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Theoretical Studies of the Factors Controlling Insertion Barriers for Olefin Polymerization by the Titanium-Chelating Bridged Catalysts. A Search for More Active New Catalysts

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In search of more active new catalysts, density functional theory was used to predict insertion barriers for ethylene polymerization for a variety of unknown Ti-chelating bridged alkoxide catalysts, $[YR'XR'Y]TiCH_3^+$, where X, Y = O, S, Se, Te, and $R' = C_6H_4$, C_2H_2, C_2H_4 with and without substituents. The use of ligands having donating and bridging atoms that are capable of donating electron density to the cationic metal center decreases the insertion barriers. For $[(C_6H_4O)X(C_6H_4O)]TiCH_3^+$, both the olefin coordination energy, X = S(21.4 kcal/mol) > Se(19.2) > Te(16.6), and migratory insertion barrier, X = S(6.4) > Se(5.9) > Te(5.7), decrease with the increasing donating capability of the bridging atom X to the metal center, i.e., via X = S < Se < Te. The oxygen bridge, however, gives the lowest insertion barrier (4.5 kcal/mol) in this group. The role of the phenyl group was explored by replacing it by C_2H_2 and C_2H_4 moieties. Having conjugation through the X−CC−Y moiety in these complexes turns out to be very important, allowing the delocalization of electron density from the incoming ethylene molecule through all atoms of the $X-[(CC)Y]_2$ ligand, which in turn makes the bridging atom less positively charged and, consequently, the M−X interaction weaker and the insertion barrier smaller. The increase in the electron density in the $X-[(CC)Y]_2$ ligand, as well as having chelating atoms (like O and S) with p-lone pair electrons, also reduces the insertion barrier. The complexes with the $Y(C_2H_2)X(C_2H_2)Y$ ligand where X = Y = O and S are predicted to have the lowest insertion barriers.

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1. Introduction

Olefin polymerization reactions have become very important processes in industry in recent years as the use of plastic materials increases dramatically. The transition metal catalyzed olefin polymerization reaction has been a focus of experimental[1] and theoretical[2] studies recently. Although the major efforts have concentrated on the metallocene compounds of the d^0- and d^0f^n-elements because of their high activities and wide applications in industry, the search for alternative catalysts has also intensified. Recent advances in this area resulted in the discovery of new classes of catalysts: diimine−M(II) (where M = Ni and Pd),[3,4] Ti- and Zr-bridged chelating alkoxide catalysts,[5−7] and other noncyclopentadienyl catalysts.[8] Many of these show high polymerization activities.

The generally accepted mechanism for olefin polymerization is the Cossee-type mechanism,[9] as shown below in reaction 1:

$$[L_2MCH_3]^+ + C_2H_4 \rightarrow [L_2M(CH_2{=}CH_2)CH_3]^+_{\pi} \rightarrow TS \rightarrow [L_2MCH_2CH_2CH_3]^+_{\gamma} \rightarrow TS \rightarrow [L_2MCH_2CH_2CH_3]^+_{\beta} \quad (1)$$

This mechanism involves the approach of an olefin (ethylene, in this case) to the active catalyst to form a π-complex and then insertion of the olefin into the

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metal−alkyl bond through the four-center transition state to form the γ-agostic alkyl intermediate, which goes through a transition state for alkyl rotation to form a usually more stable β-agostic isomer.

Our recent studies[7] on the mechanism of olefin polymerization reaction catalyzed by Ti- and Zr-chelating alkoxides show that the S-bridged chelating alkoxides have lower insertion barriers than their methylene-bridged or directly bridged analogues, which is in qualitative agreement with the known experiment.[5] This lower barrier seems to be related to several factors. The most important factor is the existence of the metal−bridge interaction in the S-bridged reactant complexes compared to their methylene-bridged or directly bridged systems. Upon coordination of the olefin, the metal center partially releases the most weakly coordinated ligand, the bridged S, and maintains its preferred tetrahedral environment. The weakening of the M−S bond results in the destabilization of the metal−alkyl−olefin complex (which is found to be the resting stage of the entire catalytic process) compared to the methylene-bridged or directly bridged systems. In the transition state (as well as in γ- and β-agostic intermediates), this M−S interaction is recovered and stabilizes the transition state relative to the π-complex and lowers the barrier. This effect was not observed with the methylene-bridged and directly bridged systems. The activation barriers for the titanium catalysts for the sulfur-bridged, methylene-bridged, and directly bridged systems are calculated to be 6.4, 10.7, and 11.0 kcal/mol, respectively. The migratory insertion barrier is found to be the rate-determining step of the reaction. We have predicted that the Ti/Zr-chelating complexes having a stronger metal−bridge bond will show even more catalytic activity than the S-bridged ones. Note, to make possible the coordination of the olefin to the metal center, this metal−bridge interaction should not be stronger than the metal−olefin interaction.

The second factor that plays a role in this reaction is the electron donor capability of the alkoxide ligands, which needs to be examined in detail. In particular, the role of the phenyl rings of the alkoxide is not clear in this process. Is the conjugation of the alkoxide through the phenyl group an essential factor for olefin polymerization? Are there other alkyl ligands that would improve this reaction? A separate question is whether the alkoxide is the best ligand. Can other ligands such as imine or thioalkoxide be used instead to improve the activity? With the results of previous papers in mind,[5−7] the present paper has three purposes.

1. To test the validity of the predictions of our previous paper that an increase in the metal−bridge interaction increases catalytic activity by lowering the insertion barrier. For this purpose we study the chain initiation reaction:

$$\begin{aligned}&[(C_6H_4O)X(C_6H_4O)]TiCH_3^+ + C_2H_4 \rightarrow\\&\qquad[(C_6H_4O)X(C_6H_4O)]TiCH_3(C_2H_4)^+ \rightarrow\\&\qquad\qquad[(C_6H_4O)X(C_6H_4O)]Ti(CH_2CH_2)CH_3^+ \quad (2)\end{aligned}$$

for X = O (**1**), S (**2**, previously studied[7]), CH_2 (**3**, previously studied[7]), Se (**4**), and Te (**5**).

2. To elucidate the electronic role of the phenyl-rings in the ethylene polymerization reaction 1. For this purpose we compare reaction 2 for the following catalysts: **2**, **4**, $[(C_2H_2O)S(C_2H_2O)]TiCH_3^+$ (**6**), $[(C_2H_2O)O(C_2H_2O)]TiCH_3^+$ (**7**), $[(C_2H_4O)S(C_2H_4O)]TiCH_3^+$ (**8**), and $[(3\text{-}OSiH_3C_6H_3O)Se(3\text{-}OSiH_3C_6H_3O)]TiCH_3^+$ (**9**).

3. To study the effect of the chelating ligand. We compare the results for a variety of systems, including **2**, **6**, **7**, $[(C_6H_4NH)O(C_6H_4NH)]TiCH_3^+$ (**10**), $[(C_2H_2NH)S(C_2H_2NH)]TiCH_3^+$ (**11**), $[(C_2H_2S)S(C_2H_2S)]TiCH_3^+$ (**12**), and $[(C_2H_2S)O(C_2H_2S)]TiCH_3^+$ (**13**).

By examining and comparing the 13 catalytic systems above, we will obtain a systematic overview of the effects of the bridging atoms, the phenyl groups, and the chelating ligands and hopefully will be able to deduce some guideline for improving the present catalytic system by decreasing the insertion barrier of olefin into the Ti−C bond.

2. Computational Methods

Geometries and energies of the reactants, intermediates, and transition states of the initiation reaction were calculated using the gradient-corrected hybrid density functional method B3LYP,[10] which had been shown to be reliable for these types of systems.[4d,11] In these calculations, we used the LANL2DZ basis set which includes a double-ζ valence basis set (8s5p5d)/[3s3p2d] with the Hay and Wadt effective core potential (ECP)[12] replacing core electrons up to 2p for the Ti atom and the Huzinage−Dunning valence double-ζ quality basis set[13] for the remaining atoms. Recently with the nickel diimine system, we examined the effect of much larger basis sets (triple-ζ quality basis with d-functions on carbons/oxygens/nitrogens, p-functions on hydrogens, and all-electron basis with up to f-functions on the nickel metal) using the B3LYP method,[4d] and for the limited number of isomers that we studied, we found that structural and energetic features using the B3LYP/LANL2DZ were quantitatively in agreement with the results of the larger basis set. The GAUSSIAN94 program,[14a] with our own modification,[14b] was used for all the calculations.

No symmetry constraints were placed on any molecules in this study. No vibrational analysis was explicitly carried out for identification of the nature of the reactants, intermediates, transition states, and products of the reaction 1, and conse-

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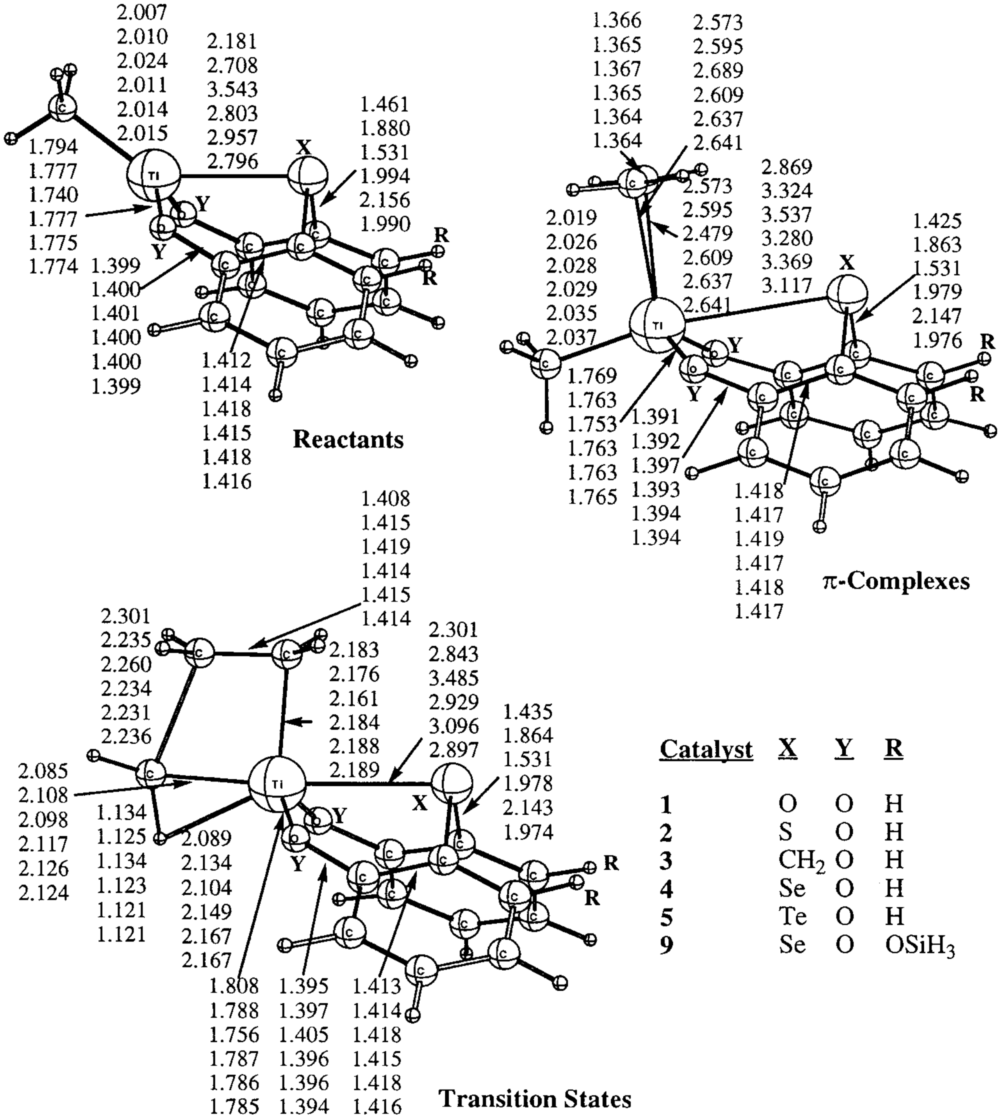

Catalyst	X	Y	R
1	O	O	H
2	S	O	H
3	CH_2	O	H
4	Se	O	H
5	Te	O	H
9	Se	O	$OSiH_3$

Figure 1. B3LYP/LANL2DZ-optimized bond distances (in Å) of the reactant, π-complex, and transition state for phenyl−alkoxide catalysts $[(RC_6H_3O)X(RC_6H_3O)]TiCH_3^+$ with the bridge (X) of oxygen (**1**), sulfur (**2**), CH_2 (**3**), selenium (**4**), tellurium (**5**), all with R = H, and with the bridge of selenium with R = $3\text{-}OSiH_3$ (**9**).

quently, the relative energies (kcal/mol) presented do not include zero-point vibrational energy corrections. However, the nature of the obtained "transition states" has been examined by performing "quasi-IRC (intrinsic reaction coordinate)" calculations in the following manner. The transition-state geometry was at first slightly changed with respect to the expected reaction coordinate, and then the entire structure was released for equilibrium geometry optimization. In each case, the calculations converged to the equilibrium structures, either π-complex or γ (or β)-agostic products, confirming these structures are indeed the transition states for the desired reactions.

3. Results and Discussion

A. Effects of the Bridge. The structures of the reactant catalyst, the olefin methyl complex, and the olefin insertion transition state for the $[(C_6H_4O)X(C_6H_4O)]TiCH_3^+$ system, where X = O (**1**), S (**2**), CH_2 (**3**), Se (**4**), and Te (**5**), as well as for the disiloxy-substituted selenium analogue $[(3\text{-}OSiH_3C_6H_3O)Se(3\text{-}OSiH_3C_6H_3O)]TiCH_3^+$ (**9**), are shown in Figure 1, and the relative energies of all species are given in Table 1. We should note that, in general, there are two different paths of addition of the incoming olefin to the transition metal center of the reactant, one from the front face of the reactant, i.e., between the methyl group and the bridging atom X, or syn to the bridge, and the other from the back face, i.e., between the methyl group and the Y ligands, anti to the bridge. We have examined both syn and anti addition in a few selected cases, as shown in Table 1, and one observes the same trend that syn is preferred to anti. Therefore, below we will discuss only the syn addition.

First, let us compare the structures and energetics for compounds **1**−**5**. As seen in Table 1, the CH_2-bridged system (**3**) has a much larger ethylene complexation energy (26.7 kcal/mol) than the other four systems. As explained previously,[7] the reason for this difference is

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Table 1. Total Energy (in au) for the Reactants, and Relative Energies (in kcal/mol, Relative to Reactant Plus Ethylene) of the π-Complex and the Transition State for Ethylene Insertion Reactions Studied in This Paper, Calculated at the B3LYP/LAN2DZ Level[a]

L[b]		reactants	π-complex	transition state	barrier[c]
[O(Ph)O(Ph)O]	**1**	−785.526 620	−23.2	−18.7	4.5
[O(Ph)S(Ph)O]	**2**	−720.424 427	−21.4 (−18.7)	−15.0 (−11.6)	6.4 (7.1)
[O(Ph)CH_2(Ph)O]	**3**	−749.634 623	−26.7	−16.0	10.7
[O(Ph)Se(Ph)O]	**4**	−719.551 829	−19.2	−13.3	5.9
[O(Ph)Te(Ph)O]	**5**	−718.382 002	−16.6	−10.9	5.7
[O(C_2H_2)S(C_2H_2)O]	**6**	−413.137 978	−24.2 (−22.8)	−18.7 (−15.8)	5.5 (7.0)
[O(C_2H_2)O(C_2H_2)O]	**7**	−478.246 850	−21.4	−18.8	2.6
[O(C_2H_4)S(C_2H_4)O]	**8**	−415.647 251	−20.2	−11.8	8.4
[O(Ph*)Se(Ph*)O][b]	**9**	−880.175 365	−16.5	−11.6	4.9
[(NH)(Ph)O(Ph)(NH)]	**10**	−745.764 929	−23.3	−12.6	10.7
[(NH)(C_2H_2)S(C_2H_2)(NH)]	**11**	−373.383 204	−19.0 (−14.4)	−9.8 (−7.5)	9.2 (6.9)
[S(C_2H_2)S(C_2H_2)S]	**12**	−282.848 373	−21.9 (−23.0)	−18.3 (−16.9)	3.6 (6.1)
[S(C_2H_2)O(C_2H_2)S]	**13**	−347.964 050	−30.4	−23.5	6.9
C_2H_4		−78.578 204			

[a] The results are for syn addition, and those for anti addition are in the parentheses. The oxygen-bridged systems (**1**, **7**, **10**, and **13**) are nearly planar across the chelating moiety, and the distinction between syn and anti addition is nearly lost. [b] Ph = C_6H_4, Ph* = 3-$OSiH_3C_6H_3$. [c] The barrier is relative to the π-complex.

the partial loss of a strong Ti−X interaction in the olefin complex which existed in the reactant between the metal and the heteroatoms (O, S, Se, Te), compared with the CH_2-bridged system, where there is no metal−bridge interaction.

As see in Figure 1, the Ti−X distance in the reactant catalyst increases as X moves down the periodic table, which is consistent with increase in the van der Waals radii of X, e.g., X = O < S < Se < Te. The approach of ethylene maintains the C_s symmetry and leads to a perpendicular π-complex, where the incoming ethylene molecule is positioned perpendicular to the CH_3−Ti−X plane. In this complex the Ti−X distance has now increased, relative to the corresponding reactants, by 0.69 (**1**, O), 0.62 (**2**, S), 0.48 (**4**, Se), and 0.41 Å (**5**, Te). These increases are consistent with the trend obtained for the complexation energies, 23.2 (O) > 21.4 (S) > 19.2 (Se) > 16.6 (Te) kcal/mol. They are all smaller than that (26.7 kcal/mol) for the noninteracting CH_2-bridged system. These values are also consistent with the calculated $C_{ethylene}$−Ti bond lengths in the π-complex, which are 2.479 (CH_2) < 2.573 (O) < 2.595 (S) < 2.609 (Se) < 2.637 Å (Te). Thus, in general, the stronger the metal−heteroatom (X) interaction, the smaller the elongation of the M−X bond distance upon ethylene coordination and, consequently, the smaller the ethylene coordination energy. The difference in the complexation energy between the X-bridged complex and the CH_2-bridged complex, 3.5 (O) < 5.3 (S) < 7.5 (Se) < 10.1 kcal/mol (Te), may be regarded as a measure of the loss of olefin binding energy due to the Ti−X interaction.

The general structural features of the transition state have also been discussed before.[7] In the transition state, the two carbons of the inserting ethylene, the metal, and the methyl carbon now lie in a coplanar arrangement. The activation energy has been calculated from the resting stage perpendicular π-complex, as parallel π-complexes, where the incoming ethylene is parallel to the CH_3−Ti−X plane, are higher in energy.[7] Thus, as ethylene starts to insert, the system passes near the geometry of the parallel complex. While the Ti−X distance is stretched in the olefin complex, it is shortened in the transition state again almost to a distance in the reactant. This fact suggests that the loss of the olefin interaction energy due to Ti−X contact at the transition state is smaller than at the π-complex. In fact, the difference in the energy of the transition state (relative to the corresponding catalyst + ethylene) between the X-bridged and the CH_2-bridged species, −2.7 (O) < 1.0 (S) < 2.7 (Se) < 5.1 kcal/mol (Te), shows the same trend as the difference at the π-complex, except for the O-bridged system. This means that for the S, Se, and Te-bridged systems, the transition state (relative to the corresponding catalyst + ethylene) is less stabilized than for the CH_2-bridged system; however, for the O-bridged system the transition state is more stabilized than for the CH_2-bridged system. Although it is not possible to pin down what caused this extra stabilization at the transition state for the O-bridged system, a donation of the lone pair from the O bridge to Ti may promote the back-donation from the metal center to ethylene, which is needed for bond breaking/formation at the transition state, and provide an extra stabilization. Thus, the migratory insertion barrier of this reaction from the π-complex changes via O (4.5) < S (6.4) > Se (5.9) > Te (5.7 kcal/mol). The geometrical parameters of the transition state for the O-bridged system indicate that this is the earliest of all the transition states in Figure 1, consistent with the lowest activation barrier.

We examined the change in charge distribution for two systems, **2** and **4**, to determine how this fact may be affecting the reaction. As seen in Table 2, the Mulliken charges summed into heavy atoms are +0.32/+1.11 (reactant), +0.29/+1.08 (π-complex), and +0.34/+0.95 (transition state) on the sulfur/titanium atoms of **2**, while on the selenium/titanium atoms of **4**, these values are +0.48/+1.07, +0.37/+1.04, and +0.47/+0.94. These values reflect a larger electron donation capability of selenium compared with sulfur, or more generally, O < S < Se < Te.

B. Electronic Effects of the Phenyl Group. The second effect that was examined was the effects of the phenyl group in the link between the bridge and the ligand. We are interested in knowing the electronic effects associated with this group and whether replacing this by an alkenyl or alkyl group would significantly affect the reaction. We compared the X = S systems: **2**, **6**, and **8**, which are the results of direct replacement of the C_6H_4 groups in **2** with unsaturated C_2H_2 (**6**) and

Table 2. Calculated Mulliken Charges (Summed into Heavy Atoms, in e, *Z) and Overlap Populations (*Q*) between the Important Atoms for the Reactant (R), π-Complex (π), and Transition State (TS) of the Catalysts [YR′XR′Y]TiCH$_3^+$: 2, 4, 6, 8, and 9**

[YR′XR′Y]			atomic charges, *Z**						overlap population, *Q*		
			Ti	Y	X	CH$_3$	C$^1_{\text{ethylene}}$[a]	C$^2_{\text{ethylene}}$[a]	Ti−X	Ti−C$^1_{\text{ethylene}}$	Ti−C$^2_{\text{ethylene}}$
[O(C$_6$H$_4$)S(C$_6$H$_4$)O]	**2**	R	+1.11	−0.54	+0.32	−0.09			0.38		
		π	+1.08	−0.55	+0.29	−0.14	+0.14	+0.14	0.13	0.15	0.15
		TS	+0.95	−0.55	+0.34	0.00	−0.03	+0.25	0.29	0.29	0.04
[O(C$_6$H$_4$)Se(C$_6$H$_4$)O]	**4**	R	+1.07	−0.54	+0.48	−0.10			0.43		
		π	+1.04	−0.55	+0.37	−0.14	+0.14	+0.14	0.18	0.15	0.15
		TS	+0.94	−0.56	+0.47	−0.01	−0.04	+0.25	0.32	0.32	0.03
[O(C$_2$H$_2$)S(C$_2$H$_2$)O]	**6**	R	+1.15	−0.49	+0.26	−0.04			0.38		
		π	+1.12	−0.50	+0.22	−0.10	+0.15	+0.15	0.12	0.15	0.15
		TS	+0.97	−0.50	+0.27	−0.02	+0.02	+0.27	0.31	0.29	0.04
[O(C$_2$H$_4$)S(C$_2$H$_4$)O]	**8**	R	+1.13	−0.50	+0.27	−0.11			0.42		
		π	+0.95	−0.50	+0.30	−0.12	+0.07	+0.21	0.39	0.18	0.07
		TS	+1.00	−0.50	+0.25	−0.01	−0.04	0.27	0.26	0.28	0.04
[O(Ph*)Se(Ph*)O][b]	**9**	R	+1.04	−0.55	+0.55	−0.12			0.45		
		π	+0.99	−0.55	+0.48	−0.16	+0.14	+0.14	0.29	0.15	0.15
		TS	+0.91	−0.56	+0.55	−0.02	−0.05	+0.28	0.37	0.33	0.04

[a] C$^1_{\text{ethylene}}$ and C$^2_{\text{ethylene}}$ are the ethylene carbons closer to and further from Ti, respectively, in the transition state. [b] Ph* = 3-OSiH$_3$C$_6$H$_3$.

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saturated C$_2$H$_4$ (**8**) moieties. To confirm the results obtained for X = S, we also carried out calculations for the oxygen-bridging C$_6$H$_4$ (**1**) and C$_2$H$_2$ (**7**) systems. Furthermore, to determine the role of strong electron-donating substituent to the activation barrier, we compared the unsubstituted (**4**) and disiloxy-substituted (**9**) selenium-bridged C$_6$H$_4$ systems. Important geometrical features of these systems are shown in Figures 1 and 2.

A comparison of the alkoxide sulfur-bridged systems with the aromatic C$_6$H$_4$ (**2**), the olefinic C$_2$H$_2$ (**6**), and saturated C$_2$H$_4$ (**8**) links should provide information on the link groups. As discussed above and in our previous paper,[7] the most interesting aspect of the geometrical changes in the reaction of the sulfur-bridged C$_6$H$_4$ system **2** is in the titanium−sulfur bond length, which is indicated by a strong interaction in the reactant, a weaker interaction in the π-complex, and a strong (nearly comparable to the reactant) interaction in the transition state. The Ti−S distance for **2** with the C$_6$H$_4$ link changes from 2.708 Å in the reactant to 3.324 Å in the π-complex to 2.843 Å in the transition state. In **6** with the C$_2$H$_2$ link, the corresponding Ti−S distances are 2.705, 3.402, and 2.865 Å. The trend with the C$_6$H$_4$ link is reproduced well with the C$_2$H$_2$ link. The fact that there is a larger Ti−S change on going from the π-complex to the transition state for **6** (0.537 Å) compared with **2** (0.481 Å) suggests that the barrier for **6** would be lower than that for **2**. Actually, the insertion barrier of 5.5 kcal/mol for **6** is smaller than 6.4 kcal/mol for **2**.

To generalize the above findings for the S-bridged systems, we compare the O-bridged C$_6$H$_4$ (**1**) and C$_2$H$_2$ (**7**) complexes. As shown in Table 1, the insertion barrier for **7** is only 2.6 kcal/mol vs 4.5 kcal/mol for **1**, while the complexation energy of 21.4 kcal/mol calculated for catalyst **7** is still relatively large. Even after the entropy factors are taken into account, which reduces this value by 10−15 kcal/mol, the olefin still appears to be bound before the insertion takes place. The activation energy can be decreased by destabilizing the π-complex, but if this effect is exaggerated, entropy effects may make the olefin unbound, an undesirable situation for the reaction. These results suggest that catalysts with a Y(C$_2$H$_2$)(X)(C$_2$H$_2$)Y ligand have a lower insertion barrier than the experimentally reported analogues with a Y(C$_6$H$_4$)(X)(C$_6$H$_4$)Y ligand and may be good catalysts.

Next, we will compare the sulfur-bridged C$_6$H$_4$ (**2**) and C$_2$H$_2$ (**6**) systems with their C$_2$H$_4$ analogue **8**, where the conjugation through O−C=C−S is destroyed. As seen in Figure 2, in the reactant of **8** there is a strong Ti−S interaction as the distance of 2.586 Å attests. This is about 0.11 Å shorter than that in the corresponding C$_6$H$_4$ (**2**) and C$_2$H$_2$ (**6**) complexes, indicative of the stronger metal−bridge interaction in **8**. Therefore, one may expect the unconjugated system **8** to have a smaller activation barrier. However, surprisingly, in the π-complex the Ti−S distance is only slightly lengthened than in the reactant (ΔR(Ti−S) = +0.14 vs +0.62 in **2** and +0.70 Å in **6**), indicating that this Ti−S interaction is not weakened significantly in the π-complex. In the transition state, the Ti−S distance even becomes longer than in the π-complex for **8** reactant (ΔR(Ti−S) = +0.35 vs −0.48 in **2** and −0.54 Å in **6**). As a result, as seen in Table 1, the calculated activation barrier, 8.4 kcal/mol, for complex **8** is a few kcal/mol higher than that for C$_6$H$_4$ (**2**), 6.4 kcal/mol, and C$_2$H$_2$ (**6**), 5.5 kcal/mol, while the complexation energy (20.2 kcal/mol) is found to be similar to other systems.

To understand the reason for this trend, we have examined the charges for the two systems, **6** and **8**. As seen in Table 2, there are little differences in the Mulliken charges between the reactants of **6** and **8**. In the π-complexes, the incoming ethylene molecule donates electrons and becomes positively charged to a similar extent, +0.30 in **6** and +0.28 in **8**. For the conjugating C$_2$H$_2$ system **6**, this −0.30 charge is spread out over all the other heavy atoms of the ligand, as each becomes slightly more negative. The bridging sulfur also becomes less positively charged. Thus, the donating capability of sulfur is decreased, leading to the weakening of the Ti−S interaction in the π-complex relative to the reactant. On the other hand, for the C$_2$H$_4$ catalyst **8**, the metal has absorbed much of the additional −0.28 charge, as the charge on titanium has gone from +1.13 in the reactant to +0.95 in the π-complex. There is less charge effect on the chelating moiety including the bridging sulfur atom, which is slightly more positive in the π-complex compared with the reactant. In **8**, there is definitely a competition between the sulfur and the

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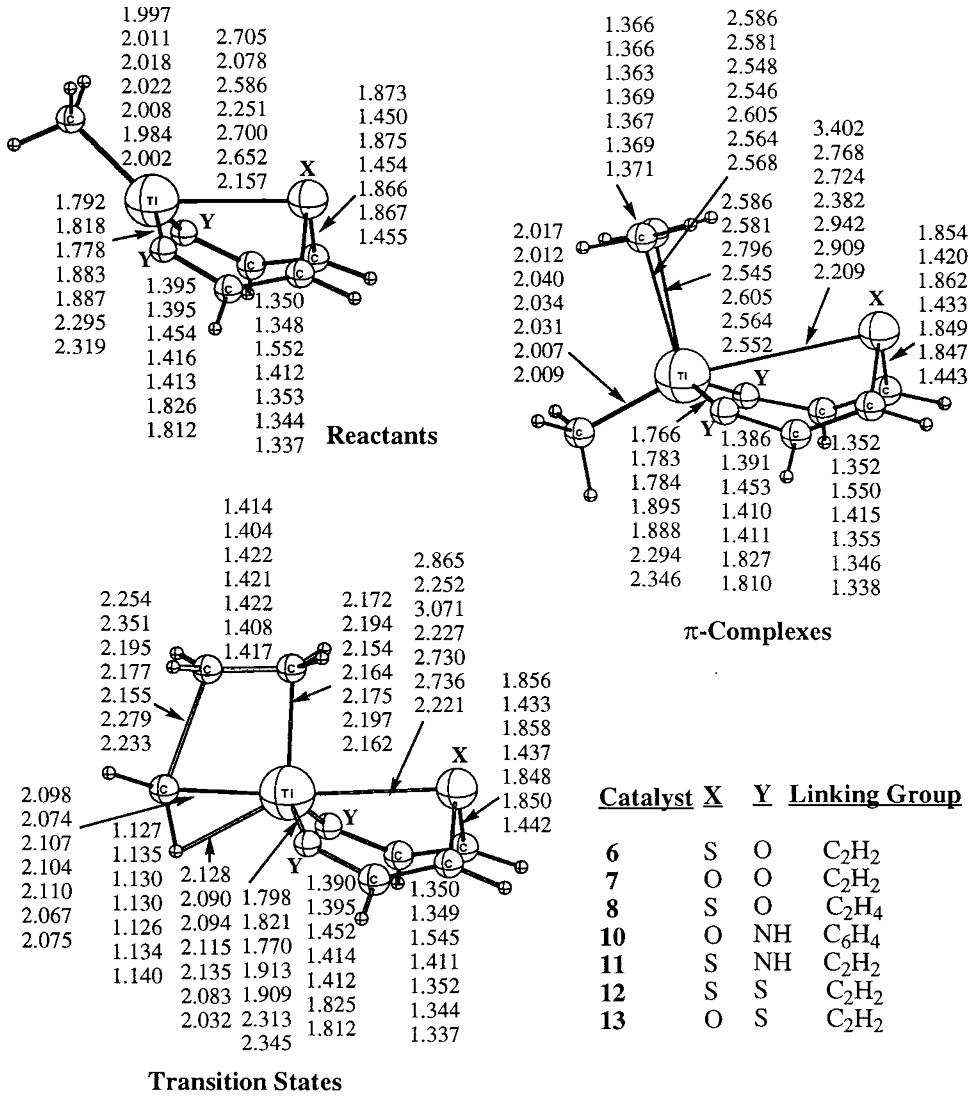

Catalyst	X	Y	Linking Group
6	S	O	C_2H_2
7	O	O	C_2H_2
8	S	O	C_2H_4
10	O	NH	C_6H_4
11	S	NH	C_2H_2
12	S	S	C_2H_2
13	O	S	C_2H_2

Figure 2. B3LYP/LANL2DZ-optimized bond distances (in Å) of the reactant, π-complex, and transition state for seven catalysts $[YR'XR'Y]TiCH_3^+$, **6**–**8** and **10**–**13**, where R′ is the link group.

incoming olefin, and although the Ti–S interaction is weaker in the π-complex than in the reactant, the difference is very small. This delocalization of charge in the π-complex of the conjugated C_2H_2 and C_6H_4 catalysts is likely to be due to the catalyst LUMO which is the metal dπ orbital through conjugation but is mostly a pure metal orbital in the C_2H_4 system.

Thus, a comparison of these results shows that the conjugation in the alkoxide moiety causes the negative charge transferred from the incoming ethylene in the π-complex to spread out over the $(O{-}C{=}C)_2{-}S$ ligand and leads to a smaller positive charge on the sulfur and a smaller interaction of S with the metal. In the unconjugated system, the transferred negative charge is not delocalized and the sulfur interacts more strongly with the cationic titanium, staying closer to the metal even in the π-complex. The Ti–X overlap populations in Table 2 also confirm that in the delocalized systems such as **2**, **4**, and **6**, there is a stronger interaction in the reactant and transition state and a much weakened interaction in the π-complex. For the saturated C_2H_4 system **8**, the Ti–X interaction decreases from the reactant to the π-complex then to the transition state. The conjugated systems (**2**, **4**, and **6**) thus act as *breathing catalysts* with the heteroatom moving in and out from the metal center as the electron density changes.

We should also note another unusual aspect in the geometries of the π-complex of the C_2H_4 system **8**. The reactant possesses C_s symmetry, but this symmetry is broken in the π-complex as the two $Ti{-}C^{\pi}$ bond lengths are 2.548 and 2.796 Å. All other π-complexes studied are symmetric except for **3**, which has no metal–bridge interaction. It appears that the conjugative effects through metal–ligand-C_6H_4 or C_2H_2–bridge X–metal induce symmetry in the metal olefin bond. If the conjugation is destroyed by the C_2H_4 group as in **8** or there is no metal–X interaction as in **3**, the π-complex is no longer symmetric.

Next, in an effort to make the bridging heteroatom more electron-rich, we have added strong electron-donating substituents on the phenyl ring next to the heteroatom. Important structural features of the reactant, π-complex, and transition state for the selenium-bridged 3,3′-disiloxy-substituted catalyst **9** are shown in Figure 1 and can be compared to the unsubstituted (R = H) catalyst **4**. In the reactant, the Se–Ti distance is slightly shorter for the siloxy-substituted system, and

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this distance difference becomes more pronounced in the π-complex. The strongly electron donating siloxy substituents weaken olefin complexation in terms of both the bond length (C^{π}−Ti lengths of 2.641 Å, compared with 2.609 Å in the unsubstituted **4**) and the energy, as the π-complex lies 16.5 kcal/mol below the reactant for **9**, compared to 19.2 kcal/mol for **4**. These donative substituents lower the activation barrier compared to the unsubstituted system from 5.9 to 4.9 kcal/mol. Thus, the electron-donating substituents on the conjugated link in the present system enhance the insertion of ethylene into the Ti−C(alkyl) bond.

C. Effects of the Chelating Group, Y. The next question to be elucidated is the effects of the chelating group, Y. For this purpose, we studied and compared three classes of complexes: (1) the oxygen-bridged C_6H_4-linked systems, **1** and **10**, with Y= O and NH, respectively, (2) the oxygen-bridged C_2H_2-linked systems, **7** and **13**, with Y= O and S, respectively, and (3) the sulfur-bridged C_2H_2-linked systems, **6**, **11**, and **12**, with Y = O, NH, and S, respectively. Important geometrical features of the structures of the relevant systems are shown in Figures 1 and 2. We believe that by comparing these three groups of catalysts, the effects of the ligand group directly bound to titanium can be determined.

First, let us compare and discuss the results for the oxygen-bridged C_6H_4-linked systems, **1** and **10**, with Y = O and NH, respectively. The first thing to compare is the $Ti-O^{bridge}$ distances in the reactants, π-complexes, and transition states. As seen in Figure 2 for **10**, the $Ti-O^{bridge}$ distances are 2.251, 2.382, and 2.227 Å, in the reactant, π-complex, and transition state, respectively, vs 2.181, 2.869, and 2.301 Å, respectively, for **1**, in Figure 1. In other words, for **10** with Y = NH, the coordination of ethylene to the metal center weakens the $Ti-O^{bridge}$ interaction only slightly (elongated only by 0.13 Å), while for **1**, this weakening is much more significant (elongated by 0.69 Å). Similar trends can be found for the $Ti-S^{bridge}$ distance by comparing reactants, π-complexes, and transition states for the S-bridged C_2H_2-linked **6** and **11** with Y = O and NH, respectively. As seen in Table 1, the activation barrier increases significantly from 4.5 (**1**) to 10.7 (**10**) kcal/mol, and from 5.5 (**6**) to 9.2 (**11**) kcal/mol when the ligand group O is replaced by NH. Thus, it appears that the use of NH instead O increases the activation barrier, which correlates with the strong π-donating capability of N to the transition metal center compared to O.

Next, let us compare and discuss the results for the oxygen-bridged C_2H_2-linked systems, **7** and **13**, with Y = O and S, and the sulfur-bridged C_2H_2-linked systems, **6** and **12**, with Y = O and S, respectively. Table 1 shows that for the oxygen-bridged system, replacement of Y = O by Y = S as chelating atoms increases the insertion barrier from 2.6 (**7**) to 6.9 (**13**) kcal/mol. In contrast, for the sulfur-bridged systems replacement of Y = O by Y = S decreases the insertion barrier from 5.5 (**6**) to 3.6 (**12**) kcal/mol. In other words, the systems **7** and **12** with X = Y have smaller insertion barriers for the insertion of ethylene into the $Ti-CH_3$ bond than those with X ≠ Y. Unfortunately, we currently have no explanation why systems with X = Y = O and X = Y = S are preferable.

4. Conclusions

From the above presented results, we can draw the following conclusions:

1. The presence of certain bridging ligands X in the Ti−alkoxide complex, $[(C_6H_4O)X(C_6H_4O)]TiCH_3^+$, which are capable of donating electron density to the cationic metal center decreases the barrier for insertion. Compared to the bare reactant, where a strong interaction exists between the bridging ligand and the metal center, the π-complex has a weaker interaction because of competition from the incoming olefin molecule, and the insertion transition state has a stronger interaction, which leads to a lower insertion barrier. In these systems, the olefin coordination energy X = S(21.4) > Se(19.2) > Te(16.6) and insertion barrier X = S(6.4) > Se(5.9) > Te(5.7) decrease in the increasing order of interaction between the bridging atom X and the metal center, i.e., via X = S < Se < Te. Oxygen as the bridging atom appears to be a special case where the complexation energy is higher than the S/Se/Te catalysts but the insertion barrier is quite low.

2. The use of the C_2H_2 link instead of the C_6H_4 link does not change the trends in the geometries of the reactant, π-complex, and transition state, while it slightly decreases the insertion barrier. In contrast, replacing the C_6H_4 link with C_2H_4 results in destroying the conjugation through the X−C═C−Y moiety and increases the insertion barrier. Without this conjugation, the delocalization of the electron density cannot take place from the interacting ethylene over all atoms of the $X-[(CC)Y]_2$ ligand, thus making the bridging atom more positively charged and, consequently, strengthening the Ti−X overlap and increasing the insertion barrier.

3. The increase of the electron density in the $X-[(CC)Y]_2$ ligand by the addition of electron-rich substituents (like $OSiR_3$) on the link reduces the olefin complexation energy and the insertion barrier.

4. The chelating atoms Y = O and S decrease and Y = NH increases the insertion barrier of the Ti−alkoxide complexes.

5. The catalysts containing X = Y = O and X = Y = S with a conjugated C═C link have the smallest insertion barriers among all studied systems in this paper.

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