

Theoretical Studies of Ethylene Polymerization Reactions Catalyzed by Zirconium and Titanium Chelating Alkoxide Complexes

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Received March 17, 1997. Revised Manuscript Received June 2, 1997[⊗]

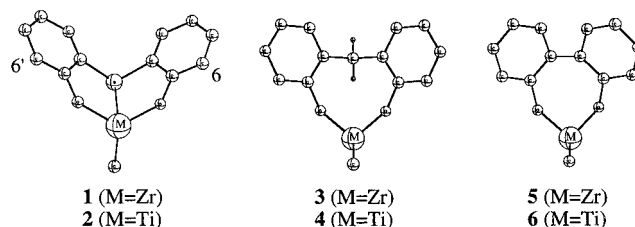
Abstract: Ethylene polymerization catalyzed by zirconium and titanium chelating alkoxide complexes has been studied using a density functional method. Activation barriers of 6.4 and 7.4 kcal/mol are found for the titanium and zirconium sulfur-bridged catalysts, respectively. The Zr/Ti CH₂- and directly-bridged catalysts have higher insertion barriers of 10–15 kcal/mol. For the S-bridged systems, there is a strong interaction between the metal and the sulfur bridge, which leads to a less stabilized π -complex and a lower activation energy. The larger exothermicity to the γ -agostic direct product by 5 kcal/mol in the titanium case compared to zirconium for all three catalysts (S-, CH₂-, and directly-bridged) is suggested to be one of the reasons why the barriers for titanium are lower than for zirconium. Flexible ligands with the ability to donate may be one method for developing more active alternative catalysts as the flexible ligand competes with the approaching olefin. The more weakly bound olefin leads to a lower activation barrier.

Introduction

The transition-metal-catalyzed olefin polymerization reaction has been an important subject of study to both theoreticians¹ and experimentalists² over the last several years. Homogeneous metallocene complexes of early transition metals, typically together with a cocatalyst, methylaluminoxane, have received special attention because of their high activities and narrow molecular weight distributions. Renewed efforts for the development of alternative catalysts have recently been rewarded by the discovery of new classes of catalysts, diimine-M(II) (where M = Ni and Pd)³ and Ti and Zr chelating alkoxide catalysts,⁴ both showing high polymerization activities.

We have studied the mechanism of the diimine-M(II)-catalyzed ethylene polymerization reactions in our previous papers^{3b–d} and compared those with the analogous metallocene

Scheme 1



systems.⁵ This paper is a continuation of our olefin polymerization project, and its goal is to study the mechanism of the ethylene polymerization reaction catalyzed by the newly discovered Ti and Zr chelating alkoxide complexes⁴ and to compare the results with those for metallocene systems.⁵

The general structures of the alkoxide complexes used in the polymerization are depicted in Scheme 1. Experimentally,⁴ the following results are known:

(1) The Zr-based catalysts are less active than Ti-based counterparts.

(2) For the titanium catalysts, the substitution of the S-bridge in the Ti/S bridged system **2** with a CH₂-bridge (**4**) dramatically reduces the activity of the complex; the measured rates of reaction are 4740 and 504 PE kg/(mol of catalyst·h) (where PE = polyethylene) for the S-bridged and 390 and 180 PE kg/(mol of catalyst·h) for the CH₂-bridged TiCl₂ and Ti(CH₂Ph)₂ systems, respectively. The directly-bridged systems also were found to be less active.

(3) In the ZrCl₂-based directly-bridged systems, the polymerization activity increases with the increase of the steric hindrance of the 6,6'-di-SiR₃ on the alkoxide ligand (see the position of the substituents SiR₃ in Scheme 1); the rates of reaction are 152, 203, and 275 PE kg/(mol of catalyst·h) for SiMe₃, SiMePh₂, and SiPh₃, respectively. In contrast to the ZrCl₂-based systems, the rate of reaction for the Zr(CH₂Ph)₂-based directly-bridged systems dramatically decreases from 1050

[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1997.

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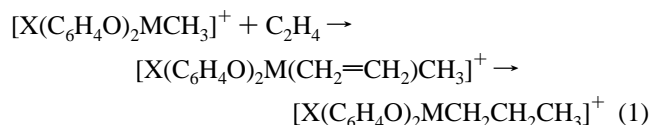
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to 0 kg/(mol of catalyst·h) upon going from the less sterically hindered SiMePh₂ substituent to SiPh₃.

However, these experiments leave several interesting questions unresolved. (i) Why are the Ti-based complexes more active than their Zr counterparts? (ii) Why are S-bridged complexes more active than CH₂- or directly-bridged systems? (iii) What is the role of the chelating alkoxide ligands? (iv) What is the role of the steric effects of the substituents on the alkoxide fragment? To answer to some of these questions, we have performed density functional calculations on the chain initiation reaction



where M = Ti and Zr and X = S, CH₂, and nothing (directly-bridged). Hopefully, these predictions can be used as a model for chain propagation. The experimental authors⁴ have pointed out that the active catalyst may not be of the form shown in Scheme 1, but rather a different structure generated from decomposition of these catalysts, but our calculations are based on the species shown in Scheme 1.

II. Computational Details

The Gaussian94 program⁶ was used for all the calculations. Geometries and energies of the reactants, intermediates, transition states, and products of the reaction 1 were calculated using the gradient-corrected hybrid density functional method B3LYP,⁷ which has been shown to be quite reliable in both geometry and energy.⁸ In this calculation, we used the LANL2DZ basis set which includes a double- ζ valence basis set (8s5p5d)/[3s3p2d] and (8s6p4d)/[3s3p2d] for Ti and Zr atoms with the Hay and Wadt effective core potential (ECP) replacing core electrons up to 2p and 3d,⁹ respectively, and the Huzinaga–Dunning valence double- ζ quality basis set¹⁰ for the remaining atoms, except for the S atom for which we also used the LANL2DZ basis set with the Hay and Wadt ECP. This basis set is referred to as basis set I. To examine the importance of polarization d functions on the S atoms, we recalculated the energetics of the reactant, intermediate, transition state and product of reaction 1 for M

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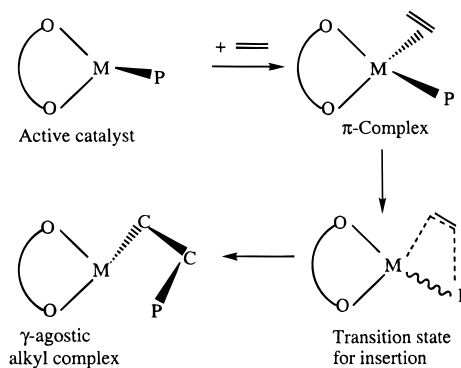
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Scheme 2. Cossee Mechanism for the Transition-Metal-Catalyzed Ethylene Polymerization Reactions



= Ti at the basis set I optimized geometries using the basis set I+d(S), basis set I plus a polarization d function (exponent 0.503¹¹) on S. No symmetry restrictions were placed on any species, and the reported symmetries of the molecules were not assumed. No systematic vibrational analysis was carried out for identification of the number of imaginary frequencies or determination of zero point energy.

III. Results and Discussion

The most widely accepted mechanism for olefin polymerization by transition metal catalysts is due to Cossee¹² (or a modified Cossee¹³). The insertion mechanism starts from the active catalyst, proceeds via a π -complex and a migratory insertion transition state, and leads to the direct product, the γ -agostic alkyl complex as depicted in Scheme 2. In this paper we will follow this mechanism. The reactant will be denoted by **a**, the olefin π -complexes with H₂C=CH₂ perpendicular and parallel to the M-CH₃ bond by **b** and **b'**, respectively, the migratory insertion transition state (TS) by **c**, and the direct product γ -agostic species by **d**. The Zr/S-bridged species are called **1**, Ti/S-bridged **2**, Zr/CH₂-bridged **3**, Ti/CH₂-bridged **4**, Zr/directly-bridged **5** and Ti/directly-bridged **6**, as indicated in Scheme 1.

The calculated relative energies of the reactant, intermediates, transition states, and products of the reaction 1 for all systems studied are given in Table 1, and the optimized geometries are presented in Figures 1–3 for the catalytic systems **1** and **2**, **3** and **4**, and **5** and **6**, respectively.

A. Zirconium and Titanium Sulfur-Bridged Complexes. The reactants, **1a** and **2a**, for the Zr and Ti sulfur-bridged catalysts, respectively, were found to possess C_s symmetry as depicted in Figure 1. All of the C–C bond lengths for the phenyl rings are similar in both cases and are calculated to be 1.407 ± 0.008 Å. The bond distances for Zr–S and Ti–S of 2.788 and 2.708 Å and the calculated M–S overlap populations, 0.20e (M = Zr) and 0.19e (M = Ti), are indicative of the existence of metal–sulfur interactions. The O–M–O angles of 121.8° (Zr) and 120.6° (Ti) are smaller than the bite angle of 139.4° in ZrCp₂.⁵ In **1a** and **2a**, the methyl ligand is nearly trans to the alkoxide ligands. One can conceive also a cis-like structure, corresponding structurally to the position of the methyl in **1b** and **2b** in Figure 1, to be discussed later. However, optimization for cis structures converged to the trans structures above, indicating that the cis structures are the only structures

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Table 1. Energies for the Insertion Step in the Ethylene Polymerization Reaction Catalyzed by Zirconium and Titanium Diimine Complexes with S, CH₂, and Direct Bridges^a

	S-bridged		CH ₂ -bridged		directly-bridged	
	Zr 1	Ti 2	Zr 3	Ti 4	Zr 5	Ti 6
a (reactant + C ₂ H ₄)	0.0	0.0	0.0 (+1.1) ^b	0.0	0.0	0.0
b' (planar π -complex)	-21.3	-19.5				
b (perp π -complex)	-22.0	-21.4 (-18.7)	-25.0 (-23.5)	-26.7	-24.9	-26.8
c (transition state)	-14.6	-15.0 (-11.6)	-10.5 (-9.8)	-16.0	-9.1	-15.8
d (γ -agostic)	-28.5	-30.1	-27.6	-32.2	-27.5	-33.0

^a All energies are at the B3LYP/LANL2DZ level in kcal/mol relative to the reactant + ethylene. Results are for the trans approach of olefin with respect to the alkoxy ligands. Numbers in parentheses are for cis approach. ^b For this reactant, two structures could be found. The reference was taken for the lower energy structure with the methyl cis to the alkoxy, shown in Figure 2. The number in parentheses here is for the structure with the methyl trans to the alkoxy.

for the reactants. Actually, the potential surface is very flat in this region and the methyl ligand can swing down easily, when ethylene approaches.

Two π -complexes, **b** and **b'**, with H₂C=CH₂ perpendicular and parallel, respectively, to the M-CH₃ bond, were found for these systems. The complexation energies of 22.0 (**1b**) and 21.3 (**1b'**) kcal/mol for zirconium and 21.4 (**2b**) and 19.5 (**2b'**) kcal/mol for titanium, as shown in Table 1, indicate that the perpendicular form **b** is more stable by up to 2 kcal/mol, presumably due to the smaller steric repulsion. Although we did not optimize the structure of the rotational transition state, the barrier from **b'** is expected to be extremely small, as was shown previously for diimine-Pd(II)^{3c} systems. Upon coordination of ethylene, the M-S distance has dramatically increased for Zr from 2.788 Å in the reactant (**1a**) to 3.213 (**1b**) or 3.272 (**1b'**) Å in the π -complexes and for titanium 2.708 Å (**2a**) to 3.241 (**2b**) and 3.286 (**2b'**) Å. This bond stretch is consistent with the decrease in the M-S overlap populations, 0.20e (**1a**) to 0.10e (**1b**) for Zr and 0.19e (**2a**) to 0.05e (**2b**) for Ti. Thus, the coordination of ethylene to the metal center is accompanied by the dramatic elongation and, consequently, weakening of the M-S bond. This effect can be understood by reviewing the well-known fact that the T₄ structure is the most stable for ML₄ complexes (M = Ti and Zr) but not for the corresponding ML₅ compound. Therefore, upon coordination of ethylene, the transition metal center partially releases the most weakly coordinated ligand and tries to keep its favorable tetrahedral environment. The slightly longer M-S bond distance in **b'** than in **b** is the result of steric repulsion between the incoming ethylene and the S atom in structure **b'**.

From the π -complex **b**, the reaction proceeds through the transition state **c** for ethylene insertion with C_s symmetry to reach the γ -agostic intermediate **d**. Since the TS has a parallel olefin, the path of reaction is expected to pass through the vicinity of the parallel complex **b'**. This migratory insertion step results in breaking of the M-alkyl σ -bonds and M-C₂H₄ π -bonds and formation of the new M-C α and C β -C γ σ -bonds. At the TS **c**, the C β -C γ bond length is closer to that of the π -complex **b** (about 0.05 Å shorter) than at the intermediate **d** (about 0.15 Å longer), and the M-alkyl bond has been stretched by only up to 5% from the π -complex. The forming C α -C β bond distance is still 0.6 Å longer than in the intermediate. These indicate that the TS is early in nature. On the other hand, the stretched M-S bond distance in the π -complex **b** is back to nearly normal in the TS **c** and more so in the intermediate **d**. A

substantial γ -agostic (if seen as the insertion product, or α -agostic if seen as the π -complex) interaction seems to be taking place in the TS, indicated by a long C-H distance of 1.125 Å for both **1c** and **2c**, which are longer than 1.115 and 1.111 Å in the insertion products **1d** and **2d**. The activation barrier calculated relative to the lower of the two π -complexes is 7.4 and 6.4 kcal/mol for the zirconium and titanium systems, respectively.

There are possibly two different reaction pathways that can be followed from the reactant; olefin can approach the metal cis or trans to the alkoxy ligands. In the actual polymerization, unless one side is energetically much less favored than the other, propagation will alternate between cis and trans addition. Olefin approaching cis implies that the alkyl group is trans and similarly olefin approaching trans requires the alkyl group (methyl in initiation) to be cis. As shown in Table 1, calculations indicated that, although the cis olefin complex is energetically higher than the trans complex by 2.7 kcal/mol, the effective barrier height to the transition state is only 0.7 kcal/mol higher for the titanium sulfur-bridged catalyst. It is reassuring that the cis addition is not much more difficult than the trans addition since polymer propagation must alternate between cis and trans addition. Thus, in most of the other complexes, we have chosen to study only the lower energy trans addition.

The direct product formed in this reaction is the γ -agostic species, **1d** and **2d**. The γ -agostic Zr complex **1d** has a relatively weak agostic interaction with a C γ -H^{agostic} distance of about 1.115 Å (vs the normal C-H bond distance of ca. 1.09 Å at the same level of theory) and a relatively long Zr-H^{agostic} bond distance of 2.459 Å. This C-H distance is shorter, and therefore, the γ -agostic interaction must be weaker than in the TS **1c**. A similar trend emerges for the titanium sulfur-bridged species. In the γ -agostic complexes, one also notices that C α -C β and C β -C γ bond distances, 1.595 and 1.577 Å for **1d** and 1.600 and 1.567 Å for **2d**, are much longer than the normal: 1.559 and 1.547 Å for an analogue (not shown) of **2d** with the all-trans alkyl group trans to S. This indicates that the C α -C β and C β -C γ bonds strongly interact with the transition metal center and that the origin of the stability of **1d** and **2d** complexes is more likely to be the C β -C γ β -agostic interactions rather than the C-H γ -agostic interaction. Similar results have been found by Koga and Morokuma,¹⁴ and the origin of these agostic C-C \cdots M interactions has been discussed in detail. The γ -agostic complexes, **1d** and **2d**, lie 28.5 and 30.1 kcal/mol below reactants, respectively.

The search for expected β -agostic complexes resulted in the γ -agostic structures **1d** and **2d**. Different β -agostic structures could be obtained, when the optimization is performed by at first rotating the alkyl group around the M-C bond, as shown in Figure 1 as **1d'** and **2d'**. The energies of these β -agostic structures are +0.2 (Zr) and -1.2 kcal/mol (Ti), relative to the corresponding γ -agostic structures; the situation is very different from zirconocene catalysts where β -agostic structures are typically 5-6 kcal/mol lower in energy than the γ -agostic structures. The reason for this unexpected instability of β -agostic complexes may be attributed to a larger deviation from the ideal tetrahedral environment around the metal center caused by the alkoxy ligands.

Comparing all the structures (**a-d**) in Figure 1 between Zr and Ti species, one recognizes that they are qualitatively very similar. The major differences are in the bond distances around the metal center. The M-O distances for Ti species are consistently nearly about 0.17 Å shorter than in the corresponding Zr species, and the M-C σ bond distances are also about

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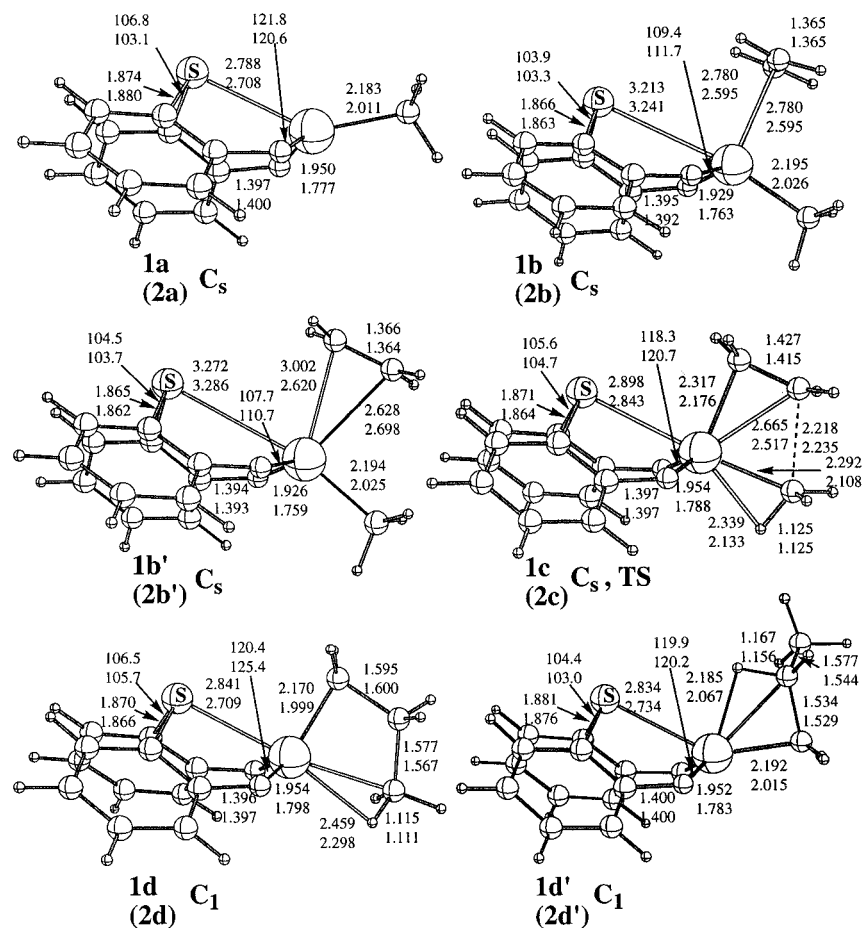


Figure 1. Important geometrical parameters of the S-bridged reactant (a), perpendicular π -complex (b), parallel π -complex (b'), insertion transition state (c), and γ -agostic (d), and β -agostic product (d') for the zirconium (1) and titanium (2) catalysts at the B3LYP/LANL2DZ level. The upper numbers are for the Zr and the lower numbers for Ti.

0.17 Å shorter. The $M\cdots C \pi$ and $M\cdots H^{\text{agostic}}$ distances are also shorter by a comparable amount. These results reflect the intrinsically smaller size of Ti in comparison with Zr. However, the smaller size does not seem to cause any visible effect of steric congestion on the geometries of any species discussed in Figure 1.

The inclusion of a polarization d function on the S atom for Ti species **2** changed the energetics only slightly, and the conclusions are unaltered. With the basis set I+d(S), the calculated π -complexation energy, migratory insertion barrier, and exothermicity changed +1.1, +0.5, and -0.2 kcal/mol, respectively, relative to those of the basis set I.

B. Zirconium and Titanium CH_2 -Bridged and Directly-Bridged Complexes. For CH_2 -bridged Zr (**3**) and Ti (**4**) systems, the important geometries of the reactants, intermediates, transition states, and products are shown in Figure 2, and for the directly-bridged Zr (**5**) and Ti (**6**) systems, the corresponding geometries are in Figure 3. In this section, we will discuss the geometrical features for these systems, mainly focusing on comparisons with the S-bridged Zr (**1**) and Ti (**2**) systems. There are several major geometrical differences between the three different bridged systems. In all of the CH_2 -bridged species in Figure 2, the $M\cdots\text{CH}_2$ distance is long, indicating that there is no interaction between them. This is also consistent with the small $M\text{---CH}_2$ overlap population (about 0.002e) for all the species.

The $\text{C}^{\text{phenyl}}\text{---S---C}^{\text{phenyl}}$ angle (e.g., 106.8° in **1a** and 103.1° in **2a**) is smaller than the $\text{C}^{\text{phenyl}}\text{---C---C}^{\text{phenyl}}$ angle (e.g., 116.5° in **3a** and 116.0° in **4a**), and therefore, the angle between the two phenyl planes is smaller in **1** and **2** than in **3** and **4**. Two

phenyl groups in **5** and **6**, directly connected and therefore intrinsically parallel to each other, are twisted slightly from each other around the $\text{C}^{\text{phenyl}}\text{---C}^{\text{phenyl}}$ bond (e.g., the $\text{O}(\text{C})\text{---C---C}(\text{O})$ dihedral angle is 38.5° in **5a** and 34.1° in **6a**) to reduce the steric repulsion. Reflecting the different structures of the bridge, the chelating O-M-O bite angle of the alkoxides is largest for the S-bridged systems (e.g., 121.8° for **1a** and 120.6° for **2a**), followed by the CH_2 -bridged systems (e.g., 98.6° for **3a** and 103.4° for **4a**), and is the smallest for the directly-bridged system (e.g., 90.9° for **5a** and 96.1° for **6a**).

As discussed above, for S-bridged π -complexes, the perpendicular structure **b** was found to be up to 2 kcal/mol more stable than the parallel **b'**, and we will not study the structure **b'** for CH_2 - and directly-bridged systems. As seen in Figure 2, the CH_2 -bridged ethylene Zr complex **3b** is nearly symmetric, while the corresponding Ti complex **4b** is nonsymmetric with the $\text{Ti}\cdots\text{C}$ distances of 2.479 and 2.689 Å. Of the two possible $M\text{---olefin}$ interaction contributions, electron donation from the occupied $\pi(\text{C}=\text{C})$ orbital into a vacant $M(\sigma)$ orbital and back-donation from the metal center into the empty $\pi^*(\text{C}=\text{C})$ orbital, for group 4 metals such as Ti(IV) and Zr(IV) without occupied d_{π} orbitals, the main contributor is the $\pi(\text{C}=\text{C}) \rightarrow M(\sigma)$ component, which may lead to either symmetrical or nonsymmetrical π -complexes. The nonsymmetric structure for **4b** is due to the smaller size of Ti d orbitals which favors the one-center interaction. These two π -complexes are calculated to be 25.0 (Zr) and 26.7 (Ti) kcal/mol below reactants. The directly-bridged ethylene complexes **6b** and **5b** are nonsymmetric, reflecting the twisted alkoxide ligand, with the asymmetry much larger again for Ti than for Zr.

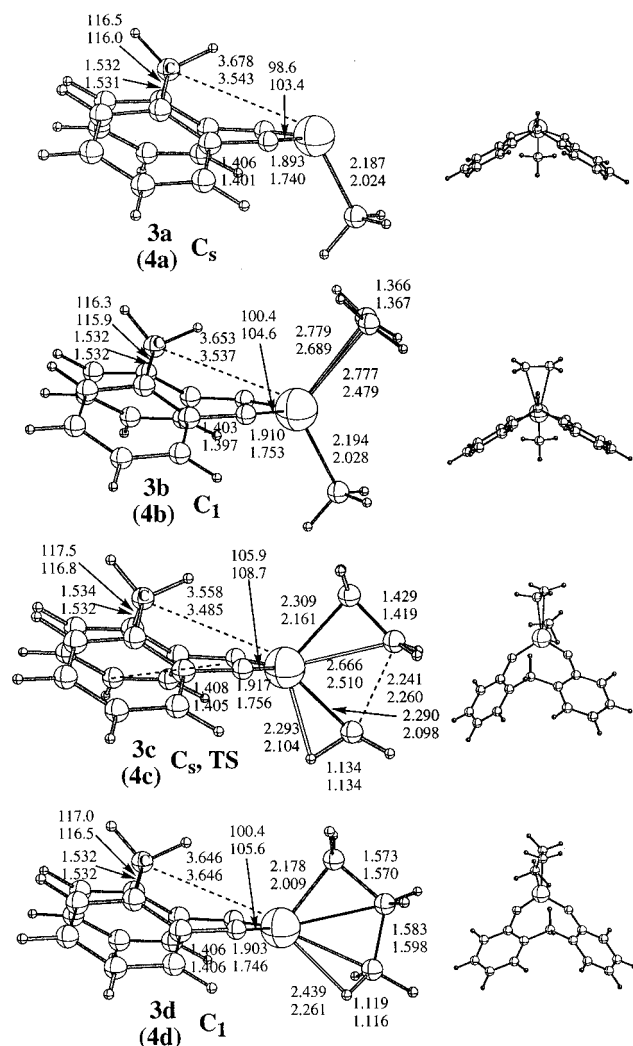


Figure 2. Important geometrical parameters of the CH₂-bridged reactant (a), perpendicular π -complex (b), insertion transition state (c), and γ -agostic product (d) for the zirconium (1) and titanium (2) catalysts at the B3LYP/LANL2DZ level. The upper numbers are for the Zr and the lower numbers for Ti. Other perspectives are also shown.

From the π -complexes, the reaction proceeds through the migratory insertion TS **c** and leads to the γ -agostic complex **d** as in the previous cases. The bond distances indicate that the TSs for CH₂- and directly-bridged systems, **3–6c**, are slightly earlier than those for S-bridged systems. The agostic interaction between C γ –H bond and metal center at the TSs **3–6c** is stronger than in the S-bridged system, as indicated by the C–H_{agostic} bond lengths of 1.134 Å in the former which is about 0.02 Å longer than the latter. The barriers for migratory insertion calculated from the corresponding π -complexes, 14.5 kcal/mol for CH₂-bridged Zr, 15.8 kcal/mol for directly-bridged Zr, 10.7 kcal/mol for CH₂-bridged Ti, and 11.0 kcal/mol for directly bridged Ti, are substantially higher than those for the S-bridged systems.

For the γ -agostic intermediate **d**, the structures of the metal–propyl moiety for CH₂- and directly-bridged systems are very similar to those of the corresponding S-bridged systems. For CH₂-bridged complexes, the β -H-agostic structure for Zr exists at higher energy than the γ -agostic structure **3d**. However, the β -H-agostic structure does not exist and converges to the γ -agostic structure for CH₂-bridged Ti and directly-bridged Zr and Ti systems.

C. Comparison of the Mechanism of Reaction 1 among S-, CH₂-, and Directly-Bridged Complexes. The “Bridge”

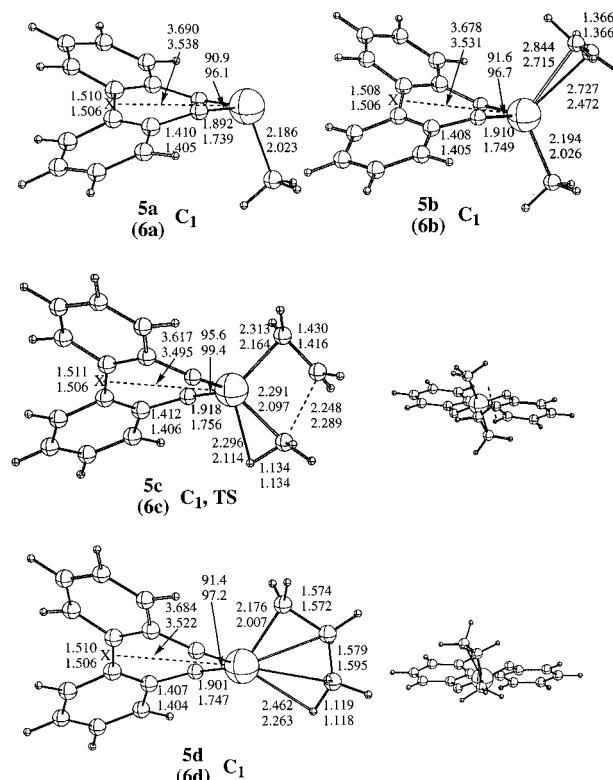


Figure 3. Important geometrical parameters of the directly-bridged reactant (a), perpendicular π -complex (b), insertion transition state (c), and γ -agostic species (d) for the zirconium (1) and titanium (2) catalysts at the B3LYP/LANL2DZ level. The upper numbers are for the Zr and the lower numbers for Ti. Other perspectives are also shown.

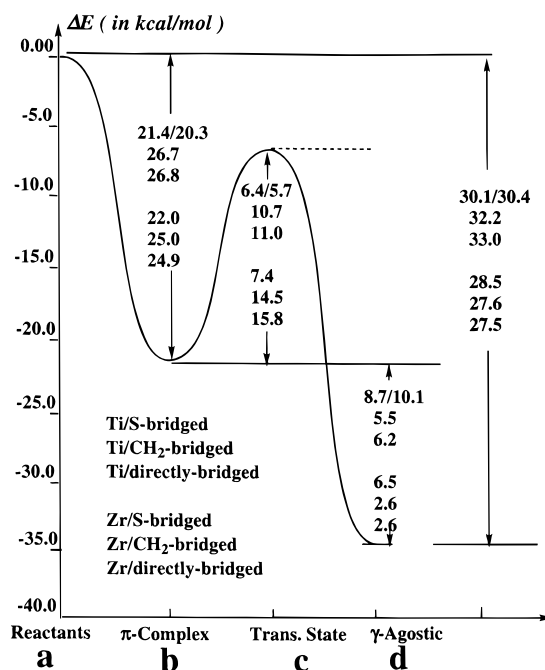


Figure 4. Schematic representation of the potential energy surfaces of reaction 1 for the complexes **1–6**. The relative energies are in kcal/mol at the B3LYP/LANL2DZ level, and the numbers after the slash are for a slightly larger basis set, LANL2DZ+d(S).

Effect. As seen from above discussions and Table 1 and Figure 4, reaction 1 for the S-, CH₂-, and directly-bridged complexes proceeds via the π -complex and migratory insertion transition state and leads to the γ -agostic complex. Table 1 shows that there is an increase of 3–5 kcal/mol in the complexation energy upon going from S-bridged systems to CH₂- or directly-bridged

ones. These changes are about 2 kcal/mol larger for Ti than Zr systems. One can explain these results by comparing the geometries of the reactants and the corresponding π -complexes given in Figures 1–3. As seen from these figures and in the above discussions, there is an attractive interaction between the metal center and the S-bridge in the reactants **1a** and **2a**, while a similar interaction is absent in the complexes **3a–6a**. The calculated Zr–S, Zr–CH₂, and Zr–X (X: the midpoint between the two directly connected carbon atoms) distances are 2.708, 3.543, and 3.538 Å and 2.788, 3.678, and 3.690 Å, for the Ti- and Zr-based S-, CH₂-, and directly-bridged complexes, respectively, indicating a substantial interaction between the metal and sulfur in the reactants. However, in the π -complexes, the M–S distance has dramatically increased to 3.241 Å in **2b** and 3.213 Å in **1b**. In other words, *coordination of ethylene to the metal center of the S-bridged reactants is accompanied by large elongation and, consequently, destabilization of the M–S bond*, which must be the main reason the stability of the π -complexes of the S-bridged systems is smaller than that of the CH₂- or directly-bridged ones, where the M-bridge bond is absent in both the reactants **3a–6a** and the π -complexes **3b–6b**.

The comparison of the relative energies of the transition states in Table 1 shows that the transition state for the S-bridged system in comparison with the CH₂- and directly-bridged systems is about 1 kcal/mol less stable for Ti and is about 4–5 kcal/mol more stable for Zr. The barrier heights relative to the π -complexes are 6.4, 10.7, and 11.0 kcal/mol and 7.4, 14.5, and 15.8 kcal/mol for the Ti- and Zr-based S-, CH₂-, and directly-bridged complexes, respectively. From these energies, we might conclude

(1) The complex with the S-bridge is much more reactive than the CH₂- or directly-bridged ones for a given metal atom. In the case of Ti-based systems, this lower barrier is mainly the result of destabilization of the π -complex of S-bridged systems compared to CH₂- or directly-bridged ones, which in turn is the result of the existence of the M/S-bridging interaction in the S-bridged reactants. On the other hand, in the Zr-based systems, this lower barrier is the result of both the destabilization of the π -complex and the stabilization of the transition state for the S-bridged systems compared to CH₂- or directly-bridged ones.

(2) In general, Ti-based alkoxides are more active catalysts than their Zr counterparts. Both of these conclusions are in agreement with the experiment.⁴ However, the fact that the Zr-based alkoxide species is completely inactive in experiment remains a mystery to us since our predicted activation energy is only slightly larger than for the highly active titanium system.

The calculated differences in the barrier heights (relative to the π -complex) between the Ti and Zr systems are also consistent with the differences in the calculated exothermicities from the π -complexes to the γ -agostic products. As seen in Table 1, for the three Zr catalysts, **1**, **3**, and **5**, the exothermicities for the γ -agostic products are 6.5, 2.6, and 2.6 kcal/mol, respectively, whereas for their Ti counterparts, **2**, **4**, and **6**, they are 6.7, 5.5, and 6.2 kcal/mol, respectively. In other words, the process π -complex \rightarrow γ -agostic product is 0.2, 2.9, and 3.6 kcal/mol more exothermic for S-, CH₂-, and directly-bridged Ti complexes than for Zr ones. This trend in the difference of exothermicity is parallel to the trend in difference of barrier height: 1.0 (S-bridged) < 3.8 kcal/mol (CH₂-bridged) < 4.8 kcal/mol (directly-bridged). These results are in agreement with available experiment⁴ and the Hammond postulate.¹⁵

D. Comparison with Metallocene-Catalyzed Ethylene Polymerization Reaction. As mentioned in the Introduction,

metallocene-catalyzed ethylene polymerization reactions have been the focus of intensive investigations over the past decade,^{1,2,16} and numerous interesting results have been accumulated. Here, we will compare our theoretical results presented above for the ethylene polymerization reaction catalyzed by chelating alkoxide complexes with those catalyzed by metallocene for both Ti and Zr. First, let us very briefly summarize the results on the polymerization mechanism catalyzed by the silylene-bridged methylbis(cyclopentadienyl)-titanium and zirconium [(SiH₂)Cp₂MCH₃]⁺ reported by our group.^{1a,5,17}

The reaction involves the coordination of an olefin to form a π -complex, followed by olefin insertion into the M–C _{α} bond via a four-center transition state to form the direct product γ -agostic complex. Then the γ -agostic complex rearranges into a more stable β -agostic complex with a few kcal/mol rotational barrier. Using single points at the QCISD level,^{1a} the olefin coordination energies are 21.9 and 29.1 (22.7 at B3LYP/LANL2DZ level⁵) kcal/mol, the insertion barriers relative to the π -complexes are 7.1 and 9.4 (7.6) kcal/mol, and the exothermicities to form the γ -agostic products from the reactant are 29.3 and 33.4 (29.3) kcal/mol for the chain initiation reaction with [(Cp)(SiH₂)Cp]MCH₃⁺ for M = Ti and Zr, respectively. The β -agostic complex is the more stable product and is 2–6 kcal/mol lower than the γ -agostic complex. Thus, according to these data, titanocene should be slightly more active than zirconocene, which is opposite to experimental observations. Similar trends have been found by Ziegler and co-workers^{1c} on studies of ethylene insertion into the M–CH₃ bond of the constrained geometry catalysts [(SiH₂C₅H₄NH)MCH₃]⁺ (M = Ti, Zr, and Hf). The insertion barrier increased via Ti (3.8 kcal/mol) < Zr (5.1 kcal/mol) < Hf (5.7 kcal/mol), while the catalytic activity of these complexes increased via Ti < Zr < Hf.

The comparison of the above-mentioned findings for metallocene catalysts with those obtained in this paper for S-, CH₂-, and directly-bridged chelating alkoxide catalysts shows the following similarities and differences:

(1) The mechanism of the chain initiation reaction 1 for the chelating alkoxide catalyst is similar to that for the metallocene catalyst. It involves the coordination of ethylene to the metal center, the insertion of ethylene into the metal–alkyl bond, and the formation of a γ -agostic product. However, for the chelating alkoxide catalyst, the β -agostic product, which was a more stable product of the metallocene catalyst, does not exist or is higher in energy than the γ -agostic product in all the cases, except for the S-bridged Ti system where a β -agostic structure is 0.2 kcal/mol lower in energy than the γ -agostic product.

(2) The calculated coordination energies of ethylene for the S-, CH₂-, and directly-bridged systems are similar for Ti and Zr. However, the coordination energies are 6–8 kcal/mol smaller for titanocenes than for zirconocenes due to the strong steric repulsion between ethylene and the methyl group on the Ti center.

(3) The rate-determining barriers calculated from the π -complexes are 6.4, 10.7, and 11.0 kcal/mol and 7.4, 14.5, and 15.8 kcal/mol for the Ti- and Zr-based S-, CH₂-, and directly-bridged complexes, respectively. Since the numbers for the CH₂- and directly-bridged systems are a few kilocalories/mole larger than those, 7.1 and 9.4 kcal/mol, for titanocene and zirconocene

(16) (a) Lohrenz, J. C. W.; Woo, T. K.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 12793. (b) Koga, N. Presented in contribution 213 in the Symposium on Computer Modeling of Polymerization Catalysts, Division of Polymeric Materials, American Chemical Society National Meeting, New Orleans, LA, March 1996.

(17) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 8687.

(15) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

systems, respectively, one might say that the intrinsic reactivity of the former is smaller than that of the latter. In contrast, the barriers of 6.4 and 7.4 kcal/mol for the S-bridged Ti and Zr systems are a few kilocalories/mole lower than those for titanocene and zirconocene systems, thus the S-bridged Ti and Zr alkoxides may be said to have a higher intrinsic reactivity than their metallocene analogues.

IV. Conclusions

We have studied using an MO method the mechanism of ethylene polymerization using a new class of catalysts, zirconium and titanium chelating alkoxide species. Very qualitatively, the present results are similar to previous theoretical results for other Zr and Ti complexes.¹⁸ However, bridged chelating ligands of these catalysts have a certain amount of flexibility which allows for certain atoms on these ligands to interact with the metal if feasible. Flexible ligands with the ability to donate may be one of the possible methods of developing more active alternative catalysts. In the case of the S-bridge, there is a definite interaction as indicated by the shortened M–S bond length and the overlap population. This interaction stabilizes the reactants more than the π -complexes as the systems prefer to be 4-coordinated and there is competition between the sulfur atom and the incoming olefin. This competition results in a destabilized π -complex. Due to the stronger exothermicity of the titanium compared to zirconium species and the destabilization of the π -complexes, the S-bridged titanium catalyst has the lowest predicted barrier which agrees with the experimentally high activity. The CH₂- and directly-bridged species do not have such an interaction with the metal, and thus, the insertion barriers are much larger. A theoretical

(18) Koga, N.; Morokuma, K. *Chem. Rev.* **1991**, *91*, 823 and references therein.

comparison of these systems with zirconocenes indicates that the titanium S-bridged system has an activity comparable to the very active zirconocene systems.

An electron-donating ligand is known to decrease the activation barrier in zirconocenes. For example, it is known experimentally^{2a} and has been predicted theoretically⁵ that methyl substituents on cyclopentadienyl rings lower the activation barrier and increase the rate of polymerization. This electron donation occurs indirectly by donation of the alkyl groups to the cyclopentadienyl fragment and then to the metal. In the present alkoxide systems, there is a direct interaction between the metal and the sulfur ligand which lowers the activation barrier. This stabilization of the cationic metal competes with the electron donation from the incoming olefin. When the olefin is a better donor, the M–S distance increases in the π -complex. However, if the donating group were better than the olefin, then complexation and thus polymerization would not occur. This approach appears to be a general way of developing more active catalysts: find ligands which have slightly less donating ability than the polymerizing olefin. Some possible ligands which could be used include selenium and tellurium or even larger groups such as a sulfoxide or carbonyl group.

Acknowledgment. The use of the computational facilities and programs at the Emerson Center is acknowledged. The present research is in part supported by grants (CHE-9409020 and CHE96-27775) from the National Science Foundation. The use of the Power Challenge Array at Illinois is acknowledged. R.D.J.F. acknowledges a Postdoctoral Fellowship from the Natural Sciences and Engineering Research Council of Canada.

JA970861G