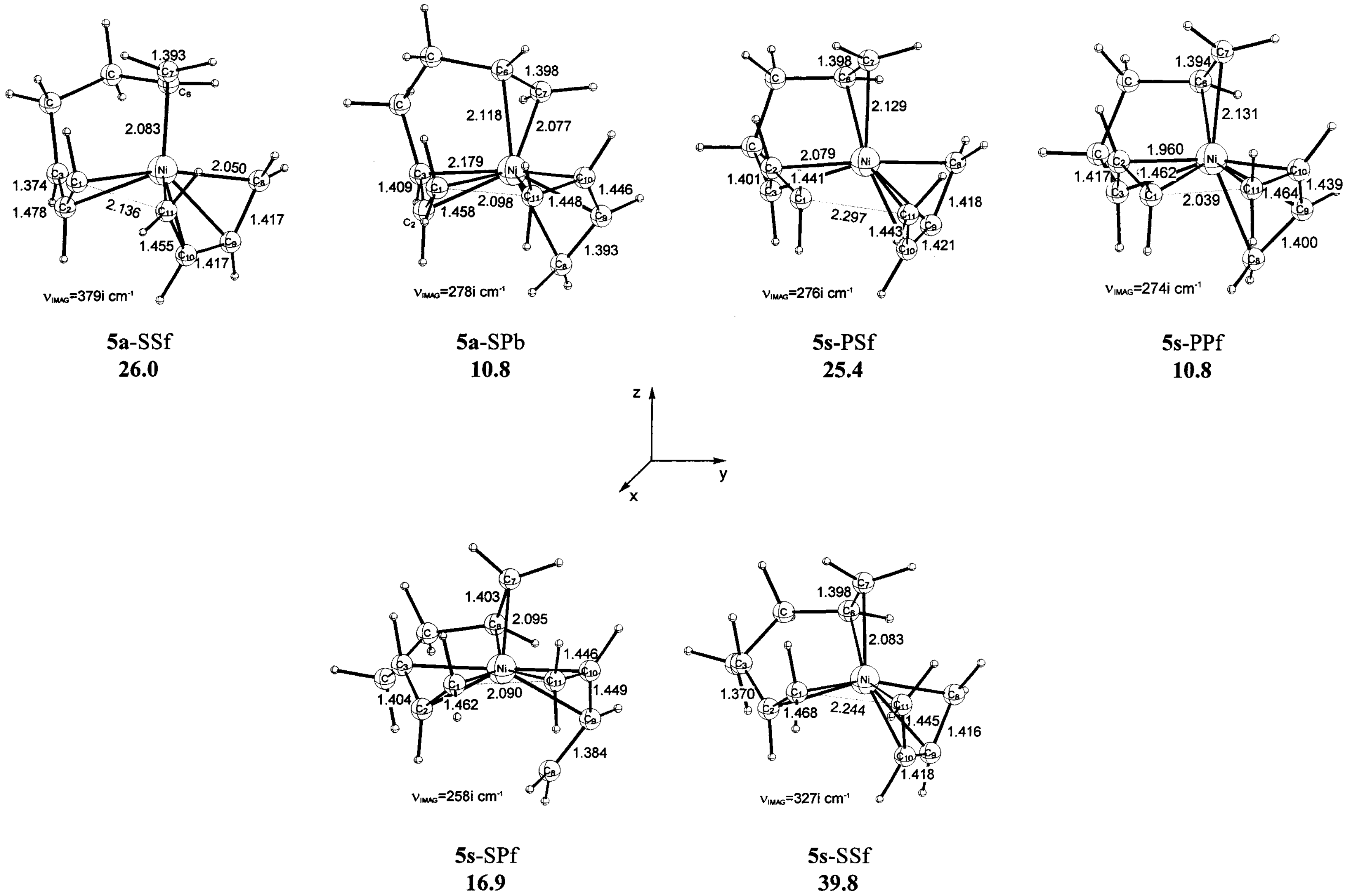
[24] Seemann, J. I. *Chem. Rev.* **1983**, *83*, 83.

[25] Only for **5s** can the PP and SP isomers be compared, since for **5a** the polybutadienyl chain coordination restricts the butenyl orientation to supine.



5a-SSf
26.0

5a-SPb
10.8

5s-PSf
25.4

5s-PPf
10.8

5s-SPf
16.9

5s-SSf
39.8

Figure 6. Selected geometric parameters of the optimized structures (Å) of transition states for *cis*-butadiene insertion together with activation energies (ΔE in kcal/mol) relative to **4a**-SSf (only the more stable of the f and b forms, if possible, are given; for abbrevations see text).

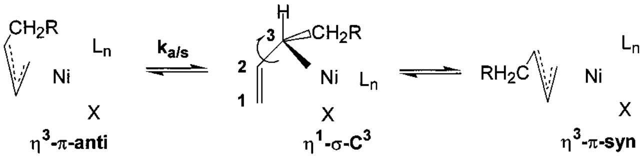


Figure 7. $\sigma \rightarrow \pi$ conversion of the butenyl group occurring during anti–syn isomerization.

et al.[26] concluded from stereochemical considerations of the Ziegler–Natta catalyst system $Ni(O_2CR)_2/BF_3{\cdot}OEt_2/AlEt_3$ that insertion very likely proceeds from the prone orientation. This is conclusively supported by our calculations.

The overall insertion reaction commencing from the most stable supine η^4-butadiene complexes **4a**-SSf and **4s**-PSf, which happens via supine to prone butadiene conversion through **5a**-SPb and **5s**-PPf and leads to the most stable kinetic insertion products **2a**-SSb(c) and **2a**-PSf(t), is calculated to be exothermic by 8.8 kcal/mol (ΔE) and 11.8 kcal/mol (ΔE), provided that the necessary steps to interconvert different isomers of **4** and **2a** are facile.

Comparison with Cationic $[Ni(C_4H_7)(C_4H_6)(C_2H_4)]^+$ Complexes.[6b] For both model systems the insertion proceeds via prone butadiene transition states. The corresponding supine butadiene species are well separated above at least by 10 kcal/mol. For the $[Ni(C_4H_7)(C_4H_6)(C_2H_4)]^+$ model the thermodynamically more stable syn forms are also more reactive than the related anti counterparts, by about 4 kcal/mol (ΔE) with a similar reactivity of SP and PP forms. By coordination of the first double bond from a chelating polybutadienyl chain the anti form's reactivity increases relatively, which gives an almost identical insertion barrier that must be overcome by walking through the competitive cis-1,4- and trans-1,4-branches.

C. Anti–Syn Isomerization. Since the chain propagation happens via *cis*-butadiene insertion, the anti–syn isomerization is a prerequisite step in order to open the trans-1,4-channel (k_{2t}). Previously, we examined the anti–syn isomerization of a π-butenyl group in cationic and neutral butenyl(butadiene)(ligand)nickel(II).[27] The isomerization most likely takes place via η^3-$\pi \rightarrow \eta^1$-σ-C^3 butenyl group conversion, followed by internal rotation of the vinyl group around the C^2–C^3 single bond (cf. Figure 7). The coordination number of the metal must always be kept as 5, to make the isomerization process energetically feasible. Thus, for the single vacant site arising during the $\pi \rightarrow \sigma$ butenyl conversion, an occupation by the polybutadienyl chain is reasonable to assume.

Several isomers of **6** were located; the trigonal-bipyramidal complexes displayed in Figure 8 constitute the rotational transition state structures which are passed through along the minimum energy isomerization path. The **6-A** and **6-B** isomers are distinguished from one another with regard to the alignment of the last coordinated polybutadienyl double bond. They were confirmed to have only one imaginary frequency. The corresponding normal mode represents a rotational displacement along the C^2–C^3 single bond. In **6** the axial position is preferentially occupied by the strongest donor,[28] which is the σ-butenyl group. For the two possible arrangements of the polybutadienyl chain, the facial arrangement, i.e., with two equatorial double bonds, is found to be in favor of the meridional arrangement, i.e., with the polybutadienyl chain occupying an equatorial and an axial position, by about 15 kcal/mol (ΔE). Since the butadiene must compete with the donating ability of the double bonds,[27] its coordination in **6** is characterized as intermediate between mono- and bidentate.

To address the question whether butadiene must participate in the isomerization process, calculations were done by replacing butadiene with two ethylene moieties, which serves as a simplified model for additional coordinated polybutadienyl chain double bonds. Despite substantial effort, no $[Ni(\sigma{:}\eta^2{:}\eta^2\text{-}C_{11}H_{17})(C_2H_4)_2]^+$ rotational transition states could be determined which make the substitution of butadiene by two ethylene units an exothermic process. We therefore conclude that the participation of butadiene is necessary in the isomerization process. Thus, it is straightforward to suppose that the isomerization most likely happens when commencing from the butadiene π-complexes.

Since isomerization is a unimolecular reaction, calculations on complexes of the same sum formula, $[Ni(C_{11}H_{17})(C_4H_6)]^+$, have been carried out in order to compare the activation energies for insertion and isomerization.[29] The barrier associated with isomerization via **6-B** is 17.7 kcal/mol (ΔE) relative to the most stable species, which occurred during the cis cycle: the bidentate butadiene π-complex **4a**-SSf. The barrier decreases slightly to 17.5 kcal/mol with inclusion of ZPC and increases to 19.0 kcal/mol using the Gibbs free energy. The energetic difference of 2.0 kcal/mol (ΔE) between **6-A** and **6-B** disappears with the Gibbs free energy.

D. Free Energy of the Entire Catalytic Cycle. The final Gibbs free energy profile of the entire catalytic cycle of the 1,4-polymerization of butadiene is given in Scheme 2 with the polybutadienylnickel(II) cation $[Ni(\eta^3{:}\eta^2{:}\eta^2\text{-}RC_{12}H_{18})]^+$ as the precatalyst. Now, different from the energetic data given in Table 2, the most stable all-cis polybutadienyl complex **2s**-SSb(c) was chosen as energetic reference. Moreover, the intrinsic energy to extend the polymer chain by an additional cis unit in subsequent chain propagation cycles (see Computational Details) is excluded from the energetic profile.

cis-Butadiene, regardless of whether it is coordinated in a mono- or bidentate fashion, is capable of replacing the last coordinated double bond of the polybutadienyl chain. Therefore, the chain propagation can proceed due to the formation of reactive η^4-butadiene π-complexes **4** in an exothermic and supposedly barrierless process.

Our calculations show the anti π-complex **4a**-SSf to be the catalyst resting state, since it is the most stable species on the potential surface. Therefore, one may conclude that anti π-complexes predominantly exist

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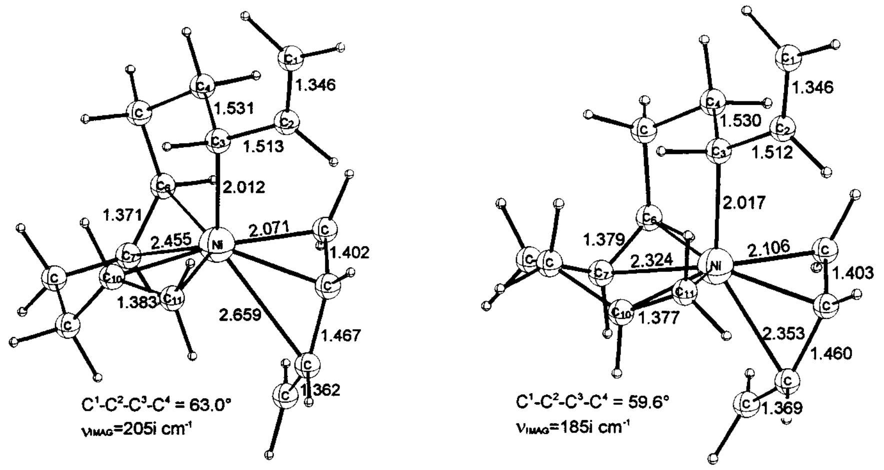
[26] Porri, L.; Giarrusso, A.; Ricci, G. *Prog. Polym. Sci.* **1991**, *16*, 405.

[27] Tobisch, S.; Taube, R. *Organometallics* **1999**, *18*, 3045.

[28] Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

[29] **4a**-SSf, **5a**-SPb, and **5s**-PPf were supplemented by an additional noncoordinating C_4 unit in the best possible arrangement. This extension does not have any significant influence on the optimized structure or on the energetics of the insertion process. Similar to the case for $[Ni(C_7H_{11})(C_4H_6)]^+$, nearly identical insertion barriers of 10.5 and 10.3 kcal/mol (ΔE) for the most reactive anti and syn π-complexes are predicted.

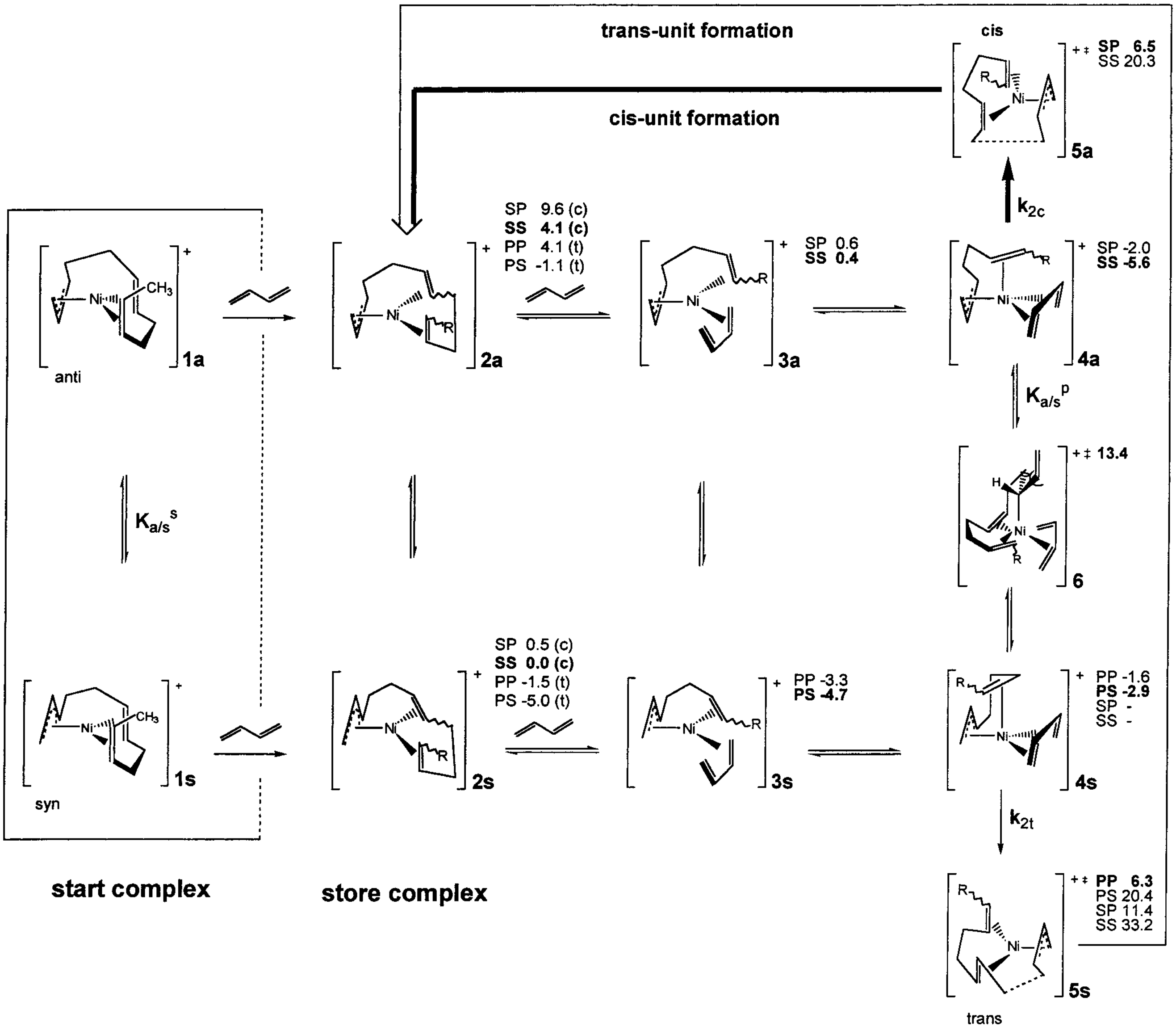


6-A
19.7

6-B
17.7

Figure 8. Selected geometric parameters of the optimized structures (Å) of transition states for anti–syn isomerization together with activation energies (ΔE in kcal/mol) relative to **4a**-SSf using the $[Ni(C_{15}H_{21})]^+$ model complex.

Scheme 2. Gibbs Free-Energy Profile (kcal/mol) of the Entire Catalytic Cycle of the 1,4-Polymerization with the Cationic Polybutadienylnickel(II) Complex $Ni(\eta^3{:}\eta^2{:}\eta^2\text{-}RC_{12}H_{18})]^+$ [a] as the Precatalyst



[a] Different isomers of a given species are distinguished (for abbrevations see text), with the most stable isomer marked in boldface type. For the different isomers only the more stable of the f and b forms, if possible, are given.

under polymerization conditions, and **4a**-SSf should be detectable by NMR.

The free activation barrier for anti−syn isomerization is 7.0 kcal/mol higher than the *cis*-butadiene insertion barrier. Therefore, one may conclude that the isomerization rate should be distinctly slower compared with the rate of insertion. We think the difference of 7.0 kcal/mol is large enough to be the discriminating factor between the cis-1,4- and trans-1,4-generation cycle, since one can expect the syn π-complexes to be negligibly populated. The k_{2t} channel, therefore, is suppressed by a slow anti−syn isomerization. The rate-determining step in the chain propagation reaction is the *cis*-butadiene insertion into the *anti*-(η^3-butenyl)nickel(II) bond, which takes place with a barrier of 12.0 kcal/mol.

The cis−trans selectivity is determined by the formation of anti π-complexes (due to the preferred anti insertion) and the much slower rate of isomerization than of insertion according to k_{2c} and k_{2t} ($k_{a/s}{}^{p} \ll k_{2c}$, k_{2t}). In agreement with experiment this gives nearly exclusively a cis-1,4-polymer, although of an almost identical reactivity of *anti*- and *syn*-butenyl forms.

Conclusions

The mechanism of stereoregulation of *cis*-1,4-polymerization of butadiene has been explored theoretically with the polybutadienylnickel(II) cation $[Ni(\eta^3:\eta^2:\eta^2\text{-}RC_{12}H_{18}]^+$ as the precatalyst. Experiment has verified it as a highly active precatalyst, which yields nearly exclusively a stereoregular cis-1,4-polymer.[1,5e,7a,10,21] The cationic $[Ni(C_7H_{11})(C_4H_6)]^+$ complex serves as a realistic model of the real catalyst. We have investigated competitive chain propagation cycles as well as anti−syn isomerization using a gradient-corrected density functional method, which has been shown to be quite reliable both in geometry and in energy. The following conclusions could be drawn.

Starting from the precatalyst, which predominantly is in the syn form **1s**, polybutadienyl complexes **2a** (note the preferred anti insertion) are formed after a short initialization period. Both **1** and **2** have a quasi planar structure with the butenyl group and the polybutadienyl chain coordinated in a $\eta^3:\eta^2:\eta^2$ fashion to Ni^{II}. **2a** represents the kinetic insertion products of the cis-1,4- (via k_{2c}) and the trans-1,4-polymer (via k_{2t}) generating cycle with an all-cis or an all-trans polybutadienyl configuration, respectively. The *syn*-butenyl counterparts **2s** are about 4 kcal/mol thermodynamically more stable. They are the thermodynamic insertion products. The calculated energy difference between the most stable all-cis and all-trans isomers of **2** is about 5 kcal/mol, in favor of the all-trans complexes. Therefore, the polymerization cycle via k_{2t} most likely would be passed through in the limit of thermodynamic control. That would give rise predominantly to trans-1,4-polymer, which contrasts with experiment.

cis-Butadiene, regardless of mono- or bidentate coordination, is capable of replacing the last coordinated double bond of the polybutadienyl chain in an exothermic process. Thus, via formation of reactive butadiene π-complexes the chain propagation can proceed. Bidentate supine butadiene coordination is found to give the most stable π-complexes. Different from our previous study on the related $[Ni(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)(C_2H_4)]^+$ complex, now, with the coordinating polybutadienyl chain, the stability of anti and syn forms of **4** is turned around. The most stable **4a** isomer, **4a**-SSf, is 2.6 kcal/mol (ΔE) below the most stable **4s** isomer. **4a**-SSf is the catalyst resting state, since it is the most stable species on the potential surface.

cis-Butadiene insertion commencing from the most stable supine butadiene isomers of **4** occurs through product-like tetragonal-pyramidal transition states. Insertion is disabled by rather large barriers of about 25−30 kcal/mol. For insertion to occur along the minimum energy pathway the butadiene orientation has to be converted into prone, which is expected to be facile. The effective interaction of prone butadiene with the d_{zz} nickel AO would stabilize the educt-like trigonal-bipyramidal transition states and, consequently, facilitate the insertion process. The free activation barrier associated with *cis*-butadiene insertion is almost identical for both the cis-1,4- and trans-1,4-polymer production cycles and amounts to 12.0 kcal/mol.

Provided that the anti−syn isomerization is much more rapid than butadiene insertion ($k_{a/s}p \gg k_{2c}$, $k_{2)}$, then our calculations indicate (in contrast to experiment) that a statistical cis/trans equibinary polybutadiene would be generated consisting of about 50% cis and 50% trans units.

The overall insertion reaction starting from the most stable *anti*- and *syn*-butenyl π-complexes which proceeds via prone butadiene transition states and yields the most stable kinetic all-cis and all-trans products is exothermic by 8.8 and 11.8 kcal/mol (ΔE), respectively.

The free activation energy for anti−syn isomerization is 19.0 kcal/mol, which is 7.0 kcal/mol higher than the insertion barrier. Isomerization proceeds via trigonal-bipyramidal σ-butenyl transition states, which constitute the internal rotation of the vinyl group around the C^2-C^3 single bond. The participation of butadiene and the occupation of the single vacant site by the polybutadienyl chain occurring during the $\pi \rightarrow \sigma$ butenyl conversion is necessary in this process.

Our calculations suggests the following mechanism of stereoregulation, provided that all the substitution equilibria involving butadiene are mobile and the steps necessary to interconvert different mutual orientations of the reacting parts are facile, which is reasonable to assume. The isomerization rate should be distinctly slower than the insertion rate ($k_{a/s}{}^{p} \ll k_{2c}$, k_{2t}), since the activation free energies differ by 7.0 kcal/mol. Accordingly, reactive *syn*-butenyl π-complexes are only sparsely populated, thus the generation of a trans-1,4-polymer via k_{2t} would be almost entirely suppressed by a slow anti−syn isomerization. The rate-determining step in the chain propagation reaction is the *cis*-butadiene insertion into the *anti*-(η^3-butenyl)nickel(II) bond. Due to the high thermodynamic population of anti π-complexes and the low free activation barrier for insertion, a high catalytic activity can be expected, which is in agreement with experiment. The cis−trans selectivity is determined by the formation of *anti*-butenyl complexes (due to the preferred anti insertion), their high reactivity, and the much slower isomerization. This gives nearly exclusively a cis-1,4-polymer, although of an almost identical reactivity of *anti*- and *syn*-butenyl forms.

Experiments determined a highly stereoregular cis-1,4-polymer[1] and concluded that butadiene insertion very likely proceeds from the prone orientation.[26] Both aspects are confirmed by our calculations. The stereoregularity in a natural way results from the controlling influence of the chelating polybutadienyl chain, which restricts the *anti*-butenyl group to a supine orientation and from the enhanced reactivity of prone butadiene.

To explain the amount of approximately 3−4% of trans units, which has been observed by experiment for highly cis-selective (C_{12}-allyl)nickel(II) complexes [Ni($C_{12}H_{19}$)]X,[5e,7a,10,21] we have to assume the participation of monoligand complexes. They are formed under thermodynamic control via displacement of the polybutadienyl chain by the counteranion. Then, the trans-1,4-channel via k_{1t}[6b] can be opened, provided that anti−syn isomerization is more rapid than butadiene insertion.

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Supporting Information Available: Tables of Cartesian coordinates of selected optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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