Closing Cycles with C_2-Symmetric Ziegler−Natta Polymerization Catalysts

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ABSTRACT: In the presence of *rac*-[CH_2(3-*tert*-butyl-1-indenyl)$_2$]$ZrCl_2$ (**1**) activated by methylaluminoxane (MAO) 1,4-pentadiene (1,4-PD), if copolymerized with ethene (E), gives unprecedented formation of methylene-1,3-cyclobutane units and a large amount of cross-links. Instead, in the presence of the same catalytic system, copolymerization of ethene with 1,3-butadiene (1,3-BD) or with 1,5-hexadiene (1,5-HD) gives exclusively a cyclization reaction, producing cyclopropane and cyclopentane units. The experimental results were rationalized by a theoretical approach, comparing the minimum energy pathways for the ring formation, after a diene insertion, with the competing ethene insertion reaction.

Introduction

Polyolefins containing cyclic group are useful materials due to solvent and chemical resistance, stiffness, and excellent transparency and, therefore, are suitable for optical applications.[1] Copolymerization of ethene (E) with cycloalkenes generates these materials even though a drawback of this method is the low reactivity of cyclic alkenes with respect to that of E.[2] A more interesting process, discovered by Waymouth et al. and based on zirconocene systems, utilizes group 4 metallocene catalysts that in the presence of α,Ω-dienes like 1,5-hexadiene (1,5-HD), 2-methyl-1,5-hexadiene, 1,6-heptadiene, and 1,7-octadiene,[3−8] lead to the formation of homopolymers and copolymers containing methylene-1,3-cycloalkane units, where the cycles involve from five to seven carbon atoms. Cross-linked materials are, instead, obtained by using α,Ω-nonconjugated dienes with double bonds that are connected by more than four carbon atoms.[9,10]

Recently, the authors reported that the copolymerization of 1,3-butadiene (1,3-BD) with E, catalyzed by the isospecific catalytic system based on a highly sterically hindered C_2 symmetric zirconocene like *rac*-[CH_2-(3-*tert*-butyl-1-indenyl)$_2$]$ZrCl_2$ (**1**), leads to E copolymers containing only methylene-1,2-cyclopropane units together with methylene-1,2-cyclopentane units, both with high trans selectivity.[11−13]

The cyclopolymerization of 1,3-BD, performed in the presence of **1**, as well as that of α,Ω-nonconjugated dienes, achieved in the presence of several zirconocenes, occurs with a mechanism consisting in a primary insertion of diene into metallocene carbon bond, followed by the 1,2 insertion of the terminal double bond into the metal−carbon σ-bond, to form the cyclic unit.[11−15]

In principle polyethenes containing 1,3-cyclobutane units could arise from cyclopolymerization of 1,4-pentadiene (1,4-PD) with E, and, although several studies, relative to the copolymerization of E with α,ω dienes, are reported in the literature, few of them concern the E−1,4-PD copolymerization.[16]

In this paper, the copolymerization of E and 1,4-PD by using **1**/methylaluminoxane (MAO) as catalyst is reported. The microstructures of E−1,4-PD copolymers were identified by ^{13}C NMR analysis and compared with those of E−1,3-BD and E−1,5-HD obtained by using **1** as the catalytic precursor. As a result, while comonomers like 1,3-BD and 1,5-HD[9,10] give exclusively cyclization reaction, 1,4-PD produces unprecedented detected methylene-1,3-cyclobutane units and a large amount of cross-links.

The experimental data were rationalized by density functional theory (DFT) calculations. In particular, intermediates and insertion transition states, relative to the pathways for the ring formation, after a diene insertion, and the competing E insertion reaction, were modeled.

Table 1. Copolymerizations of E with 1,3-BD (A), 1,4-PD (B), and 1,5-HD (C) in the Presence of 1/MAO Catalytic System

run	[E]^c (mol/L)	[comonomer]^d (mol/L)	*t* (min)	yield (g)	X_{com}^{e} ($\times 10^2$)	f_O^{f} ($\times 10^2$)
A^a	1.02	1,3-BD (1.50)	9	1.20	2.1	100
B^b	0.11	1,4-PD (0.50)	90	1.90	2.6	30
C^b	0.11	1,5-HD (0.14)	15	2.00	2.9	100

[a] The polymerization was carried out in dry toluene using 2×10^{-5} mol of **1** and 1×10^{-2} mol of MAO (based on Al) at 50 °C. [b] The polymerization was carried out in dry toluene using 1×10^{-5} mol of **1** and 5.0 mmol of MAO (based on Al) at 50 °C. [c] E concentration in the reaction mixture. [d] Comonomer concentration in the reaction mixture. [e] Fraction of comonomer units in the copolymer chains. [f] Fraction of comonomer leading to cyclized units.

Results

In Table 1, the results of copolymerizations of E with 1,3-BD, 1,4-PD, and 1,5-HD performed in the presence of **1** activated by MAO, are reported. All the samples contain very close concentrations of inserted dienes, though comonomer reactivity increases in the order 1,5-HD > 1,3-BD > 1,4-PD.

NMR Analysis. Figure 1 shows the ^{13}C NMR spectra of samples A, B, and C of Table 1. As expected, the spectrum of sample A, a E/1,3-BD copolymer sample, shows only the signals attributable to a polyethene containing 1,2-cyclopropane and 1,2-cyclopentane units (see Figure 1a).[11−13] The spectrum of sample C, a E/1,5-HD copolymer sample, shows only the resonances

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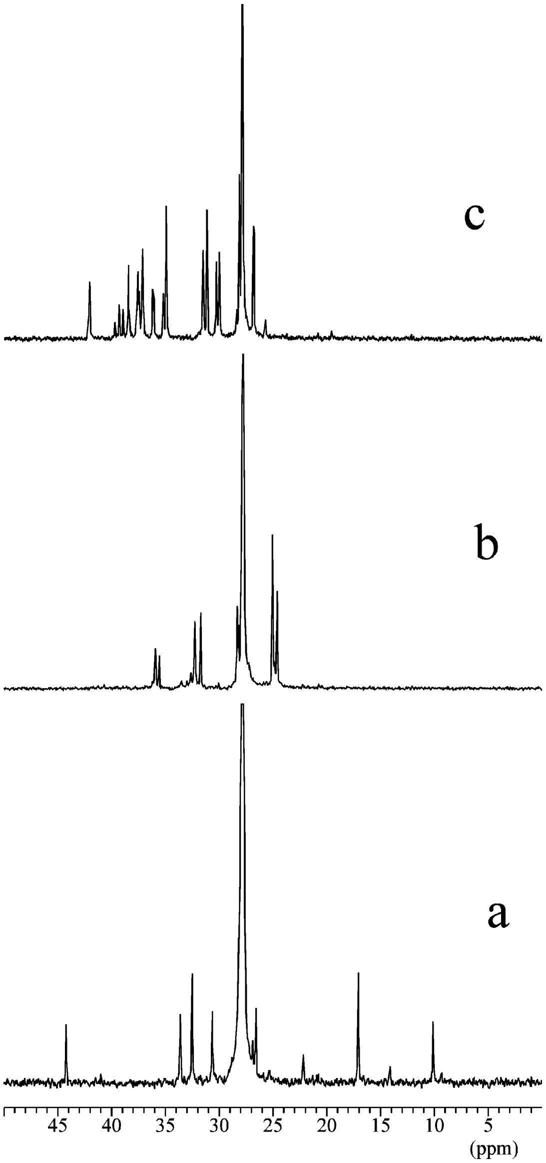


Figure 1. ^{13}C NMR spectra of samples A, B, and C of Table 1.

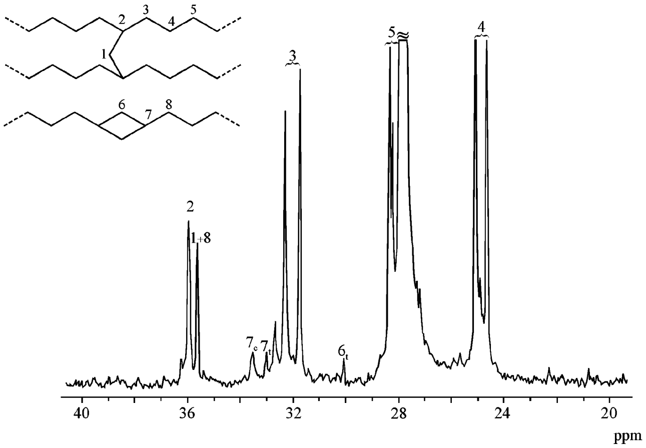
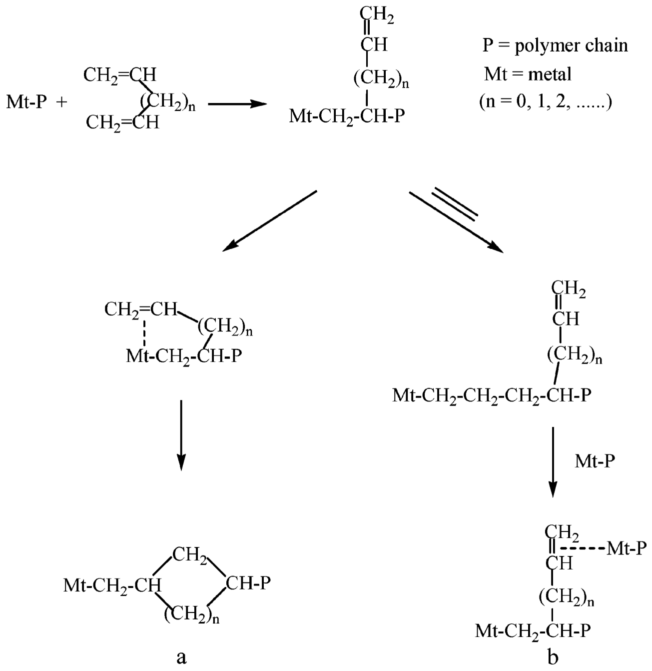
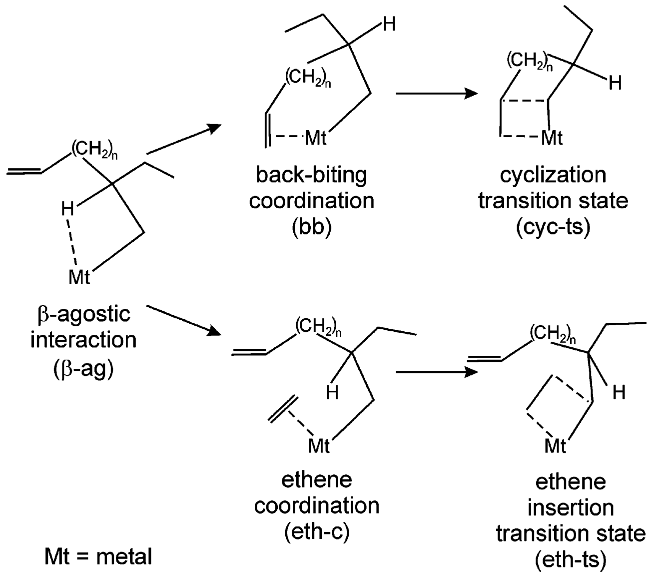


Figure 2. Zoom of ^{13}C NMR spectrum of sample B.

Scheme 1



Scheme 2



expected for a polyethene containing 1,3-cyclopentane units[3−6] (see Figure 1c). As in the case of samples A and C, the spectrum of sample B (see Figure 1b), relative to the E/1,4-PD copolymer, does not present signals in the unsaturated region proving that both double bonds of 1,4-PD units are always involved in an addition reaction. In the saturated region, signals attributable to 1,3-cyclobutane units and resonances relative to cross-linked structures can be observed (see Figure 2).

The resonances of these structural units have been attributed on the basis of the data reported in the literature for carbon in similar environments,[3,11,17] by distortionless enhancement by polarization transfer 90 and 135 (DEPT-90 and DEPT-135) ^{13}C NMR experiments, and by using additivity rules .[18−20]

1,3-Cyclobutane units arise from 1,2-addition of 1,4-PD into a metal−polymeryl σ-bond followed by coordination and intramolecular insertion of a pendant vinyl group. Analogously, it occurs for 1,3-BD and 1,5-HD (see Scheme 1, pathway a). Cross-links likely arise from coordination of a pendant double bond, of 1,4-pentadiene units inserted in a polymer chain, to another catalytic center followed, by insertion in other propagating chain (see Scheme 1, pathway b). It is worth noting that while

1,3-BD and 1,5-HD insert in the polymer chains giving exclusively cyclization reaction, the insertion of 1,4-PD leads to only 30% of 1,3 cyclobutane units and almost 70% of cross-links.

Molecular Modeling Studies. The origin of the easy formation of cyclopropane and cyclopentane rings compared to the formation of cyclobutane rings have been investigated with a theoretical approach. As reported in refs 13−15, the ring closing mechanism involves a primary diene insertion followed by the backbiting coordination of the double bond of the last diene inserted unit, which would insert in the metal−carbon bond leading to the formation of the ring. The coordination and insertion of the backbiting double bond can, obviously, compete with the coordination and insertion of a new E unit. The competition between these two possible pathways could be responsible of the percentage of rings in the polymer. To rationalize the experimental data reported, intermediates and insertion transition states relative to those possible two pathways were modeled, using DFT methods (see computational details section) for copolymerization of E with 1,3-BD, 1,4-PD, and 1,5-HD in the presence of **1**.

Models. For each copolymerization the minimum energy geometries were calculated for the following:

•the β-agostic interaction intermediates of the terminal growing chain after the diene insertion (β-ag of Scheme 2);

•the backbiting coordination intermediates after the diene insertion (bb);

•the backbiting insertion transition states which correspond to the cyclization transition states (cyc-ts);

•the E coordination intermediates after the diene insertion (eth-c);

•the E insertion transition states (eth-ts).

"A"($n = 0$ in Scheme 2), "B"($n = 1$), and "C"($n = 2$) always refer to intermediates relative to the copolymerization of E with 1,3-BD, 1,4-PD, and 1,5-HD, respectively. Previous inserted units are simulated by the ethyl group bound to the tertiary carbon atom. Mt represents the metal center.

Results. Minimum energy pathways are sketched in Scheme 3, and the energies are also collected in Table 2.

The geometries relative to backbiting coordination and insertion are shown in Figures 3 and 4, respectively. Structures A, B, and C of both figures are relative to the formation of cyclopropane, cyclobutane, and cyclopentane units, respectively.

The energy barrier for the backbiting insertion is $\Delta E^{\neq} = 4.1$, 2.5, and 1.1 kcal/mol for A, B and C, respectively. Thus, it decreases in the order cyclopropane > cyclobutane > cyclopentane, as would have been expected considering that the ring angular strain decreases in the same order. The minimum energy pathways for the cyclization reaction are always related to the formation of trans cycles. Energies corresponding to the formation of cis cycles are higher than those reported for the trans cyclization ($\Delta\Delta E^{\neq} \geq 2.8$ kcal/mol). On the other hand, the coordination and insertion of an ethene molecule seem to be particularly favored in the E−1,4-PD copolymerization. A deeper look shows that the E coordination energy is not strongly different for the three models if compared with the β-agostic intermediate relative to the three growing chains. The main difference between the three models is the lower stability of the backbiting coordination for 1,4-PD (B) with respect to 1,3-BD (A) and 1,5-HD (C). The higher energy of structure B (Figure 2) depends on the conformation of the terminal growing chain presenting a θ_2 dihedral angle of about 0°, which causes a strong non bonding interaction between the metal and the eclipsed carbon atom (Mt−C = 3.04 Å).

Thus, according to our calculations, while the cyclization reaction is clearly favored in E−1,3-BD and E−1,5-HD, the E insertion competes with the cyclization reaction in the E−1,4-PD copolymerization ($\Delta\Delta E^{\neq} \approx 0$ kcal/mol), due to the low stability of the backbiting coordination intermediate.

Conclusions

Ethene-α,ω-diene copolymerizations were performed in the presence of highly hindered catalytic precursor

Scheme 3

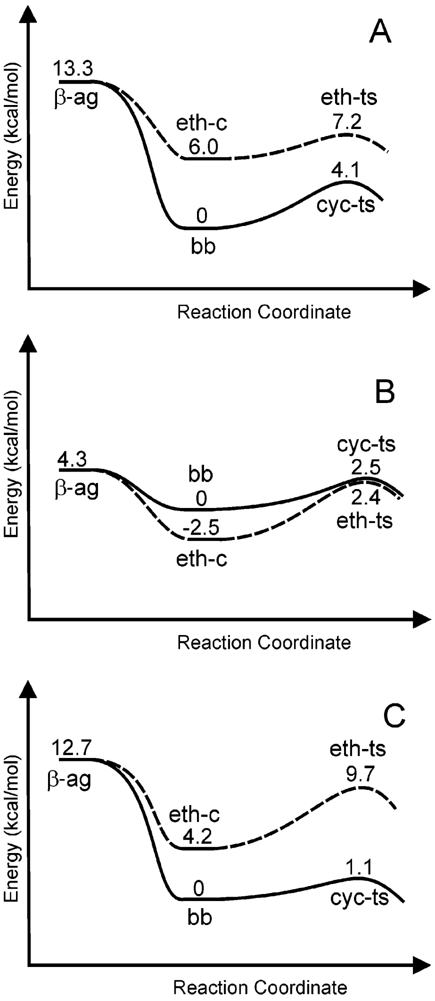


Table 2. Calculated Energies (kcal/mol) for the β-Agostic Interaction Intermediates of the Terminal Growing Chain (β-ag), the Backbiting Coordination Intermediates (bb), the Cyclization Transition States (cyc-ts), the E Coordination Intermediates (eth-c), and the E Insertion Transition States (eth-ts)[a]

	A	B	C
β-ag	13.3	4.3	12.7
bb	0	0	0
cyc-ts	4.1	2.5	1.1
eth-c	6.0	−2.5	4.2
eth-ts	7.2	2.4	9.7

[a] A, B, and C refer to geometries relative to the copolymerization of E with 1,3-BD, 1,4-PD and 1,5-HD, respectively.

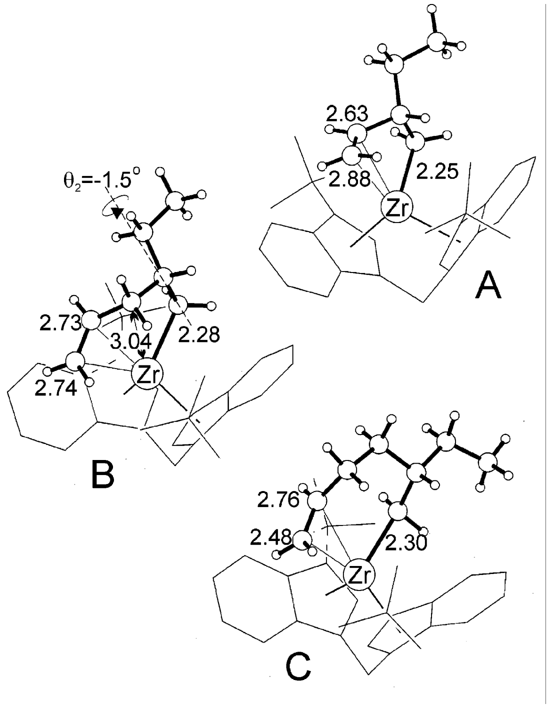


Figure 3. Backbiting coordination intermediates. Structures A, B, and C are relative to the formation of cyclopropane, cyclobutane and cyclopentane units, respectively.

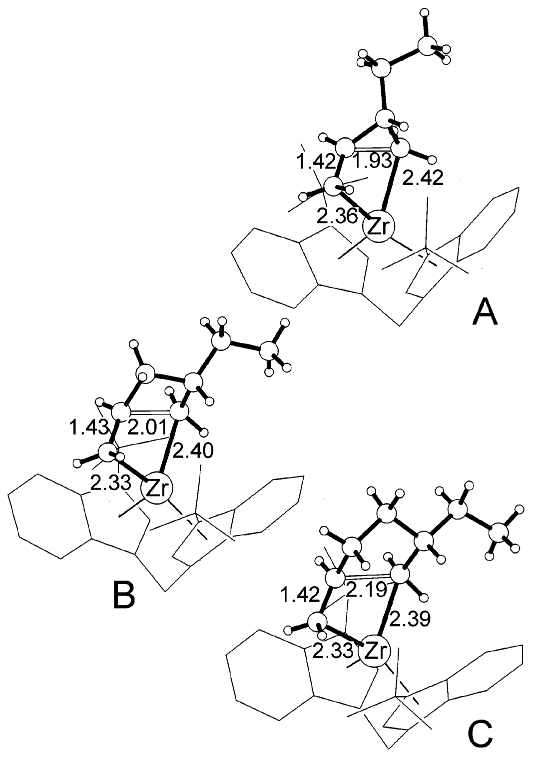


Figure 4. Cyclization transition states. Structures A, B, and C are relative to the formation of cyclopropane, cyclobutane and cyclopentane units, respectively.

1. Both 1,3-BD and 1,5-HD generate, under specific conditions, only cyclic units, rising from 1,2-diene primary insertion, followed by backbiting coordination and insertion. Similarly 1,4-PD gives 1,2-primary insertion, followed for 30% by coordination and insertion of the backbiting and for 70% by the insertion of ethene units. The pendant unreacted double bond coordinates to another catalytic center, generating cross-links. The experimental results can be related to the low stability of the backbiting coordination intermediate of the 1,4-PD inserted unit, as shown by molecular modeling studies.

Experimental Part

General Procedure. All 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-BD and E were purchased from Società Ossigeno Napoli (SON) and used without further purification. MAO was purchased from Witco and used as a solid after distillation of solvent. 1,4-PD and 1,5-HD were purchased from Aldrich and purified by distillation in the presence of Al(*i*-Bu)$_3$. *rac*-[CH$_2$(3-ter-butyl-1-indenyl)$_2$]-ZrCl$_2$, was synthesized according to the literature.[21]

Run A. In a 250 mL glass autoclave, thermostated at 50 °C (see Table 1), 100 mL of toluene, MAO (580 mg, 10.0 mmol, based on Al), 1,3-BD, and the catalyst (20 μmol) were introduced. The autoclave was fed with E (5 atm) and kept under magnetic stirring over the run, and then it was vented and the copolymer was recovered by precipitation with ethanol/HCl and dried under reduced pressure at room temperature.

Runs B and C. In a 100 mL glass flask 0.290 g (5.0 mmol, based on Al) of MAO and 38 mL of dry toluene were charged. The flask was thermostated at 50 °C and the inert atmosphere was removed and replaced with E at 1 atm. The amount of diene reported in Table 1 was charged in the flask. E concentration in the liquid phase was calculated by Lewis and Luke's equation in conjunction with the fugacity function chart of E as reported in the literature.[22] The concentration of 1,4-PD was considered constant during all the run of polymerization. The polymerization started by injecting a solution of 1×10^{-5} mol of **1** in 2 mL of dry toluene. The copolymers were recovered by precipitation with ethanol/HCl and dried under reduced pressure.

Polymer Analysis. 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 tetrachlorodideuteroethane. Hexamethyldisiloxane was used as internal chemical shift reference.

The resonances were assigned on the base of the data reported in the literature for carbons in similar environments,[3,11,17] on the DEPT (distortionless enhancement by polarization transfer) ^{13}C NMR experiment and on additivity rules.[18–20]

Copolymer compositions were calculated by summarizing the concentration of following resonances:

$$E = [{}^1/_2(\Sigma \text{ saturated carbons} - (n/2)\,\Sigma \text{ methine carbons})]/[{}^1/_2(\Sigma \text{ saturated carbons} - (n/2)\,\Sigma \text{ methine carbons}) + (n/2)\,\Sigma \text{ methine carbons}]$$

$$D = [(n/2)\,\Sigma \text{ methine carbons}]/[{}^1/_2(\Sigma \text{ saturated carbons} - (n/2)\,\Sigma \text{ methine carbons}) + (n/2)\,\Sigma \text{ methine carbons}]$$

where n = 4, 5, and 6 for 1,3-BD, 1,4-PD, and 1,5-HD, respectively.

Computational Details. Stationary points on the potential energy surface were calculated with the Amsterdam density functional (ADF) program system,[23] developed by Baerends et al.[24,25] 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.[26] and augmented in a self-consistent manner with Becke's[27] exchange-gradient correction and Perdew's[28] correlation gradient correction. Geometry optimizations were terminated if the largest component of the Cartesian gradient was smaller than 0.002 au.

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Supporting Information Available: Table giving the Cartesian coordinates of all modeled structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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