E Stereoregular 1,1 and 1,3 Constitutional Units from 1,3-Butadiene in Copolymerizations Catalyzed by a Highly Hindered *C*₂ Symmetric Metallocene

Pasquale Longo,* Stefania Pragliola, Giuseppe Milano, and Gaetano Guerra

Contribution from the Università di Salerno, Dipartimento di Chimica Via S. Allende, I-84081 Baronissi Salerno, Italy

Received September 9, 2002; E-mail: plongo@unisa.it

Abstract: Unprecedented 1,1 and 1,3 constitutional units from 1,3-butadiene, both presenting only the *E* configuration of the double bond, have been achieved by copolymerization with ethene, conducted at high temperature and low ethene concentration, when catalyzed by a highly hindered *C*₂ symmetric metallocene. Ethene/butadiene copolymerizations by this catalyst generally lead to prevailing methylene-1,2-cyclopropane units from butadiene. Polymer microstructures obtained for different comonomer concentrations clearly indicate that the rate-determining step leading to cyclopropanation involves ethene, while that leading to 1,1 and 1,3 constitutional units does not. A general copolymerization scheme and a molecular modeling study of the cyclopropanation reaction are presented. Molecular modeling also indicates that the *E* stereoselectivity for 1,1 and 1,3 constitutional units can be rationalized, in the assumption that an allyl isomerization of the terminal of the growing chain would occur.

Introduction

Metallocene-based polymerization catalytic systems are generally regioselective in favor of primary (or 1,2) propene insertion.[1] In particular, the regioselectivity of syndiospecific or aspecific systems is nearly complete,[2] while substantial amounts of regioirregularities are obtained for isospecific catalytic systems based on zirconocenes and hafnocenes.[3] This complete regioselectivity has been rationalized by a mechanism involving the rotation of the coordinated monomer from the orientation suitable for secondary insertion toward that suitable for primary insertion, which would not be available for the wrong enantioface coordinated to isospecific catalysts.[2b]

A different mechanism of regioselectivity, which can operate also for isospecific zirconocenes and hafnocenes, involves the inhibition of secondary monomer coordination, through suitable substitutions of the π-ligand.[4,5] In particular, a substantially complete regioselectivity has been observed for isospecific catalytic systems based on the *C*₂ symmetric zirconocene *rac*-[CH₂(3-*tert*-butyl-1-indenyl)₂]ZrCl₂ (**1**), discovered by Resconi and co-workers, which presents a large gap aperture associated with large substituents.[5]

Recent polymerization studies have shown that only this latter regioselectivity, due to π-ligand substitution, is retained for other hydrocarbon monomers, forcing them to unusual reaction paths also leading to new polymeric structures. In particular, the catalytic system **1**/MAO promotes an unusual primary insertion of styrene,[6] rather than the usual secondary insertion. The same catalytic system for copolymerization of 1,3-butadiene with ethene can lead to ethene copolymers only containing unprecedented methylene-1,2-cyclopropane together with methylene-1,2-cyclopentane units. Both cycloalkane units present a prevailing trans configuration and would be obtained by cyclization reactions involving the intermediate produced by an unusual primary vinyl insertion of 1,3-butadiene (upper part of Scheme 1).[7]

In this paper, we report results of ethene/1,3-butadiene copolymerizations performed with the same catalytic system, under different conditions of temperature and monomer concentration. ¹³C NMR analysis of the obtained products, with full attribution of signals to microstructures, shows that, in suitable conditions, Resconi's catalyst can lead to ethene copolymers only containing unprecedented 1,1 and 1,3 constitutional units from 1,3-butadiene, both presenting only the *E* configuration of the double bond.

Experimental Section

All of the operations were performed under nitrogen atmosphere by using conventional Schlenk-line techniques. Toluene was refluxed over sodium diphenylketyl for 48 h and distilled before use. 1,3-Butadiene

(1) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355−6364. (b) Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015−1018.
(2) (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256. (b) Guerra, G.; Longo, P.; Cavallo, L.; Corradini, P.; Resconi, L. *J. Am. Chem. Soc.* **1997**, *119*, 4394−4402.
(3) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617−622.
(4) (a) Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 339−341. (b) Toto, M.; Cavallo, L.; Corradini, P.; Moscardi, G.; Resconi, L.; Guerra, G. *Macromolecules* **1998**, *31*, 3431−3438.
(5) Resconi, L.; Piemontesi, F.; Camurati, I.; Sundmeijer, O.; Ninfant'ev, I. E.; Ivchenko, P. V.; Kuz'mina, L. G. *J. Am. Chem. Soc.* **1998**, *120*, 2308−2321.
(6) Caporaso, L.; Izzo, L.; Sisti, I.; Oliva, L. *Macromolecules* **2002**, *35*, 4886−4870.
(7) Pragliola, S.; Milano, G.; Guerra, G.; Longo, P. *J. Am. Chem. Soc.* **2002**, *124*, 3502−3503.

Table 1. Copolymerization of Ethene and 1,3-Butadiene Performed in the Presence of Zirconocene-Based Catalytic Systems

run	cat.	[E][a]	[B][a]	[E]/[B]	T (°C)	t (h)	yield (g)	$X_B{}^b$ ($\times 10^2$)	$f_\Delta{}^c$ ($\times 10^2$)	$f_\bigcirc{}^c$ ($\times 10^2$)	$f_{1,1}{}^c$ ($\times 10^2$)	$f_{1,3}{}^c$ ($\times 10^2$)
1	**1**	4.6×10^{-2}	0.525	8.8×10^{-2}	−20	59	0.14	4.8	73	27		
2	**1**	4.6×10^{-2}	0.525	8.8×10^{-2}	0	19	0.15	4.4	79	21		
3	**1**	4.6×10^{-2}	0.525	8.8×10^{-2}	16	21	0.12	4.0	80	20		
4	**1**	4.6×10^{-2}	0.525	8.8×10^{-2}	73	1.5	0.40	5.6			76	24
5	**1**	1.02	1.5	0.68	50	0.15	1.20	2.1	66	34		
6	**1**	1.4×10^{-3}	8.0×10^{-3}	0.17	50	3.50	1.60	1.5	16	7	53	24
7	**1**	8.0×10^{-4}	8.0×10^{-3}	0.1	50	25	0.55	2.6			66	34
8	**2**	4.6×10^{-2}	0.525	8.8×10^{-2}	73	1	0.40	26.0^d		25		

[a] Concentration in the feed. [b] Molar fraction of butadiene units in the polymer chain. [c] Fraction of butadiene leading to cyclopropane ring units (f_Δ), cyclopentane ring units ($f_\bigcirc$), 1,1-inserted units ($f_{1,1}$), and 1,3-inserted units ($f_{1,3}$). [d] 75% of inserted butadiene gives 1,4-trans units.

Scheme 1
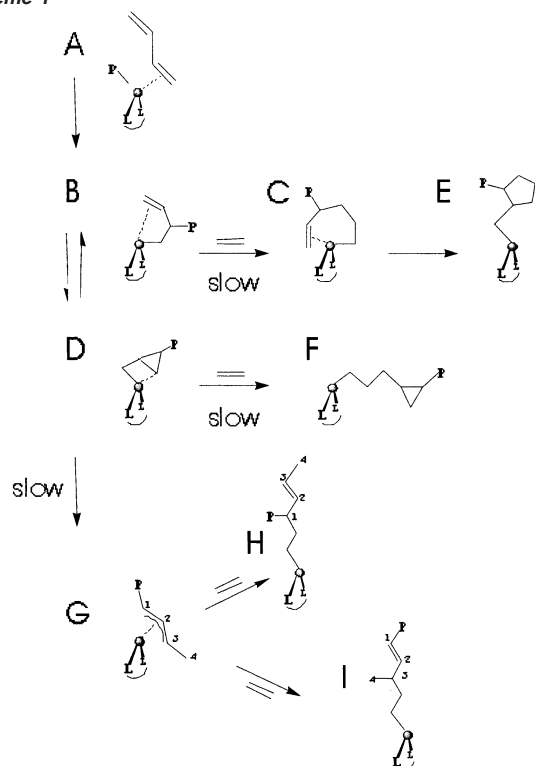
and ethylene were purchased from Società Ossigeno Napoli (SON) and used without further purification. Methylaluminoxane (MAO) was purchased by Witco and used as a solid after distillation of solvent. The catalysts *rac*-(CH₂(3-*tert*-butyl-1-indenyl)₂)ZrCl₂ and *rac*-(CH₂(1-indenyl)₂)ZrCl₂ were prepared according to the procedures described in ref 8.

The copolymerizations were carried out in toluene feeding the diene as a liquid and pumping the ethylene on the reaction mixture (the amounts are also reported in Table 1) using 1×10^{-5} mol of catalyst and 1×10^{-2} mol of MAO (based on Al). In the comonomer feed composition $f(E) = [E]_{feed}/[B]_{feed}$, the ethylene composition in the liquid phase was calculated by Lewis and Luke's equation in conjunction with the fugacity function chart of ethylene as reported in the literature.[9] The concentration of 1,3-butadiene was considered constant during all of the polymerization runs.

NMR spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz at 393 K. The samples were prepared by dissolving 40 mg of polymer in 0.5 mL of tetrachlorodideutero ethane. Hexamethyldisiloxane was used as the internal chemical shift reference.

(8) Resconi, L.; Balboni, D.; Baruzzi, G.; Fiori, C.; Guidotti, S.; Mercandelli, P.; Sironi, A. *Organometallics* **2000**, *19*, 420−429.
(9) Maxwell, J. B. *Data Book on Hydrocarbons*; Van Nostrand Co. Inc.: New York, 1950.

Table 2. Attributions of the Signals Related to the ¹³NMR Spectra of E/B Copolymers

carbon	chemical shift		refs
	observed	calculated	
1	10.08	9.84	10a, 10d
2	17.06	16.84	10a, 10d
3	32.45	32.50	10a
4	27.77	27.80	10a
1′	9.28	9.84	10a
2′	14.12	14.35	10a
3′	30.54	30.72	10a
4′	24.57	25.10	10a
5	22.22	22.21	25
6	33.91	33.61	25
7	44.22	44.30	25
8	30.54	30.82	25
9	26.22	26.22	25
7′	40.96	40.02	25
10	25.31	25.30	a
11	33.61	33.61	a
12	40.92	40.04	11b
13	134.77	134.70	11b
14	121.75	121.77	11b
15	15.78	15.76	11b
16	126.47	126.50	10b
17	134.62	134.25	10b
18	35.48	34.30	10b
19	34.54	34.54	a
20	18.85	18.81	10b

[a] Attributed in the present paper.

The resonances were assigned on the basis of the data reported in the literature for carbons in similar environments (see Table 2), of the DEPT ¹³C NMR experiment, and of the additivity rules.[10a−c,11a−c]

The molar fractions of ethylene and butadiene (X_E and X_B) in the copolymers were calculated by the following equations:

$$X_E = E/(E + B) \qquad X_B = B/(E + B)$$

where $E = {}^1/_2(\Sigma C_s - 2C_2 - 2C_{2'} - 2C_7 - 2C_{7'} - 2C_{15} - 2C_{20})$, $B = [{}^1/_2(C_2 + C_{2'} + C_7 + C_{7'}) + C_{15} + C_{20}]$, $f_{B\Delta} = {}^1/_2(C_2 + C_{2'})/B$, $f_{B\bigcirc} = {}^1/_2(C_7 + C_{7'})/B$, $f_{B1,1} = C_{15}/B$, and $f_{B1,3} = C_{20}/B$. E and B are the molar fractions of ethene and butadiene units in the polymer chain, respectively. $f_{B\Delta}$, $f_{B\bigcirc}$, $f_{B1,1}$, and $f_{B1,3}$ are the fractions of butadiene leading to cyclopropane, cyclopentane, 1,1-, and 1,3-inserted units. ΣC_s is the sum of the areas of the resonances of all saturated carbons; the subscripts of the carbon atoms refer to those indicated in Figure 1a and 1b.

(10) (a) O'Connor, E. J.; Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1987**, *109*, 3739−3747. (b) Sozzani, P.; Di Silvestro, G.; Grassi, M.; Farina, M. *Macromolecules* **1984**, *17*, 2532−2538. (c) Porri, L.; Di Corato, A.; Natta, G. *Eur. Polym. J.* **1969**, *5*, 1−13. (d) Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1964**, *86*, 1870−1871.
(11) (a) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323−327. (b) Aubert, P.; Sledz, J.; Schué, F.; Brevard, C. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 955−972. (c) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984−2990.
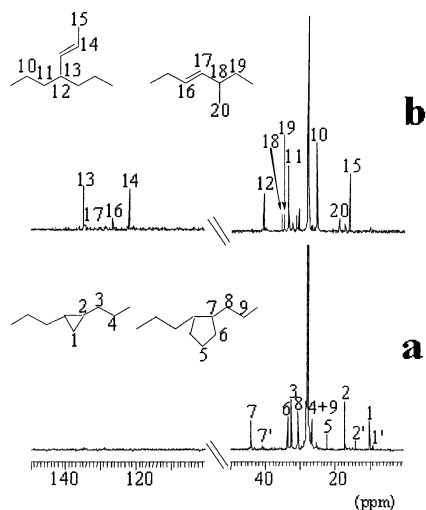
Figure 1. ^{13}C NMR spectra of samples 1 (a) and 4 (b) of Table 1 (hexamethyldisiloxane scale).

Chart 1. Partitioning of the Systems into QM and MM Parts
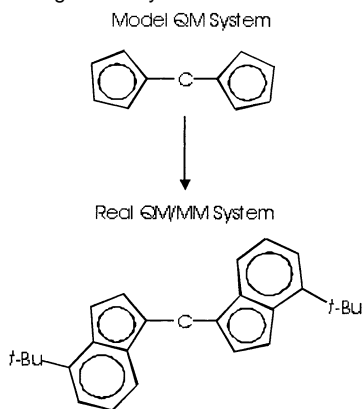
Computational Details. Stationary points on the potential energy surface were calculated with the Amsterdam density functional (ADF) program system,[12] developed by Baerends et al.[13,14] The electronic configuration of the molecular systems was described by a triple-basis set on zirconium for 4s, 4p, 4d, 5s, and 5p. Double-STO basis sets were used for carbon (2s,2p) and hydrogen (1s), augmented with a single 4d, 3d, and 2p function, respectively. The inner shells on zirconium (including 3d) and carbon (1s) were treated within the frozen core approximation. Energetics and geometries were evaluated by using the local exchange-correlation potential by Vosko et al.,[15] and augmented in a self-consistent manner with Becke's[16] exchange-gradient correction and Perdew's[17,18] correlation gradient correction.

The ADF program was modified[19−21] to include standard molecular mechanics force fields in such a way that the quantum mechanic (QM) and molecular mechanic (MM) parts are coupled self-consistently, according to the method prescribed by Morokuma and Maseras.[22] The model QM and the real QM/MM systems are reported in Chart 1.

The partitioning of the systems into QM and MM parts only involves the skeleton of the catalyst's ligand. Hence, the growing chain and the

monomer are always totally composed by pure QM atoms. Moreover, the metal atom, the five-membered Cp rings of all of the catalysts, and the H$_2$C bridge connecting the two Cp rings are also composed by pure QM atoms. The only MM atoms, hence, are the carbon and hydrogen atoms needed to transform the pure QM H$_2$CCp$_2$ skeleton of the ligand into the CH$_2$(3-*tert*-butyl-1-indenyl)$_2$ ligand. The connection between the QM and MM parts occurs by means of the so-called capping "dummy" hydrogen atoms, which are present in the model system only. These capping atoms are replaced in the real system by the corresponding "linking" carbon atom.

The QM and MM parts are thus linked by the "capping" hydrogen atoms and coupled by van der Waals interactions. The geometry optimization on the whole system was carried out within this coupling scheme between QM and MM atoms. In the optimization of the MM part, the ratio between the C−C bonds crossing the QM/MM border and the corresponding optimized C−H distances was fixed equal to 1.36. This coupling scheme is described in detail in ref 19. Further details on the methodology can be found in previous papers.[19,20]

The molecular mechanics potential developed by Bosnich for bent metallocenes has been adopted.[23] This approach substantially corresponds to an extension of the Karplus's CHARMM force field[24] to include group 4 metallocenes.

All of the structures which will follow are stationary points on the combined QM/MM potential surface. Geometry optimizations were terminated if the largest component of the Cartesian gradient was smaller than 0.002 au.

Results and Discussion

Polymerization Tests. Copolymerization runs of 1,3-butadiene and ethene in the presence of catalyst **1**/MAO, effected at different reaction temperatures and at low ethene concentration, are described in rows 1−4 of Table 1.

For the copolymers obtained at lower polymerization temperatures, as already observed for copolymer samples obtained at higher ethene concentrations,[7] the ^{13}C NMR spectra (shown for sample 1 in Figure 1a) do not show any signal in the region of the unsaturated carbons, while the aliphatic region includes, besides the intense peak placed at 27.8 ppm related to methylene sequences, three resonances placed at 10.1, 17.1, and 32.5 ppm which can be attributed to trans 1,2 disubstituted cyclopropane rings as well as five resonances of trans 1,2-disubstituted cyclopentane rings[25] and minor resonances which can be attributed to cis 1,2 disubstituted rings (primed numbers in Figure 1a). The ratio between cyclopropane and cyclopentane units increases from 2/1 to 4/1, as the polymerization temperature increases from −20 to 16 °C (rows 1−3 of Table 1).

For the copolymer obtained at higher polymerization temperature (sample 4 of Table 1), the ^{13}C NMR spectrum of Figure 1b shows the presence of a polyethylene, containing *E* propenyl branches and *E* double bonds along the main chains with methyl branches in the α position (inset of Figure 1b), which correspond to 1,1 and 1,3 constitutional units from butadiene, respectively.

These assignments have been confirmed by ^{13}C NMR spectra of hydrogenated samples. In particular, the spectrum of sample 4, after hydrogenation with *p*-toluenesulfonylhydrazide,[26] shows

(12) ADF 2.3.0; Vrije Universiteit Amsterdam, Amsterdam, The Netherlands, 1996.
(13) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41−51.
(14) te Velde, B.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84−98.
(15) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.
(16) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098−3100.
(17) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824.
(18) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.
(19) Cavallo, L.; Woo, T. K.; Ziegler, T. *Can. J. Chem.* **1998**, *76*, 1457−1466.
(20) Woo, T. K.; Cavallo, L.; Ziegler, T. *Theor. Chim. Acta* **1998**, *100*, 307−313.
(21) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177−6186.
(22) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *16*, 1170−1179.

(23) Doman, T. N.; Hollis, T. K.; Bosnich, B. *J. Am. Chem. Soc.* **1995**, *117*, 2793−2804.
(24) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187−217.
(25) Galimberti, M.; Albizzati, E.; Abis, L.; Bacchilega, G. *Makromol. Chem.* **1991**, *192*, 2591−2601
(26) (a) Harwood, H. J.; Russel, D. B.; Verthe, J. J. A.; Zymonas, J. *Makromol. Chem.* **1973**, *163*, 1. (b) Mango, L. A.; Lenz, R. W. *Makromol. Chem.* **1973**, *163*, 13.
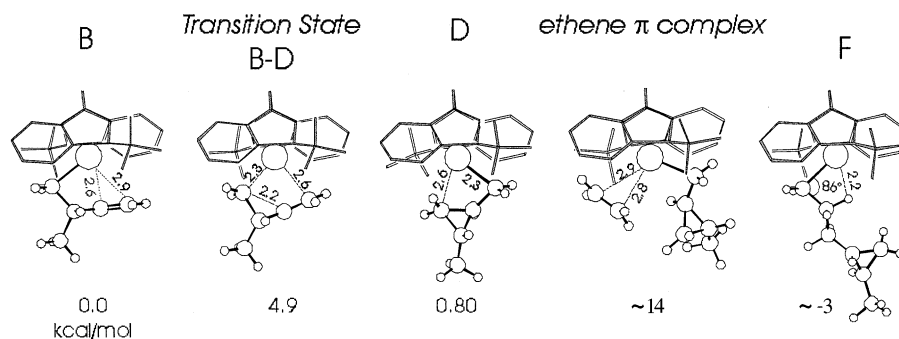
Figure 2. Calculated QM/MM geometries and energies of intermediates and transition states for the cyclopropanation reaction.

only the presence of methyl and *n*-propyl branches along polyethylene chains.

Attributions of the signals related to the ^{13}C NMR spectra of E/B copolymers are reported in Table 2.

Copolymerization runs of 1,3-butadiene and ethene in the presence of catalyst **1**, effected at a given temperature (50 °C) for different comonomer concentrations, are described in rows 5−7 of Table 1. It is apparent that, also for high polymerization temperatures, for high ethene concentrations this catalytic system produces ethene copolymers containing only methylene-1,2-cyclopropane and methylene-1,2-cyclopentane units, in a ratio not far from 2/1, as already observed for polymerization tests conducted at room temperature and high ethene concentrations.[7] The 1,1 and 1,3 constitutional units from 1,3-butadiene gradually appear, by decreasing the ethene concentration (sample 6 in Table 1), and are the only constitutional units from butadiene for the lowest ethene concentration (sample 7 in Table 1).

For the sake of comparison, we also report results of a copolymerization test conducted at high temperature and at low ethene concentration (same conditions of runs 1−4) for the catalytic system based on *rac*-[CH$_2$(1-indenyl)$_2$]ZrCl$_2$ (**2**), that is, the ansa-metallocene, similar to **1**, but not presenting *tert*-butyl substituents on the indenyl group (run 8 of Table 1). It is apparent that catalyst **2** more efficiently inserts butadiene but leads to usual 1,4 and methylene-1,2-cyclopentane units in a ratio close to 3/1, as it does in tests at room temperature.[7]

Copolymerization Scheme. The copolymerization scheme presented in our previous communication[7] is recalled and extended on the basis of the present results. In the presence of **1**, butadiene would prefer a primary η^2 coordination (model A of Scheme 1); that is, the coordinated double bond, being nearly parallel to the σ metal−polymeryl bond, would present the noncoordinated double bond on the same side of the growing polymer chain (P). This primary butadiene coordination would give rise, through a 1,2 insertion into the σ metal−polymeryl bond, to a primary growing chain, that is, a growing chain bound to the metal by a methylene group (model B of Scheme 1). The resulting 1,2 inserted butadiene unit would be bonded to the metal also by a back-biting coordination of the closest double bond of the chain. This four carbon atoms back-biting chain (B in Scheme 1) could give rise to a six carbon atoms back-biting chain (C in Scheme 1), through ethene insertion.[25] Both types of back-biting chains B and C could give rise to cyclization reactions leading to formation of cyclopropane and cyclopentane rings, respectively, through intramolecular insertion of the coordinated double bond into the σ metal−alkyl bond (D and E in Scheme 1, respectively).

The lower part of Scheme 1 is an attempt to rationalize the achievement, for high polymerization temperatures and low ethene concentration, of (*E*)-1,1 and (*E*)-1,3 constitutional units from butadiene. First, it is worth noting that these two stereostructures are those expected for 1,4 trans and 1,2 insertions of (*E*)-1,3-pentadiene. This clearly suggests that they could be rationalized by assuming the formation of the allyl intermediate, corresponding to (*E*)-1,3-pentadiene homopolymerization, being syn with respect to both substituents (G in Scheme 1). In fact, the insertion of ethene into the external allyl carbons (1 and 3 in G of Scheme 1), which are bound to the growing chain (P) or to the methyl substituent, would produce 1,1 (H in Scheme 1) and 1,3 (I in Scheme 1) constitutional units, respectively, both with *E* configuration of the double bond. In a following section, molecular modeling results will suggest the molecular origin of the high *E* stereoselectivity, for both 1,1 and 1,3 constitutional units, as well as of the driving force for the possible B → D → G allyl isomerization.

The poor dependence on comonomer concentrations of the ratio between cyclopropane and cyclopentane inserted rings (Table 1 of present paper and Table 1 of ref 7) and the disappearance of 1,1 and 1,3 constitutional units, by increasing ethene concentration (at any temperature), can be rationalized by assuming that the rate-determining step leading to 1,1 and 1,3 units H and I would not involve ethene while the rate-determining steps leading both to cyclopropane and to cyclopentane rings would involve ethene. The detailed QM/MM study of the cyclopropanation reaction, discussed in the following section, indicates that the intermediate D would be in equilibrium with intermediate B, while the higher free energy barrier would correspond to the ethene insertion reaction (D → F).

Mechanism of Cyclopropanation. The possible cyclopropanation route (B → D → F in Scheme 1) has been investigated by a recently developed hybrid quantum mechanics (density functional theory) and molecular mechanics approach (QM/MM). Calculated geometries and energies of intermediates and transition states are shown in Figure 2. It is clearly apparent that the rearrangement leading to cyclopropane formation (B → D) involves small nuclear motions, and correspondingly the free energy barrier is lower than 5 kcal/mol. Hence, an equilibrium between the nearly isoenergetic intermediates B and D is expected. Moreover, according to our calculations, a lower energy product including a methylene-cyclopropane unit (F in Scheme 1 and in Figure 2) would be only achieved after an ethene monomer insertion. This ethene insertion reaction (D → F) presents a higher free energy barrier, being entropic (the entropy loss associated with ethene coordination has been
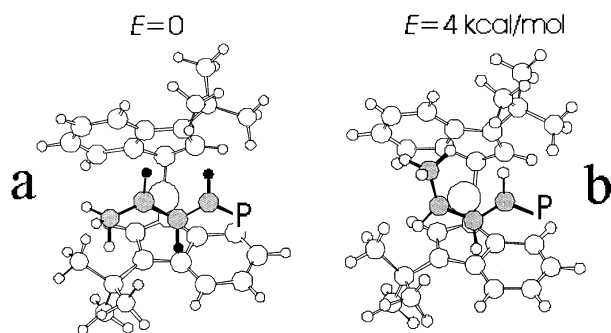
Figure 3. Minimum energy allyl coordinated intermediates presenting the growing chain (P) and a methyl as substituents of the two external allyl carbons. The absolute minimum energy intermediate **a** leads, as a consequence of ethene insertion, to the formation of (*E*)1,1 and (*E*)1,3 configurational units from butadiene.

roughly assumed close to 10 kcal/mol[27]), that is, definitely higher than the energy barrier for cyclopropane formation (B → D).

These results hence show the feasibility of the proposed cyclopolymerization mechanism and are able to rationalize the same dependence on ethene concentration, which has been observed for formation of methylene-1,2-cyclopropane (B → D → F) and methylene-1,2-cyclopentane (B → C → E) units.

The molecular origin of the trans stereoselectivity of the cyclopropanation reaction has been already investigated.[7] In particular, minimum energy intermediates of type B of Scheme 1, leading to trans and cis cyclopropane units, have been compared (Figure 2A and B of ref 7, respectively). The minimum energy envelope conformation for the five-membered ring (four carbon atoms + metal) is essentially the same for both models, while the growing chain (P) is in equatorial or axial (more hindered) position for intermediates leading to trans and cis cyclopropane rings, respectively. This results in a calculated energy difference in favor of the intermediate for trans cyclization of nearly 2.5 kcal/mol. It is worth adding that this energy difference is only in part due to the bulkiness of the cyclopentadienyl substituents. In fact, an energy difference in favor of the intermediate for trans cyclization of nearly 1.7 kcal/mol is also calculated when the substituents (six-membered rings and *tert*-butyl groups) of the cyclopentadienyl ligands are removed.

Allyl Intermediates for 1,1 and 1,3 Constitutional Units from 1,3-Butadiene. An extensive QM/MM analysis relative to all possible disubstituted allyl intermediates, coordinated to metallocene (**1**), shows that the minimum energy corresponds to the allyl group being syn with respect to both substituents (G in Scheme 1 and Figure 3a). The essentially complete stereoselectivity of the reaction can be easily accounted for by considering the higher energy (3−4 kcal/mol) for allyl intermediates presenting anti substituents when coordinated to the hindered metallocene. This is clearly apparent on inspection of the minimum energy allyl coordinated model shown in Figure 3a. In fact, larger steric interactions characterize the models with alkyl substituents replacing the allyl hydrogens indicated as black spheres in Figure 3a.

As an example, the minimum energy intermediate presenting the syn growing chain and the anti methyl substituent is shown in Figure 3b.

It is also worth noting that the allyl coordinated intermediate of Figure 3a (G in Scheme 1) presents an energy definitely lower (∼8 kcal/mol) than that of the product of primary vinyl butadiene insertion (B in Scheme 1 and in Figure 2). This energy difference could provide the driving force for the B → D → G allyl isomerization of Scheme 1.

Conclusions

For copolymerization of 1,3-butadiene with ethene, the isospecific catalytic systems based on the C_2 symmetric zirconocene *rac*-[CH$_2$(3-*tert*-butyl-1-indenyl)$_2$]ZrCl$_2$ (**1**), which presents a large gap aperture associated with large substituents, generally lead to ethene copolymers only containing unprecedented methylene-1,2-cyclopropane together with methylene-1,2-cyclopentane units.

The copolymerization of the same monomers with the same catalytic system, when conducted at high temperature and low ethene concentration, can lead to ethene copolymers only containing unprecedented 1,1 and 1,3 constitutional units from 1,3-butadiene, both presenting only the *E* configuration of the double bond.

Both cyclization reactions would occur starting from an intermediate (B of Scheme 1) produced by the unusual and complete primary vinyl insertion of 1,3-butadiene, due to the large metallocene substituents. For low ethene concentration, this intermediate would have sufficient lifetime to rearrange to the thermodynamically most stable allyl intermediate (G of Scheme 1). The insertion of ethene into the external allyl carbons would produce 1,1 and 1,3 constitutional units (inset of Figure 1a).

A detailed QM/MM study of the cyclopropanation reaction shows the feasibility of the proposed cyclopropanation mechanism and is able to rationalize the same dependence on ethene concentration, observed for the formation of methylene-1,2-cyclopropane and methylene-1,2-cyclopentane units.

Nonbonded interactions with the bulky metallocene substituents, as evaluated for intermediates of types B and G of Scheme 1, are able to rationalize the stereoselectivities which have been observed for cyclopropanation reactions and for formation of 1,1 and 1,3 constitutional units, respectively.

This catalytic process, which allows one to achieve new constitutional units from 1,3-butadiene, with well-defined configurations, could be possibly helpful also for stereoselective oligomerization reactions.

Supporting Information Available: Experimental and computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA028462V

(27) (a) Margl, P.; Deng, L.; Ziegler, T. *Organometallics* **1998**, *17*, 933. (b) Musaev, D. G.; Froese, R. J.; Svensson, M.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 367.