justed with KOH under helium purge before the solution was sealed into the sample cell.

Control flashes delivered to solutions containing cresol red but from which diazo compound was omitted (Figure 2A, dotted trace) showed that flash duration and detector recovery did not limit time resolution.

In Vivo Biological Tests. For preliminary biological tests, Fisher rat embryo fibroblasts of the REF52 cell line were cultured as previously described.[9b] For testing diazo-2, REF52 cells were incubated for 30 min at 25 °C in Dulbecco's modified Eagle's medium (DMEM), buffered at pH 7.4 with 20 mM HEPES and containing 1 μM diazo-2/AM and 10 μM fluo-3/AM. For control experiments using diazo-3, the cells were incubated for 90 min at 25 °C in DMEM, buffered to pH 7.4 with 20 mM HEPES and containing 1 μM diazo-3/AM and 10 μM fluo-3/AM. After loading, the cells were gently washed, transferred into Hanks' balanced salt solution containing 0.2 mM sulfinpyrazone to inhibit nonspecific organic anion transport,[41] and mounted on a 25 °C microscope stage for experimentation.

Flash photolysis of trapped cellular diazo-2 and the concomitant monitoring of intracellular free Ca^{2+} concentration with fluo-3, a fluorescent Ca^{2+} indicator,[9a] were performed by methodology and instrumentation developed previously.[9b] Briefly, output from a Xe arc lamp was passed through a monochromator to yield the 490-nm light used to probe the fluo-3 trapped intracellularly. The fluo-3 fluorescence images of the cells were recorded with a silicon-intensified target camera. Images were stored on a high-resolution monochrome laser disc recorder (Panasonic TQ-2028) for delayed processing. Photolyses were performed by briefly moving a chopper mirror to send broad-band UV from an XBO 75-W xenon arc lamp and a UG-2 filter into the microscope instead of 490-nm fluo-3 excitation. The microscope objective (Nikon UV-CF, 40X) was chosen for its high UV transmission and numerical aperture (1.3). A custom dichroic mirror (DR505LP, Omega Optical, Inc., Brattleboro, VT) was placed in the microscope epifluorescence filter cube to reflect both UV and 490-nm light efficiently while retaining high transmission at wavelengths greater than 510 nm, where fluo-3 emits strongly. Data acquisition by the camera and the flash photolysis were under the coordinated control of a Micro-PDP-11/73 computer. The same computer was used to analyze the fluorescence images acquired during the experiment.

Covalent Modification of Lysine by Photochemical Intermediates. To study the extent to which biological substrates may be covalently modified by reactive intermediates generated by the photolysis of the diazoketones, we photolyzed 100 μM diazo-3 in the presence of 10 mM phosphate and either 100 mM KCl or 100 mM lysine hydrochloride, at pH 7.2. The photolysates were analyzed by HPLC (Waters Associates, Inc., Milford, MA; C-18 column, Supelco, Inc., Bellefonte, PA), with 10 mM KH_2PO_4/K_2HPO_4 buffer at pH 7.2 as eluting solvent. The absorbance of the eluate at 254 nm was monitored. Before being injected onto the column, concentrated stock solutions of either KCl or lysine hydrochloride were added to the photolysate to ensure that the electrolyte compositions of the injected samples were identical. Thus, 10 μL of 1 M KCl was added to 100 μL of the sample of diazo-3 photolyzed in lysine hydrochloride, while 10 μL of 1 M lysine hydrochloride was added to 100 μL of the sample of diazo-3 photolyzed in KCl.

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The Direct Insertion Mechanism in Ziegler–Natta Polymerization: A Theoretical Study of $Cp_2TiCH_3^+ + C_2H_4 \rightarrow Cp_2TiC_3H_7^+$

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Abstract: The direct insertion mechanism for the polymerization of ethylene using a real Ziegler–Natta initiator has been studied using PRDDO and ab initio electronic structure calculations. Geometries were optimized at the PRDDO level and energetics were reevaluated at the ab initio Hartree–Fock level with and without MP2 corrections. The calculated barrier for the direct insertion reaction $Cp_2TiCH_3^+ + C_2H_4 \rightarrow Cp_2TiC_3H_7^+$ is +9.8 kcal/mol at the MP2 level. This is in excellent agreement with the experimental barrier of 6–12 kcal/mol. The calculated ΔE for the overall reaction is −12.4 kcal/mol. The geometries of several structures along the reaction pathway including the transition state are presented. The structure of the transition state was found to resemble a metallocyclobutane ring as is generally assumed for the direct insertion mechanism. Localized molecular orbitals are employed to qualitatively analyze the bonding in these complexes. A comparison of our results with similar calculations on the model system $Cl_2TiCH_3^+ + C_2H_4 \rightarrow Cl_2TiC_3H_7^+$ is also presented.

The insertion of olefins into transition-metal alkyl bonds is the fundamental process in Ziegler–Natta polymerization. Yet, despite more than 30 years of study, the mechanism of polymerization is still not fully understood. Several schemes[1] have been proposed for the olefin insertion step; however, experimental results have not definitely proven any one mechanism. The problem in determining the mechanism arises from the fact that most of the Ziegler–Natta initiators are heterogeneous, making them very difficult to study quantitatively. Three basic mechanisms have been proposed. The first and most widely accepted mechanism is the direct four-center olefin insertion mechanism suggested by Cossee and Arlman (Figure 1).[1a–c] The transition state in this scheme may be loosely described as a metallocyclobutane ring-type complex. In some variations on this mechanism, an alkyl-aluminum species is also involved in the mechanistic details; however, in the simplest version of this mechanism the alkyl-aluminum species is required only to alkylate a transition-metal complex, thus forming an active initiator. Second, a metathesis-type mechanism has been proposed by Green and Rooney (Figure 2).[1e,f] In this scheme, there is an α-hydrogen shift from the growing

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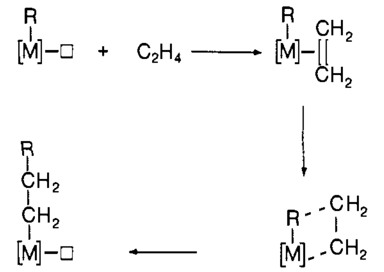


Figure 1. Direct insertion mechanism as proposed by Cossee and Arlman.

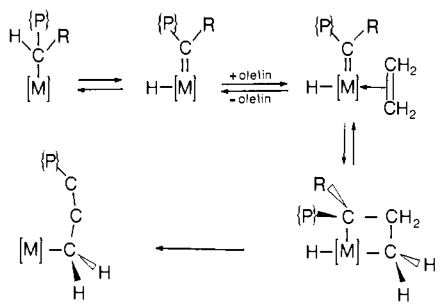


Figure 2. Metathesis mechanism as proposed by Green and Rooney.

polymer chain to the transition metal to form a metal carbene. A third mechanism, more recently proposed by Brookhart and Green,[2,3] is actually a synthesis of the two previously mentioned schemes. Instead of a hydride shift, an α-hydrogen on the growing alkyl side chain forms an "agostic" C–H→Ti bridge with no C–H bond breakage involved.

Each of these proposed mechanisms is supported by experimental evidence. For example, studies on the reaction of $Cp(CH_3)_2(PPh_3)Co$ with C_2H_4,[4] using deuterium labeling experiments, support the direct insertion mechanism of polymerization, since no α elimination was observed in the reaction. Kinetic studies on the $(Cl)Cp_2(C_2H_5)Ti$ system[5] were also consistent with similar conclusions. Experimental evidence supporting the Green–Rooney mechanism generally involves second- or third-row transition-metal complexes. In particular, it has been observed that both $(CHCMe_3)(H)(PMe_3)_3I_2Ta$[6] and $(\eta^5\text{-}C_5Me_5)_2(C_2H_4)(H)Nb$[7] insert ethylene via a metathesis-type mechanism. The suggestion of an agostic interaction in Ziegler–Natta polymerization can be justified by several arguments. Formation of a C–H→Ti bridge could assist in the carbon–carbon bond formation by allowing other atoms on the α carbon to move away from an approaching carbon of the olefin, reducing steric hindrance. Also, the stereochemistry of the alkyl chain with respect to the olefin could be controlled by a C–H→Ti interaction. When compared to available experimental evidence, this mechanism seems quite realistic, since no large isotope effects have been observed in the initiator systems, suggesting no C–H bond breaking is involved. In addition, a recent study by Schmidt and Brookhart[8] suggests an agostic structure for the ethylene polymerization initiator $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)(P(OMe)_3)$, as evidenced by NMR data.

Superficially, olefin insertion reactions, such as the kind found in Ziegler–Natta polymerization, are reminiscent of symmetry forbidden[9] 2 + 2 reactions; however, they are known[10] to proceed with a very low activation energy (6–12 kcal/mol). Recently, Upton[11a] and others[11b] have demonstrated that the low barriers in processes of this type which involve transition metals can be rationalized by simple arguments based on the Pauli principle. From the perspective of qualitative MO theory, it is also easy to show that these reactions should be facile. Consider the $2_\sigma + 2_\sigma$ reaction, $H_2 + H_2 \rightarrow 2H_2$. In the D_{4h} transition state formed by the four hydrogen 1s orbitals there is one bonding (A_{1g}), two nonbonding (E_u), and one antibonding (B_{2g}) interaction. The result is a high-energy barrier for this symmetry-forbidden four-electron reaction. Now, if we replace one of the 1s orbitals with a low-lying 3d orbital (equivalent to replacing one hydrogen atom with an early transition metal in a high oxidation state), we find that one of the previous nonbonding molecular orbitals is now bonding.

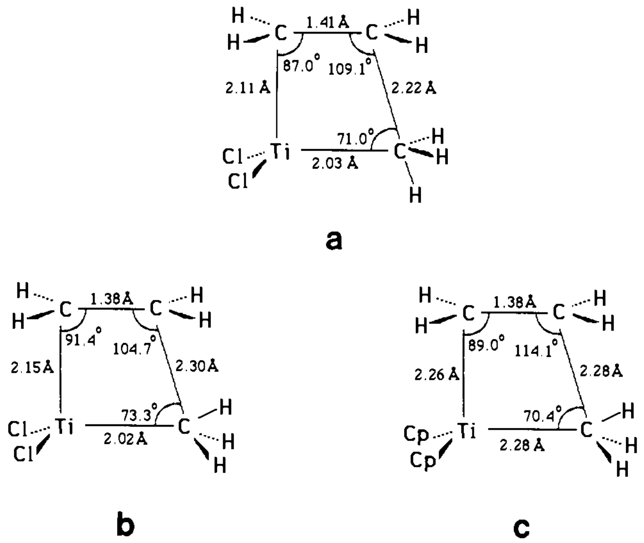
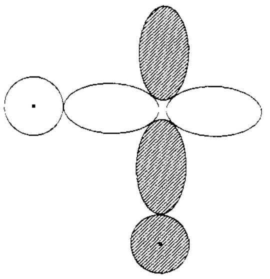


Figure 3. Comparison of transition-state geometries for (a) $Cl_2TiCH_3^+$ initiator from Fujimoto's[16] work, (b) $Cl_2TiCH_3^+$ initiator from this work, and (c) $Cp_2TiCH_3^+$ initiator.



This leads to a stabilization of the transition state and thus a lower energy barrier for the reaction. Therefore, the available d orbitals on the transition metal make this reaction symmetry allowed. Similar qualitative arguments hold for $2_\pi + 2_\sigma$ reactions. Results from calculations[10,12] on various 2 + 2 reactions support this concept.

In an attempt to resolve the question of the mechanism for Ziegler–Natta polymerization, theoretical studies have been performed by various groups. CNDO calculations[13] have been

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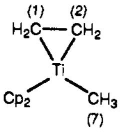
Table I. Geometrical Parameters[a] for Structures **4a–e**

structure	geometrical parameter[b]	calc'd
4a	C(1)-C(2)	1.32
	C(2)-C(7)	3.21
	Ti-C(1)	3.08
	Ti-C(2)	2.76
	Ti-C(7)	2.17
	Ti-Cp[c]	2.06
	Ti-H[d]	2.68
	Ti-H[e]	2.78
	C(1)-C(2)-C(7)	132.6
	C(2)-C(7)-Ti	57.8
	C(7)-Ti-C(1)	105.9
	Ti-C(1)-C(2)	63.7
	Cp-Ti-Cp	137.5
4b	C(1)-C(2)	1.35
	C(2)-C(7)	2.34
	Ti-C(1)	2.43
	Ti-C(2)	2.63
	Ti-C(7)	2.22
	Ti-Cp	2.07
	Ti-H[d]	3.06
	Ti-H[e]	2.67
	C(1)-C(2)-C(7)	119.2
	C(2)-C(7)-Ti	70.3
	C(7)-Ti-C(1)	87.8
	Ti-C(1)-C(2)	82.8
	Cp-Ti-Cp	134.8
4c	C(1)-C(2)	1.38
	C(2)-C(7)	2.28
	Ti-C(1)	2.26
	Ti-C(2)	2.63
	Ti-C(7)	2.28
	Ti-Cp	2.08
	Ti-H[d]	3.16
	Ti-H[e]	2.67
	C(1)-C(2)-C(7)	114.2
	C(2)-C(7)-Ti	70.5
	C(7)-Ti-C(1)	86.3
	Ti-C(1)-C(2)	89.0
	Cp-Ti-Cp	133.6
4d	C(1)-C(2)	1.41
	C(2)-C(7)	2.21
	Ti-C(1)	2.19
	Ti-C(2)	2.62
	Ti-C(7)	2.36
	Ti-Cp	2.08
	Ti-H[d]	3.38
	Ti-H[e]	2.69
	C(1)-C(2)-C(7)	115.3
	C(2)-C(7)-Ti	68.9
	C(7)-Ti-C(1)	84.4
	Ti-C(1)-C(2)	91.4
	Cp-Ti-Cp	137.8
4e	C(1)-C(2)	1.53
	C(2)-C(7)	1.51
	Ti-C(1)	2.15
	Ti-C(2)	2.96
	Ti-C(7)	2.88
	Ti-Cp	2.05
	Ti-H[d]	3.95
	Ti-H[e]	2.71
	C(1)-C(2)-C(7)	116.7
	C(2)-C(7)-Ti	77.8
	C(7)-Ti-C(1)	59.7
	Ti-C(1)-C(2)	105.9
	Cp-Ti-Cp	139.6

[a] In Å and deg. [b] The atom numbering scheme is



[c] Cp refers to the center of the cyclopentadienyl ring. [d] In-plane methyl hydrogen. [e] Out-of-plane methyl hydrogen.

used to study a soluble titanium Ziegler–Natta initiator. The geometries for the compounds in this study were estimated by analogy to related molecules. Ab initio calculations (with a minimum basis set without 4p orbitals on titanium) on the reaction of a $TiCl_4$–$Al(CH_3)_3$ complex with ethylene[14] have been performed by Clementi and co-workers. The quasi-trigonal-bipyramidal geometry for the assumed initiator was taken primarily from experimental structures, however, partial geometry optimizations were performed on the olefin–initiator complex. An SCF–Xα–SW molecular orbital calculation[15] has been reported for $CH_3TiCl_4(C_2H_4)$ using an assumed geometry. Fujimoto et al.[16] carried out a study of the direct insertion of C_2H_4 into the Ti-C bond of $CH_3TiCl_2^+$ as a model of more realistic Ziegler–Natta systems. The geometries for the cyclic structures were determined by ab initio gradient optimizations; however, a complete potential energy surface was not calculated and only the geometry of the cyclic intermediate was reported.

Although many theoretical studies attempting to elucidate the mechanism of Ziegler–Natta polymerization have been reported, none have given an accurate picture of the entire process for a realistic Ziegler–Natta initiator. In light of this, there seems to be a need for a thorough theoretical study of the direct insertion mechanism in which all geometries along the complete potential energy surface are optimized.

In this paper we present the first theoretical study of a true Ziegler–Natta initiator system,[17] $Cp_2TiCH_3^+ + C_2H_4$. We will describe the complete potential energy surface for the direct insertion of ethylene in which all structures have been optimized. The goal of this study was 2-fold. First, we wished to ascertain the viability of the direct insertion process in a realistic Ziegler–Natta system at the highest practical theoretical level. Second, we were interested in comparing the results for the chlorine-containing complexes studied earlier with those obtained for the cyclopentadienyl-containing compounds. This was done to determine the validity of the common practice of substituting chlorines for cyclopentadienyl ligands when performing theoretical studies.

Calculations

The geometries for all of the complexes reported in this work were determined by the PRDDO method.[18,19] PRDDO is a minimum basis set approximate molecular orbital technique which has been shown to reproduce the results of ab initio calculations with a high degree of accuracy while requiring only a fraction of the computing time. PRDDO also gives excellent optimized geometries for a wide range of transition-metal complexes.[20]

In order to explore the potential energy surface and locate the transition state without the evaluation of costly second derivatives, we employed the synchronous transit method[21] for determining least energy pathways in chemical reactions. This approach involves an initial estimate of the transition-state geometry by constructing a linear synchronous transit between the Cartesian coordinates of the reactant and product. Path coordinates are defined as

$$P = d_r/(d_r + d_p)$$

where d_r and d_p are the distances of the current geometry from the reactant and product, respectively. These parameters are defined as

$$d_r = [(1/N) \sum_{\omega=x,y,z} \sum_{a=1}^{N} [(\omega_a(c) - \omega_a(r))^2]]^{1/2}$$

with a similar definition of d_p. This definition of the path coordinate has the advantage of being general for all reactions.

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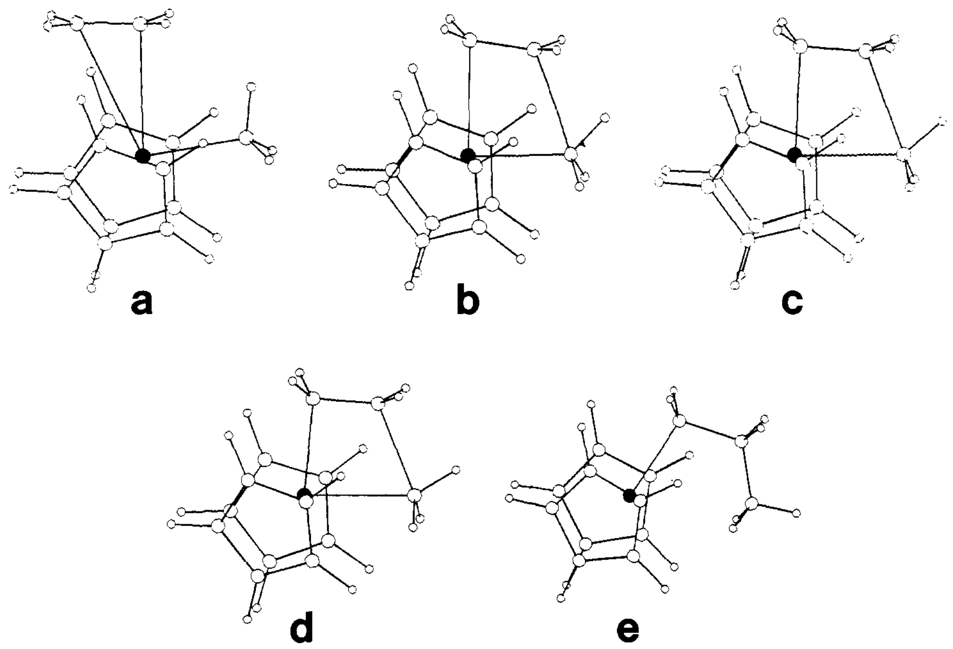

Figure 4. Molecular geometries for points along the potential energy surface: (a) titanium–ethylene complex (reactant, path coordinate 0.0); (b) intermediate structure between reactant and transition state (path coordinate 0.51); (c) estimated transition state for ethylene insertion (path coordinate 0.55); (d) intermediate structure between transition state and product (path coordinate 0.61); (e) product (path coordinate 1.0).

Table II. Comparison of $Cl_2TiC_3H_7^+$ and $Cp_2TiC_3H_7^+$ Parameters[a] with Those of the Agostic Structure $Ti(CH_2CH_2\text{-}\mu\text{-}H)Cl_3(dmpe)$[b]

compound	M–H	C–H	M–C	M–C–H
$Ti(CH_2CH_2\text{-}\mu\text{-}H)Cl_3(dmpe)$	2.29	1.02	2.52	70.0
$Cl_2Ti\text{-}CH_2\text{-}CH_2\text{-}CH_3^+$	2.28	1.09	2.37	72.2
$Cp_2Ti\text{-}CH_2\text{-}CH_2\text{-}CH_3^+$[c]	2.71	1.07	2.88	70.1
$Cp_2Ti\text{-}CH_2\text{-}CH_2\text{-}CH_3^+$[d]	2.18	1.09	2.95	37.0

[a] In Å and deg. [b] See ref 32. [c] Structure **4e**. [d] Structure **4e** with methyl group rotated 180° and reoptimized.

Table III. Overlap Populations for Compounds **4a–e**

compd	C_1–C_2	C_2–C_7	C_1–Ti	C_2–Ti	C_7–Ti
4a	1.126	−0.007	0.061	0.115	0.441
4b	1.040	0.029	0.162	0.030	0.394
4c	0.966	0.089	0.215	0.003	0.357
4d	0.852	0.209	0.272	−0.003	0.256
4e	0.736	0.749	0.427	−0.118	−0.037

Table IV. Degrees of Bonding for Compounds **4a–e**

compd	C_1–C_2	C_2–C_7	C_1–Ti	C_2–Ti	C_7–Ti
4a	1.765	0.004	0.203	0.263	1.027
4b	1.512	0.115	0.494	0.261	0.916
4c	1.348	0.229	0.655	0.243	0.814
4d	1.133	0.476	0.858	0.244	0.577
4e	0.973	1.000	1.009	0.050	0.096

Full geometry optimizations were performed for all structures with the following exceptions: (1) C_s symmetry was preserved in all cases and (2) the C–C and C–H distances in the cyclopentadienyl rings were fixed. Orthogonal optimizations[21] for a model initiator system, $Cl_2TiCH_3^+ + C_2H_4$, revealed that the bond length between the interacting methyl and ethylene carbons (C_2 and C_7) varies monotonically with the path coordinate. This geometrical parameter was employed to define the path coordinate in the more complicated $Cp_2TiCH_3^+ + C_2H_4$ surface.[22] Optimizations were performed while holding the C_2–C_7 bond length fixed at the value obtained from the synchronous transit calculations. The path coordinates for the resulting optimized complexes were computed by linear interpolation of the C_2–C_7 internuclear distance. The path coordinates for the reactant and product were set at 0.0 and 1.0, respectively. The conformation of the methyl group in structure **4a** was intentionally chosen to prevent the possibility of agostic interactions and thus allows the simplest form of the reaction to be studied.

After the optimized geometries were obtained, the energetics of the structures along the reaction pathway were reevaluated at the Hartree–Fock ab initio level. These ab initio calculations were performed with the program GAMESS.[23] The choice of basis set for complexes such as these is often difficult. The basis set must be economical in order for the calculations to be tractable, yet it must be large enough to accurately describe the system. Our first concern was to get a realistic picture of the energetics at the Hartree–Fock level. With this in mind, we performed calculations using a very large basis set. This basis set consisted of 4-31G*[24] plus diffuse sp functions[25] on the methyl and ethylene carbons, 3-21G[26] on the remaining ligands except for the cyclopentadienyl hydrogens which were described by an STO-3G[27] expansion. The metal basis was triple-ζ in the 3d space, double-ζ for the 4s and 4p functions, and single-ζ for the core orbitals and included a diffuse 4d function.[28] This corresponds to basis set A′ in ref 28 with Slater exponents of: 3s/3d, 8.041, 3.770, and 1.752; 4s/4p, 2.215 and 1.355; 4d, 1.00. Diffuse s and p functions were included on the methyl and ethylene ligand to account for the potential anionic character of alkyl groups coordinated to early transition metals. Other basis sets were tested and an optimum basis set was chosen. This basis set is smaller, and thus more economical, while giving an energy barrier within 1.4 kcal/mol of the large basis set. The basis set consisted of a 4-31G[24a,29] basis on all the ligands except for the

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[22] For molecules containing groups with high *local* symmetry (e.g., cyclopentadienyl ligands) and low rotational energy barriers about the local symmetry axis, the orthogonal optimization approach proposed in ref 18 sometimes fails, owing to an ambiguity in defining the path coordinate when equivalent, energetically accessible rotational conformers are present. For this reason, the C_2–C_7 distance was chosen to define the path coordinate.

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Table V. LMO Hybridizations and Populations

	population				hybridization				
orbital	Ti	C_1	C_2	C_7	Ti	C_1	C_2	C_7	% delocalization
8a	0.23	0.86	0.94	*a*	$sp^{0.6}d^{0.4}$	$sp^{5.9}$	$sp^{5.6}$		12.1
8b	0.90	*a*	*a*	1.13	$sp^{0.7}d^{3.8}$			$sp^{2.5}$	17.0
9a	0.51	1.13	0.38		$sp^{0.7}d^{2.9}$	$sp^{4.3}$	$sp^{13.5}$		13.1
9b	0.68	*a*	0.20	1.14	$sp^{1.3}d^{4.5}$		$sp^{8.1}$	$sp^{2.4}$	18.6

[a] Less than 0.2.

cyclopentadienyl rings which were described by a minimum (STO-3G) basis. The metal basis (basis B′, ref 28) was double-ζ in the 3d and 4p space and single-ζ for the inner shells and the 4s region. The Slater orbital exponents for the valence orbitals were: 3s/3d, 4.661 and 1.983; 4s, 2.075; 4p, 2.429 and 1.477. For both metal basis sets, the 3d functions included a sixth Cartesian d functon used to represent the 3s space.[28] Both metal basis sets consisted of 3G expansions on the core orbitals and 2G expansions on the valence 3d, 4s, and 4p orbitals.

In order to account for electron correlation in these systems, MP2[30] corrections were added using the GRADSCF[31] program of Komornicki. The basis set employed in these calculations was identical with the small basis set described above except that a 6-31G basis was used on the methyl and ethylene carbons and hydrogens and only 1G expansions were used on the 4s and 4p orbitals of the metal. These modifications in the basis set resulted in insignificant changes in the calculated energies at the Hartree–Fock level.

Discussion

$Cl_2TiCH_3^+$. The reaction of ethylene with $Cl_2TiCH_3^+$ was studied in our laboratory as a precursor to the cyclopentadienyl system. Although the results for the $Cp_2TiCH_3^+$ initiator will be presented more fully, a few points about the less complicated chlorine system are worth mentioning. For example, our PRDDO optimized geometry for the transition state in the model Ziegler–Natta reaction $Cl_2TiCH_3^+ + C_2H_4 \rightarrow Cl_2TiC_3H_7^+$ is remarkably similar to the geometry Fujimoto and co-workers[16] found in their study of the same system at the ab initio level with an expanded basis set. The two geometries are compared in Figure 3 (the methyl group in our optimized transition state is rotated 180° compared to the orientation of the methyl group in Fujimoto's calculations). The bond angles describing the metallocyclobutane ring structure differ by no more than 4.4° between our PRDDO optimized geometry and the ab initio gradient optimized geometry of Fujimoto. Furthermore, the largest discrepancy between bond lengths was only 0.08 Å, for the weakly formed C_2–C_7 bond (see footnote *b*, Table I). The product geometry obtained from the model $Cl_2TiC_3H_7^+$ complex differs considerably from the cyclopentadienyl case. In particular, the distance between the methyl hydrogens and the titanium is 2.28 Å, suggesting the presence of an agostic interaction. Upon further inspection we note that the geometrical parameters involving the methyl hydrogens and the metal in the chlorine-containing complex are very similar to those for the complex $Ti(CH_2CH_2\text{-}\mu\text{-}H)Cl_3(dmpe)$[32] which is known to have an agostic structure; for a comparison, see Table II. Furthermore, overlap populations obtained from PRDDO population analyses show an overlap of 0.04 for the titanium-methyl nearest-neighbor hydrogens. This is not an insignificant value when considering agostic interactions.

The reaction barrier at the ab initio Hartree–Fock level for the reaction of ethylene with $Cl_2TiCH_3^+$ was found to be 11.9 kcal/mol, while the overall ΔE for the insertion reaction of $Cl_2Ti(C_2H_4)(CH_3)^+$ is -2 kcal/mol. Our calculations yield an ethylene binding energy of 34.1 kcal/mol, compared to a binding energy of 35.3 kcal/mol reported by Fujimoto and co-workers.[16] Addition of MP2 correlation corrections increases the binding energy to 48.8 kcal/mol, significantly larger than that found for the cyclopentadienyl initiator (see below). Thus, the energies of ethylene binding are not well-modeled by the $Cl_2TiCH_3^+$ system. We note that the optimized geometry of $Cl_2TiCH_3^+$ is unusual, in the sense that the chlorines, carbon, and titanium are not coplanar (Cl-Ti-Cl = 118.6°, C-Ti-Cl = 108.3°, C_s symmetry). This is a characteristic of many low coordination number, high oxidation state metal complexes which can be attributed to the ability of the metal to more efficiently utilize its d orbitals in a nonplanar geometry. Further details, including optimized geometries for a variety of complexes at the ab initio level, will appear elsewhere.[33]

$Cp_2TiCH_3^+$. Geometries. Five structures are used to describe the reaction of ethylene with the $Cp_2TiCH_3^+$ initiator. These molecular structures correspond to points along the reaction pathway and are presented in Figure 4. The important bond lengths and angles for the complexes are given in Table I. Structure **4a**, the "reactant" in our olefin insertion process, is a π-type complex. The ethylene moiety is not bound symmetrically by the titanium, but instead is shifted away slightly from the methyl group. The titanium–carbon distances associated with this interaction are quite long (3.08 and 2.76 Å) compared to typical Ti–C single bonds (~2.2 Å). Partial optimization of a structure with a symmetrically bound ethylene yielded a calculated energy only 1 kcal/mol higher than the energy of **4a** at the PRDDO level. Structure **4b** is a complex which is intermediate between the reactant and the transition state. This structure illustrates the ethylene "sliding" over in preparation for insertion into the Ti–CH_3 bond.

The transition state for this reaction, structure **4c**, is very similar to the metallocyclobutane ring-type complex as described by Cossee.[1a] The transition state strongly resembles the reactant, the major differences being that (1) the ethylene has migrated over toward the methyl group and (2) the methyl group has pivoted to avoid unfavorable steric interactions between the ethylene hydrogens and the in-plane methyl hydrogen and to enhance the bonding interaction between C_2 and C_7. The ethylene C–C bond and the methyl–titanium bond have lengthened slightly in the transition state as compared to the reactant. The ethylene–methyl distance (C_2–C_7) has shortened to 2.28 Å; however, it is still much longer than a typical C–C single bond. The "reactant-like" nature of the transition state is nicely demonstrated by the overlap populations and degrees of bonding shown in Tables III and IV, respectively. A comparison between **4c** and Fujimoto's[16] transition state for the $Cl_2TiCH_3^+$ model initiator is also shown in Figure 3.

Structure **4d** is intermediate between the transition state and the product (**4e**). Upon studying the product geometry, **4e**, it is noted that the methyl-titanium bond has completely broken as evidenced by the long bond length, and that the methyl hydrogens show no significant agostic interaction with the titanium (Ti-H = 2.71 Å). This is in contrast to the product geometry obtained from the model $Cl_2TiC_3H_7^+$ complex (see above). The geometry of this complex differs considerably from the cyclopentadienyl case. These results for the cyclopentadienyl initiator are not surprising considering the steric hindrance between the out-of-plane hydrogens and the cyclopentadienyl rings. In order to reduce this steric hindrance and investigate the possibility of an agostic

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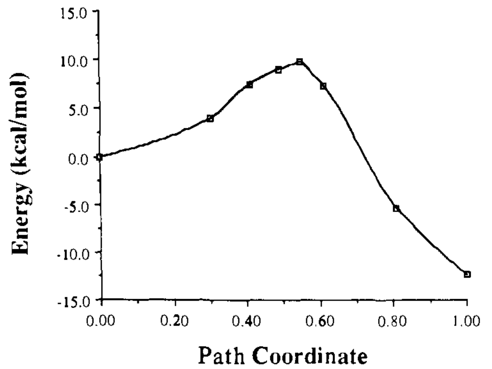

Figure 5. Potential energy surface for the reaction $\mathrm{Cp_2TiCH_3^+ + C_2H_4 \rightarrow Cp_2TiC_3H_7^+}$ (eq 1) calculated at the MP2 level. Path coordinates 0.0 and 1.0 correspond to structures **4a** and **4e**, respectively. The energy of the initial transition metal-alkyl-olefin complex is set to 0.0 kcal/mol and all other energies are plotted relative to this value.

Figure 6. Localized molecular orbital plots showing the (a) titanium-ethylene and (b) titanium-methyl bonding orbitals for the metal-olefin complex (**4a**). The contour levels are ±0.5, ±0.4, ±0.3, ±0.2, ±0.1, ±0.05, ±0.02, ±0.01, ±0.005, ±0.0035, and ±0.002 e/au^3.

interaction in the real initiator system, the methyl group in **4e** was rotated 180° and the structure was reoptimized. This revealed the presence of an agostic interaction between the in-plane hydrogen and the metal. The optimized hydrogen-titanium distance was found to be 2.18 Å with a corresponding overlap of 0.05. The ΔE between the product (**4e**) and the product with the methyl group rotated was found to be 0.42 kcal/mol at the PRDDO level. Although there is a significant agostic interaction, it appears to be masked energetically by the less favorable eclipsing of the methyl hydrogens with the neighboring methylene hydrogens.

The calculated reaction profile for eq 1 is shown in Figure 5.

$$\mathrm{Cp_2TiCH_3^+ + C_2H_4 \rightarrow Cp_2TiC_3H_7^+} \qquad (1)$$

The reaction barrier, computed at the PRDDO level, was determined to be +21.1 kcal/mol. The barrier at the ab initio Hartree-Fock level was found to be +22.1 kcal/mol. Upon adding electron correlation effects, the barrier dropped to +9.8 kcal/mol. Remarkably, the transition state at all levels of theory was found to be at path coordinate 0.55 ± 0.01. The MP2 results are in excellent agreement with the estimated activation energies of 6–12 kcal/mol[10] for similar systems. The overall ΔE for the insertion process **4a** → **4e** is calculated to be −12.4 kcal/mol at the MP2 level, almost exactly what one would expect based upon the relative average bond dissociation energies of C–C single and double bonds (~80 and ~105 kcal/mol, respectively).

In order to further investigate the possibility of an agostic interaction in this initiator system and its effects on the energetics of the reaction, the methyl groups in both the reactant (**4a**) and product (**4e**) were rotated 180° and the structures reoptimized. A transition state was then located for this new surface using the methods described previously. A slightly lower activation energy was found for this reaction, specifically 14.3 kcal/mol at the PRDDO level, and 15.3 kcal/mol at the ab initio Hartree-Fock level (MP2 calculations were not done for this conformation). The 7 kcal/mol difference between the energy barriers with the methyl group in the two different conformations could be due to nonbonded interactions in the transition state or to agostic interactions. In order to investigate this, nonbonded van der Waals interaction calculations were performed on the two different transition states using the CHEMX software package.[34] The difference in the nonbonded interactions between the two structures was found to be 5.4 kcal/mol, favoring the second conformation. This suggests that the lower energy barrier found for the second conformation is not due to agostic interaction effects. These results show that the direct insertion mechanism is a viable one even without agostic interactions. The exact nature of the transition state and energy barrier for an experimental Ziegler-Natta system will greatly depend on the amount of steric hindrance in the initiator.

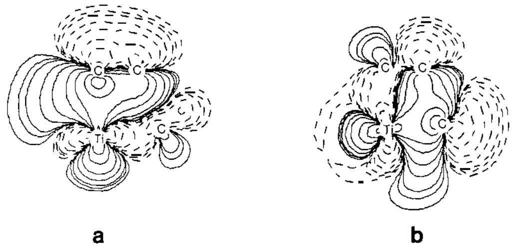

Figure 7. Localized molecular orbital plots showing the (a) titanium-ethylene and (b) titanium-methyl bonding orbitals for the transition state (**4c**). The contour levels are the same as those of Figure 6.

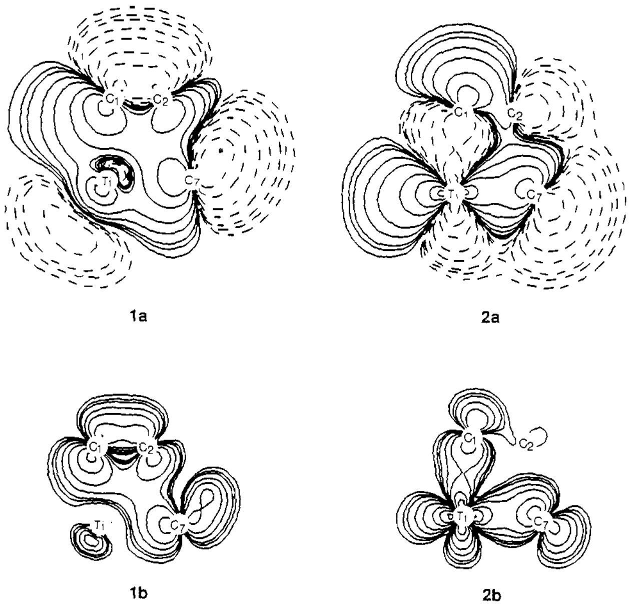

Figure 8. Canonical molecular orbital plots for the transition state (**4c**) showing the (1a) full MO wave-function plot for the second HOMO, (1b) electron density plot for the second HOMO, (2a) full MO wave-function plot for the HOMO, and (2b) electron density plot for the HOMO. The contour levels are the same as those of Figure 6.

Our calculations on the $\mathrm{Cp_2TiCH_3^+}$ system yielded an ethylene binding energy of 15.9 kcal/mol at the MP2 level, significantly different from the value of 48.8 kcal/mol found for $\mathrm{Cl_2TiCH_3^+}$. Unlike the $\mathrm{Cl_2TiCH_3^+}$ system, the geometry for the cyclopentadienyl initiator is not unusual; the cyclopentadienyl centroids, Ti, and methyl C are coplanar.

Localized and Canonical Molecular Orbitals. Localized molecular orbitals are very useful for analyzing the bonding in these complex transition-metal systems. The Boys criterion[35] was employed for calculating localized molecular orbitals with the PRDDO program. The important localized molecular orbital wave-function plots for the ethylene complex (**4a**) are presented in Figure 6. The LMO representing the titanium-ethylene bond, Figure 6a, shows the titanium bound to the ethylene through the olefin π system. Figure 6b shows the titanium-methyl bonding LMO. The transition-state (structure **4c**) LMO's are shown in Figure 7. The titanium-ethylene LMO (Figure 7a) is very similar

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(34) CHEMX. Developed and distributed by Chemical Design Ltd., Oxford, England, 1988.

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to that seen for the ethylene complex. The titanium-methyl LMO (Figure 7b), however, shows the new bonding interactin between C_2 and C_7. This interaction may be loosely described as donation of the Ti–CH_3 bonding pair into the ethylene π^* orbital. The atomic populations and calculated hybridizations[36] for orbitals 6a, 6b, 7a, and 7b are presented in Table V. Clearly, d-orbital participation is very important in both the reactant and the transition state.

In the Introduction, symmetry arguments were presented to explain why the 2 + 2 reaction in Ziegler–Natta polymerization is not symmetry forbidden. To further illustrate this fact, wave-function plots and electron density plots for the two important bonding canonical molecular orbitals (the first two HOMO's) in the $Cp_2TiCH_3^+$ transition state are shown in Figure 8. As the symmetry analysis showed, we have two bonding orbitals in the transition state for this reaction. Plot 1a illustrates the bonding interaction between the ethylene carbons (C_1 and C_2) and the titanium, as well as the bonding interaction between the methyl carbon (C_7) and one of the ethylene carbons (C_2). In the second molecular orbital, 2a, we see bonding between the methyl carbon (C_7) and the titanium and C_1 and titanium. There is no interaction, however, between C_2 and C_7. This is further exemplified by the electron density plot, 2b, and supports the fact that the C_2–C_7 bond in the transition state has not fully formed yet.

Conclusions

We have presented a full reaction profile for the direct insertion polymerization of ethylene by a real Ziegler–Natta initiator system, $Cp_2TiCH_3^+$. Geometries for the structures along the reaction pathway were optimized using the PRDDO method. Ab initio Hartree–Fock calculations with and without MP2 corrections were used to reevaluate the energetics of these structures. The activation energy at the MP2 level of theory is +9.8 kcal/mol for the $Cp_2TiCH_3^+$ system. The binding energy of ethylene was found to be 15.9 kcal/mol for the $Cp_2TiCH_3^+$ initiator, while the overall ΔE for the insertion process is −12.4 kcal/mol.

The results of this study indicate that direct insertion without alkyl-aluminum assistance and without agostic interactions is indeed a viable mechanism for the Ziegler–Natta polymerization of ethylene using a titanium-based initiator system.

Finally, this work indicates that the substitution of chlorines for cyclopentadienyl ligands in theoretical studies on organometallic complexes must be done with caution. While the calculated transition states and overall exothermicities for the two reactions studied are fairly similar, the ethylene binding energies are significantly different.

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Photochemistry in a Box. Photochemical Reactions of Molecules Entrapped in Crystal Lattices: Mechanistic and Exploratory Organic Photochemistry[1,2]

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Abstract: An exploration was made of the photochemical behavior in the crystalline state of a series of molecules we have previously studied in solution. The reactions studied fall into the categories of cyclohexenone rearrangements, reactions of di-π-methane systems, and the behavior of a molecule giving a long-range phenyl migration in solution. The 4,4-diarylcyclohexenones differed from the solution behavior in giving the trans-bicyclic photoproducts without the cis isomers and the 3,4-diarylcyclohexenones. In the case of 4,5,5-triphenylcyclohexenone, the bicyclic photoproduct had inverted stereochemistry compared with solution and otherwise showed entirely different photochemistry than the usual solution cyclobutanone formation. The di-π-methane systems gave rise to three types of behavior: (1) An intramolecular $2_\pi + 2_\pi$ cycloaddition between a dicyanovinyl and a phenyl group, (2) di-π-methane reactivity but with reversed regioselectivity, and (3) cyclopentene formation where the reactant has an additional vinyl group on the methane carbon. Finally, 1,1,5,5-tetraphenyl-3,3-dimethyl-1-penten-5-ol afforded five- and six-membered ring ethers rather than the solution phenyl migration. Solid-state quantum yields were determined with use of a newly designed apparatus. Several quantitative approaches for correlating solid-state reactivity to molecular geometry and crystalline constraints were devised.

For several decades our research group has pursued the investigation of solution photochemistry with an aim of encountering new organic transformations, determining the corresponding reaction mechanisms, and then correlating excited-state reactivity with structure. This reactivity was shown to be controlled by various intramolecular factors such as excited-state bond orders, electron densities, and hypersurface energy effects.[3]

However, organic photochemistry has included many studies of crystalline solids. The dimerization of crystalline cinnamic acid to the truxillic and truxinic acids was first studied at the beginning of the century.[4] With the advent of X-ray crystallography

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[1] This is Paper 158 of our photochemical series and Paper 218 of our general series.

[2] For Paper 157 see: Zimmerman, H. E.; Cassel, J. M. *J. Org. Chem.*, **1989**, *54*, 3800–3816.

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