

Computational Studies into Ziegler-Natta Catalysis

by

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Dr. Kumar Vanka



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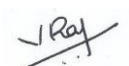


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Dedicated to My Parents

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Abbreviations

Z-N	Ziegler-Natta
DFT	Density Functional Theory
B3LYP	Becke, 3-parameter, Lee-Yang-Parr
M06	Minnesota 06
ID	Internal Donor
ED	External Donor
MM	Molecular Mechanics
DNA	Deoxyribonucleic acid
TISE	Time Independent Schrödinger Equation
1-D	1-Dimensional
H-K	Hohenberg-Kohn
K-S	Kohn-Sham
PBE	Perdew–Burke-Ernzerhof
TZVP	Triple Zeta Valence plus Polarization
RI	Resolution of Identity
MARIJ	Multipole Accelerated Resolution of Identity
D3	Dispersion correction (version 3)
IRC	Intrinsic Reaction Coordinate
KP	Ketone Pathway
AP	Aldehyde Pathway
NCI	Non-Covalent Interaction
D	Donor
DIPDMS	diisopropyl dimethoxysilane
DCPDMS	dicyclopentyl dimethoxysilane
DSBDMS	disec-butyl dimethoxysilane
SBMDMS	sec-butyl(methyl) dimethoxysilane
TEAL	Triethylaluminum
SVP	Single Valence plus Polarization

M06-L	Minnesota 06 Local
TPSS	Tao-Perdew-Staroverov-Scuseria
+I	+Inductive
AFE	Adduct Formation Energy
AS	Active Site
TS	Transition State

Physical Constants

Avogadro's Constant	$(N_A) = 6.02214129 \times 10^{23} \text{ mol}^{-1}$
Atomic Mass Unit	$(u) = 1.660538921 \times 10^{-27} \text{ kg}$
Boltzmann's Constant	$(k) = 1.3806488 \times 10^{-23} \text{ JK}^{-1}$
Bohr Radius	$(a_0) = 5.291772109 \times 10^{-11} \text{ m}$
Elementary Charge	$(e) = 1.602176565 \times 10^{-19} \text{ C}$
Gas Constant	$(R) = 8.3144621 \text{ JK}^{-1} \text{ mol}^{-1}$
Mass of Electron	$(m_e) = 9.10938291 \times 10^{-31} \text{ kg}$
Mass of Proton	$(m_p) = 1.672621777 \times 10^{-27} \text{ kg}$
Mass of Neutron	$(m_n) = 1.674927351 \times 10^{-27} \text{ kg}$
Rydberg Constant	$(R) = 1.097373157 \times 10^7 \text{ m}^{-1}$
Speed of Light	$(c) = 2.99792458 \times 10^8 \text{ ms}^{-1}$
Planck's Constant	$(h) = 6.62606957 \times 10^{-34} \text{ Js}$

Chapter 1

Introduction to Ziegler-Natta Catalysis

Chapter 1

Introduction to Ziegler-Natta Catalysis

Abstract: Ziegler-Natta (Z-N) catalysts are the global working horse in producing polyethylene and isotactic polypropylene. Despite their success as industrial catalytic systems, their nature and reactivity remain unclear. The multi-component (MgCl_2 , TiCl_4 , alkyl aluminum species, donors, and monomer) and multi-site nature of the Z-N catalysts make them challenging to understand completely at the atomic level. Furthermore, the reaction is stereoselective and regioselective, and depends on multiple factors. The parallel reactions also occur in the system, which can adversely affect the primary polymerization reaction. This chapter provides a brief overview of the components in Z-N catalysts and their roles, reaction mechanisms, the factors influencing stereoselectivity and regioselectivity, and a discussion about the parallel reactions taking place in these systems.

1.1. Introduction

The invention of the Ziegler-Natta (Z-N) catalyst in the 1950s was one of the most influential chemistry discoveries of the last century, which profoundly impacted the polyolefin industry.^{1,2} For this remarkable discovery, Karl Ziegler and Giulio Natta were awarded the Nobel Prize in Chemistry in 1963. Ziegler was the director of Max-Planck-Institut für Kohlenforschung from 1943 to 1969. In 1953, he discovered that a mixture of aluminum triethyl or diethyl aluminum chloride with titanium tetrachloride could act as catalysts for synthesizing long-chain molecules (polymers) from smaller molecules (monomers).³ Natta was a full professor and director of the Department of Industrial Chemistry at the Milan Polytechnic from 1938. Later, in 1955, Natta extended the discovery by Ziegler and discovered a catalyst that could produce long-chain molecules in which parts of the molecules were oriented in a specific direction (isotactic polymers).⁴

The Z-N catalysts show excellent catalytic activity, are highly stereoselective, and produce polymers with high molecular mass, making the Z-N catalysts one of the most critical industrial heterogeneous catalysts.^{1,2} The annual production of polyolefin, mainly polyethylene and isotactic polypropylene, using the Z-N catalysts are more than 150 million tons. Compared to homogeneous catalysts, the Z-N catalysts are more efficient, less costly, and offer better control over the morphology of polymer granules. Despite all these facts, the understanding of Z-N catalysts at an atomistic scale is still poor. There are four components in a modern-day Z-N catalyst: (1) an inert MgCl_2 surface, which acts as a support, (2) TiCl_4 , which is the precatalyst and can convert into the active form by the intervention of an alkyl aluminum species, (3) an alkyl aluminum species, which acts as the cocatalyst, and finally (4) Lewis base donors, which are small molecules containing oxygen atoms, which act as potential electron donors. There are two categories of donors, depending on when they are added to the system. Internal donors are added to the system during the precatalyst preparation, and external donors are added to the system along with the alkyl aluminum species. The multisite nature of Z-N catalysts arises from the innumerable possibilities of interactions between these components, which make them very difficult to understand by any experimental or computational techniques alone. Understanding the Z-N catalyst is like solving a jigsaw puzzle. In the following sections, I will briefly summarize the roles of each component in the Z-N system, which will help the reader get an overall picture of how it works.

1.2. MgCl₂ surface

For more than a decade after the discovery of the Z-N catalyst, people had used TiCl₃ catalyst to produce polyolefins. However, a significant breakthrough happened in 1968 when Kashiwa (of Mitsui Petrochemical Industries) discovered that MgCl₂-supported TiCl₄ catalysts are far superior to the old generation of catalysts in terms of both activity and selectivity.⁵ Even though many surfaces like MgCl₂.nROH,^{6–9} MgCl(OR),¹⁰ Mg(OR)₂,¹¹ FeCl₃ doped Mg(OR)₂,¹¹ and SiO₂¹² have been employed in the Z-N catalysts; the most efficient and extensively used support is MgCl₂. There are three forms of MgCl₂: α , β , and γ .¹³ The α MgCl₂ form is available commercially and is used to prepare the support (mixed with internal donors) by the ball milling method, which produces small MgCl₂ crystallites. There are different terminations for MgCl₂; (001), (110), (104) (see Figure 1.1), and the recently identified (015) facets.^{14–17} The (001) facet is unsuitable for the adsorption of TiCl₄ because it consists of only Cl atoms. However, both (104) and (110) facets are suitable for TiCl₄ adsorption, where the (104) facet is composed of penta-coordinated Mg atoms and the (110) facet is composed of tetra-coordinated Mg atoms. This means that an Mg²⁺ ion in the (104) facet has a single vacancy, but an Mg²⁺ ion in the (110) facet has two vacancies.

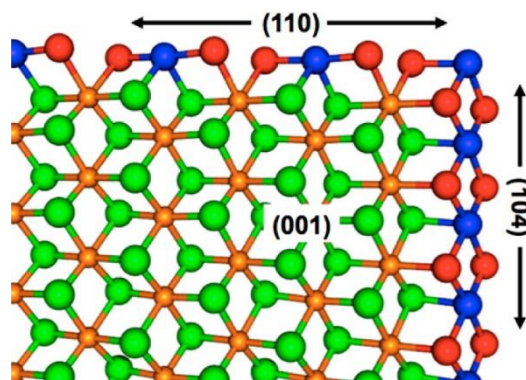


Figure 1.1. Model of the MgCl₂ layer demonstrating the (001), (110), and (104) terminations. Adapted with permission from ref. 33. Copyright 2015 American Chemical Society.

A periodic DFT study by Credendino *et al.* proposed that the (104) facet is more stable than the (110) facet.¹⁸ Later, Cavallo and co-workers also concluded the same using DFT calculations. However, more interestingly, they found that the order of stability reversed in the presence of donors because of the higher Lewis acidity of the (110) facet.^{19,20} Similarly, other studies have also shown that the presence of

adsorbates/donors can tremendously influence the microstructure of the MgCl_2 facets.^{21–23} Even though the (104) facet was considered catalytically relevant for an extended period, later computational and experimental studies suggested that the (110) facet is catalytically essential.^{22,24} This change in the paradigm is because of the revelation (mainly due to DFT studies) that it is only to the (110) facet that both the TiCl_4 and donors can strongly coordinate. However, a few studies still suggest that, along with the (110) MgCl_2 facet, the (104) MgCl_2 facet is also catalytically relevant.^{25,26}

1.3. TiCl_4

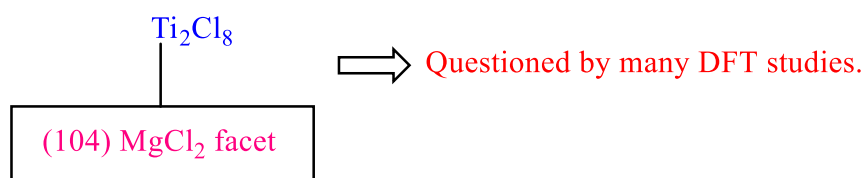
Initial models suggested that the adsorption of the TiCl_4 (which is the precatalyst) happens on the (104) facet as a dimeric species (Ti_2Cl_8), which would mimic the stereoselective site. The proposal was based on the similarity of such a dimeric species with stereoselective sites proposed earlier for the TiCl_3 .^{27–29} However, this model was challenged by many DFT studies that showed that the adsorption of TiCl_4 on the (104) facet is not energetically favorable, and the formation of Ti_2Cl_8 is dubious.^{16,30,31} For example, a study by Monaco *et al.* showed that the adsorption of TiCl_4 and TiCl_3 on the (110) MgCl_2 facet is more favorable (15.3 and 29.8 kcal/mol, respectively) than the adsorption on the (104) MgCl_2 facet (5.0 and 24.9 kcal/mol, respectively).³² Furthermore, Ziegler and co-workers questioned the binding of TiCl_4 on the MgCl_2 facets because of the low adsorption energies (~ 10.0 kcal/mol in various models) and the high loss of translational and rotational degrees of freedom.³³ They suggested that the binding of TiCl_4 on the facet would be favorable only if the titanium replaced one of the magnesium atoms.

Furthermore, the effect of donors in the binding energy of TiCl_4 and TiCl_3 on the (110) and (104) MgCl_2 facets has been studied by Taniike and Terano.³⁴ Intriguingly, they found that the use of donors causes a preferential co-adsorption of the titanium species and the donor on the (110) MgCl_2 facet. However, such a trend was not observed on the (104) MgCl_2 facet. An interesting study of the zip-coordination (coordination of a species into different layers of the MgCl_2) of titanium species has been done by Stukalov *et al.*, where they found that among various possibilities of Ti(IV) coordinated to the (104) facet, the zip-coordination of the Ti_2Cl_8 species on the (104) facet is the most favorable one.³⁵ However, unlike Ti_2Cl_8 coordinated to the

monolayer of the (104) facet, the zip-coordinated Ti_2Cl_8 on the (104) facet can produce both stereoselective and non-stereoselective active sites.

A recent study by D'Amore using better functionals such as B3LYP, PBE0, and M06 also shows that the coordination of TiCl_4 on the (110) facet is feasible, but the coordination on the (104) facet is too weak.³⁶ Experimental studies have also proven that TiCl_4 prefers to coordinate with the (110) MgCl_2 facet.^{14,37} Liu and co-workers have performed an interesting study to understand the competition between the ethyl benzoate donor and TiCl_4 to coordinate to various MgCl_2 surfaces. They have considered regular and defective surfaces, where the defective surfaces are modeled by the omission of either chlorine atoms or chloride ions. They have concluded that the surface model, for which the TiCl_4 coordination is more favorable than the ethyl benzoate coordination, is the most likely model for the active site.³⁸ Recently, Cavallo and co-workers proposed the formation of a step defect on the (104) surface.³⁹ The energy cost for the formation of such a single-step defect is only 7.0 kcal/mol, and the calculated surface energies for various percentages (10%, 20%, and 30%) of defects indicate that even a 30% defective (104) facet is more stable than the (110) facet. More interestingly, they have also calculated the adsorption energy of TiCl_4 on the step defect of the (104) facet. The calculated binding energy (12.5 kcal/mol) is much higher than the binding energy on the (104) facet and comparable to that on the (110) facet (2.8 kcal/mol and 13.9 kcal/mol, respectively), which suggests a new type of active site for the polymerization reaction. The main differences between the early and current models proposed for Z-N catalysts are summarized in Figure 1.2, shown below.

Early model



Current model

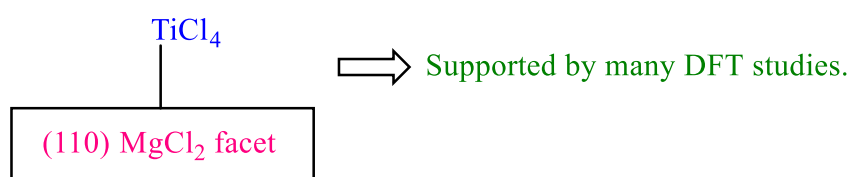


Figure 1.2. Schematic representation comparing early and current models proposed for Z-N catalysts.

There are mainly three active sites proposed in the literature (see Figure 1.3): the (a) Corradini site, where titanium is bound to the (110) facet *via* two bridging chlorine atoms and two surface chlorine atoms, (b) the edge site, where the titanium is coordinated to the (110) facet *via* two bridging chlorine atoms and one surface chlorine atom, and (c) the slope site, where the titanium is bound to the (104) facet *via* two bridging chlorine atoms and one surface chlorine atom. The edge and the slope sites have two vacancies, but there is only one vacancy in the Corradini site. This means that both donor and monomer can coordinate to the edge and the slope sites, but either the monomer or the donor can coordinate to the Corradini site. Seth *et al.* studied the 18 various active site models and concluded that only three edge sites (two TiCl_3 based edge sites and one TiCl_4 based edge site of TiCl_2) were suitable as the active sites.³³ The other considered models were either unstable or produce only short-length polymer chains.

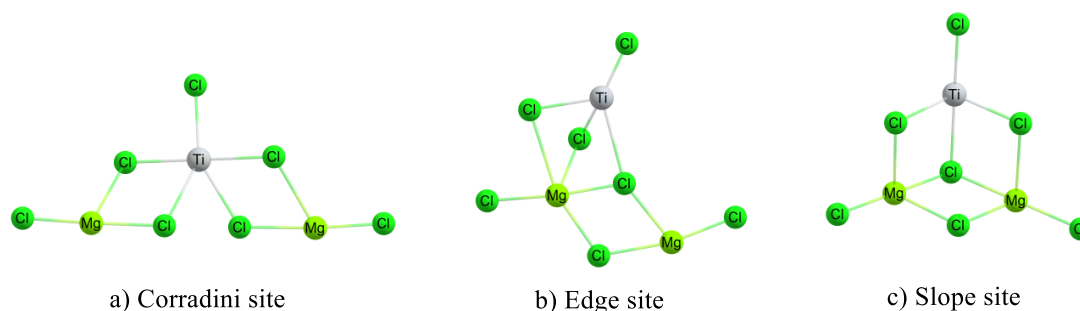


Figure 1.3. Different active sites proposed for the Z-N catalysts.

One interesting thought is what will happen when Ti--Cl bond/bonds are replaced with Ti--OR (where R is alkyl) bond/bonds. Such titanium alkoxy species can be formed by the reaction between TiCl_4 and $\text{Mg}(\text{OR})_2$, as well as by the decomposition reaction of the titanium center by donor molecules. Studies indicate that the formation of titanium alkoxy species can influence the activity and selectivity of the Ziegler-Natta catalysts, provided that the R groups are carefully selected.⁴⁰⁻⁴²

1.4. Co-catalyst

The TiCl_4 coordinated to the (110) MgCl_2 facet is not a catalytically active species for performing polymerization reactions. Hence, the necessity of a co-catalyst

arises, which can reduce the Ti(IV) to Ti(III) or Ti(II) and also alkylate the TiCl_n species.^{43,44} In Z-N catalysts, alkyl aluminum compounds are used as co-catalyst, and studies show that the activity and selectivity of the polymerization reaction can be altered by changing the R groups of the AlR_3 co-catalyst (where R can be alkyl groups or Cl ligands).^{35,45,46} A study by Stukalov *et al.* revealed that even though the barriers to the reduction of Ti(IV) to Ti(III) and Ti(II) are similar, the formation of Ti(III) is more favorable. Interestingly, the R groups on the AlR_3 impact the reduction of Ti(IV). Among various alkyl aluminum compounds, $\text{Al}(i\text{-Bu})_3$ is the best reductive agent and AlEt_2Cl is the worst reductive agent. The transalkylation step can happen through two possible transition states, which depends on the concentration of the alkyl aluminum species in the system: a four-membered transition state of barrier 9.7 kcal/mol and a six-membered transition state of barrier 10.3 kcal/mol (see Figure 1.4).^{47,48}

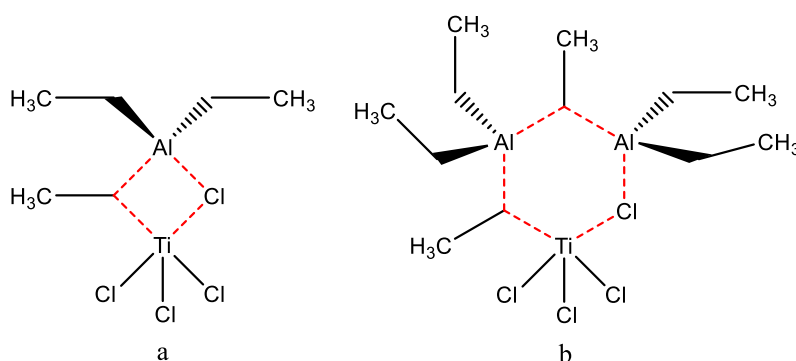


Figure 1.4. Two possible transition states for the transalkylation process.

A rigorous study of the possible pathways of conversion of Ti(IV) to Ti(III) with a coordination vacancy has been done by Bahri and co-workers.⁴⁹ They have calculated the energy required to homolytically cleave the Ti-Cl bond (ΔE_{diss}) by AlEt_3 , AlCl_3 , C_2H_4 , and Al_2Cl_6 , and the results suggest that the only energetically feasible reaction is with AlEt_3 ($\Delta E_{\text{diss}} = 8.8$ kcal/mol), and that the other species have very high ΔE_{diss} values. Moreover, they have also studied the transalkylation of Ti(III) via two possible mechanisms: (1) direct transalkylation of Ti(III) and (2) oxidation of Ti(III) to Ti(IV) by AlEt_3Cl with the formation of a Ti-C bond formation, followed by the reduction of Ti(IV) to Ti(III) by AlEt_3 . They concluded that the single-step direct transalkylation pathway is more favorable than the two-step pathway. Similarly, Champagne *et al.* have studied the effect of the R group in the R- AlEt_2 type of cocatalysts.⁵⁰ They have considered many groups such as Et, O-Me, O-*i*Pr, Cl, S-*i*Pr,

S-Me, and NH-Me as R, and their study indicates that AlEt_3 is the most potent *trans* alkylating agent among all the considered candidates. In addition to the most studied transalkylation process of the alkyl aluminum species, a recent study by Cavallo and co-workers have shown that AlEt_3 and AlEt_2Cl could coordinate on the (104) MgCl_2 facet to moderately enhance the stereoselectivity of the active site formed on the step defect of the (104) facet.³⁹

1.5. Lewis Donors

The performance of the Z-N catalysts enhanced drastically in the 1970s due to the introduction of Lewis base ‘donors’ into the system.^{51,52} Montedison and Mitsui introduced the first donor as a result of their collaborative effort to increase the efficiency of the MgCl_2 -based Z-N catalysts. The term donor arises because these additives are Lewis bases with the ability to donate electrons. Ethyl benzoate was used as a donor in the third generation of Z-N catalysts, and experimental studies based on ^{13}C NMR indicate the coordination of such donors to the MgCl_2 facets.^{53,54} In later generations of Z-N catalysts, several other donors have been employed. Donors are classified into two based on when they are added to the system: (1) internal donors (ID) are those added during the catalyst preparation step, and (2) external donors (ED) are those added along with the alkyl aluminum species. A proper choice of a pair of ID and ED can remarkably improve the properties of the resulting polymers. Studies show that the donors can influence the stereoregularity of the polymer, the molecular mass as well as the hydrogen response.^{55–57} Moreover, a recent study by Vanka and co-workers has shown that donors can also help utilize the (104) MgCl_2 surface for polymerization.²⁵ Various molecules have been used as donors in the Z-N system (see Figure 1.5), such as succinates, phthalates, 1,3-diethers, alkoxysilanes, 1,3-diol ester, 1,3-dione, malonic ester, 1,4-diol, glutaric acid ester, and isocyanate. In terms of performance, succinates, phthalates, 1,3-diethers, and alkoxysilanes are better than other donors. Although oxygen-containing molecules have generally been used as donors, nitrogen-containing molecules such as amino silanes have also been employed to enhance the activity and selectivity of Z-N catalysts.⁵⁸

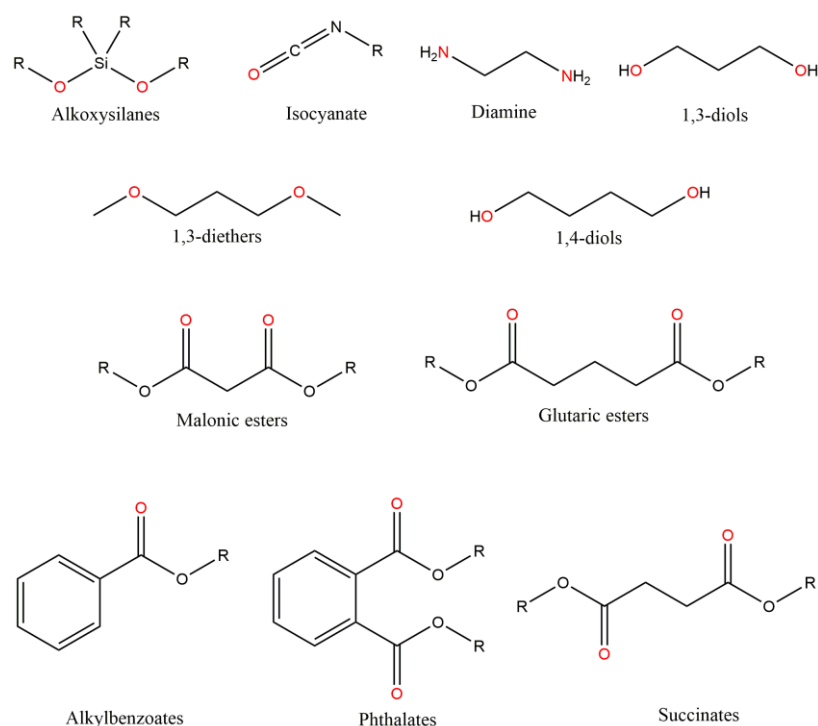


Figure 1.5. Examples of donors used in the Z-N catalysts.

Corradini and co-workers came up with the first explanation for the role of donors.^{59,60} According to them, donors coordinate on the (110) MgCl_2 facets that force the TiCl_4 to coordinate on the (104) MgCl_2 facets. At that time, the prevailing belief was that the TiCl_4 coordinated on the (104) MgCl_2 facet as a dimer (Ti_2Cl_8), which was responsible for the stereoselectivity. TiCl_4 could coordinate to the (110) and the (104) MgCl_2 facets without donors, thereby reducing the stereoselectivity. Even though the explanation of Corradini and co-workers correlated with the experimental observations, it was an oversimplified model. Furthermore, Lee and Jo performed a detailed study of eight 1,3-diethers, which revealed that the donors prefer to coordinate on the (110) MgCl_2 facet compared to the (104) MgCl_2 facet.⁶¹ The reason for this preference is that, in order to coordinate on the (104) MgCl_2 facet, the 1,3-diether donors must cross a rotational barrier, whereas such a rotation is not required for coordination on the (110) MgCl_2 facet.

Donors can coordinate to the (110) and (104) MgCl_2 facets through four possible modes⁶² (see Figure 1.6): (1) mono-coordination, where one donor atom coordinates to one magnesium atom, (2) bridge-coordination, where two donor atoms coordinate to two magnesium atoms, (3) chelate-coordination, where two donor atoms

coordinate to the same magnesium atom, and (4) zip-coordination, where two donors atoms coordinate to two magnesium atoms of different layers.

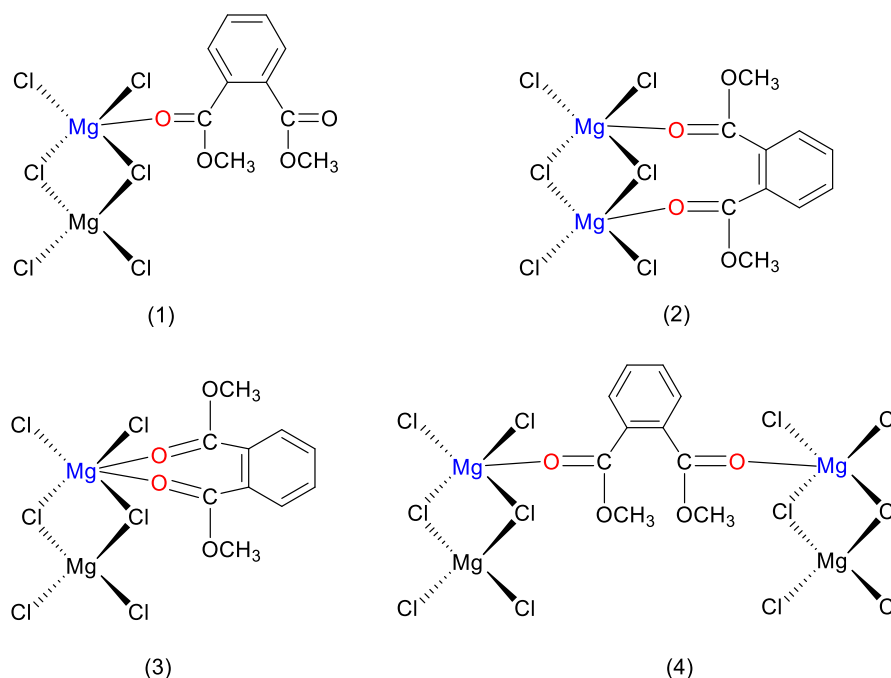


Figure 1.6. Schematic representation of four modes of coordination of a phthalate donor: (1) mono-coordination, (2) bridge-coordination, (3) chelate-coordination, and (4) zip-coordination.

Cavallo and co-workers have studied the above-mentioned coordination modes of various donors on both (110) and (104) facets.⁶² They found that the coordination of the sp^2 hybridized oxygen atom (for example, succinate) on the MgCl_2 surface is more favorable than that of the sp^3 hybridized oxygen atom (for example, 1,3-diethers). Another fascinating insight that emerged from their study is the relationship between the flexibility of the donor and the Mw/Mn ratio. A flexible donor causes the formation of diverse active sites, leading to a higher Mw/Mn ratio. In contrast, a less flexible donor leads to a lower Mw/Mn ratio. Their findings matched the experimental observation that 1,3-diethers lead to a lower Mw/Mn ratio in propylene polymerization, while phthalates lead to a higher Mw/Mn ratio. However, why does flexibility lead to various active sites? If a donor is flexible, it can do various coordination modes near the active site, but if the donor is not flexible enough, the number of coordination modes is limited to near the active site. For example, 1,3-diethers and alkoxysilanes prefer chelate coordination on the (110) MgCl_2 facet over other modes, which restricts the

diversity of the active sites, but such a restriction is not there in the case of succinates or phthalates.

Vanka and co-workers explored various roles of donors in the Z-N catalysts.^{25,63–65} Their DFT studies suggest that the direct coordination of a donor to the active titanium site can lead to high molecular weight polymers, which happens due to the increase in the difference between the insertion and termination barriers.⁶⁴ If no donors are coordinated with the titanium, the difference between the barriers mentioned above is 1.2 kcal/mol. However, the difference significantly increased to 5.5–8.9 kcal/mol when donors (they have considered four donors: ethyl benzoate, ethyl *p*-ethoxybenzoate, ethyl *p*-isopropoxybenzoate, and ethyl decanoate) coordinated to the titanium. In another study, Vanka and co-workers have shown that the donors can influence the activation process of the pre-catalyst to the catalyst.⁶⁵ Their calculations indicate that the rate-limiting step is the *trans* alkylation, and the coordination of a phthalate or silyl ester donor in the vicinity of the active site can increase the barrier significantly. The higher barrier for the activation step when using a phthalate donor explains the induction period in the polymerization reaction.

1.6. Mechanism of Polymerization

The Cossee and Arlman mechanism (see Figure 1.7) for inserting a monomer into the Ti-C bond has been widely accepted in the scientific community.^{66–68} The first step of the reaction is the formation of a π complex between the electropositive titanium atom and the monomer, followed by a four-member transition state, which leads to the insertion of the monomer between the Ti-C (C of the polymer chain) bond. The insertion of the monomer to the Ti-C bond again creates a vacant coordination site in the active site, where another monomer molecule can coordinate, and the reaction continues.

Ziegler and co-workers studied the effect of various oxidation states of titanium.⁶⁹ Titanium can be present in II, III, and IV oxidation states, and they found that the insertion barriers are in the range of 8.0–16.0 kcal/mol. Cavallo and co-workers obtained similar values in another study: the barriers of 8.6 and 6.6 kcal/mol for ethylene insertion for methyl and ethyl groups are modelled as polymer chains attached to the active site, respectively.⁷⁰ One of the earlier studies by Ziegler and co-workers obtained a surprising result of a lower insertion barrier for propylene compared to

ethylene, whereas the experimental observations indicated the opposite. However, the authors concluded that the discrepancy was due to the poor selection of the active model. Later, Bahri *et al.* chose two active models and showed that the propylene insertion barriers (12.6 kcal/mol and 13.9 kcal/mol for 1,2- and 2,1-insertion, respectively) are higher than the ethylene insertion barrier (6.2 kcal/mol).⁵⁷ Furthermore, experimental studies suggest that the activation barrier for the polymerization of ethylene is in the range of 6-12 kcal/mol.⁷¹

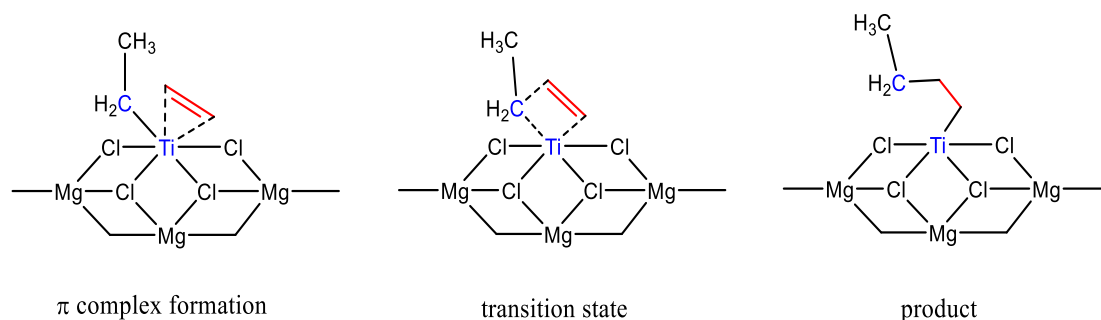


Figure 1.7. The Cossee and Arlman mechanism of monomer (ethylene) insertion between the Ti-C bond.

1.7. Stereo- and Regio-selectivity

The production of stereoregular polymers (cellulose and rubber) was considered the monopoly of nature. However, Natta broke this monopoly of nature by producing stereoregular polypropylene. Moreover, Natta also proposed that the stereo control is because of the chiral nature of the catalytic sites on the surface of TiCl_3 crystal. Later, Corradini *et al.* rationalized the factors that influence the stereoselectivity in Z-N catalysts. They are (1) the pro-chiral nature of the monomer, (2) the chiral active site, and (3) the orientation of the growing polymer chain.¹ One more factor that influences the stereoselectivity is the presence of coordinated Lewis bases (donors) or alkyl aluminum species in the vicinity of the active site.^{72,73,39} It is possible to calculate the theoretical stereoselectivity of the Z-N catalysts by computing the barriers for *re*- and *si*-face insertions for a particular model. The ΔG_{stereo} is the difference between the *re*- and *si*- barriers ($\Delta G_{\text{si}}^\ddagger - \Delta G_{\text{re}}^\ddagger$). However, due to the multisite nature of the Z-N catalyst, the correlation between the computed values and the tacticity of the polymer chains may not precisely match.

Busico and co-workers proposed a three-site model to explain the stereo defects in the Z-N catalyst: (1) the active site, without any steric hindrance on both sides, (2) the active site, with steric hindrance on only one side, and (3) the active site, with steric hindrance on both sides.⁷⁴ According to them, these three active sites lead to syndiotactic, isotactoid, and isotactic polymers. The interconversion between these active sites, which is faster than the termination, is responsible for the stereo defects in the polymer chains. Wondimagegn and Ziegler showed that alkoxysilane donors could enhance the stereoselectivity and molecular weight of the polymer by coordinating with the magnesium atom and active titanium site in a bridge fashion.⁷⁵ Their computed values were in good correlation with the experimental results. Computational studies by Cavallo and co-workers also clearly indicate that the coordination of donors in the vicinity of the active site can enhance the stereoselectivity irrespective of the difference in the MgCl_2 surface model.^{76,77}

Furthermore, Taniike and Terano also showed that the adsorption of ethyl benzoate in the vicinity of the active site could enhance the stereoselectivity, and the calculated ΔE_{stereo} was 2.3 kcal/mol.⁷⁸ Later, Terano and co-workers performed a combined experimental and computational study, where they found a correlation between the yield of the polymer and the binding energy of the alkoxysilane donor on the MgCl_2 surface.⁷⁹ In the same study, they have also found that it is not the bulkiness of the donor; it is the conformation of the donor in the vicinity of the active site that determines the stereoselectivity. A study by Bahri and co-workers showed that di-*n*-butyl phthalate could enhance the stereoselectivity better than the ethyl benzoate donor.¹¹ Moreover, the studies by Kumawat *et al.* and Liu and co-workers also showed the enhancement in the stereoselectivity due to various donors.^{72,73,80} Please note that Z-N catalysts produce isotactic polymers, while homogeneous catalysts are required for the production of syndiotactic polymers.⁸¹⁻⁸⁵

Interestingly, the Z-N polymerization reaction is also regioselective. The reaction can proceed either via 1,2-insertion or 2,1-insertion. Unlike stereoselectivity, regioselectivity is less studied because Z-N catalysts produce very few regioerrors in the polymer. However, the interest in studying the regioselectivity of the Z-N catalysts resumed when Chadwick *et al.* found 20% butyl chain ends in the polymers due to the 2,1-insertion of the monomers.⁸⁶ According to them, 2,1-insertion can convert an active site into a dormant form because of the bulky secondary polymeryl chain attached to

the active site. Later, Busico and co-workers found that the percentage of regiomistakes in an $\text{MgCl}_2/\text{TiCl}_4$ catalyst (activated by $\text{Al}(\text{iBu})_3$) is 0.7%.⁸⁷ However, another study by Cipullo and co-workers showed that the regiomistakes reduced to 0.26% and 0.18% when 1,3-diethers and alkoxysilane donors were employed along with the catalyst.⁸⁸

DFT studies based on simple models suggest that the 1,2-insertion is more favorable than the 2,1-insertion by 1.5 kcal/mol.⁸⁷ Later, similar results were obtained from studies based on cluster models by the groups of Ziegler and Cavallo.^{77,89} The active site is regioselective even in the absence of donors, and the presence of donors had not profoundly impacted the regioselectivity. They also found that the 2,1-insertion is more enantioselective than the 1,2-insertion. A recent study by Cavallo and co-workers on the (104) step defects suggests a similar regioselectivity trend.³⁹ Furthermore, Taniike and Terano found that the probability of regiomistakes reduced to 6% in the presence of donors from 15% (where there are no donors in the vicinity of the active site).⁷⁸

1.8. Parallel Reactions

The complexity of the Z-N systems is due to their multicomponent nature. Even though the primary reaction is the polymerization on the active titanium site, many parallel reactions are also taking place in the system. An understanding at the molecular level of these parallel reactions will help to design reactions in such a way as to increase the rate of the primary polymerization reaction and reduce the undesired parallel reactions. For instance, donors are prone to react with the Lewis acidic species (such as Al_2Et_6 and TiCl_2Et) in the system due to their Lewis basicity. Such reactions are undesirable because they reduce the performance of the catalyst. Hence, a suitable donor increases the activity and selectivity of the polymerization reaction without undergoing any undesirable reactions with the Lewis acidic species in the Z-N system. Chien and co-workers reported that the ester donors undergo decomposition reactions with AlEt_3 and produce aldehyde and ketone. They have characterized the products using GC-MS analysis.⁹⁰ Later, Vanka and co-workers performed rigorous DFT calculations of the decomposition reaction of three donors (ethyl *p*-ethoxybenzoate, ethyl *p*-isopropoxybenzoate, and ethyl benzoate) with Al_2Et_6 and TiCl_2Et (coordinated on the surface).⁹¹ Interestingly, they found that donors tend to react more with titanium

because of the lower barriers compared to aluminum for the slowest step in the reaction mechanism.

Finally, some potentially poisonous molecules are present in the Z-N system, such as water, methanol, and hydrogen sulfide. Studies show that these molecules can coordinate on the (110) and (104) MgCl_2 facets and make stable complexes with the active titanium species, reducing the catalytic activity.⁹²

1.9. Objective of this Thesis

The commencement of the Z-N catalyst in the 1950s was a remarkable discovery, which helped to produce large quantities of polymers with desirable qualities. The annual production of polyethylene and polypropylene is around 190 million metric tons, giving rise to a billion-dollar market. Since its discovery, various experimental and computational studies (mainly based on DFT) have led to an increase in the performance of the catalysts and a better understanding at the molecular level. However, a complete and thorough understanding remains elusive due to the multisite and multicomponent nature of the Z-N catalysts. Without adequate understanding, it is not possible to improve the performance of the system, as well as solve some existing challenges in the Z-N industry.

For instance, one major issue in Z-N industrial plants is reactor fouling. The polymerization reaction is exothermic, and an uncontrollable increase in the temperature inside the reactor causes the melting of the polymers. Such melted polymers can stick to the reactor walls, which is called reactor fouling. Reactor fouling is an undesirable process because cleaning the reactor requires its shutdown, which causes substantial economic loss. How does one avoid such an undesirable situation? A few patents show that some donors can be used to self-extinguish the reaction. However, why does this self-extinguishing take place? What factors determine the self-extinguishing capacity of a donor?

Another interesting aspect of Z-N catalysis is the stereo and regioselectivity of the reaction. There is a consensus that stereoselectivity will increase when donors coordinate in the vicinity of the active site. The phthalate and succinate derivative donors can do bridge coordination in the vicinity of the active site. However, alkoxysilane donors cannot do bridge coordination because of the lower bite angle compared to phthalates and succinates. Then, how do alkoxysilanes positively influence

the stereoselectivity of the reaction? One possibility is that alkoxysilane donors can get help from other components in the system. For instance, Lewis acidic species such as AlEt_3 or AlEt_2Cl can form adducts with alkoxysilane donors. It is interesting to study the stability of such adducts and the effect of such adducts on the stereoselectivity of the reaction. Regioselectivity is a less explored area in Z-N catalysis. The impact of Lewis acid-base adducts on regioselectivity would be interesting to explore.

The donors can influence the reaction only if they are coordinated in the vicinity of the active site. However, how does such a donor find the titanium active site? One possibility is that a donor coordinates to the MgCl_2 surface and can migrate through the surface towards the TiCl_4 . However, can a donor have a migration preference toward TiCl_4 ? If so, what are the factors that affect such a migration? Computational chemistry, especially density functional theory (DFT) calculations, can be utilized to answer the questions raised above. The primary objectives of the thesis are:

- To understand the factors that determine the self-extinguishing property of a donor.
- To study the formation of Lewis acid-base adducts in the Z-N system and the effect of such adducts on the stereoselectivity.
- To explore the effect of Lewis acid-base adducts on the regioselectivity.
- To investigate the directional migration ability of various donors towards TiCl_4 .

1.10. Organization of the Thesis

The thesis titled “Computational Studies into Ziegler-Natta Catalysis” is divided into seven chapters. The summary/conclusions of each chapter are provided below along with the chapter titles.

Chapter 1: Introduction to Ziegler-Natta Catalysis

This chapter briefly introduces Z-N catalysis. I have outlined the history of this remarkable discovery, the components in the catalytic system, and their respective roles. I have also discussed the origin of stereoselectivity and regioselectivity in the polymerization reaction and the mechanism for the insertion and propagation steps. Finally, I have included a brief discussion about the parallel reactions in the system.

Chapter 2: Fundamentals of Computational Chemistry

This chapter discusses the fundamentals of computational chemistry, such as the Schrödinger equation, the Born-Oppenheimer approximation, the Hartree-Fock method, the Hohenberg-Kohn Theorem, the Kohn-Sham approach, and the exchange-correlation energy.

Chapter 3: Insights into the Nature of Self-Extinguishing External Donors for Ziegler Natta Catalysis: A DFT Study

In this chapter, we have explored the reason behind the difference in the self-extinguishing property between two donors, using DFT. A systematic study of the decomposition reaction of D1 and D2 with Al_2Et_6 and titanium attached to the (110) MgCl_2 surface has been done. With Al_2Et_6 , both D1 and D2 show a tendency to form monomer donor adducts, and these adducts can undergo decomposition reactions with the help of another AlEt_3 molecule, either through the ketone pathway (KP) or the aldehyde pathway (AP), leading to the formation of a ketone or an aldehyde respectively. Such species act as poisons in Z-N systems, thereby explaining why D1 and D2 have self-extinguishing properties. Both donors have similar barriers for KP and AP, and among the two possible pathways, KP is more favorable, which corroborates experimental observations. With titanium, both D1 and D2 bind strongly in comparison to Al_2Et_6 , and KP is a significantly more facile pathway. It is also interesting to note that the alkyl chain makes the binding significantly stronger through non-covalent interactions. Even though the barriers are similar for both D1 and D2 for the decomposition reactions (both KP and AP) with titanium, the thermodynamic binding preference of D2 over D1 makes D2 a better self-extinguishing donor, which agrees with the polymerization studies.

Chapter 4: Hidden Role of Lewis acid-base adducts in enhancing the stereoselectivity of Ziegler-Natta Catalysis: Insights from Theory

In this chapter, we have employed DFT calculations to understand the role of Lewis acid-base adducts on the stereoselectivity of Z-N catalysis. We have selected five alkoxysilane donors; DCPDMS, DIPDMS, DSBDMMS, DIBDMS, and SBMDMS. These five external donors tend to form adducts with both the AlEt_3 and AlEt_2Cl acidic species in the system. Since the adducts with AlEt_2Cl are more favorable, we have further investigated their affinity to bind to the (110) MgCl_2 surface. It has been revealed that an alkoxysilane donor prefers to bind away from the active site because

of the favorable chelate coordination. Still, such a preference is not there in the case of adducts because adducts can do bridge coordination next to the active site. Furthermore, the presence of adducts in the vicinity of the active site significantly improves the stereoselectivity of the Z-N catalysis compared to cases where there are no donors, or only internal donors, near the active site. In conclusion, our detailed computational studies indicate that external donors such as alkoxysilane alone are not responsible for the high stereoselectivity observed in Z-N polymerization. The Lewis acid-base adducts that they make with the aluminum species present in the system are the real drivers of stereoselectivity in Z-N systems.

Chapter 5: The Effect of Lewis Acid-Base Adducts in the Regioselectivity of Ziegler-Natta Catalysis: A DFT Study

In this chapter, we have explored the effect of Lewis acid-base adducts on the regioselectivity of Z-N catalysts. Compared to stereoselectivity, regioselectivity is less explored in Z-N catalysis. We have shown in Chapter 4 that the formation of Lewis acid-base adducts and their coordination in the vicinity of the active site are energetically feasible. We have taken identical adducts to study the regioselectivity, and our calculations indicate that the effects of such adducts in the regioselectivity are not very profound compared to stereoselectivity. It is also interesting to note that 2,1-insertion is more enantioselective than 1,2-insertion.

Chapter 6: Directional Migration of Internal Donors in Ziegler-Natta Catalysis: Insights from Theory

In this chapter, we have studied the directional migration of internal donors, through DFT calculations. Cavallo and co-workers proposed that donors can migrate on the MgCl_2 surface. However, such migrations are helpful only if they are directional. We have taken three internal donors; (1) dimethyl succinate, (2) dimethyl phthalate, and (3) 1,3-dimethoxy-2,2-dimethylpropane, for the study. Our study suggests that if only a donor is coordinated to the MgCl_2 surface, then it will not have any migration preference. In other words, a donor can migrate randomly in any direction if there are no other species present on the surface. Interestingly, if there is a TiCl_4 coordinated one step away from the donor, it has a thermodynamic preference to migrate toward the TiCl_4 . Such a preference increases if there is an extra donor in the vicinity of the donor. Further, we have considered the four-step migration of donors. The calculated values

indicate that dimethyl succinate and dimethyl phthalate have a thermodynamic gradient to migrate toward the TiCl_4 in the presence of an extra donor. However, 1,3-dimethoxy-2,2-dimethylpropane does not show such a trend. Finally, we have also demonstrated that the barriers to migration are feasible under reaction conditions.

Chapter 7: Conclusions and Future Outlook

This chapter provides the main conclusions as well as the future outlook of this thesis.

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Chapter 2

Fundamentals of Computational Chemistry

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Abstract: Computational chemistry has become one of the most important branches of modern chemistry research. In order to improve any existing chemical systems or predict a chemical system with a desirable property, understanding at the atomic level is mandatory. Even though quantum mechanics developed by the mid of 1900s, its applicability to real-world problems was limited due to the non-availability of computer resources. However, the improvement in the performance and availability of computers in the last few decades exponentially increased the number of studies using computational chemistry. Density functional theory (DFT) is the most widely used method among various computational chemistry methods due to its balance between accuracy and computational cost. This chapter provides the fundamentals of quantum mechanics and a brief overview of density functional theory.

2.1. Introduction

Chemistry is the branch of science that deals with molecules, their construction, their properties, and their transformation. Theoretical chemistry is the sub-field of chemistry where mathematical methods (based on the fundamental laws of physics) are used to study processes of chemical significance. The molecules are constructed by charged particles, positively charged nuclei, and negatively charged electrons. Molecules differ because of the difference in the number of nuclei or electrons or the geometrical position of nuclear centers. Using theoretical chemistry, we can calculate (in principle) many properties, such as (a) which geometrical arrangement is the most favorable for a given set of nuclei and electrons, (b) the properties of a given arrangement of a molecule, (c) the interaction between molecules and (d) the rate of transformation of one molecule to another. However, one needs to solve complex mathematical equations in order to calculate such properties, which was a daunting task for real-world chemical reactions before the 1950s. Later, the 1960s and the 1970s witnessed the remarkable rise of electronic computers that helped many researchers around the globe to access computers to calculate mathematical models relatively faster, which caused the origin of a new branch in chemistry called computational chemistry. In simpler terms, computational chemistry aims to calculate the values for a given chemical problem based on an existing mathematical model. Even though computational chemistry does not seek to develop any mathematical models directly, the results obtained from the computational calculations can reveal the accuracy of a mathematical model and help to improve it further.

Hartree was the first scientist who used a computer to calculate the properties of molecules. In the modern world, computational chemistry has flourished into a matured and essential branch of chemistry, which has significantly contributed to understanding various molecular chemical phenomena at the molecular level. Such understanding has helped to design better chemical systems for various applications.

There are various approaches in computational chemistry, depending on the size of the system we need to study and our desired accuracy:

(a) Molecular mechanics (MM) treat molecules as a collection of balls held by springs, where a ball represents an atom, and the spring represents a bond. MM is based on

classical laws of physics and ignores the electronic effects in the system; hence it is fast compared to other methods and can be employed to study large biological systems.

(b) *Ab initio* (from Latin, which means “from scratch”) methods based on the time independent Schrodinger equation, one of the most fundamental equations in physics. An *ab initio* method solves the Schrodinger equation of a molecule to obtain its energy. However, solving the Schrodinger equation for many body problems is still challenging (even after various approximations), and the method is time-consuming compared to other methods.

(c) Semi-empirical methods are also based on the Schrodinger equation, but instead of evaluating all the integrals, they try to guess the integrals to fit with the experimental observations. Compared to *ab initio* methods, these methods are faster.

(d) Density functional theory (DFT) calculations are based on the calculation of the ground state energy of a molecule from its electron density. These methods are less complex to solve than the *ab initio* methods, hence they are faster. DFT became a popular and widely used method because of the ability to study bigger chemical structures with a balance between accuracy and computational cost.

(e) *Ab initio* molecular dynamics are based on combining Schrodinger equations and classical mechanics.

How do we choose a method for a chemical problem of interest? It depends on mainly two factors: (1) the size of the system and (2) the desired accuracy. MM methods are the best choice for very large biomolecules like proteins or DNA. *Ab initio*, DFT, or semi-empirical methods would take a long time to get results. For studying the bonding of unusual molecules, *ab initio* methods are the best choice. Semi-empirical methods can be used to study moderately big systems such as steroids. DFT, the most popular method for bond forming and breaking chemistry, can be used to study many homogenous and heterogeneous catalytic systems and even study the bonding scenario of bigger molecules. However, choosing a functional is a critical task in DFT methods, which should be done very carefully, based on the benchmarking studies. In the following sections, I will briefly describe the fundamental theories of quantum mechanics and eventual developments in density functional theory.

2.2. Time Independent Schrodinger Equation

Erwin Schrödinger proposed one of the most important equations in physics, the time-dependent Schrödinger equation, in 1926. Since the potential energy of molecules is independent of time, quantum mechanics aims to solve the time-independent Schrodinger equation (TISE) of the systems to calculate the energy. The TISE for a system consisting of n electrons and m nuclei is given below.

$$\hat{H}\Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_n, \vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_m) = E\Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_n, \vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_m) \quad (2.1)$$

This equation $\hat{H}$ represents the Hamiltonian operator, $\Psi(\vec{x}_n, \vec{r}_m)$ is the wave function of the many-body system, and E is the total energy of the system. $\vec{x}$ and $\vec{r}$ denote the coordinates of the electrons and nuclei. It is important to note that the wave function depends on the $3n$ space coordinates, n spin coordinates of electrons, and $3m$ space coordinates of nuclei. This equation (2.1) is called the eigenvalue equation, where $\hat{H}$ (a Hermitian operator) operates on a wave function $\Psi(\vec{x}_n, \vec{r}_m)$ and returns only the real value for E (known as eigenvalue). The Hamiltonian operator is represented as (in atomic units),

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \frac{1}{2} \sum_{a=1}^m \frac{\nabla_a^2}{m_a} - \sum_{a=1}^m \sum_{i=1}^n \frac{Z_a}{r_{ia}} + \sum_a \sum_{b>a}^m \frac{Z_a Z_b}{r_{ab}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} \quad (2.2)$$

The first two terms in equation (2.2) describe the kinetic energy of electrons and nuclei. The subsequent three terms denote nuclear-electron attraction, nuclear-nuclear repulsion and electron-electron repulsion. Indices i and j denote the number of electrons, and indices a and b represent the number of nuclei.

We must solve the TISE for such systems if we want to apply quantum mechanics to real-world chemical problems. Unfortunately, the TISE is not precisely solvable for multi-electron multi-nuclear molecular systems. The exact solution of TISE is only known for a few simple, ideal systems such as a particle in a 1-D box, rigid rotor, simple harmonic oscillator, and the hydrogen atom. Hence, we need approximations to solve the TISE for practical problems.

2.3. Born-Oppenheimer Approximation

Nuclei move much slower relative to electrons because of their heaviness. Hence, the assumption of all the electrons exists in the field of fixed nuclei. Therefore, one can assume the nuclei kinetic energy to be zero, and the potential energy to be

considered constant, which is known as the Born-Oppenheimer approximation. This approximation helps to separate the electronic and nuclear parts in the TISE. As a result, the Hamiltonian operator shown in equation (2.2) can be simplified as,

$$\hat{H}_{el} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{a=1}^m \sum_{i=1}^n \frac{Z_a}{r_{ia}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} \quad (2.3)$$

This electronic Hamiltonian operator $\hat{H}_{el}$ operated on the electronic wave function yields the electronic energy E_{el} .

$$\Psi_{el}, \hat{H}_{el} \Psi_{el} = E_{el} \Psi_{el} \quad (2.4)$$

Then the total energy of the system can be calculated as the sum of electronic energy and nuclear repulsion energy, as given below:

$$E_{tot} = E_{el} + E_{nn} \quad (2.5)$$

Where E_{nn} is provided by the formula,

$$E_{nn} = \sum_a^m \sum_{b>a}^m \frac{Z_a Z_b}{r_{ab}} \quad (2.6)$$

2.4. Wave Function

We have seen how energy can be obtained from the wave function using the Hamiltonian operator. However, what is a wave function? According to the Copenhagen interpretation, a wave function contains all the information about a system in a given state. The information can be extracted from the wave function using a suitable quantum mechanical operator. A wave function is not physically observable and has no physical significance. The physical significance of the wave function arises when we calculate the square of the wave function, which gives the probability density.

$$probability\ density = |\Psi(x_1, x_2, \dots, x_n)|^2 \quad (2.7)$$

A wave function can be complex or negative values, but the probability density will always be positive. For a system consisting of n electrons, the probability density is given by

$$|\Psi(x_1, x_2, \dots, x_n)|^2 dx_1 dx_2 \dots dx_n \quad (2.8)$$

The above equation calculates the probability of finding the electrons 1, 2, 3, ..., n simultaneously in the volume $dx_1.dx_2.dx_3....dx_n$. Interestingly, even if two electrons interchange their position, the probability density will be the same. This is because the electrons are indistinguishable particles.

$$|\Psi(x_1, x_2, \dots, x_i, x_j, \dots, x_n)|^2 = |\Psi(x_1, x_2, \dots, x_j, x_i, \dots, x_n)|^2 \quad (2.9)$$

According to Pauli's exclusion principle, a wave function of fermions ($s=1/2$) must be antisymmetric. What does it mean? See the equation given below. An interchange between two electrons will cause a change in the sign of the wave function. However, the probability density is calculated by taking the square of the wave function, and it will be the same.

$$\Psi(x_1, x_2, \dots, x_i, x_j, \dots, x_n) = -\Psi(x_1, x_2, \dots, x_j, x_i, \dots, x_n) \quad (2.10)$$

Finally, a wave function must be normalized, meaning the probability of finding all the electrons over space must be unity.

$$\int \dots \int |\Psi(x_1, x_2, \dots, x_n)|^2 dx_1 dx_2 \dots dx_n = 1 \quad (2.11)$$

2.5. The Variational Principle

In the TISE, there are two unknown quantities: wave function and energy. In order to solve the TISE, we need to find the wave function for a system and operate with the Hamiltonian operator to get the energy of the system. Unfortunately, there is no concrete way to find the actual wave function for a system. However, the variational principle offers a solution to this problem. Consider a system described by a wave function Ψ , then the expectation value for the energy of that system is,

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2.12)$$

$$\text{Where } \langle \Psi | \hat{H} | \Psi \rangle = \int \Psi^* \hat{H} \Psi d\tau.$$

The variational principle says that the energy obtained by solving the TISE using a guess wave function Ψ is always higher than the actual ground state energy of the system.

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \quad (2.13)$$

In equation (2.13), E_0 is the actual ground state energy of the system and Ψ_0 is the exact wave function for the system. Furthermore, the trial wave function will be acceptable only if it obeys a few conditions. Otherwise, a wave function does not make any physical sense. A trial wave function must be normalized and continuous, which is expressed as,

$$E_0 = \min_{\Psi \rightarrow n} E[\Psi] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} | \Psi \rangle \quad (2.14)$$

$\Psi \rightarrow n$ denotes that Ψ is an acceptable wave function for an n-electron system. However, searching over all the possible wave functions is impossible. So, to overcome this issue, we can adopt some algebraic scheme on a particular subset so that the procedure will lead to the best approximation for the actual wave function corresponding to the system.

2.6. Functional

It is essential to understand what a functional is before discussing the fundamentals of density functional theory. A functional is a function of a function, which is commonly represented with a function in the square bracket, $F[f]$. How does one distinguish a function from a functional? The fundamental difference is that a function takes a number as input and delivers a number as output. In contrast, a functional takes a function as input and delivers a number as output. It is possible to find the derivatives of a functional, like in the case of functions. The differentiation of a functional is,

$$\partial F[g] = F[g + \delta x] - F[g] = \int \frac{\partial F}{\partial g(x)} \delta g(x). dx \quad (2.15)$$

Similar to the functions, the rules for differentiation of functional are,

$$\frac{\partial}{\partial f(x)} (c_1 F_1 + c_2 F_2) = c_1 \frac{\partial F_1}{\partial f(x)} + c_2 \frac{\partial F_2}{\partial f(x)} \quad (2.16)$$

$$\frac{\partial}{\partial f(x)}(F_1, F_2) = \frac{\partial F_1}{\partial f(x)} F_2 + \frac{\partial F_2}{\partial f(x)} F_1 \quad (2.17)$$

2.7. Density Functional Theory

The problem with conventional quantum mechanics is the complexity of solving the TISE, where the electronic wave function depends on the spatial and spin coordinates of the electron. Hence, an increase in the number of electrons in the system makes it very expensive to apply wave function-based methods on relatively more extensive systems. Enter the most popular method due to its balance between accuracy and computational cost: the density functional theory (DFT) method. DFT utilizes electron density as a fundamental parameter from which we can calculate other chemical and physical parameters. Electron density has mainly two advantages over the wave function: (1) the electron density is a measurable quantity, whereas wave function is not, and (2) electron density is only dependent on three coordinates, but a wave function depends on $4n$ variables (three spatial and one spin coordinates of n electrons). Because of the less complexity compared to the wave function methods, DFT is significantly faster and provides reasonable accuracy. Many computational packages are available with robust algorithms that help to study various chemical systems using DFT. The following sections will give a brief introduction to density functional theory.

2.8. Electron Density

The probability of finding an electron (of arbitrary spin) within a particular volume is known as electron density. It can be measured using experimental techniques like transmission electron microscopy, scanning tunneling microscopy, X-ray diffraction, and atomic force microscopy. For a system consisting of n electrons, the electron density can be given by the following equation,

$$\rho(\vec{r}) = n \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_n \quad (2.18)$$

where $\vec{x} = \vec{r}.s$ ($\vec{r}$ is the spatial coordinates and s is the spin coordinates). $\rho(\vec{r})$ is the probability of finding any n electrons with an arbitrary spin in a particular volume, where the rest of the $n-1$ electrons (with random positions and spin) are represented by the wave function Ψ . The electron $\rho(\vec{r})$ density has some specific properties: (1) $\rho(\vec{r})$ is a positive function of three spatial coordinates, and its integration results in the

total number of electrons, (2) $\rho(\vec{r})$ exhibits an asymptotic exponential decay at very large distances from the nuclei, and (3) at a given position in an atom, the electron density exhibits a maximum possessing a finite value due to the attractive force exerted by the positively charged nuclei. Furthermore, the density gradient at this position shows a discontinuity, resulting in a cusp.

2.9. Pair Density

Pair density is the probability of finding two electrons with spins simultaneously at two different volumes. The remaining $n-2$ electrons have arbitrary spatial coordinates and spin. The equation gives the pair density is given below,

$$\rho(\vec{x}_1, \vec{x}_2) = n(n-1) \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n)|^2 d\vec{x}_3 \dots d\vec{x}_n \quad (2.19)$$

It is interesting to note that pair density contains all the information about electron correlation. It is a positive quantity, like electron density.

2.10. Thomas-Fermi Model

The attempts to use electron density to get information about chemical systems began long before modern density functional theory calculations. In 1927, Thomas and Fermi introduced a model (known as the Thomas-Fermi model) in which electron density was used instead of the wave function to understand the electronic structure of many-body systems. They came up with an expression for the kinetic energy,

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d\vec{r} \quad (2.20)$$

However, other contributions, such as nuclear-electron interaction and electron-electron repulsion, were treated classically. Hence, the equation for the total energy is,

$$E_{TF}[\rho(\vec{r})] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d\vec{r} - Z \int \frac{\rho(\vec{r})}{r} d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad (2.21)$$

The Thomas-Fermi model has serious disadvantages. The kinetic energy expression is very crude and does not give an accurate value. Moreover, the model also ignores the electron exchange and correlation effects. Hence, when applied to real chemical systems, the Thomas-Fermi model failed to describe the chemical bonds in the systems. However, the importance of the model is that it is the first model that

employed the electron density to calculate the energy of a system without wave function information.

2.11. Hohenberg-Kohn (HK) Theorems

The modern density functional theory was born in 1964 when Hohenberg and Kohn published their landmark paper in Physical Review. They proposed two theorems with mathematical proofs, which solve the doubtfulness towards the approximation used by Thomas and Fermi regarding whether it is justifiable to calculate the energy from electron density. Moreover, their theorems also provide a robust theoretical foundation for using DFT in the ground state.

Theorem 1 *The external potential $\hat{V}_{ext}(\vec{r})$ is (to within a constant) a unique functional of $\rho(\vec{r})$; since, in turn $\hat{V}_{ext}(\vec{r})$ fixes $\hat{H}$ we see that the full many particle ground state is a unique functional of $\rho(\vec{r})$.*

Let us consider a non-degenerate system with n number of electrons, where $\rho(\vec{r})$ is the exact ground state electron density, and Ψ is the wave function of the system. Let us further assume that two different external potentials, $\hat{V}_{ext}$ and $\hat{V}'_{ext}$, exist for this electron density $\rho(\vec{r})$. The $\hat{V}_{ext}$ and $\hat{V}'_{ext}$ are different from each other more than a constant because otherwise, the wave function and electron density remain unaffected. If such two different external potentials exist, there will be two corresponding Hamiltonians ($\hat{H}$ and $\hat{H}'$), two different ground state wave functions (Ψ and Ψ'), and finally, two different ground state energies (E_0 and E'_0), where $E_0 = \langle \Psi | \hat{H} | \Psi \rangle$, $E'_0 = \langle \Psi' | \hat{H}' | \Psi' \rangle$ and $E_0 \neq E'_0$.

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} \quad (2.22)$$

$$\hat{H}' = \hat{T} + \hat{V}_{ee} + \hat{V}'_{ext} \quad (2.23)$$

We can represent the overall scenario of both wave functions giving rise to the same electron density as,

$$V_{ext} \Rightarrow \hat{H} \Rightarrow \Psi \Rightarrow \rho(\vec{r}) \Leftarrow \Psi' \Leftarrow \hat{H}' \Leftarrow V'_{ext}$$

Now, apply the variational principle for the Ψ' with the Hamiltonian $\hat{H}$,

$$E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle = \overbrace{\langle \Psi' | \hat{H}' | \Psi' \rangle}^{E'_0} + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \quad (2.24)$$

Take the values of $\hat{H}$ and $\hat{H}'$ from equations (2.22) and (2.23) and use them in equation (2.24)

$$E_0 < E'_0 + \langle \Psi' | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} - \hat{T} - \hat{V}_{ee} - \hat{V}'_{ext} | \Psi' \rangle = E'_0 + \int \rho(r) \{ \hat{V}_{ext} - \hat{V}'_{ext} \} dr \quad (2.25)$$

Similarly, if we perform the variational principle on Ψ with the Hamiltonian $\hat{H}'$,

$$E'_0 < \langle \Psi | \hat{H}' | \Psi \rangle = \overbrace{\langle \Psi | \hat{H} | \Psi \rangle}^{E_0} + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle = E_0 - \int \rho(r) \{ \hat{V}_{ext} - \hat{V}'_{ext} \} dr \quad (2.26)$$

Addition of two equations (2.25) and (2.26) leads us to a mathematically impossible result,

$$E_0 + E'_0 < E'_0 + E_0 \quad \text{or} \quad 0 < 0 \quad (2.27)$$

Hence it is proven that for a particular ground state electron density, there cannot be two different external potentials. Furthermore, the total energy of the system can be represented as a functional of electron density,

$$E[\rho] = \underbrace{E_{ne}[\rho]}_{\text{system dependent}} + \underbrace{T[\rho] + E_{ee}[\rho]}_{\text{universally valid}} = \int \rho(\vec{r}) \hat{V}_{ne}(\vec{r}) d\vec{r} + T[\rho] + E_{ee}[\rho] \quad (2.28)$$

Here, $T[\rho] + E_{ee}[\rho]$ is universal because it only depends on the electron density.

However, $E_{ne}[\rho] = \int \rho(\vec{r}) \hat{V}_{ne}(\vec{r}) d\vec{r}$ is the potential energy due to the nuclear-electron attraction, and it is system dependent. Now the system independent parts can be combined as *Hohenberg-Kohn functional*, which is defined as,

$$F_{HK}[\rho] = T[\rho] + E_{ee}[\rho] \quad (2.29)$$

Then the total energy can be rewritten as,

$$E[\rho] = \int \rho(\vec{r}) \hat{V}_{ne}(\vec{r}) d\vec{r} + F_{HK}[\rho] \quad (2.30)$$

We have seen that HK theorem 1 assures that the ground-state electron density is sufficient to calculate the ground-state energy. However, how do we know that the assumed electron density is the correct electron density of our system of interest? A formal remedy to this problem was provided by HK theorem two, which states as follows,

Theorem 2 $F_{HK}[\rho]$, the functional that delivers the ground state energy of the system delivers the lowest energy if and only if the input density is the true ground state density, ρ .

Mathematically it means,

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}] \quad (2.31)$$

The proof for the equation (2.31) is straightforward. Consider a trial electron density; it has a corresponding wave function and a Hamiltonian. Then this wave function can operate with the Hamiltonian corresponding to the original wave function, which gives,

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = T[\tilde{\rho}] + E_{ee}[\tilde{\rho}] + \int \tilde{\rho}(\vec{r}) V_{ext} d\vec{r} = E[\tilde{\rho}] \geq E_0[\rho] = \langle \Psi | \hat{H} | \Psi \rangle \quad (2.32)$$

2.12. The Kohn-Sham (K-S) Approach

As discussed in the previous sections, HK theorems allow us to express the energy of a many-body system in terms of electron density.

$$E_0[\rho] = \min_{\rho \rightarrow n} \left(\int \rho(\vec{r}) \hat{V}_{ne}(\vec{r}) d\vec{r} + F_{HK}[\rho] \right) \quad (2.33)$$

The $F_{HK}[\rho]$ term can be further divided into kinetic energy, classical Coulomb, and non-classical contributions, as given in the expression below,

$$F_{HK}[\rho] = T[\rho] + J(\rho) + E_{nc}(\rho) \quad (2.34)$$

Only the classical Coulomb term is known among the three terms in equation (2.34), and the other two terms are not known explicitly. Unfortunately, kinetic energy is the major part of the overall energy. Without an accurate kinetic energy expression, we would not be able to use the HK theorems applicable to real-world problems. In 1965, Kohn and Sham came up with the second paper, which is the pillar of modern DFT methods. Their focus was to calculate the kinetic energy with accuracy, and in

order to do that, they introduced the concept of a non-interacting reference system. According to them, a non-interacting system is simply a collection of non-charged fermions so that there is no Coulomb interaction with each other. However, it is essential to note here that there is still a portion of unknown kinetic energy (reasonably small), which they merged into a non-classical contribution. Thus,

$$T_s = -\frac{1}{2} \sum_i^n \langle \psi_i | \nabla^2 | \psi_i \rangle \quad (2.35)$$

and

$$\rho_s(\vec{r}) = \sum_i^n \sum_s |\psi_i(\vec{r}, s)|^2 = \rho(\vec{r}) \quad (2.36)$$

T_s and ψ_i are the kinetic energy and the wave function of the non-interacting system. It is apparent that the $T_s \neq T$, but a major part of the total kinetic energy is recovered in T_s . Kohn and Sham further partitioned the $F_{HK}[\rho]$ into,

$$F_{HK}[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \quad (2.37)$$

Where $E_{xc}[\rho]$ is known as the *exchange-correlation energy* and is given by,

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) \quad (2.38)$$

The exchange-correlational energy functional $E_{xc}[\rho]$ contains all the unknown contributions to the total energy. It includes the contributions from electron exchange, electron correlation, the residual portion of kinetic energy, and the correction for the self-interaction energy. In a nutshell, all the contributions of the total energy of a system, which are explicitly unknown to us, have put it in the exchange-correlational energy functional $E_{xc}[\rho]$.

The following vital question is how to calculate the potential of the non-interacting system. It should lead us to the antisymmetrized wave function, which is associated with the same electron density of the real interacting system. To answer this, rewrite the total energy as,

$$E[\rho] = T_s[\rho] + J[\rho] + E_{EX}[\rho] + E_{ne}[\rho] \quad (2.39)$$

The equation (2.39) can be further expanded to

$$E[\rho] = T_s[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{EX}[\rho] + \int V_{ne}\rho(\vec{r})d\vec{r} \quad (2.40)$$

$$= -\frac{1}{2} \sum_i^n \langle \psi_i | \nabla^2 | \psi_i \rangle + \frac{1}{2} \sum_i^n \sum_j^n \iint |\psi_i(\vec{r}_1)|^2 \frac{1}{r_{12}} |\psi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 + E_{EX}[\rho] - \sum_i^n \int \sum_a^m \frac{Z_a}{r_{1a}} |\psi_i(\vec{r}_1)|^2 d\vec{r}_1$$

..... (2.41)

Apply the variational principle on equation (2.41) under the constraint $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ to minimize the energy, then it will lead to the *Kohn-Sham equation*,

$$\left(-\frac{1}{2} \nabla^2 + \left[\int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_a^m \frac{Z_a}{r_{1a}} \right] \right) \psi_i = \left(-\frac{1}{2} \nabla^2 + V_{eff}(\vec{r}_1) \right) \psi_i = \varepsilon_i \psi_i \quad (2.42)$$

If we compare this equation with the one particle equations (from the non-interacting reference system), it appears that V_s is nothing but V_{eff} .

$$V_s(\vec{r}) = V_{eff}(\vec{r}) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_a^m \frac{Z_a}{r_{1a}} \quad (2.43)$$

ψ_i in the equation (2.42) is known as the *Kohn-Sham orbital*, which can be obtained from equation (2.42). Then use the *Kohn-Sham orbital* to calculate the electron density and use the density to get an improved V_{eff} that will lead to a self-consistent cycle (see Figure 2.1). Since the V_{eff} depends on the electron density and the orbitals, the one-electron Kohn-Sham equations must solve iteratively until the self-consistency is achieved.

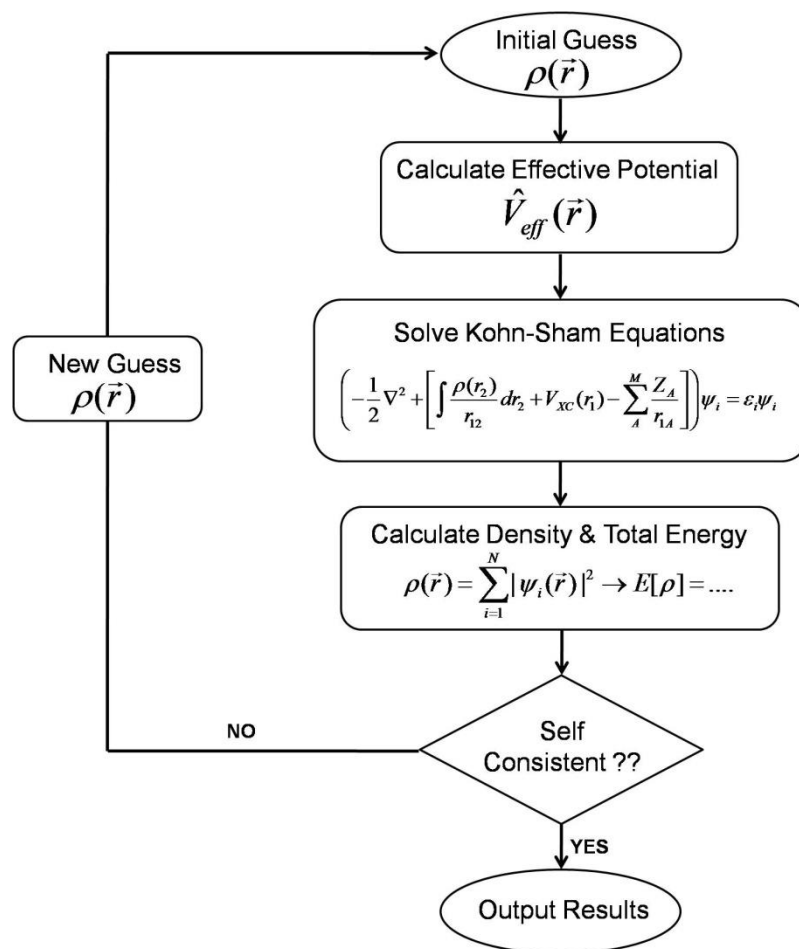


Figure 2.1. The flow chart for the Kohn-Sham iterations.

It is intriguing to note that, unlike the Hartree-Fock method, the Kohn-Sham method is exact in principle. The Hartree-Fock method uses approximations from the beginning, but in the Kohn-Sham method, we need approximation when we try to find the explicit form of the exchange-correlation energy. The major research in the theoretical DFT is to develop better approximations for this unknown part. There are many functionals available in any modern DFT software package. However, no universal functional is available for every system, and the performance of functionals varies from system to system. So, it is crucial to be cautious in choosing a particular functional for a system of interest.

2.13. Conclusions

From just two theoretical proofs in the 1960s, today, DFT has become one of the pivotal tools extensively used by a vast range of chemists and physicists. Even though the DFT is not the most accurate method compared to the wave function-based methods, its balance between accuracy and computational cost makes it the most

suitable choice for studying various problems in chemistry, biology, and material sciences, which is impractical with any wave function method. With the further betterment of computational resources and new functionals or approximations, DFT will continue to perform fruitful calculations for larger and larger systems, provide better molecular-level understanding, and predict new chemistry.

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Chapter 3

Insights into the Nature of Self-Extinguishing External Donors for Ziegler Natta Catalysis: A DFT Study

Chapter 3

Insights into the Nature of Self-Extinguishing External Donors for Ziegler Natta Catalysis: A DFT Study

Abstract: Developing new donors for Ziegler-Natta (Z-N) catalysis to control the polymerization reaction and produce polymers with desirable properties has always been challenging due to the multi-component nature of the catalytic systems. One of the challenges in the industrial production of polyolefins using Z-N catalysts is reactor fouling, a phenomenon of polymer melting due to the uncontrollable rise in temperature. Recently, it has been reported that using self-extinguishing external donors can overcome reactor fouling. However, insights into the origin of the self-extinguishing property of such donors still need to be discovered. Here, we have performed a systematic DFT study to understand the self-extinguishing property of two donors: **D1** (2,2,2-trifluoroethyl myristate) and **D2** (2,2,2-trifluoroethyl palmitate). **D1** and **D2** can undergo parallel reactions with the aluminum and titanium species present in the system to produce ketones and aldehydes, which are poisons for Z-N catalytic systems, thus explaining their self-extinguishing nature. The non-covalent interaction between the long alkyl chain of the donors with the surface plays a vital role in determining the donors' self-extinguishing nature. There is a significant thermodynamic preference for the binding of the donor with the longer alkyl chain at the titanium center. The current work, therefore, provides interesting insights into how self-extinguishing donors function in Z-N catalytic systems.

3.1. Introduction

Ziegler-Natta (Z-N) catalysis is one of the most important catalytic processes, which produces around 150 million tons of polyolefins/year, and has a billion dollar market.¹⁻⁴⁹ Donors are vital components of the Z-N polymerization process that can enhance the stereo- and regioselectivity of the product by coordinating in the vicinity of the active titanium center.^{9,42,43,46} It can influence the kinetics of the activation, insertion and termination steps in the polymerization reaction, and can also help the titanium to coordinate to the (104) MgCl₂ surface, which is otherwise unutilized.^{30,31,33} It is interesting to note that tuning the structure of existing donors and developing new donors has always been challenging and a prominent area of research in Z-N catalysis, because of their potential to produce polyolefins with desirable properties.

Olefin polymerization is an exothermic process that releases heat, and an increase in the temperature inside the reactor results in increase in the rate of the polymerization reaction, and vice versa. The reaction temperature is a crucial factor for polymerization as the heat generation causes polymer melting, which leads to the agglomeration of polymer particles that further causes lump formation. Such situations are detrimental to the continuous production of polymer resin. There is, therefore, considerable incentive to develop new ways over the existing ones to overcome this problem without affecting the desirable properties of the polymerization reaction. One of the promising ideas is to use one of the components itself to “self-extinguish” the process at a higher temperature. There are several patents regarding the use of long-chain fatty acid external donors as activity limiting agents and bringing self-extinguishing behavior in the catalyst system.⁵⁰⁻⁵⁵ However, to the best of our knowledge, there are no detailed studies available about such systems that can shed light into the underlying reasons leading to the self-extinguishing of the donors, which can help to modify them to eliminate reactor fouling.

In the current work, we report a systematic density functional theory study (DFT) of a new class of self-extinguishing molecules **D₁** and **D₂** (see Figure 3.1) that can be used as self-extinguishing donors in Z-N polymerization. **D₁** and **D₂** are fluorine-containing ester derivatives of myristic acid and palmitic acid, respectively. These compounds, when employed as donors (as D_{ES}), reduce the activity at elevated temperatures. The most probable reason for the lowering of the activity is parallel

reactions in the Z-N system. In 2014, the parallel reactions of various ester donors with Al_2Et_6 and TiCl_2Et on the MgCl_2 surface was investigated.³⁴ We have now performed a systematic study using DFT to develop an understanding of this peculiar behavior of these D_{ES} .

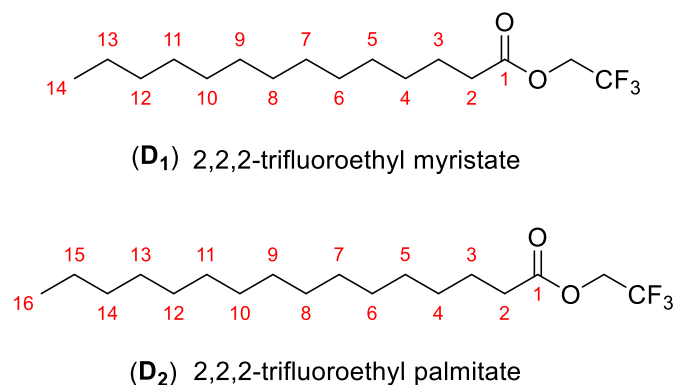


Figure 3.1. Structures of the two self-extinguishing donors **D₁** and **D₂**.

3.2. Computational Details

The Turbomole 7.0 suite of program⁵⁶ has been employed to optimize all the structures including intermediates and transition states using density functional theory (DFT). Geometry optimizations have been performed using the Perdew, Burke, and Ernzerhof (PBE) functional⁵⁷ and TZVP basis set.⁵⁸ The dispersion correction (DFT-D3) developed by Grimme et al. has been used to increase the accuracy of the calculations.⁵⁹ The resolution of identity (RI)⁶⁰ and the multipole accelerated resolution of identity (marij)⁶¹ approximations were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations. Closed-shell calculations were done for the Al_2Et_6 -donor model system cases, while open-shell calculations have been considered for the TiCl_2Et -donor model system cases. For better accuracy, we have performed single point calculations using PBE0 functional,⁶² TZVP basis set, and dispersion correction (DFT-D3). Our choice of the PBE-D3/TZVP//PBE0-D3/TZVP level of theory is based on benchmarking and computational studies.^{63,64,34} For the calculations that we have performed, the energy convergence criteria was 10^{-6} H, and the norm for the cartesian gradients was 10^{-3} . And the second-order derivatives of the potential energy obtained numerically. Further, to check whether our chosen level of theory is adequate to address the interactions in the system, especially in alkyl aluminum species (many functionals are known to underestimate the dimerization energy of bridged alkyl aluminum species),⁶⁵ we have

calculated the dimerization energy of AlEt_3 . Our calculations indicate that dimeric Al_2Et_6 is more favorable by 8.7 kcal/mol over monomeric AlEt_3 , suggesting that the chosen level of theory is sufficient to address the interactions. We have employed a 15 molecule MgCl_2 cluster (see Figure 3.2) and have not employed any periodic boundary conditions. This model is chopped from the MgCl_2 model proposed by Cavallo and co-workers.²⁷ The values reported are ΔG values, with zero-point energy, internal energy, and entropic contributions (including translational, rotational, and vibrational entropy contributions) included through frequency calculations on the optimized minima and transition state structures, with the temperature taken to be 298.15 K. This was done in order to ensure that all the reported transition state structures contained only one imaginary frequency corresponding to the correct normal mode. IRC calculations have been considered for the confirmation of the transition states. In every case, the IRC calculations have yielded the correct reactant and product structures.

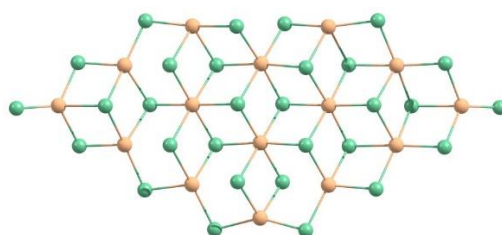


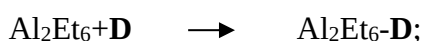
Figure 3.2. The MgCl_2 cluster model employed for this study.

3.3. Results and Discussion

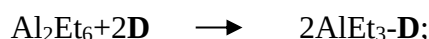
In order to understand the reason for the difference in the self-extinguishing property of **D**₁ and **D**₂, we have performed a systematic full quantum mechanical study at the PBE0-D3/TZVP//PBE-D3/TZVP level of theory using density functional theory. Since **D**₁ and **D**₂ both have a long alkyl chain attached to the carbonyl carbon (see Figure 3.1), they can exist in different conformations. Before starting the study of the interaction of these **D**_{ES} with aluminum and titanium, we have performed a conformational analysis using the HyperChem software package.⁶⁶ Our calculations indicate that the linear chain conformation of the alkyl chain is preferable among the other possible structures, and therefore, these most stable conformations of **D**₁ and **D**₂ have been used for further computational studies.

3.3.1. Decomposition Reaction of **D**₁ and **D**₂ with Al_2Et_6

D₁ and **D₂** can react with Al₂Et₆, and lead to two different products. It can either form a dimer-donor adduct (Al₂Et₆-**D₁**/**D₂**) or two monomer-donor adducts (2AlEt₃-**D₁**/**D₂**). Our calculations indicate that the formation of two monomer-donor adducts is more favorable than the formation of a dimer-donor adduct (see below). We have taken the monomer-donor adduct (AlEt₃-**D₁**/**D₂**) as the reference energy for further calculations of the formation of ketone and aldehyde.



$$\Delta G = -2.0 \text{ kcal/mol } (\mathbf{D}_1), -1.9 \text{ kcal/mol } (\mathbf{D}_2)$$



$$\Delta G = -4.4 \text{ kcal/mol } (\mathbf{D}_1), -5.1 \text{ kcal/mol } (\mathbf{D}_2)$$

3.3.2. Ketone Pathway (KP)

Once the monomer-donor adduct formation takes place, it can pass through a six-membered transition state with the help of one more molecule of AlEt₃ (TS_{1KPM} and TS_{1KPP} for **D₁** and **D₂** respectively), in which one ethyl group from aluminum is transferred into the carbonyl carbon of the donor (see Figures 3.3 and 3.4). The barriers are 21.3 kcal/mol and 21.2 kcal/mol for **D₁** and **D₂**, respectively. The second transition state is also six-membered, which involves the transfer of one ethyl group from AlEt₃ to AlEt₂, which is already bonded with the carbonyl O of the donor, along with the breakage of the C-O bond and the formation of the Al-O bond, leading to the formation of the ketone. The corresponding barriers are minimal for **D₁** (5.0 kcal/mol) and **D₂** (4.9 kcal/mol). Our calculations therefore suggest that the formation of ketone by the reaction of **D₁** and **D₂** with Al₂Et₆ is thermodynamically and kinetically favourable. It should also be noted that since the corresponding barriers for the **D₁** and **D₂** cases are almost the same, the results also indicate that there is no difference in the reactivity of **D₁** and **D₂** in this particular reaction.

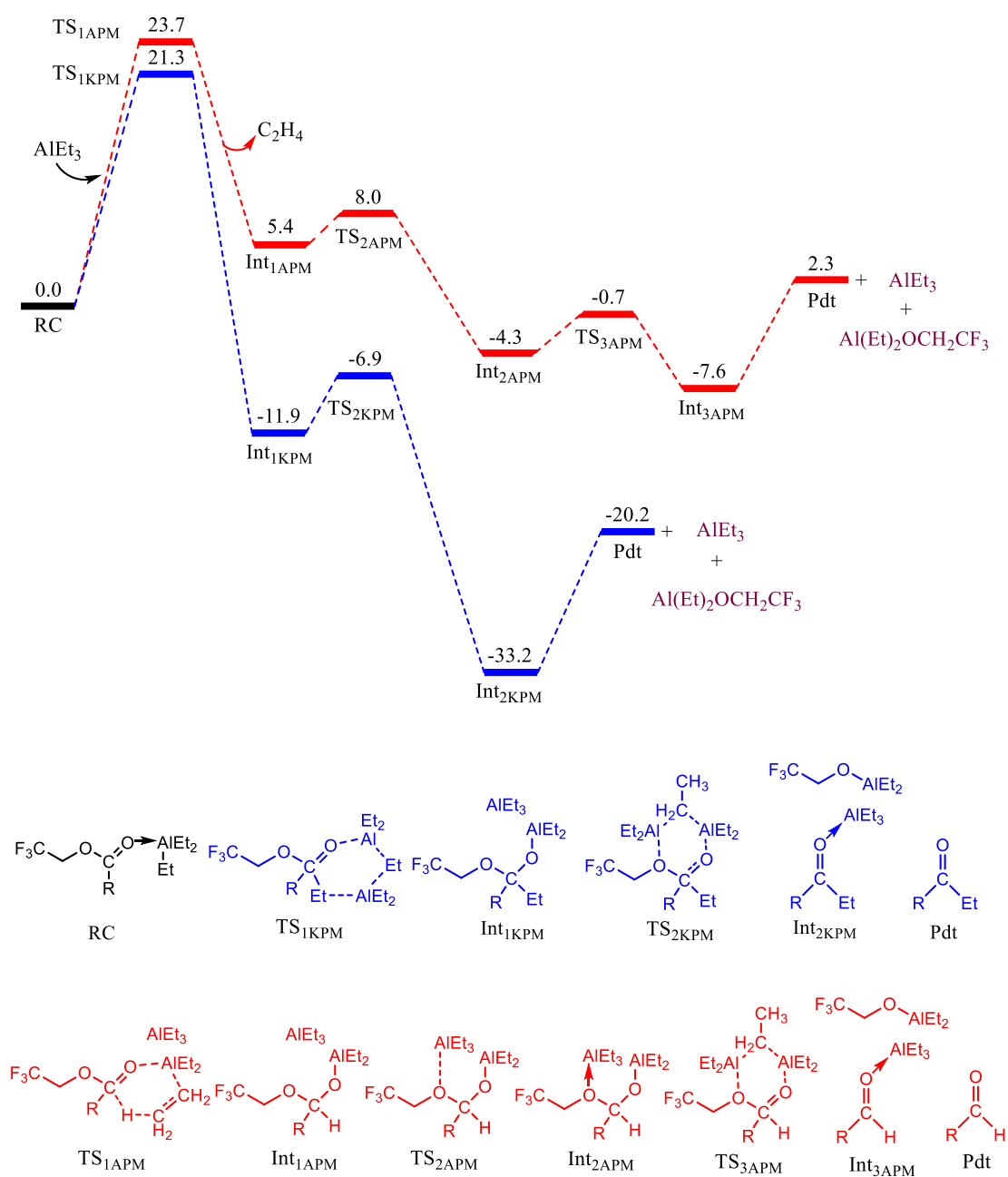


Figure 3.3. The free energy profile for the decomposition reaction of **D1** ($R = (\text{CH}_2)_{12}\text{CH}_3$) with Al_2Et_6 . The values are in kcal/mol. Blue indicates the ketone pathway (KP) and red indicates the aldehyde pathway (AP).

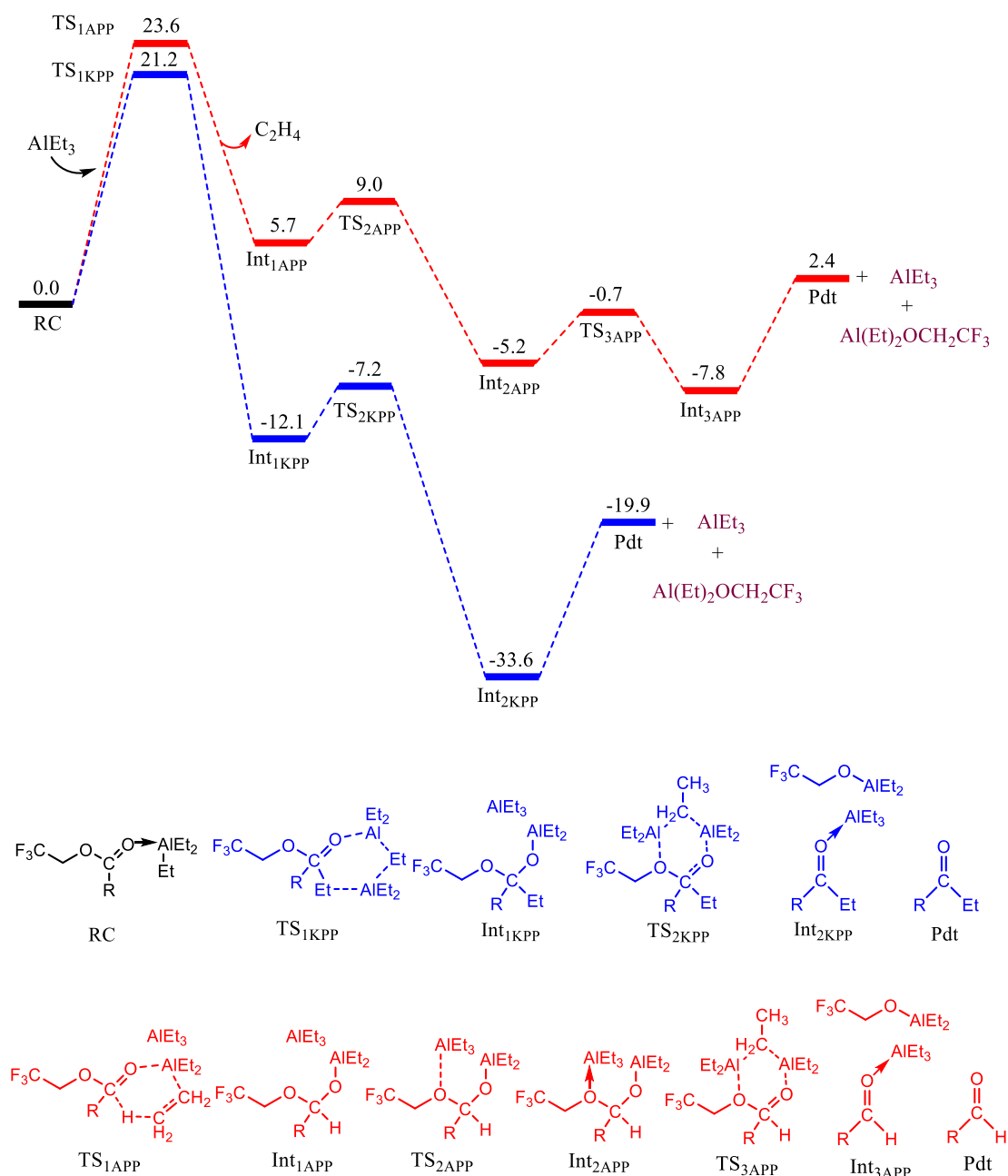


Figure 3.4. The free energy profile for the decomposition reaction of **D**₂ (R = (CH₂)₁₄CH₃) with Al₂Et₆. The values are in kcal/mol. Blue indicates the ketone pathway (KP) and red indicates the aldehyde pathway (AP).

3.3.3. Aldehyde Pathway (AP)

Another possible pathway for the donor-AlEt₃ adduct to proceed is the AP, in which the first transition state (TS_{1APM} and TS_{1APP}) is the rate-determining one for both **D**₁ and **D**₂. The transition state involves the transfer of a hydride ion and the elimination of an ethylene molecule in the presence of one more molecule of AlEt₃, with a barrier of 23.7 kcal/mol for **D**₁ and 23.6 kcal/mol for **D**₂ (see Figures 3.3 and 3.4). It is

interesting to note that the extra AlEt_3 molecule is not covalently interacting like in the case of KP. The second transition state is different from KP because the AP has a new stable intermediate ($\text{Int}_{2\text{APM}}$ and $\text{Int}_{2\text{APP}}$ for **D₁** and **D₂**, respectively). We were not able to optimize such an intermediate for KP, probably due to the electron-donating effects of the ethyl group, which facilitates the C-O bond breakage and leads to the formation of the final product. The second transition state involves the formation of the Al-O bond alone, with a barrier of 2.6 kcal/mol for **D₁** and 3.3 kcal/mol for **D₂**. Subsequent to this, the intermediate surmounts a barrier of 3.6 kcal/mol for **D₁** and 4.5 kcal/mol for **D₂**, which leads to the formation of aldehyde.

Our calculations therefore suggest that the AP is less favorable compared to the KP, thermodynamically and kinetically, which corroborates with NMR studies. However, like KP, **D₁** and **D₂** do not show any considerable difference for the AP as well.

3.3.4. The Effect of the $-\text{CF}_3$ Group and the Length of Alkyl Chain on the Decomposition with Al_2Et_6

In order to understand the effect of the $-\text{CF}_3$ group and the length of the alkyl chain in the decomposition reactions, we have chosen three donors; **D₃**, **D₄**, and **D₅** (see Figure 3.5). Experimental studies with **D₃** (where trifluoroethyl group is replaced with isopropyl group) indicate that it is less reactive than **D₁** and **D₂**. On the other hand, **D₄** and **D₅** are two model donors that we considered here for computational purposes, in which the $-\text{CF}_3$ group has been replaced with $-\text{CH}_3$, and a long alkyl chain has been replaced with a $-\text{CH}_3$ group, respectively. Since the rate of the reaction depends on the slowest step in a reaction profile, we have calculated barriers for only the rate-determining steps for both KP and AP and compared the same with the barriers of **D₁** (see Figure 3.6). It was found that the alkyl chain has a small effect on the barriers (for **D₅**, the barriers were 21.7 kcal/mol and 23.4 kcal/mol for KP and AP, respectively), but replacing the $-\text{CF}_3$ group with other alkyl groups had a significant impact on the barriers (the barriers increased by around 2.1 to 3.2 kcal/mol in both **D₃** and **D₄**, see Figure 3.6). These calculated values indicate that a long alkyl chain would not help significantly to facilitate the decomposition reaction of a donor with Al_2Et_6 , but having an electron-withdrawing group attached to it (such as $-\text{CF}_3$) can increase the rate of decomposition reactions with Al_2Et_6 .

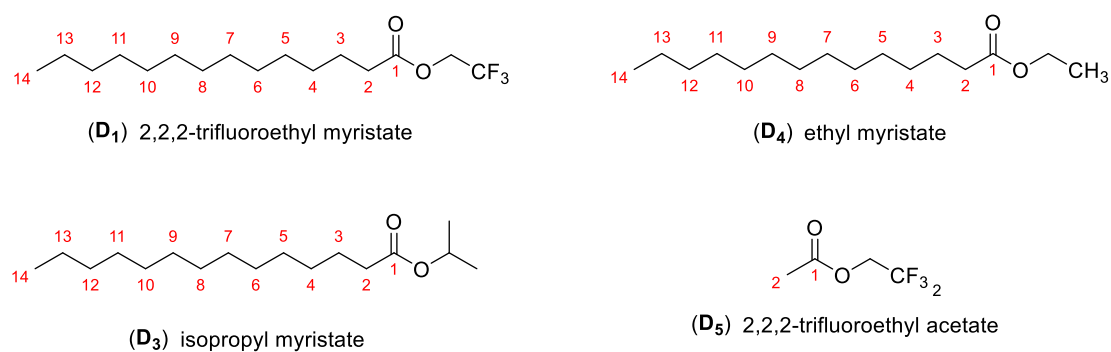


Figure 3.5. Structures of **D₁** and **D₃**, and the two model donors **D₄** and **D₅**.

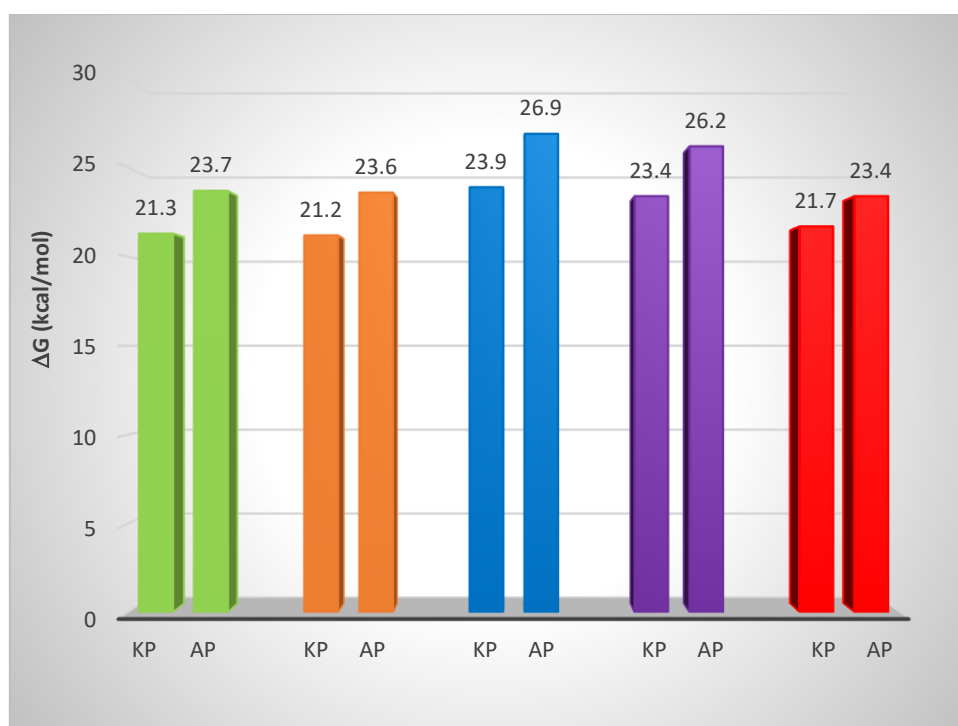


Figure 3.6. Barriers (values in kcal/mol) for the rate determining step for the decomposition donors **D₁** (green), **D₂** (orange), **D₃** (blue), **D₄** (purple), and **D₅** (red), in the decomposition reaction with Al₂Et₆.

It is interesting to note that **D₁** and **D₂** did not show any considerable difference in their reactivity towards Al₂Et₆, either thermodynamically or kinetically. However, there is a difference in their self-extinguishing properties, according to experimental observations.

3.3.5. Decomposition Reaction of **D₁** and **D₂** with Titanium on the (110) MgCl₂ Surface

As mentioned in the Introduction, a donor can interact with titanium as well. We have calculated the binding energy of **D**₁ with titanium on the (110) MgCl₂ surface, where the choice of MgCl₂ model is based on work reported earlier.³⁴ Here, one important thing to be noted is the orientation of the alkyl chain concerning the (110) MgCl₂ surface. We have considered two extreme cases: (i) the alkyl chain oriented away from the MgCl₂ surface and (ii) the alkyl chain oriented just above the MgCl₂ surface (see Figure 3.7). The calculated values indicate that the structure in which the alkyl chain is oriented just above the MgCl₂ surface is more stable than the other possibility by 21.0 kcal/mol. This vast difference in the binding energy is due to the favorable non-covalent interactions between the alkyl chain and the MgCl₂ surface. In other words, the long alkyl chain helps the donor to bind to the titanium more strongly. If the above hypothesis is correct, then there should be a considerable difference in the binding energies of **D**₁ and **D**₂ with titanium on the (110) MgCl₂ surface, because there is a difference of the alkyl chain length (by two carbon units) among these D_{ES}. However, our results do not show any significant difference in the binding energies, due to the limitation of our chosen small MgCl₂ surface model. The use of a sizeable MgCl₂ surface model that can completely interact with the long alkyl chain of **D**₁ and **D**₂ can provide the exact difference between the binding energies of **D**₁ and **D**₂, but such a computationally expensive approach is beyond the scope of the current work.

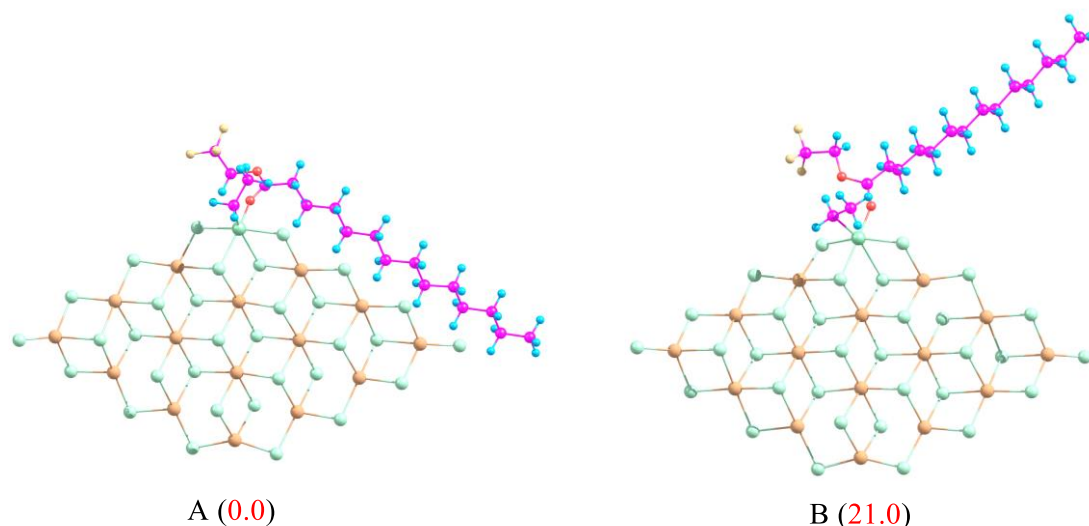


Figure 3.7. The relative binding energies (for **D**₁) of two possible orientations of the alkyl chain concerning the MgCl₂ surface (values are in kcal/mol); (A) the alkyl chain is oriented just above the (110) MgCl₂ surface, and (B) the alkyl chain is oriented away from the (110) MgCl₂ surface.

However, another way to proceed forward is to use the same MgCl_2 surface model but choose new donors in such a way that the difference between them is the same as between **D**₁ and **D**₂. We have chosen three model donors **D**₆, **D**₇, and **D**₈ (see Figure 3.8) with small alkyl chains so that complete interaction is possible between the alkyl chain and the (110) MgCl_2 surface. The binding energy values obtained (-11.5 kcal/mol for **D**₆, -14.5 kcal/mol for **D**₇ and -16.6 kcal/mol for **D**₈) for these new model donors clearly show an increase in the binding energy around 2.0 to 3.0 kcal/mol per addition of an extra CH_2CH_3 group in the structure of the donor. It is reasonable to assume that the same would be true for the case of **D**₁ and **D**₂, which means that **D**₂ has a thermodynamic preference over **D**₁ to bind with titanium on the (110) MgCl_2 surface.

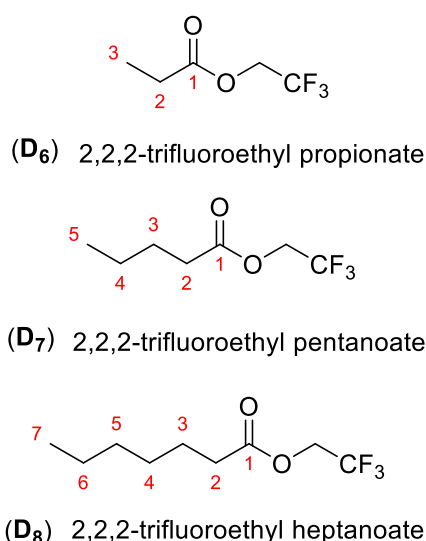


Figure 3.8. Structures of new model donors **D**₆, **D**₇, and **D**₈ with small alkyl chains compared to **D**₁ and **D**₂.

In order to obtain more insights into the interaction between the alkyl chain and the (110) MgCl_2 surface, we have done non-covalent interaction (NCI) plots⁵⁹ for the binding of **D**₆, **D**₇, and **D**₈. The NCI plots indicate that there is a weak attractive interaction (the area colored in green between the alkyl chain and the MgCl_2 surface, see Figure 3.9) between the alkyl chain and the (110) MgCl_2 surface and, more importantly, the area of attraction increases with increase in the length of the alkyl chain.

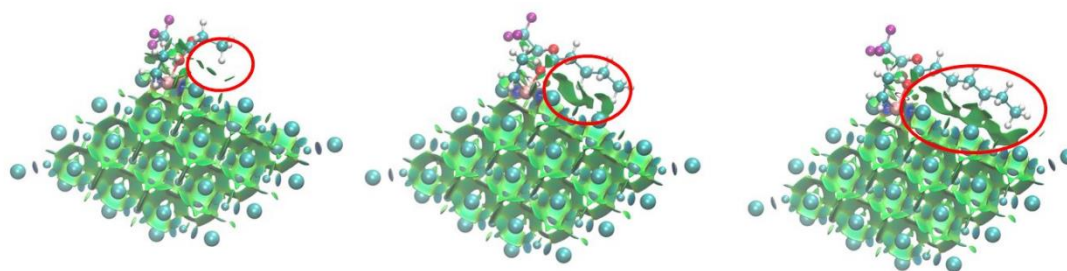


Figure 3.9. The non-covalent interaction (NCI) plots for **D**₆, **D**₇, and **D**₈ binding to titanium, with the alkyl chain interacting with the MgCl₂ surface (the area of interest encircled in red). The color code for the NCI plots is as follows: blue - strongly attractive, green - weakly attractive, and red - strongly repulsive.

Once the donor binds with titanium, it can undergo decomposition through KP and AP. It is already reported that the first step, involving ethyl transfer in KP and hydride transfer in AP, are the rate-determining transition states. We have, therefore, calculated the barriers for both **D**₁ and **D**₂ (see Figure 3.10), and our calculations suggest that KP is much more favorable than AP, both in cases of **D**₁ and **D**₂. However, the alkyl chain length does not have any influence on the barriers. It is important to note here that for **D**₁ and **D**₂, the alkyl chain does not entirely interact with the (110) MgCl₂ surface. Therefore, in order to make sure that the alkyl chain length is not affecting the barriers, we have calculated the barriers for AP for **D**₆ (29.0 kcal/mol), **D**₇ (29.1 kcal/mol), and **D**₈ (29.3 kcal/mol), and found that there is no difference in the barriers. Our study also indicates that among various possibilities of decomposition reactions of **D**₁ and **D**₂ with Al₂Et₆ and titanium, the KP with the help of titanium is the most preferred pathway for both **D**₁ and **D**₂.

Our calculations indicate that difference in the reactivity of **D**₁ and **D**₂ is due to the difference in the chain length. However, in the slurry phase polymerization, there could be a competition between the alkyl chain of the donor and the n-hexane molecules for the MgCl₂ surface. We have calculated the free energy required to displace the alkyl chain from the MgCl₂ surface by the n-hexane molecule. For **D**₁ and **D**₂, the values are found to be the same (17.6 kcal/mol and 17.4 kcal/mol, respectively), which is due to the reason discussed earlier: our surface model is not big enough to quantify the complete interaction of alkyl chain with the MgCl₂ surface. Hence, we have calculated the corresponding free energy for **D**₆ (-4.7 kcal/mol), **D**₇ (-3.1 kcal/mol), and **D**₈ (-0.9 kcal/mol). Results indicate that with an increase in the alkyl chain length, it is difficult

for the n-hexane molecule to displace the alkyl chain from the MgCl_2 surface, which is applicable for the case of **D**₁ and **D**₂ donors as well.

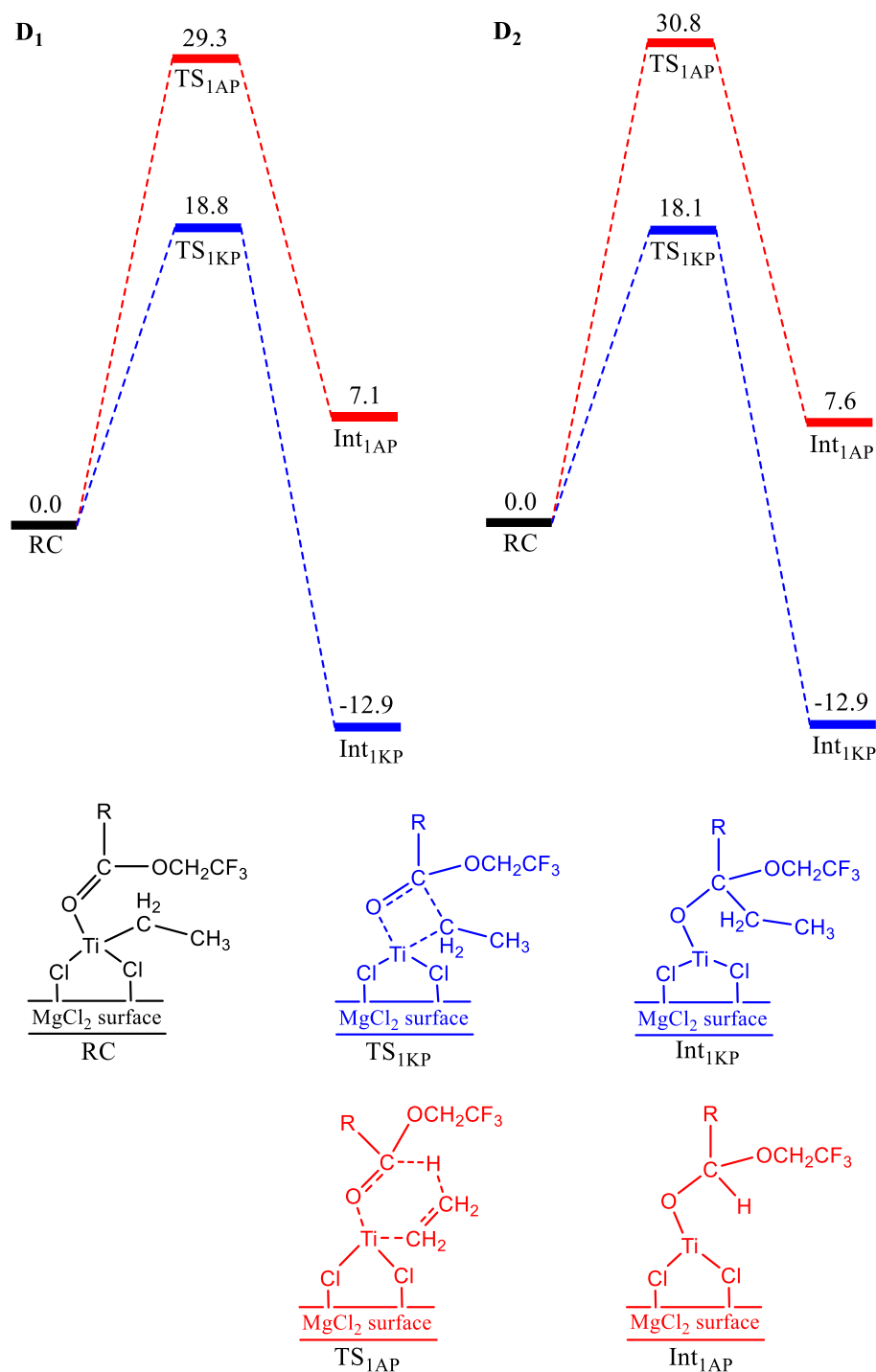


Figure 3.10. The free energy profile for the rate determining steps for the decomposition reaction of **D**₁ ($\text{R} = (\text{CH}_2)_{12}\text{CH}_3$) and **D**₂ ($\text{R} = (\text{CH}_2)_{14}\text{CH}_3$) with titanium. The values are in kcal/mol. Blue indicates the ketone pathway (KP) and red indicates the aldehyde pathway (AP).

3.4. Conclusions

Reactor fouling is a significant issue in Z-N catalyst systems, caused by overheating of the reactor vessel during the exothermic polymerization process. An interesting means of avoiding this problem is to employ donors with the ability to stop the polymerization process if the temperature were to exceed a certain value. In the current work, we have explored the reason behind the self-extinguishing property between the two donors using density functional theory (DFT). A systematic study of the decomposition reaction of **D1** and **D2** with Al_2Et_6 and titanium attached on the (110) MgCl_2 surface has been done. With Al_2Et_6 , both **D1** and **D2** show a tendency to form monomer-donor adducts, and these adducts can undergo decomposition reactions with the help of another AlEt_3 molecule, either through the ketone pathway (KP) or the aldehyde pathway (AP), leading to the formation of a ketone or an aldehyde respectively. Such species are known to act as poisons in Z-N systems, thereby explaining why **D1** and **D2** have the self-extinguishing property. Both donors have similar barriers for KP and AP, and among the two possible pathways, KP is more favorable, which corroborates with experimental observations. With titanium, both **D1** and **D2** bind strongly compared to Al_2Et_6 , and KP is a significantly more facile pathway. It is also interesting to note that the alkyl chain plays a significant role in making the binding stronger through non-covalent interactions. Even though the barriers are similar for both **D1** and **D2** for the decomposition reactions (both KP and AP) with titanium, the thermodynamic binding preference of **D2** over **D1** makes **D2** a better self-extinguishing donor, which agrees with the polymerization studies. In summary, our work provide insight into how the donors interact with Al_2Et_6 , TiCl_4 and, importantly, also the MgCl_2 surface, in order to undergo the self-extinguishing process.

3.5. References

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Chapter 4

Hidden Role of Lewis Acid-Base Adducts in Enhancing the Stereoselectivity of Ziegler-Natta Catalysis: Insights from Theory

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Abstract: Ziegler-Natta (Z-N) systems have been well established as heterogeneous catalysts that produce isotactic polypropylene and polyethylene with great efficiency. Such systems benefit considerably from donors (Lewis bases), whose addition significantly improves the stereoselectivity of polymerization. There is a consensus that the primary role of the external donors is to coordinate at the vacant site created by the extraction of internal donors and thus maintain the stereoselectivity. However, the bite difference between internal donors such as phthalates or succinate derivatives and external donors such as alkoxysilanes raises the question of how external donors can effectively replace internal donors. In order to investigate this, we have chosen four external alkoxysilane donors: (1) diisopropyl dimethoxysilane (DIPDMS), (2) dicyclopentyl dimethoxysilane (DCPDMS), (3) disec-butyl dimethoxysilane (DSBDMS), and (4) sec-butyl(methyl) dimethoxysilane (SBMDMS). Density functional theory (DFT) studies reveal that the bite difference problem is overcome by the favourable formation of adducts between the alkoxysilane external donors and AlEt_2Cl , which is present in the Z-N systems. Such adducts prefer to coordinate in the vicinity of the active site. Finally, it is seen that it is not the alkoxysilane donors, but these Lewis acid-base adducts (the alkoxysilane donor coordinated to AlEt_2Cl) that are primarily responsible for the stereoselectivity.

4.1. Introduction

Ziegler-Natta (Z-N) catalysis is widely regarded as the cornerstone of the polyolefin industry, serving as the primary method for producing isotactic polypropylene and polyethylene. In this process, Lewis base donors play a critical role in the catalytic mechanism.¹⁻²⁵ Initially, an indirect role of donors was proposed by the groups of Busico and Corradini. They proposed that donors bind to the more acidic (110) MgCl_2 surface, which prevents the coordination of TiCl_4 on the non-stereoselective (110) surface.^{4,26} However, subsequent experiments revealed that the role of donors in the Z-N system is direct.^{11,27} Donors can coordinate next to the active site and enhance the stereoselectivity of the reaction.^{7,11,28-34} Stereoselectivity in the heterogeneous Z-N catalyst is a complex phenomenon, depending on several factors: (a) the chiral site, (b) two different enantiofaces of the prochiral monomer, (c) chirality in the growing chain, (d) orientation of the long growing chain, and finally (e) adsorption of a donor in the vicinity of the active site.³⁵ In 1999, Busico *et al.* put forward a three-site model explaining the isotactic, isotactoid, and syndiotactic sequences in the polymer.³⁶

Ziegler and co-workers performed a systematic study regarding the relationship between the structure of alkoxysilane external donors and the stereoselectivity.²⁹ To this end, they selected 14 industrially relevant donors and calculated the energy difference between the two transition states responsible for the stereoselectivity. They noted that the alkoxysilane structure influences the gap in the barrier and corroborated the results with experimental observations. Moreover, the structure of alkoxysilanes was correlated with the average molecular weight of the polymer by calculating the energy difference between the insertion and termination barriers.

Taniike *et al.* did a similar study in 2012.³⁷ They studied the effect of ethyl benzoate co-adsorption (along with TiCl_4) on the surface using periodic density functional studies and concluded that the presence of EB in the vicinity of an active site could influence the catalytic process in three ways: (a) by converting an aspecific active site into a stereospecific site, (b) by improving the regioselectivity, and (c) by preventing chain transfer to the monomer. Terano *et al.* have extensively investigated the structure-performance of alkoxysilane donors by combining stopped-flow propylene polymerization and periodic density functional studies.³⁸ They found that

those silane donors that bind more strongly to the surface show high polymerization activity. One crucial aspect revealed from their work is that only increasing the bulkiness of the silane donor will not necessarily enhance the stereoselectivity: the conformation of the hydrocarbon group near the active site is also an important contributing factor. Recent computational studies by Liu and co-workers show that donor coordination and the presence of the AlEt_2Cl cocatalyst have a significant influence on the stereoselectivity.^{32,34}

The Z-N polymerization process is also regioselective in nature. It can proceed through either 1,2- or 2,1-insertion, and various studies show that 1,2-insertion is favourable compared to the 2,1 case.^{39,40} In 1994, Chadwick *et al.* experimentally detected around 20.0% n-butyl chain ends, indicating 2,1-insertion followed by a chain transfer with hydrogen.⁴¹ Later, Busico and co-workers also detected a lower amount of regio-irregularities (0.26% and 0.18%) in the isotactic polypropylene produced by employing the Z-N catalyst, where 1,3-diether and alkoxy-silanes were used as donor pairs.³⁹ Calculations by Cavallo and co-workers indicate that considerable ΔE_{regio} (i.e., the difference in the barriers between different reaction possibilities, leading to regioselectivity) is present even in the absence of any donors (~ 1.2 kcal/mol) and that there is a slight improvement in the regioselectivity with donor presence (~ 1.2 to 2.0 kcal/mol).⁷ Recently, Cavallo's group calculated the ΔE_{regio} of insertion on an active site based on a unified model created by defects on the (104) MgCl_2 surface. The results are also in agreement with previous studies.⁴²

It is interesting to note that a combination of internal and external donors is used in the modern Z-N systems, which helps to increase the isotacticity of the polymer.¹ However, a random selection of such a pair will not always be helpful. Experimentalists have tried to improve the effectiveness of such pairs through trial and error. An internal donor can adsorb beside the active titanium site and enhance the stereoselectivity of the polymerization. In other words, an internal donor can convert a non-stereoselective active site into a stereoselective active site. However, it is known that internal donors can be extracted from the MgCl_2 surface by the aluminum species present in the system and can undergo subsequent decomposition reactions, which would result in the loss of stereoselectivity.^{43,44} The primary role of the external donors is assumed to be the conversion of such non-stereoselective active sites back again into stereoselective active sites through the occupation of the empty sites on the MgCl_2 surface created by

the internal donor extraction. Among various internal : external donor combinations, it has been seen that the phthalates : alkoxysilanes and succinates : alkoxysilanes combinations provided the best activity and selectivity.¹

However, while there is consensus on the role of external donors – they occupy the vacant sites created by internal donor extraction, it is worth noting that there is considerable difference in the “bite” (i.e., the distance between two donor oxygen atoms) of phthalate and alkoxysilane molecules (see Figure 4.1). This leads to a pertinent, and potentially very significant, question: how are the alkoxysilane molecules effectively coordinating to the vacant sites on the MgCl_2 surface and enhancing the stereoselectivity of the polymerization reaction? The current work proposes to address this question by considering an expanded role of the aluminum species, TEAL, and its influence on donor chemistry in Z-N catalysis.

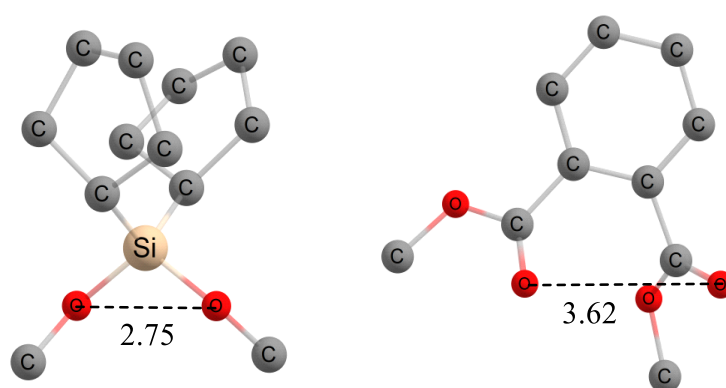


Figure 4.1. The bite difference between alkoxysilane (DCPDMS) and phthalate donors. Values are in angstrom. Hydrogen atoms have been omitted for the purpose of clarity.

The primary role of the aluminum species is to activate the pre-catalyst by exchanging one of its alkyl groups with a chloride from a surface coordinated TiCl_4 species, and AlR_2Cl is the by-product of the activation. Credendino *et al.* have showed that coordinated AlEt_3 and AlEt_2Cl on the step-defected (104) MgCl_2 surface can enhance the stereoselectivity.⁴² Similar results have been reported by Fallah *et al.*, who showed that the coordination of AlEt_3 and AlEt_2Cl next to the active site on the (110) MgCl_2 surface influences the stereoselectivity.⁴⁵ Recently, Khatri *et al.* have shown that interactions are possible between external donors and triethylaluminum.⁴⁶ Coming back to the question that we have raised above, it is possible that the key player in the Z-N system is not the alkoxysilane donor. *Instead, one can consider the possibility that*

Lewis acid-base adducts formed by the interaction of acidic aluminum species and basic alkoxysilane donors creates new “external” donors that have the proper ‘bite’ distance. This is illustrated further in Figure 4.2 below. To the best of our knowledge, there are no studies done to understand the role of such Lewis adducts in the stereoselectivity of Z-N catalysis.

In this work, we have employed full quantum chemical calculations with density functional theory (DFT), in order to understand the feasibility of the formation of Lewis acid-base adducts between four alkoxysilane donors and AlEt_3 or AlEt_2Cl . Then, the possibility of such adducts coordinating next to the active site compared to alkoxysilane donors has been considered. Finally, the effect of the adduct in enhancing the stereoselectivity in Z-N catalysis has been investigated.

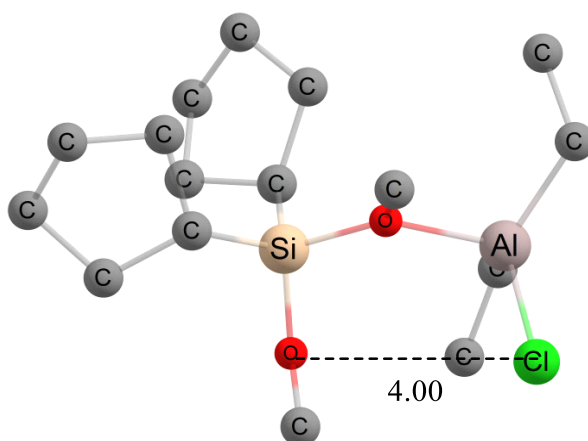


Figure 4.2. The bite distance in the Lewis acid-base adduct (DCPDMS- AlEt_2Cl). The value is in angstrom. Hydrogen atoms have been omitted for the purpose of clarity.

4.2. Computational Details

The Turbomole 7.5 suite of the programs⁴⁷ has been employed to optimize all the structures, including intermediates and transition states, using density functional theory (DFT). Geometry optimizations have been performed using the B3-LYP functional⁴⁸ and the def2-SVP basis set.⁴⁹ The dispersion correction (DFT-D3), developed by Grimme *et al.*,⁵⁰ has been employed to increase the accuracy of the calculations. The resolution of identity (RI)⁵¹ and the multipole accelerated resolution of identity (marij)⁵² approximations have been used to efficiently treat the electronic Coulomb term in the DFT calculations. Open-shell calculations have been considered for the active site transition state optimizations. For the calculations that we have performed, the energy convergence criteria was 10^{-7} H, and the norm for the Cartesian

gradients was 10^{-3} . The second-order derivatives of the potential energy were obtained numerically. For better relative energies, we have performed single point calculations for all the geometries obtained from optimization at the M06-L/TZVP (RI and marij approximations employed) level of theory.^{53,54} Furthermore, we have employed the m4 grid size for both optimization and single point calculations, in order to achieve better accuracy. We note here that no solvent corrections have been included in the calculations. This is because Ziegler-Natta (Z-N) catalysis is a heterogenous process, and a predominant portion of the global polypropylene production is carried out either in the bulk phase or in gas phase polymerizations, where there are no solvents. This, indeed, is the norm for computational studies on Z-N catalysis, as evidenced by the many recently published computational studies in various journals, which investigate various aspects of Z-N catalysis through gas phase calculations.^{7,29,30,32,34,42,43,55-57} We further note that our choice of the level of theory (M06L/TZVP//B3LYP-D3/def2-SVP) is based on recent computational studies of stereoselectivity in Ziegler-Natta catalysis, which had been found to corroborate with experimental observations.^{32,34} Another point that should be discussed is the reliability of predictions on stereoselectivity if the barrier gaps are small. In order to address this, we have considered three representative cases: (1) the bare site, (2) DCPDMS-AlEt₂Cl, where the ethyl groups are oriented towards the active site, and (3) DCPDMS-AlEt₂Cl, where the cyclopentyl groups are oriented towards the active site, and calculated the $\Delta\Delta G^{\ddagger}_{\text{Stereo}}$ values at a different level of theory (TPSS-D3/def2-SVP).⁵⁸ Even though the absolute values do show changes (0.3 kcal/mol for Case 1, 1.2 kcal/mol for Case 2, and 4.3 kcal/mol for Case 3), the trend in the stereoselectivity remains the same. This is also discussed in the last paragraph of the Results and Discussion section.

We have employed a 30 MgCl₂ cluster for the calculations (described in Section 3.2). Furthermore, in order to reduce the computational cost of the barrier calculations, a 22 MgCl₂ cluster has been employed for the transition state calculations (described in Section 3.3). The values reported are ΔG values, with zero-point energy, internal energy, and entropic contributions (including translational, rotational, and vibrational entropy contributions) included through frequency calculations on the optimized minima and transition state structures, with the temperature taken to be 298.15 K. This was done to ensure that all the reported transition state structures contained only one imaginary frequency corresponding to the correct normal mode. IRC calculations have

been considered for the confirmation of the transition states. In every case, the IRC calculations have yielded the correct reactant and product structures.

4.3. Results and Discussion

4.3.1. Formation of Lewis Acid-base Adducts

Alkoxysilane donors are Lewis bases that can form adducts with Lewis acidic species in the system. Since the alkoxysilane donors are the conventional external donors for the Z-N catalysts, they add along with the alkyl aluminum species into the catalytic system. Alkoxysilane donors can bind to AlEt_3 and AlEt_2Cl (the species formed as the by-product of the activation of the pre-catalyst by AlEt_3). We have chosen four alkoxysilane donors for the study (see Figure 4.3): (1) diisopropyl dimethoxysilane (DIPDMS), (2) dicyclopentyl dimethoxysilane (DCPDMS), (3) disec-butyl dimethoxysilane (DSBDMS), and (4) sec-butyl (methyl) dimethoxysilane (SBDMS). The formation energy for the alkoxysilane donors and the $\text{AlEt}_3/\text{AlEt}_2\text{Cl}$ adducts are shown in Table 4.1.

All the alkoxysilane donors show significant adduct formation energies (AFE), with both AlEt_3 and AlEt_2Cl . With AlEt_3 , the DCPDMS donor shows the highest AFE of -4.6 kcal/mol, and the DIPDMS donor shows the lowest AFE of -1.0 kcal/mol. The remaining donors, DSBDMS and SBDMS, show intermediate AFE values of -4.2 kcal/mol and -4.3 kcal/mol, respectively. The difference in the binding energies arises due to the differences in the +I effect and the bulkiness of alkyl groups in the alkoxysilane donors. With AlEt_2Cl , all the donors show an increase in the AFE of around 4-5 kcal/mol, which is due to the higher Lewis acidity of the aluminum center in AlEt_2Cl compared with AlEt_3 , probably due to the -I effect of the chloride ion. The trend in the AFE remains similar: DCPDMS shows the highest AFE of -9.0 kcal/mol, and DIPDMS shows the lowest AFE of -5.9 kcal/mol. The other two donors, DSBDMS and SBDMS, show intermediate AFE values of -8.2 kcal/mol and -8.8 kcal/mol, respectively. Furthermore, alkoxysilane donors can also form adducts with two molecules of $\text{AlEt}_3/\text{AlEt}_2\text{Cl}$, due to two potential donor oxygen atoms. The AFE values for forming D--2AlEt_3 or $\text{D--2AlEt}_2\text{Cl}$ (where D = alkoxysilane donor) are given in Table 4.1, which shows the same trend as in the D--AlEt_3 or $\text{D--AlEt}_2\text{Cl}$ adduct formation cases. Furthermore, in order to ensure that the formation of adducts is

feasible, we have also calculated the AFE at a different level of theory. It is seen that even though the absolute values change, the conclusion remains the same.

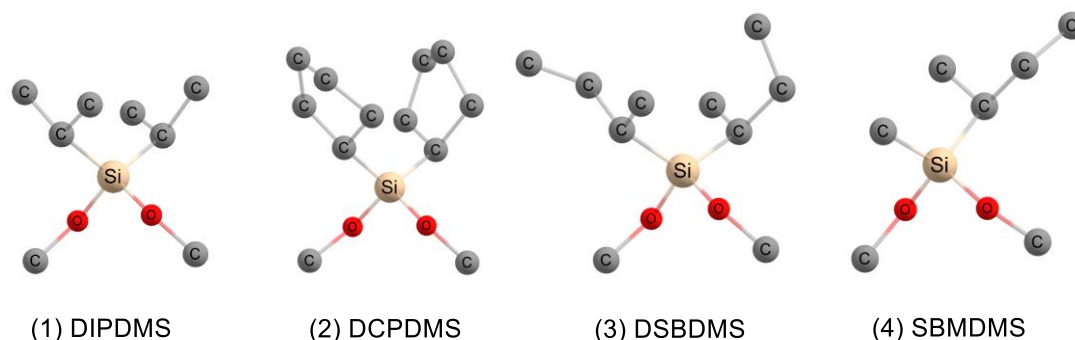


Figure 4.3. The structures of the four alkoxy silanes donors considered in this study. Hydrogen atoms have been omitted for the purpose of clarity.

Table 4.1. Adduct formation energy (AFE) for the four alkoxy silane donors with AlEt_3 and AlEt_2Cl . ΔG values are in kcal/mol.

Alkoxy silane donor (D)	Adduct formation energy (AFE)			
	D-- AlEt_3	D-- AlEt_2Cl	D-- 2AlEt_3	D-- $2\text{AlEt}_2\text{Cl}$
DIPDMS	-1.0	-5.9	-3.3	-11.5
DCPDMS	-4.6	-9.0	-8.6	-17.2
DSBDMs	-4.2	-8.2	-6.9	-14.9
SBMDMS	-4.3	-8.8	-7.7	-14.3

The calculated values of AFE indicate that the formation of Lewis acid-base adducts between the alkoxy silane donors and $\text{AlEt}_3/\text{AlEt}_2\text{Cl}$ is feasible in Z-N catalysis systems. What would be the role of such Lewis adducts in the system? In the following sections, we have addressed this question. Since the AFE of alkoxy silane donors with AlEt_2Cl is significantly higher than that of AlEt_3 , we have considered D-- AlEt_2Cl adducts for further calculations.

4.3.2. Binding of Lewis Acid-base Adducts to the (110) MgCl_2 Surface

There is a consensus that donors enhance the stereoselectivity of Z-N catalysts by coordinating near the active titanium site, and if the donors are coordinating away from the active site, the influence is minor. Hence, an effective donor must bind next

to the active site. We have considered a model active titanium site on the (110) MgCl_2 surface, in which an internal donor (the phthalate derivative donor is taken as a representative donor for the internal donor) coordinates on one side of the active site (see Figure 4.4). An external alkoxysilane donor has two possibilities: it can either coordinate next to the active site or away. Due to the short bite of alkoxysilane donors, they must bind through mono-coordination (one oxygen atom coordinated to one magnesium atom) to sit next to the active site. However, they can bind through chelate-coordination (two oxygen atoms coordinated to the same magnesium atom) or mono-coordination on the (110) MgCl_2 surface, in order to sit away from the active site. The calculated values suggest that the alkoxysilane donor prefers to coordinate away from the active site (-37.1 kcal/mol for chelate-coordination and -22.5 kcal/mol for mono-coordination) than next to the active site (-16.5 kcal/mol for mono-coordination). The difference arises from the stability gained from the coordination of two oxygen atoms to the same magnesium atom in chelate-coordination instead of only one oxygen atom coordinating to the magnesium atom in mono-coordination. Moreover, the mono-coordination away from the active site is more favorable than the mono-coordination near the active site, due to reduced sterics and non-covalent interactions between the cyclopentyl group and the MgCl_2 surface.

The situation changes in the Lewis acid-base adduct case: there are now two donor atoms (oxygen and chlorine) with a larger bite. This adduct can coordinate next to the active site *via* bridge-coordination or coordinate away from the active site by bridge- or chelate-coordination. We have not considered the mono-coordination of the adduct, because it is a less favorable mode in comparison to the chelate- and bridge-coordination modes. One additional complexity that arises in the case of the adduct is due to its non-symmetrical nature. There are two possibilities even for the bridge-coordination near the active site: either the Cl donor atom can coordinate near the active site, or the O donor atom can coordinate. Such a difference in coordination causes a change in the sterics around the active site. If Cl coordinates, the alkyl groups of the aluminum species orient towards the active site (ethyl groups in this case), and in the case of O coordination, the R groups of alkoxysilane orient towards the active site. Both would have implications with regard to the eventual properties of the polymers formed in the reactions.

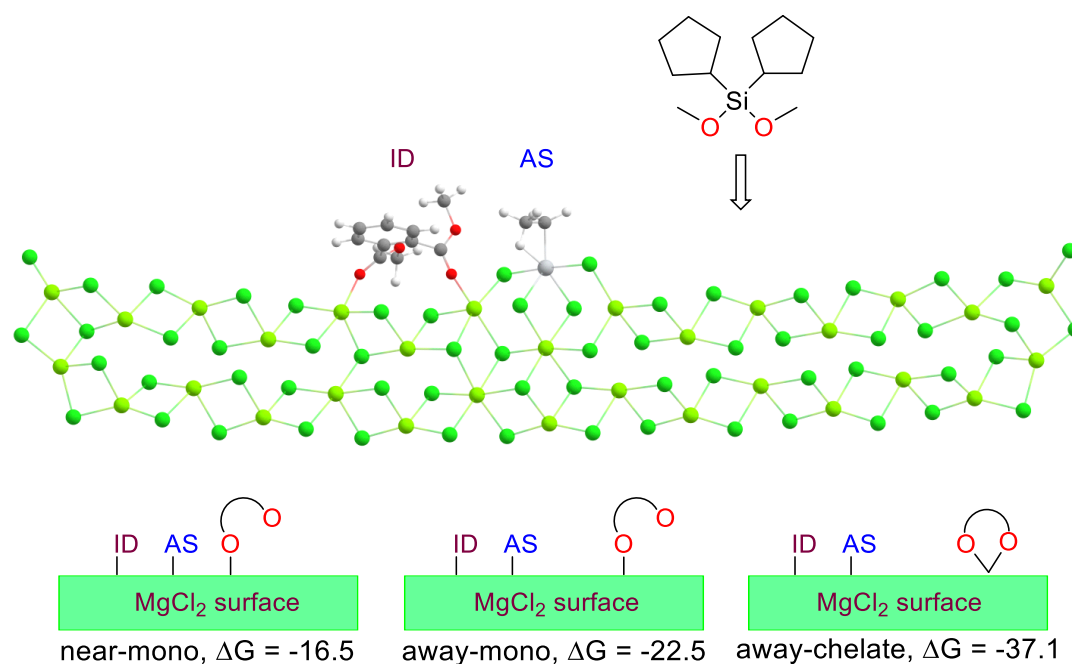


Figure 4.4. The three possibilities (near and away from the active site) of coordination by DCPDMS with respect to the active site. Values are in kcal/mol. ID: Internal Donor, AS: Active Site.

The calculated values indicate that the adduct (taking the DCPDMS- AlEt_2Cl adduct as the representative) prefers to coordinate away from the active site when the O donor atom coordinates faces the active site (see Figure 4.5): the ΔG values for the adduct coordination for away coordination by bridge- and chelate-coordination modes are -31.6 kcal/mol and -29.1 kcal/mol, respectively. In contrast, ΔG for the near coordination is only -22.1 kcal/mol. There is a change in the trend in the case of the Cl donor atom facing the active site. The ΔG values for away coordination by bridge- and chelate-coordination modes are -32.1 kcal/mol and -29.0 kcal/mol, but, interestingly, the near coordination is equally probable (-31.7 kcal/mol) in the case of the Cl donor atom facing the active site (see Figure 4.5).

Why does the Cl donor atom prefer to coordinate in the vicinity of the active site in comparison to O? The difference arises mainly due to the increased sterics caused by two cyclopentyl groups around the active site, in comparison to two ethyl groups. However, it is essential to note that we have assumed no other donors in the vicinity of the adduct on the MgCl_2 surface for these calculations, which is unlikely from the experimental point of view. Such an extra ID or ED can alter the binding preferences because of change in the sterics. In order to take this factor into account, we have

considered four cases; (i) only adduct case, (ii) ED in the vicinity of the adduct in chelate-coordination, (iii) ID in the vicinity of the adduct in chelate-coordination, and (iv) ID in the vicinity of the adduct in bridge-coordination (see Figure 4.6). The calculated relative energy values indicate that when no extra donor is present, the Cl coordination near the active site is favored by 9.6 kcal/mol.

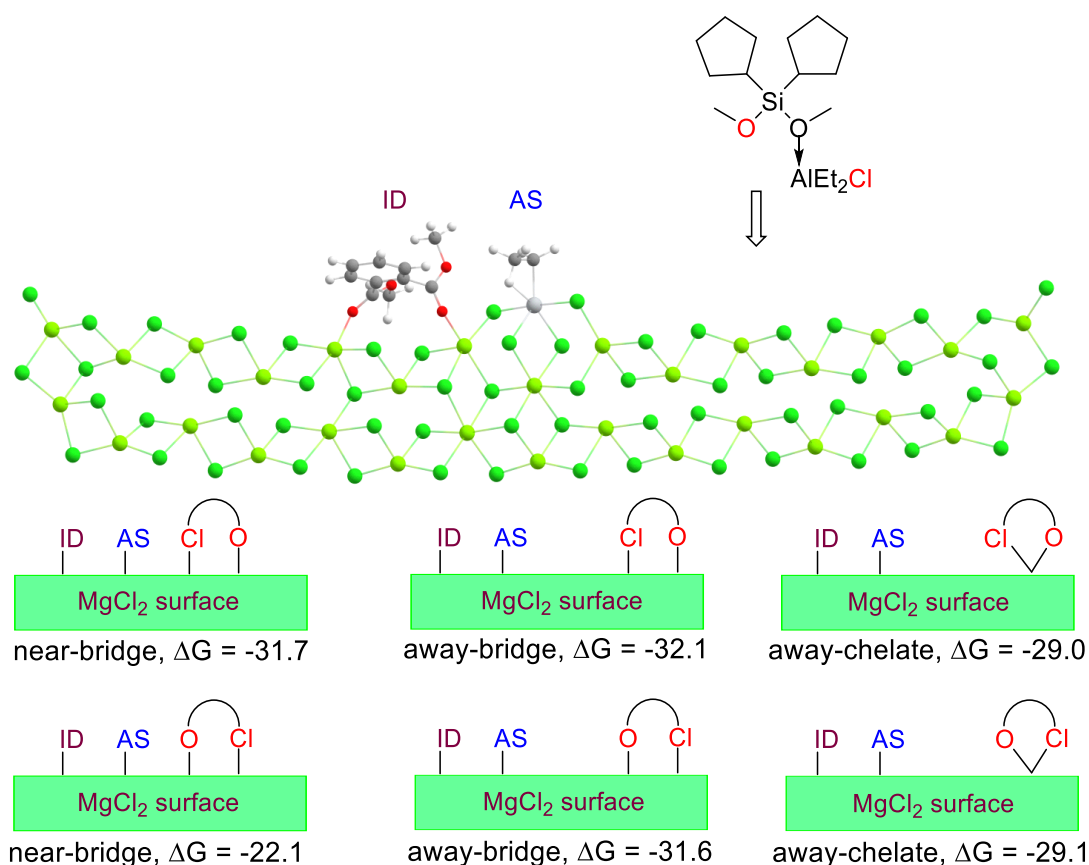


Figure 4.5. The six possibilities (near and away from the active site) of coordination by the Lewis acid-base adduct. Values are in kcal/mol. ID: Internal Donor, AS: Active Site.

Interestingly, the preference for the Cl coordination is reduced in the presence of an extra donor: to 8.8 kcal/mol for case (ii), 6.8 kcal/mol for case (iii) and 1.3 kcal/mol for case (iv). The results suggest that we cannot wholly ignore the possibility of O coordinating in the vicinity of the active site. Hence, we have considered the two possibilities of adduct coordination in the vicinity of the active site to study the effect of adducts in the stereoselectivity.

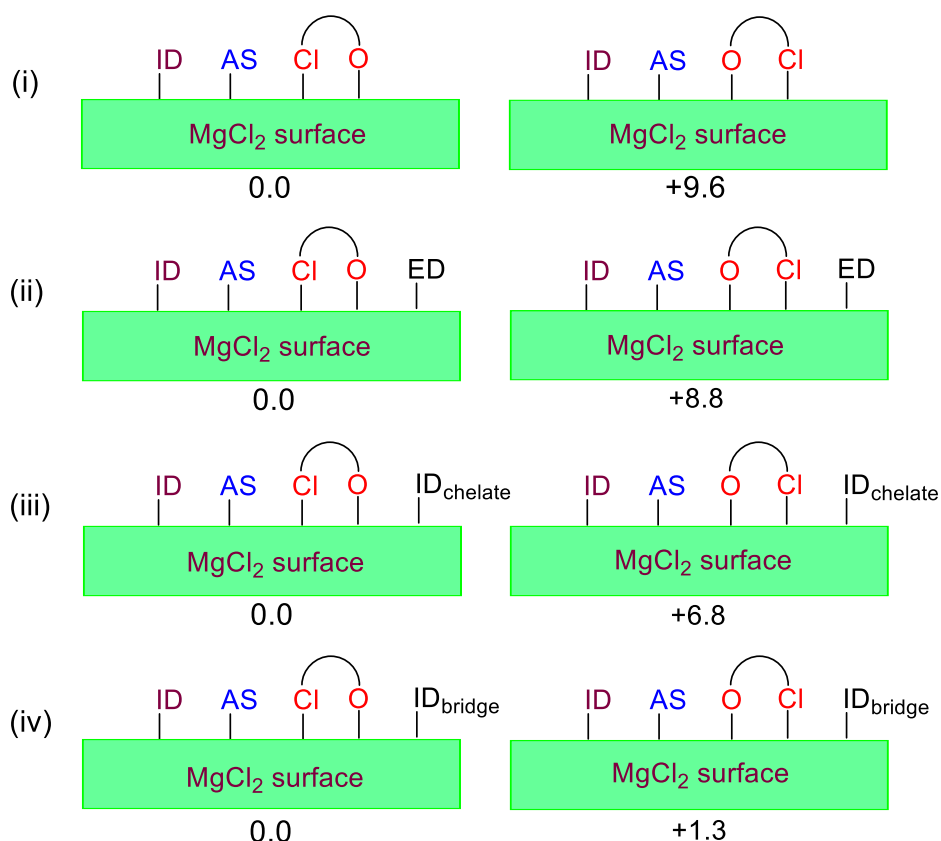


Figure 4.6. The relative energy difference between two binding possibilities of adduct in presence of another donor. Values are in kcal/mol. ID: Internal Donor, AS: Active Site.

4.3.3. Role of Lewis Acid-base Adducts in the Stereoselectivity of Propylene Polymerization

Stereoselectivity in Z-N catalysis arises due to factors such as the prochiral nature of the monomer, the chirality of the active site, the orientation of the growing chain, and the presence of coordinated donors in the vicinity of the active site. The insertion of propylene monomer to the Ti-C (of the growing polymer chain) proceeds *via* the Cossee-Arlman mechanism. The first step is the formation of the π complex, followed by a four-membered transition state. To understand the effect of Lewis adducts on the stereoselectivity, we have calculated the barriers for the *re*- and *si*-transition states for 1,2-insertion using models in which the chirality of the active site is the same, and an ethyl group is taken to mimic the growing polymer chain. We have chosen only 1,2-insertion because, as mentioned in the Introduction, various studies show that 1,2-insertion is favorable over 2,1-insertion in Z-N catalysis. There are eight possibilities (four each for *re*- and *si*- face coordination) of π complexes depending on

the relative position of the propylene monomer and the growing polymer chain (see Figure 4.7). Then, the insertion can take place through a four-membered *re*- or *si*-transition state (TS). Again, there are two possibilities for each *re*- and *si*- coordination case (see Figure 4.8).

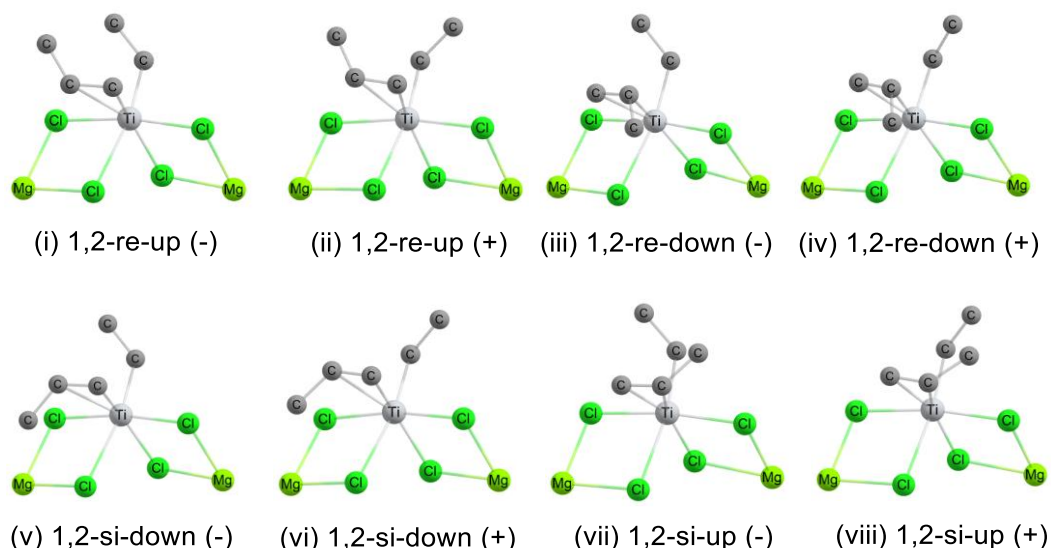


Figure 4.7. Representation of the eight possibilities for the formation of π complexes. Hydrogen atoms are omitted for the purpose of clarity.

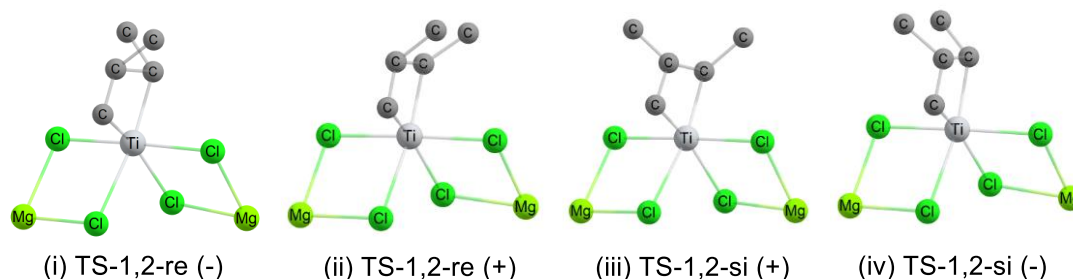


Figure 4.8. Representations of the four transition state possibilities for 1,2-insertion. Hydrogen atoms are omitted for the purpose of clarity.

First, we have considered a bare site without any donor in the vicinity (see Figure 4.9a). The $\Delta\Delta G^{\ddagger}_{\text{Stereo}}$ is the difference between the barriers of 1,2-*si* and 1,2-*re* insertions ($\Delta G^{\ddagger}_{1,2\text{-}si} - \Delta G^{\ddagger}_{1,2\text{-}re}$). We have taken the most stable π complex and the TS for calculating the barriers for *re*- and *si*- insertions (the relative stabilities of π complexes and TSs are provided in Figure 4.10 and 4.11). TS-1,2-*re* (-) is stable by 3.0 kcal/mol compared to TS-1,2-*re* (+) in the case of *re*- insertion, and TS-1,2-*si* (+) is stable by 2.4 kcal/mol compared to TS-1,2-*si* (-) in the case of *si*- insertion (see Figure

4.11). This is due to less steric repulsion between the CH₃ group of the propylene monomer and the CH₃ group of the growing polymer chain. The $\Delta\Delta G^{\ddagger}_{\text{Stereo}}$ for the bare site is -0.5 kcal/mol (see Table 4.2), which indicates that the bare site without any adjacent donor species is poor from a stereoselective point of view. Furthermore, in order to understand the effect of one donor in the vicinity of the active site, we have calculated the $\Delta\Delta G^{\ddagger}_{\text{Stereo}}$ by coordinating one phthalate derivative donor (see Figure 9b), a well-known ID in Z-N catalysis. We have only considered the TS-1,2-*re* (-) and TS-1,2-*si* (+) cases, because of the stability factor discussed above but considered all the four π complex possibilities for both *re*- and *si*- coordination (see Figure 4.12 for the relative free energy values) to get the most stable π complex. However, the calculated value (0.8 kcal/mol) suggests that there is no significant improvement in the stereoselectivity (see Table 4.2).

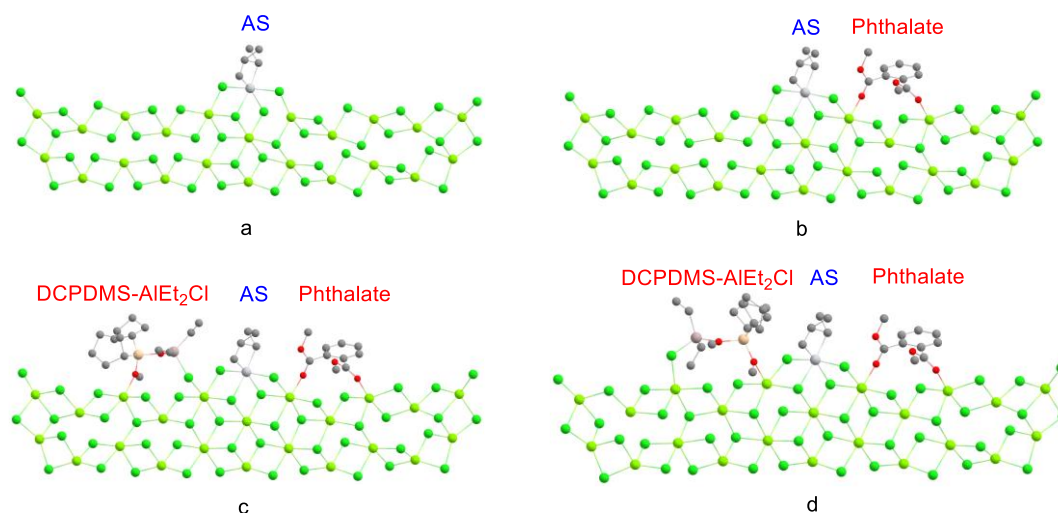


Figure 4.9. Side view of four different cases considered for the study: (a) bare active site (AS), (b) only one phthalate donor coordinated in the vicinity of the active site, (c) phthalate donor and DCPDMS-AlEt₂Cl adduct are coordinated in the vicinity, where the ethyl groups are oriented towards the active site, and (d) phthalate donor and DCPDMS-AlEt₂Cl adduct are coordinated on the vicinity, where the cyclopentyl groups are oriented towards the active site. Hydrogen atoms have been omitted for clarity, and in all four cases, we have shown *re*-propylene with (-) growing chain on the active site.

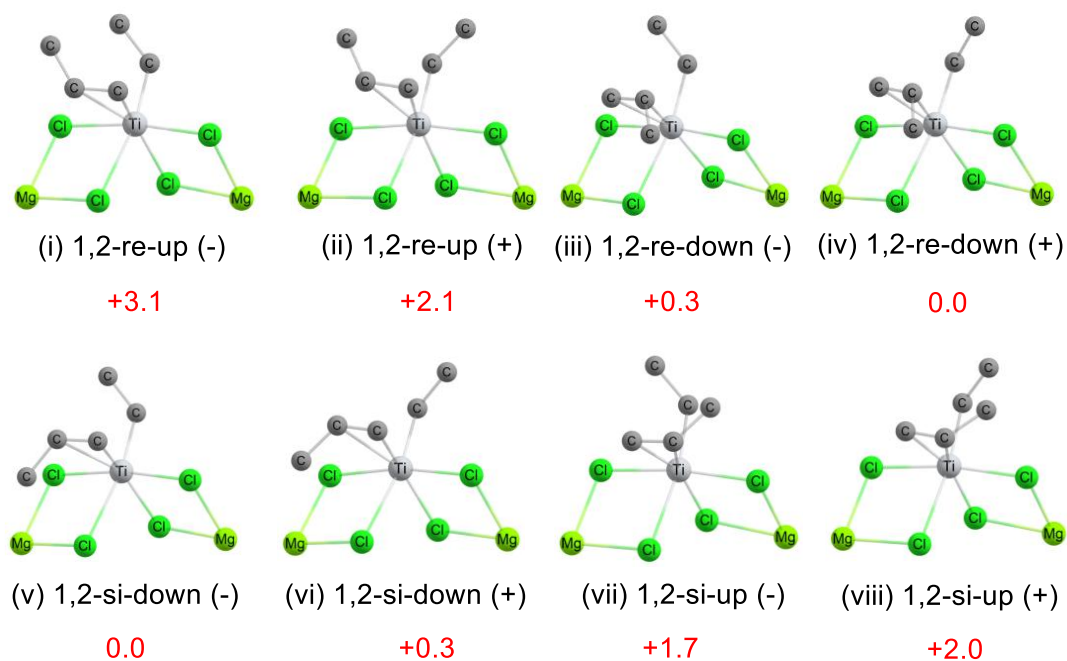


Figure 4.10. Relative free energy values (in kcal/mol) of the π complexes for *re*- and *si*-coordination, for the bare site. For clarity, we have shown schematic representations, not the optimized structures.

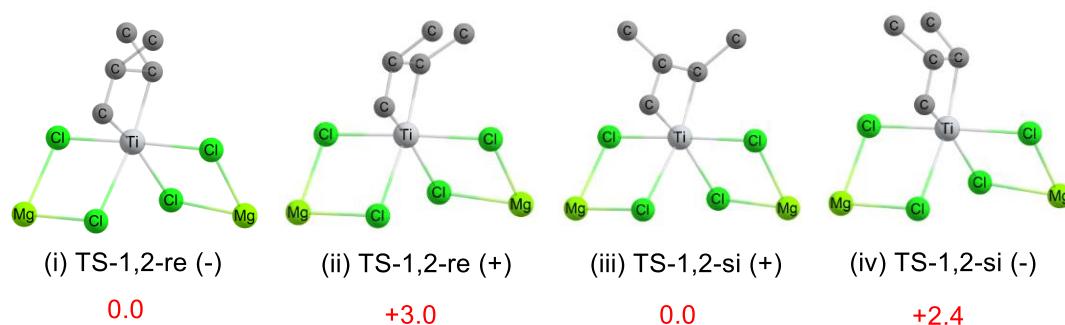


Figure 4.11. Relative free energy values (in kcal/mol) of the TSs for *re*- and *si*-coordination, for the bare site. For clarity, we have shown schematic representations, not the optimized structures.

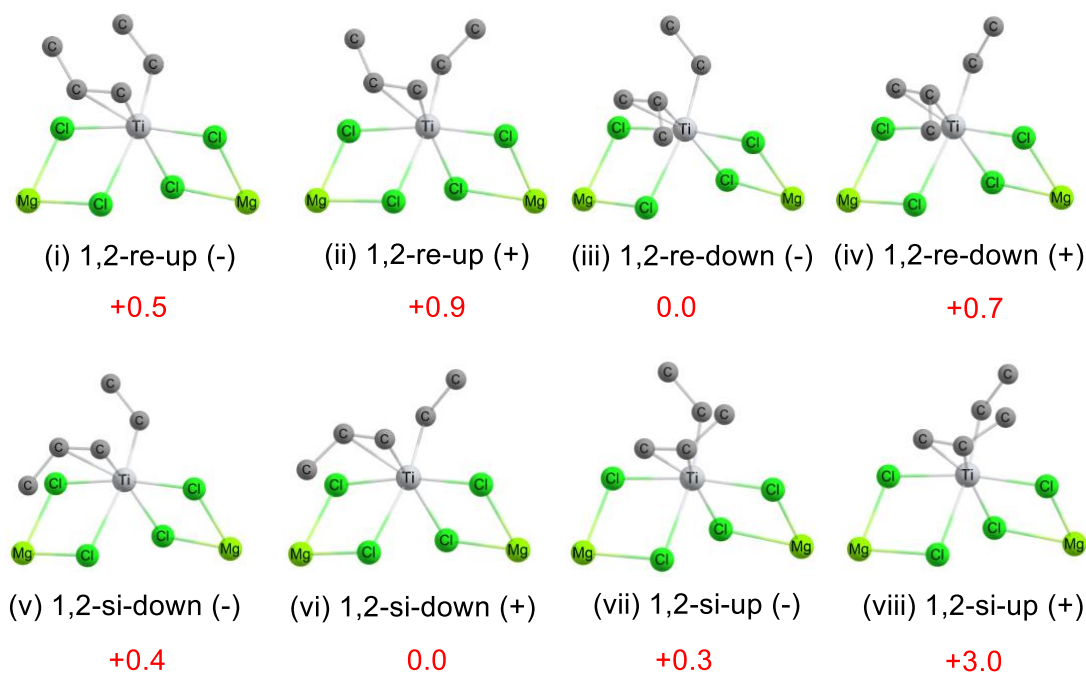


Figure 4.12. Relative free energy values (in kcal/mol) of the π complexes for *re*- and *si*- coordination, for the “only phthalate” case. For clarity, we have shown schematic representations, not the optimized structures.

Next, we have considered the case where, in addition to the phthalate donor coordinating to one side of the active site, the Lewis acid-base adduct is coordinated to the other side (see Figure 9c). As discussed in Section 3.2, there are two possibilities for an adduct to coordinate in the vicinity of an active site; either the ethyl groups of AlEt_2Cl can orient towards the active site, or R groups of the alkoxysilane donors can orient towards the active site. Out of these two possibilities, we have first considered the ethyl groups oriented towards the active site, since such coordination is more thermodynamically favorable. Like in the above case, we have only looked at TS-1,2-*re* (-) and TS-1,2-*si* (+) to calculate the *re*- and *si*-barriers for all the adduct cases. Moreover, for such adduct coordination in the vicinity of the active site, the possibilities for π complex formation is reduced to two, where the CH_3 group of the monomer is oriented away from the bulky adduct. We have calculated the relative free energies for two possibilities of the simplest DIPDMS- AlEt_2Cl case (see Figure 4.13) and considered the most favorable π complex possibility for the remaining three adduct cases.

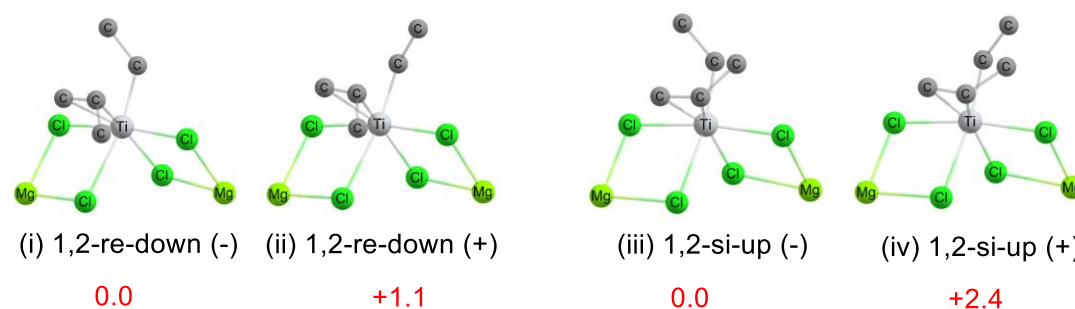


Figure 4.13. Relative free energy values (in kcal/mol) of the π complexes for *re*- and *si*- coordination, for the DIPDMS- AlEt_2Cl case (ethyl groups oriented towards the active site). For clarity, we have shown schematic representations, not the optimized structures.

Interestingly, all four adducts formed by DIPDMS, DCPDMS, DSBDMS, and SBMDMS show a significant improvement in the stereoselectivity, compared to the bare site. The $\Delta\Delta G^\ddagger_{\text{Stereo}}$ values are 2.2 kcal/mol, 2.2 kcal/mol, 2.9 kcal/mol, and 3.0 kcal/mol, respectively (see Table 4.2). This better stereoselectivity is due to the orientation of the ethyl groups of AlEt_2Cl towards the active site. Such an active site makes the *si*-insertion difficult, because of the repulsive interaction between the CH_3 group of the propylene and the ethyl groups.

Table 4.2. The *re*- and *si*- insertion barriers and the difference for four-selected alkoxyasilane- AlEt_2Cl adducts. The values are in kcal/mol.

	$\Delta G^\ddagger_{1,2-re}$	$\Delta G^\ddagger_{1,2-si}$	$\Delta\Delta G^\ddagger_{\text{Stereo}}$ ($\Delta G^\ddagger_{1,2-si} - \Delta G^\ddagger_{1,2-re}$)
Bare active site	13.3	12.8	-0.5
Only phthalate	13.3	14.1	0.8
Adduct and phthalate (Et groups towards AS)			
DIPDMS	13.6	15.8	2.2
DCPDMS	14.0	16.2	2.2
DSBDMS	12.6	15.5	2.9
SBMDMS	13.2	16.2	3.0
Adduct and phthalate (R groups towards AS)			

DIPDMS	14.5	16.7	2.2
DCPDMS	14.3	17.3	3.0
DSBDMS	13.6	16.4	2.8
SBDMS	13.7	15.3	1.6

Next, we have considered the second case where the R groups of the alkoxy silane donors are oriented towards the active site (see Figure 9d). Even though the formation of such sites is less favorable in the absence of a nearby donor, as discussed in Section 3.2, their formation is possible in the presence of another donor. The calculated values indicate (see Table 4.2) that the active sites formed by coordinating DCPDMS-AlEt₂Cl and DSBDMS-AlEt₂Cl adducts show the highest stereoselectivity (the $\Delta\Delta G^{\ddagger}_{\text{Stereo}}$ values are 3.0 kcal/mol and 2.8 kcal/mol, respectively). The higher stereoselectivity is due to the increased sterics provided by the cyclopentyl groups and the secondary butyl groups of the alkoxy silane donors near the active site compared to that of the ethyl groups in the last considered examples. Such a higher steric hindrance between the R groups of the alkoxy silane donors significantly destabilizes the *si*-insertion transition state compared to the re-insertion transition state, leading to improved stereoselectivity.

The adduct formed by DIPDMS shows the same selectivity (the $\Delta\Delta G^{\ddagger}_{\text{Stereo}}$ value is 2.2 kcal/mol) compared to the ethyl group oriented towards the active site case, which is probably because there is not much improvement in the sterics, whereas that of SBDMS shows lower stereoselectivity (the $\Delta\Delta G^{\ddagger}_{\text{Stereo}}$ value is 1.6 kcal/mol). Our calculated $\Delta\Delta G^{\ddagger}_{\text{Stereo}}$ values for all four cases correlate with experimental observations that DCPDMS, DSBDMS, and DIPDMS are known as donors that increase the stereoselectivity significantly. Furthermore, we have selected three representative cases, (1) the bare site, (2) DCPDMS-AlEt₂Cl, where the ethyl groups are oriented towards the active site, and (3) DCPDMS-AlEt₂Cl, where the cyclopentyl groups are oriented towards the active site and calculated the $\Delta\Delta G^{\ddagger}_{\text{Stereo}}$ values at a different level of theory (TPSS-D3/def2-SVP). Even though the absolute values change (0.3 kcal/mol for Case 1, 1.2 kcal/mol for Case 2, and 4.3 kcal/mol for Case 3), the trend in the stereoselectivity remains the same. Even though our calculated values suggest that the adducts improve the stereoselectivity of the active site for the polymerization of

propylene monomers, we must caution the reader not to take the absolute values as a direct measure of the stereoselectivity, due to the multi-site nature of the heterogeneous Z-N catalysis.

4.4. Conclusions

Density functional theory (DFT) calculations have been employed to understand the role of Lewis acid-base adducts on the stereoselectivity of Z-N catalysis. We have selected four alkoxy silane donors; DIPDMS, DCPDMS, DSBDMS, and SBMDMS. These four external donors form adducts with the AlEt_3 and AlEt_2Cl acidic species in the system. Since the adducts with AlEt_2Cl are more favorable, we have further investigated their affinity to bind to the (110) MgCl_2 surface. It has been revealed that an alkoxy silane donor prefers to bind away from the active site because of the favorable chelate-coordination, but such a preference is not there in the case of adducts because adducts can do bridge-coordination next to the active site. Furthermore, the presence of adducts in the vicinity of the active site significantly improves the stereoselectivity of the Z-N catalysis compared to cases where there are no donors, or only an internal donor, near the active site. In conclusion, our detailed computational studies indicate that the Lewis acid-base adducts formed by the alkoxy silane donors and the aluminum species are the real players in enhancing the stereoselectivity in Z-N systems.

4.5. References

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Chapter 5

The Effect of Lewis Acid-Base Adducts in the Regioselectivity of Ziegler-Natta Catalysis: A DFT Study

Chapter 5

The Effect of Lewis Acid-Base Adducts in the Regioselectivity of Ziegler-Natta Catalysis: A DFT Study

Abstract: Heterogeneous Ziegler-Natta (Z-N) catalysis is well known for the large-scale industrial production of polyethylene and isotactic polypropylene. Lewis base donors are an inevitable component of the system. Donors can influence the activity and selectivity of the reaction by coordinating in the vicinity of the active site. Our previous study shows that it is not the alkoxysilane donor; it is the alkoxysilane- AlEt_2Cl adduct that plays a vital role in increasing the stereoselectivity of the reaction. However, what would be the role of such adducts in the regioselectivity of the Z-N catalysis? In order to understand that, we have chosen the adducts of four alkoxysilanes: (1) diisopropyl dimethoxysilane (DIPDMS), (2) dicyclopentyl dimethoxysilane (DCPDMS), (3) disec-butyl dimethoxysilane (DSBDMS), and (4) sec-butyl(methyl) dimethoxysilane (SBMDMS). Our DFT studies suggest that the adducts can enhance the stereoselectivity without much reduction in the regioselectivity of the reaction. Furthermore, 2,1-insertion was found to be more stereoselective compared to 1,2-insertion in the presence of adducts in the vicinity.

5.1. Introduction

Ziegler-Natta (Z-N) catalysis is one of the most important heterogeneous catalytic processes ever discovered. The global production of polyethylene and isotactic polypropylene predominantly depends on Z-N catalysis, which has opened up a multi-billion-dollar market worldwide.^{1,2} Donors were not part of Z-N catalysts in the initial days. However, later, it was found that using oxygen-containing molecules such as ethyl benzoate could improve the activity and stereoselectivity of the reaction. Donors are of two types, and this classification is based on when they are introduced to the system. Donors like ethyl benzoate, 1,3-diethers, phthalates, and succinates are examples of internal donors,³⁻¹⁹ which add to the system during the preparation of the catalyst. Alkoxysilanes are used as external donors. External donors are added to the system along with the co-catalyst.²⁰⁻²⁵ A suitable combination of internal and external donors is employed in Z-N catalysts to maintain the stereoselectivity of the active site.¹

In Chapter 4, we have addressed an important question: how can the alkoxysilane donors enhance the stereoselectivity of the active site despite their considerable bite difference in comparison to phthalate donors? Our DFT studies revealed that it is not the alkoxysilane donors responsible for the enhancement in the stereoselectivity. The Lewis adducts formed by the interaction of alkoxysilane donors and alkyl aluminum species such as AlEt_2Cl are majorly responsible for the stereoselectivity. However, what would be the effect of such adducts on the regioselectivity in Z-N catalysis? Regioselective studies are less reported in the literature because early studies in Z-N suggest that Z-N catalysts are regioselective.^{7,26-28} However, experimental studies show that a considerable amount of regio-errors exist in Z-N catalysis.²⁹ According to them, these can reduce the activity of the catalyst by increasing the sterics at the active site. Hence, it is crucial to understand the regioselectivity of the newly identified active sites in the Z-N catalysts where the alkoxysilane adducts are coordinated in the vicinity of the active site. In this work, we have employed full quantum mechanical studies to understand the effect of adducts on the regioselectivity of the Z-N reaction.

5.2. Computational Details

The Turbomole 7.5 suite of the programs³⁰ has been employed to optimize all the structures, including intermediates and transition states, using density functional

theory (DFT). Geometry optimizations have been performed using the B3-LYP functional³¹ and the def2-SVP basis set.³² The dispersion correction (DFT-D3)³³, developed by Grimme *et al.*, has been employed to increase the accuracy of the calculations. The resolution of identity (RI)³⁴ and the multipole accelerated resolution of identity (marij)³⁵ approximations have been used to efficiently treat the electronic Coulomb term in the DFT calculations. Open-shell calculations have been considered for the active site transition state optimizations. For the calculations that we have performed, the energy convergence criteria was 10^{-7} H, and the norm for the Cartesian gradients was 10^{-3} . The second-order derivatives of the potential energy were obtained numerically. For better relative energies, we have performed single point calculations for all the geometries obtained from optimization at the M06-L/TZVP (RI and marij approximations employed) level of theory.^{32,36,37} Furthermore, we have employed the m4 grid size for both optimization and single point calculations, in order to achieve better accuracy.

We have employed a 22 MgCl₂ cluster has been employed for the transition state calculation. The values reported are ΔG values, with zero-point energy, internal energy, and entropic contributions (including translational, rotational, and vibrational entropy contributions) included through frequency calculations on the optimized minima and transition state structures, with the temperature taken to be 298.15 K. This was done to ensure that all the reported transition state structures contained only one imaginary frequency corresponding to the correct normal mode. IRC calculations have been considered for the confirmation of the transition states. In every case, the IRC calculations have yielded the correct reactant and product structures.

5.3. Results and Discussion

We have considered four alkoxysilanes (see Figure 5.1): (1) diisopropyl dimethoxysilane (DIPDMS), (2) dicyclopentyl dimethoxysilane (DCPDMS), (3) disec-butyl dimethoxysilane (DSBDMS), and (4) *sec*-butyl(methyl) dimethoxysilane (SBMDMS), in order to study the effect of alkoxysilane-AlEt₂Cl on the regioselectivity.

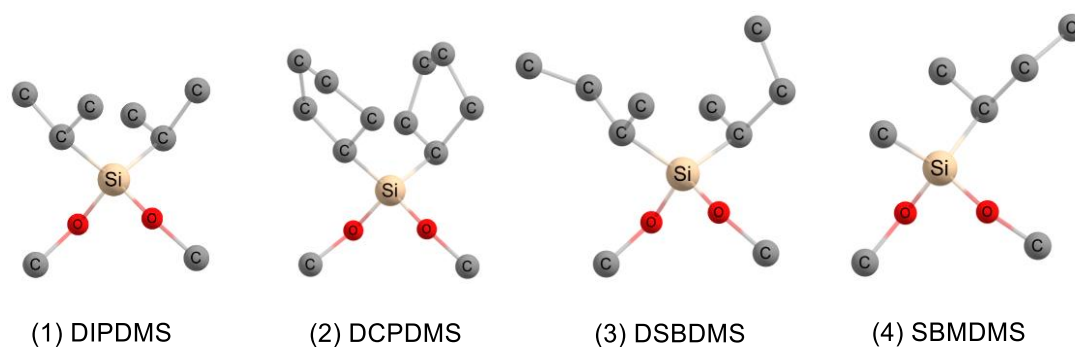


Figure 5.1. The structures of the four alkoxy-silane donors considered in this study. For the purpose of clarity, hydrogen atoms have been omitted. The same figure is also used in Chapter 4 as Figure 4.3.

The regioselectivity of Z-N catalysts is defined as the energy difference between the lowest transition states in 1,2- and 2,1-insertions. However, for 1,2- insertion, there are two possibilities: 1,2-*re* and 1,2-*si*. Similarly, 2,1-insertion also has two possible transition states: 2,1-*re* and 2,1-*si*. Hence to calculate the $\Delta\Delta G^{\ddagger}_{\text{Regio}}$, we need to compute these four barriers and find out the lowest barriers for 1,2- and 2,1- insertions (can be *re*- or *si* in both cases depending on the nature of the active site) and take the difference. It is important to note here that additional factors, such as the chirality of the active site and the orientation of the growing polymer chain, can also influence these barriers.

5.3.1. Regioselectivity of Bare Site and Active Site with Only Phthalate Donor in the Vicinity

First, we have considered a bare site to understand the regioselectivity of the active site without any donors/adducts coordinated in the vicinity (see Figure 5.2a). The insertion of propylene monomer (both 1,2- and 2,1-insertions) to the Ti-C (of the growing polymer chain) proceeds *via* the Cossee-Arlman mechanism. The first step is the formation of the π complex, followed by a four-membered transition state. Eight possibilities exist for π complex formation between the active titanium site and propylene monomer (see Figure 5.3). These possibilities are due to the prochiral nature (*re*- or *si*-face coordination) of the propylene monomer and the relative orientation between the growing alkyl chain and the methyl group of the propylene monomer. Then, similarly, there are four possible transition states for both 1,2-insertion and 2,1-insertion (see Figure 5.4). For the sake of computational cost, we have kept the chirality

of the active site the same for all calculations and taken an ethyl group to mimic the growing polymer chain. Moreover, to calculate the barriers, we have taken the most stable π complex and transition state among all the possibilities in each case.

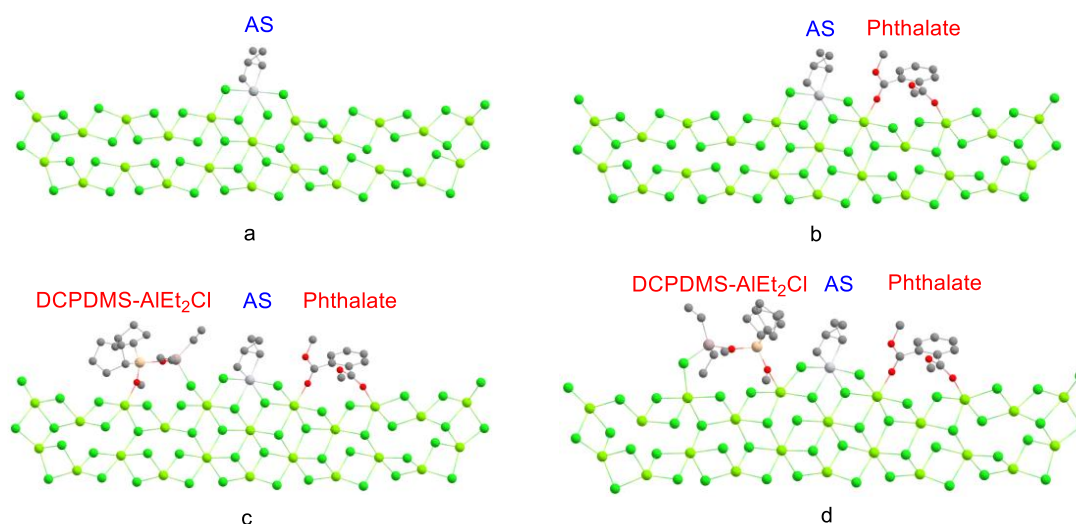


Figure 5.2. Side view of four different cases considered for the study: (a) bare active site (AS), (b) only one phthalate donor coordinated in the vicinity of the active site, (c) phthalate donor and DCPDMS-AlEt₂Cl adduct are coordinated in the vicinity, where the ethyl groups are oriented towards the active site, and (d) phthalate donor and DCPDMS-AlEt₂Cl adduct are coordinated on the vicinity, where the cyclopentyl groups are oriented towards the active site. Hydrogen atoms have been omitted for clarity, and in all four cases, we have shown *re*-propylene with (-) growing chain on the active site. The same figure is also used in Chapter 4 as Figure 4.9.

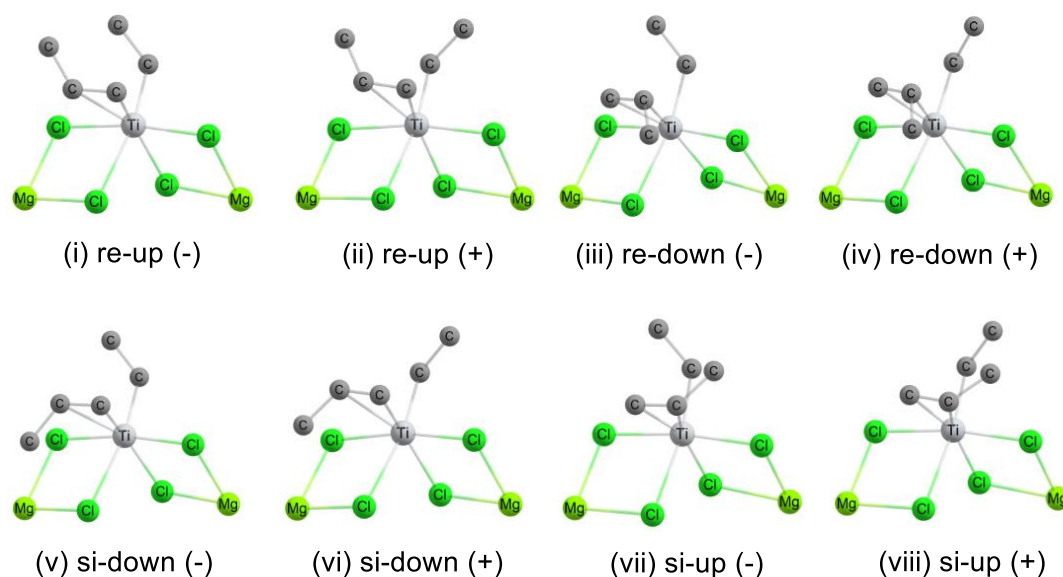


Figure 5.3. Representation of the eight possibilities for the formation of π complexes. For clarity, hydrogen atoms have been omitted. The same figure is also used in Chapter 4 as Figure 4.7, but with different denotations.

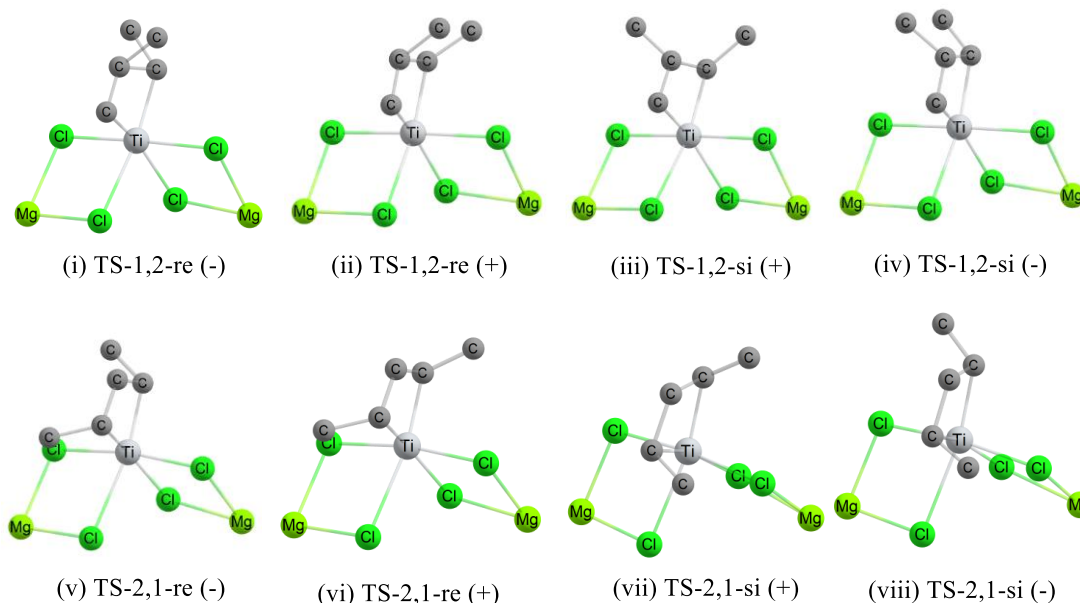


Figure 5.4. Representations of the four possible transition states for 1,2-insertion and 2,1-insertion. For clarity, hydrogen atoms have been omitted. The upper part of this figure is also used in Chapter 4 as Figure 4.8.

The barriers for the bare active site for 1,2-*re* and 1,2-*si* insertions are 13.3 kcal/mol and 12.8 kcal/mol, respectively. Likewise, the barriers for 2,1-*re* and 2,1-*si* insertions are 15.2 kcal/mol and 15.1 kcal/mol, respectively (see Table 5.1). Hence the $\Delta\Delta G_{\text{regio}}^{\ddagger}$ of the bare active site is 2.3 kcal/mol, which means that the bare active site is significantly regioselective even without any coordinated donors/adducts in the vicinity. It is intriguing to note here that for 1,2-insertions, the orientation of the growing polymer chain plays a vital role in deciding the stable transition states. For 1,2-*re* insertion, TS-1,2-*re* (-) (see Figure 5.4), and for 1,2-*si* insertion, TS-1,2-*si* (+) are stable transition states compared to the other possibilities. The stabilization is around 2.7 kcal/mol for both transition states, and this is due to the reduced sterics in these two transition states between the growing polymer chain and methyl group of the propylene monomer.

However, such an effect of the growing polymer chain in deciding the stable transition state geometry is not observed in the 2,1-insertions. The computed free

energy values suggest that the free energy difference between TS-2,1-*re* (-) and TS-2,1-*re* (+) and that between TS-2,1-*si* (+) and TS-2,1-*si* (-) is negligible (less than 0.5 kcal/mol). This is understandable from the geometries of corresponding transition states, which show that the growing polymer chain and the methyl group of the propylene monomer are far from each other. Hence, there is no preference for one transition state possibility over another in 2,1-*re* and 2,1-*si*. Thus, for the remaining calculations, we have only considered TS-1,2-*re* (-) and TS-1,2-*si* (+) for 1,2-insertions and TS-2,1-*re* (+) and TS-2,1-*si* (+) for 2,1-insertions. Moreover, we have taken the stable π complex in each case, as described in Chapter 4, to calculate the barriers in each case.

Next, we have considered an active site where only a phthalate donor was coordinated in the vicinity (see Figure 5.2b). The barriers for the 1,2-*re* and 1,2-*si* insertions are 13.3 kcal/mol and 14.1 kcal/mol, while the barriers for the 2,1-*re* and 2,1-*si* insertions are 14.1 kcal/mol and 17.2 kcal/mol. This implies that such an active site is poorly regioselective with a $\Delta\Delta G^\ddagger_{\text{Regio}}$ value of only 0.8 kcal/mol.

Table 5.1. The *re*- and *si*- barriers for the 1,2- and 2,1-insertions and the $\Delta\Delta G^\ddagger_{\text{Regio}}$ for the four-selected alkoxy silane-AlEt₂Cl adducts. The values are in kcal/mol, and the lowest values for 1,2- and 2,1-insertions are given in bold.

	$\Delta G^\ddagger_{1,2-re}$	$\Delta G^\ddagger_{1,2-si}$	$\Delta G^\ddagger_{2,1-re}$	$\Delta G^\ddagger_{2,1-si}$	$\Delta\Delta G^\ddagger_{\text{Regio}}$
Bare active site	13.3	12.8	15.2	15.1	2.3
Only phthalate	13.3	14.1	14.1	17.2	0.8
Adduct and phthalate (Et groups towards AS)					
DIPDMS	13.6	15.8	19.8	15.4	1.8
DCPDMS	14.0	16.2	20.1	16.5	2.5
DSBDMS	12.6	15.5	19.4	15.2	2.6

SBDMS	13.2	16.2	19.0	15.8	2.6
Adduct and phthalate (R groups towards AS)					
DIPDMS	14.5	16.7	21.3	15.7	1.2
DCPDMS	14.3	17.3	22.4	16.0	1.7
DSBDMS	13.6	16.4	22.2	15.0	1.4
SBDMS	13.7	15.3	21.9	16.1	2.4

5.3.2. Effect of Lewis Acid-base Adducts in the Regioselectivity of Propylene Polymerization

The intriguing question here is whether coordinating an adduct on the other side of the active site would increase the regioselectivity. As discussed in Chapter 4, the coordination of an alkoxysilane- AlEt_2Cl adduct can give rise to two possibilities: (i) the ethyl groups of the alkoxysilane- AlEt_2Cl adduct can orient toward the active site (see Figure 5.2c) and (ii) the R groups of the alkoxysilane- AlEt_2Cl adduct can orient toward the active site (see Figure 5.2d). The origin of these two possibilities is due to the unsymmetrical nature of the adduct that has two potential donor atoms (O and Cl). Among these two possibilities, first, we have considered the case where the ethyl groups are oriented toward the active site and calculated the $\Delta\Delta G^\ddagger_{\text{Regio}}$ for all four alkoxysilane- AlEt_2Cl adducts cases, as we had done for the bare site and only phthalate cases (see Table 5.1).

The $\Delta\Delta G^\ddagger_{\text{Regio}}$ values for the DIPDMS-, DCPDMS-, DSBDMS-, and SBDMS- AlEt_2Cl adducts are 1.8 kcal/mol, 2.5 kcal/mol, 2.6 kcal/mol and 2.6 kcal/mol, respectively. This implies that the regioselectivity remains similar to the bare active site, which is good in that such active sites improve the stereoselectivity (as discussed in Chapter 4) without compromising the regioselectivity of the reaction. Interestingly, our calculations also suggest that 2,1-insertion is more stereoselective than 1,2-

insertion. Even though the *si*- barriers for both 1,2- and 2,1-insertions remains similar, the higher *re*- barriers for 2,1-insertion compared to that of 1,2-insertion is the reason for the higher stereoselectivity in 2,1-insertion. The high *re*-barriers of 2,1-insertion result from the higher sterics between the methyl group of the propylene monomer and the coordinated adduct.

Next, we have considered the second possibility, where the R groups are oriented toward the active site. The $\Delta\Delta G^{\ddagger}_{\text{Regio}}$ values for the DIPDMS-, DCPDMS-, DSBDMS-, and SBDMS-AlEt₂Cl adducts are 1.2 kcal/mol, 1.7 kcal/mol, 1.4 kcal/mol, and 2.4 kcal/mol, respectively. The results indicate the R group orientation toward the active site can lead to slight decrease in the regioselectivity of the reaction, except for the SBMDMS-AlEt₂Cl case. However, the regioselectivity appears to be reasonable, considering that such active sites are highly stereoselective. Furthermore, the 2,1-*re* insertion barriers are significantly higher than the corresponding barriers for 1,2-*re* insertion, which is due to the reduced interaction of the oxygen donor atom of the adduct and the magnesium of the surface. Such a slight detachment of the adduct is due to the greater sterics between the R groups of alkoxy silanes and the methyl group of the propylene monomer. Moreover, the 2,1-insertions in such active sites are more stereoselective compared to the other cases we have considered.

5.4. Conclusions

Density functional theory (DFT) calculations have been employed to understand the role of Lewis acid-base adducts on the regioselectivity of Z-N catalysis. We have selected four alkoxy silane donors; DIPDMS, DCPDMS, DSBDMS, and SBMDMS. DFT calculations reveal that the bare active site (without any donors/adducts in the vicinity) is regioselective. The active sites with adducts on one side and phthalate on the other have two possibilities in terms of sterics: a less steric active site where the ethyl groups are oriented toward the active site and a more steric active site where the R groups are oriented toward the active site. The regioselectivity of the active site remains the same if ethyl groups are oriented towards the active site, but the regioselectivity is slightly reduced in the case of the R group orientation toward the active site. However, the overall results suggest that such active sites are suitable for enhancing the stereoselectivity without compromising the regioselectivity of the

reaction. Furthermore, the calculations also suggest that 2,1-insertions are more stereoselective than 1,2-insertions.

5.5. References

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Chapter 6

Directional Migration of Internal Donors in Ziegler-Natta Catalysis: Insights from Theory

Chapter 6

Directional Migration of Internal Donors in Ziegler-Natta Catalysis: Insights from Theory

Abstract: Directionality is a fascinating property, and it is challenging to achieve it at a molecular level. Recent years witnessed remarkable development in the directional motion of molecules, which was inspired by following nature's example. However, the directional migration of molecules in chemical systems, known to us for decades, is less investigated. In this DFT study, we have chosen three internal donors (ID) that are well-known in the Ziegler-Natta (Z-N) catalytic systems: dimethyl succinate (**ID-1**), dimethyl phthalate (**ID-2**), and 1,3-dimethoxy-2,2-dimethylpropane (**ID-3**). Among the three IDs, **ID-1** and **ID-2** exhibit a thermodynamic preference to migrate toward TiCl_4 . The migrational preference was observed in two cases: (1) **ID-1** and **ID-2** coordinated at one step away from the TiCl_4 and (2) at three steps away from the TiCl_4 . However, the three steps migration is favorable only in the presence of a second ID. Finally, the obtained barriers to the migration of **ID-1** suggest that those barriers are very much accessible at the reaction conditions. Hence, we have shown that directional migration of IDs takes place, which helps explain why donors and the catalyst are found in close proximity on the MgCl_2 surface in Z-N systems.

6.1. Introduction

Biological molecular machines such as kinesin, myosin, and dynein inspired the scientific community to synthesize artificial molecular motors that can move along a particular direction and perform functional tasks.^{1,2} The outstanding contribution of Sauvage, Stoddart, and Feringa in molecular interlocks, molecular shuttles, and molecular motors resulted in the commencement of active research in artificial molecular motors. For their remarkable contributions, they received the Nobel Prize in chemistry for the year 2016.³ The most relevant aspect of molecular motors is their directionality, because a machine without directionality is ineffective. Hence, achieving unidirectionality at a molecular level is one of the holy grails in chemistry. In recent years, the group of David Leigh has reported several examples of the directional motion of molecules at the molecular level.⁴⁻¹¹

One can wonder whether such directional processes are already happening in well-known chemical systems. Recently, aryl migration on graphene has been demonstrated experimentally,¹² and subsequent density functional theory (DFT) based studies showed the curvature dependence of the graphene layer on the aryl group migration.¹³ Cavallo and co-workers have shown that migration of donors such as alkoxysilanes, phthalates, and 1,3-diethers on the MgCl_2 facets is possible.^{14,15} However, these areas have yet to explore the possibility of directionality in such processes.

Modern-day Z-N catalytic systems consist of four main components: (a) TiCl_4 as pre-catalyst, (b) MgCl_2 as support, (c) AlR_3 as co-catalyst, where R represents alkyl groups, and (d) donors.^{16,17} Donors are Lewis bases. Donors are classified into two categories, based on when they are introduced into the system. Internal donors (ID) are those that are added during the catalyst preparation,¹⁸⁻³⁴ and external donors (ED) are those added to the system along with the alkyl aluminum species.³⁵⁻⁴⁰ Examples of IDs are succinates, phthalates, 1,3-diethers and ethyl benzoate. Furthermore, alkoxysilane donors are widely used as EDs in the Z-N catalytic systems. Using a proper ID: ED pair can significantly change the properties of the polymer.¹⁷

Donors can enhance the stereoselectivity of the polymerization reaction, which will produce isotactic polymers.^{29,30,41-47} They can also increase the rate of the transalkylation step,⁴⁸ influence the molecular weight of the polymer,⁴⁹ and help to

utilize the dominant (104) MgCl_2 facet for the polymerization reactions.⁵⁰ It is important to note here that in order to influence these properties, donors need to coordinate in the vicinity of the active site. This immediately raises the question: *how do the donors find the active site on the MgCl_2 facet? Since donors can migrate on the MgCl_2 facet, do they have a migrational preference toward the active site?*

This work explores the possibility of the directional migration of three well-known IDs in the Z-N catalytic systems. We have performed full quantum chemical calculations with DFT to shed light on the thermodynamic preference of IDs for the migration toward TiCl_4 . Furthermore, we have also calculated the migration barriers for one ID case. The results obtained demonstrate that donors indeed do display a short range directional preference in Z-N systems, which provides insights into how catalysts and donors find each other on the MgCl_2 surface during Z-N catalysis.

6.2. Computational Details

The Turbomole 7.5 suite of programs⁵¹ has been employed to optimize all the structures, including intermediates and transition states, using density functional theory (DFT). Geometry optimizations have been performed using the TPSS functional⁵² and the def2-SVP basis set.⁵³ The dispersion correction (DFT-D3),⁵⁴ developed by Grimme *et al.*, has been employed to increase the accuracy of the calculations. The resolution of identity (RI)⁵⁵ and the multipole accelerated resolution of identity (marij)⁵⁶ approximations have been used to treat the electronic Coulomb term in the DFT calculations efficiently. For the calculations we performed, the energy convergence criteria was 10^{-7} H, and the norm for the Cartesian gradients was 10^{-3} . The second-order derivatives of the potential energy were obtained numerically. Furthermore, we have employed the m5 grid size for both optimization calculations to achieve better accuracy. We note here that no solvent corrections have been included in the calculations. This is because Ziegler-Natta (Z-N) catalysis is a heterogenous process, and a predominant portion of the global polypropylene production is carried out either in the bulk phase or in gas phase polymerizations, where there are no solvents. This, indeed, is the norm for computational studies on Z-N catalysis, as evidenced by the many recently published computational studies in various journals, which investigate various aspects of Z-N catalysis through gas phase calculations.^{14-16,30,42,44,46-48}

We have employed a 39MgCl_2 cluster model for the calculations (see Figure 6.1). The values reported are ΔG values, with zero-point energy, internal energy, and entropic contributions (including translational, rotational, and vibrational entropy contributions) included through frequency calculations on the optimized minima and transition state structures, with the temperature taken to be 298.15 K. This was done to ensure that all the reported transition state structures contained only one imaginary frequency corresponding to the correct normal mode. IRC calculations have been considered for the confirmation of the transition states. In every case, the IRC calculations yielded the correct reactant and product structures.

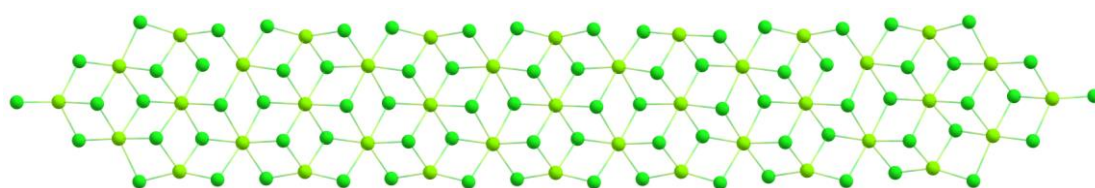


Figure 6.1. The 39 MgCl_2 cluster model used for this study.

6.3. Results and Discussion

6.3.1. Thermodynamics of Migration

An ID coordinated to the (110) MgCl_2 facet can migrate to another position in any direction (in principle). However, if a TiCl_4 is also present on the (110) MgCl_2 facet, does the donor prefer to move towards the TiCl_4 or away from the TiCl_4 ? In order to answer this intriguing question, we have selected three well-known internal donors in Z-N catalysts (see Figure 6.2): (1) dimethyl succinate (**ID-1**), (2) dimethyl phthalate (**ID-2**), and (3) 1,3-dimethoxy-2,2-dimethylpropane (**ID-3**). First, we have calculated the ΔG values for the migration of an ID to either right or left (see Case 1 in Figure 6.3) on the bare (110) MgCl_2 facet. The calculated ΔG values for the three internal donors (**ID-1**, **ID-2**, and **ID-3**) suggest no specific preference for migration in any direction (see Table 6.1). In other words, if only an ID is coordinated to the (110) MgCl_2 facet, then it would be expected move randomly on the surface, without displaying any directionality.

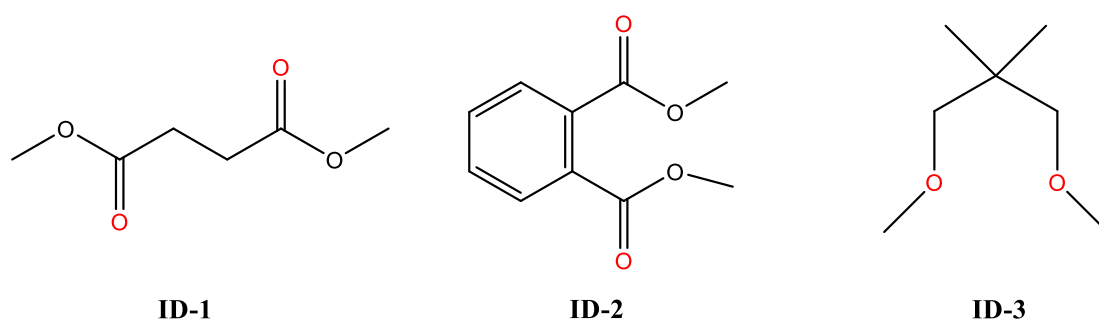


Figure 6.2. The three internal donors considered for this study.

Furthermore, in order to understand whether there is any directionality in the migration of an ID in the presence of TiCl_4 , we have considered the second case (Case 2). Case 2 is where an ID coordinated one step away from TiCl_4 on the (110) MgCl_2 (see Case 2 in Figure 6.3). Unlike in case 1, now an ID can have a bias in the migration: either it can move towards TiCl_4 or away from TiCl_4 . The calculated values suggest that among the three IDs, **ID-1** and **ID-2** prefer to migrate toward TiCl_4 . The movement of **ID-1** toward TiCl_4 is favorable by 4.6 kcal/mol, while movement away from the TiCl_4 is favorable by only 0.1 kcal/mol (see Table 6.1). Similarly, **ID-2** shows a preference for the migration towards TiCl_4 by 3.9 kcal/mol, while the migration in the opposite direction is unfavorable by 0.5 kcal/mol. On the contrary, the third internal donor, **ID-3**, does not show similar directionality in the presence of TiCl_4 . The migration of **ID-3** toward the TiCl_4 is unfavorable by 0.8 kcal/mol, and the migration in the opposite direction is also unfavorable by 0.1 kcal/mol.

Under experimental conditions, multiple donors are likely coordinated to the (110) MgCl_2 facet. What would be the effect of a second ID on the directionality of an ID migration toward the TiCl_4 ? In order to understand this, we have considered Case 3, where two IDs and a TiCl_4 molecule are coordinated on the (110) MgCl_2 facet (see Case 3 in Figure 6.3). The TiCl_4 and second ID are one step away from the middle ID (both the middle ID and second ID are the same species). Now, the middle ID has two choices: either it can move toward TiCl_4 or it can move toward the second ID. Interestingly, our calculations suggest that the directionality in the migration of **ID-1** and **ID-2** toward TiCl_4 significantly improved in the presence of a second donor. In the case of **ID-1**, the migration towards the TiCl_4 is favorable by 5.0 kcal/mol, while migration towards the second ID is unfavorable by 2.6 kcal/mol. Similarly, in the case of **ID-2**, migration towards TiCl_4 is favorable by 5.0 kcal/mol, while migration towards

the second donor is unfavorable by 3.4 kcal/mol. Finally, **ID-3** does not show a similar trend in migration. **ID-3** shows a higher unfavorability compared to **ID-1** and **ID-2** for migrating toward the second donor (6.8 kcal/mol). At the same time, **ID-3** prefers to migrate toward the TiCl_4 by only 0.5 kcal/mol, which is a significantly lower preference in comparison to **ID-1** and **ID-2**.

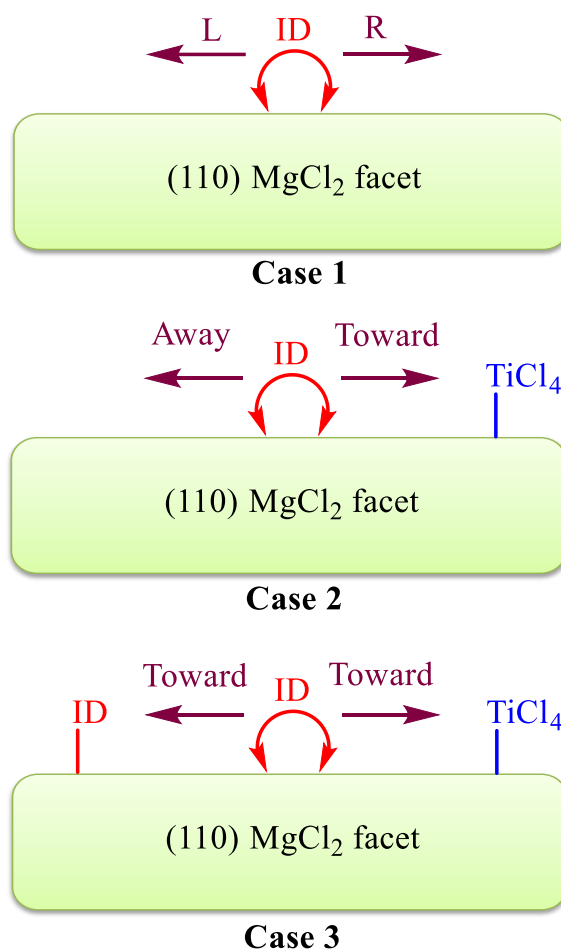


Figure 6.3. The three cases (Cases 1, 2, and 3) considered for studying the one step directional migration of an ID.

Table 6.1. The free energy (ΔG in kcal/mol) values for the migration of IDs in Cases 1, 2, and 3.

Internal Donor (ID)	Free energy change for migration (ΔG , in kcal/mol)	
	Case 1	
	Toward left	Toward right
ID-1	0.0	-0.5
ID-2	-0.1	0.1

ID-3	0.2	-0.5
	Case 2	
	Away from TiCl₄	Toward TiCl₄
ID-1	-0.1	-4.6
ID-2	0.5	-3.9
ID-3	0.1	0.8
	Case 3	
	Toward second ID	Toward TiCl₄
ID-1	2.6	-5.0
ID-2	3.4	-5.0
ID-3	6.8	-0.5

Nevertheless, till now, we have considered only a single-step migration of the IDs; either towards TiCl₄ or away from it. If an ID were to be coordinated three steps away from the TiCl₄, would it show the same migrational preference towards TiCl₄? Please note that we have restricted our study to only three steps because of the high computational cost of dealing with bigger MgCl₂ cluster models. Like in the one-step migration study, we have considered three cases (see Figure 6.4). In case 4, an ID is coordinated on one end of the (110) MgCl₂ facet, and then it can migrate from one end to another by taking three steps. Three IDs (**ID-1**, **ID-2**, and **ID-3**) do not show any thermodynamic gradient for such a migration from one end of the (110) MgCl₂ facet to another (see Table 6.2). Then, we considered Case 5, where TiCl₄ is coordinated on one end of the (110) MgCl₂ facet, so that an ID can migrate toward the TiCl₄ by taking three steps (see Figure 6.4). Similar to Case 4, there is no clear thermodynamic preference for the migration of three IDs toward the TiCl₄. In the case of **ID-1**, migration from positions 1 to 2 (Step 1) and 2 to 3 (Step 2) do not show any thermodynamic favorability (see Table 6.2). However, the migration from Position 3 to 4 (Step 3) is favorable by 3.4 kcal/mol (see Table 6.2). Similarly, in the case of **ID-2**, migration from Positions 1 to 2 (Step 1) and 2 to 3 (Step 2) do not indicate any favourability. On the other hand, migration from Position 3 to 4 is favorable by 3.8 kcal/mol. Coming to the case of **ID-3**, again, migration of **ID-3** from Positions 1 to 2 (Step 1) and 2 to 3 (Step 2) do not show any preference. Interestingly, unlike **ID-1** and **ID-2**, **ID-3** shows unfavorability in the migration of Position 3 to 4 by 1.3 kcal/mol.

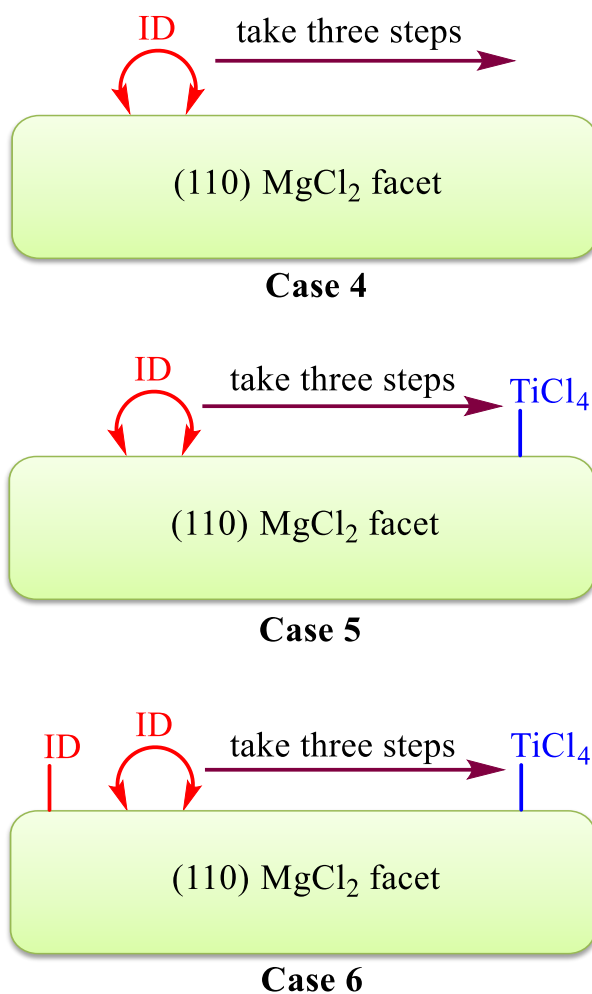


Figure 6.4. The three cases (Cases 4, 5, and 6) considered for studying the three steps directional migration of an ID.

Table 6.2. The relative free energy (ΔG in kcal/mol) values for the positions 2, 3, and 4 with respect to the Position 1 for the cases 4, 5, and 6.

Internal Donor (ID)	Free energy change for migration (ΔG , in kcal/mol)			
	Case 1			
	Position 1	Position 2	Position 3	Position 4
ID-1	0.0	0.2	0.6	0.3
ID-2	0.0	-0.6	-0.4	0.3
ID-3	0.0	0.0	0.3	0.1
	Case 2			
	Position 1	Position 2	Position 3	Position 4
ID-1	0.0	-0.3	0.0	-3.4

ID-2	0.0	-0.4	-0.1	-3.9
ID-3	0.0	0.4	0.1	1.3
	Case 3			
	Position 1	Position 2	Position 3	Position 4
ID-1	0.0	-4.2	-4.7	-8.8
ID-2	0.0	-5.1	-6.4	-10.8
ID-3	0.0	-8.8	-10.0	-9.1

The results suggest no directionality in the migration if the ID is coordinated even at three steps away from the TiCl_4 . However, what would be the effect of a second ID in such a scenario? To understand this, we have considered Case 6 (see Figure 6.4), where the ID starts migrating from a second ID toward the TiCl_4 . Interestingly, **ID-1** and **ID-2** show a thermodynamic gradient for the migration toward the TiCl_4 . In the case of **ID-1**, migration from Positions 1 to 2 (Step 1) is favorable by 4.2 kcal/mol, 2 to 3 (Step 2) is favorable by 0.5 kcal/mol, and 3 to 4 (step 3) is favorable by 4.1 kcal/mol. Similarly, in the case of **ID-2**, the migrations from Positions 1 to 2, 2 to 3, and 3 to 4 are favorable by 5.1 kcal/mol, 1.3 kcal/mol, and 4.4 kcal/mol, respectively. Finally, the third ID, **ID-3**, again shows a difference in migration preference even in the presence of a second donor. Even though **ID-3** prefers to move away from the second ID, it does not prefer to coordinate next to the TiCl_4 . Migration from Positions 1 to 2 and 2 to 3 are favorable by 8.8 kcal/mol and 2.2 kcal/mol, respectively. However, in the third step, migration from Position 3 to 4 is unfavorable by 0.9 kcal/mol.

Hence, in a nutshell, **ID-1** and **ID-2** prefer to migrate toward TiCl_4 if it is coordinated one step away from the TiCl_4 , and the presence of a second ID increases the favourability to migrate toward the TiCl_4 . Furthermore, **ID-1** and **ID-2** also show a migrational preference, even if they coordinated three steps away from the TiCl_4 in the presence of a second donor. However, **ID-3** does not such a migrational preference, even in the presence of a second ID. It is important to note here that **ID-1** and **ID-2** are known for their ability to increase the stereoselectivity of the polymerization reaction, but **ID-3** is considered less stereoselective. The current work therefore suggests one possible reason for this: **ID-3** displays less preference for migrating towards TiCl_4 , a fact that would result in fewer stereoselective active sites. Contrary to this, **ID-**

1 and **ID-2** can migrate towards the catalyst and convert those sites into stereoselective active sites.

While the results from the thermodynamics studies are insightful, it has to be noted that to migrate from one position to another, an ID must overcome multiple barriers, which should be accessible under the reaction conditions. We will discuss the kinetics of donor migration in the next section.

6.3.2. The Kinetics of Migration

In the previous section, we have seen that the donors have a migrational preference towards TiCl_4 in the presence of another donor. However, the values are just an indication of the thermodynamics of the process. In order to move from one position to another, it must cross multiple barriers. We have selected **ID-1** to calculate the barriers for the single-step migration on a bare (110) MgCl_2 facet. The first step is the breakage of the O-Mg bond and the formation of a bond between the same O with a nearby Mg (see **TS1_L** and **TS1_R** in Figure 6.5), which leads to the formation of chelate coordination of the ID (**Int1_L** and **Int1_R**) to the (110) MgCl_2 facet. Then, the **ID-1** passes through a second transition state, where again the O-Mg bond breaks, and the same O forms a bond with the nearby Mg (see **TS2_L** and **TS2_R** in Figure 6.5), which leads to the bridge coordination of the ID. Hence, one step in the migration is completed. The same chemistry can take place in both the left and right directions (see Figure 6.5).

We have considered the same three cases for calculating thermodynamics for single-step migration (see Figure 6.3) to calculate the barriers for ID migration: (a) only **ID-1** coordinated on the (110) MgCl_2 facet, (b) Both **ID-1** and TiCl_4 coordinated at a one-step distance from each other, and (c) two **ID-1** donors and TiCl_4 coordinated, where each species is at one step-distance from the nearby coordinated species. In the first case, **ID-1** must surmount barriers of 21.5 kcal/mol (**TS1_L**) and 19.6 kcal/mol (**TS2_L**) to migrate toward the left. In comparison, the migrational barriers toward the right are 23.1 kcal/mol (**TS1_R**) and 19.0 kcal/mol (**TS2_R**). In the second case, where **ID-1** has two choices, it can move either towards or away from TiCl_4 . The barriers for migration towards TiCl_4 are 22.7 kcal/mol and 17.4 kcal/mol, while the barriers to the migration away from TiCl_4 are 21.4 kcal/mol and 19.1 kcal/mol. The values suggest no clear preference for migration toward the TiCl_4 . However, all the obtained barriers are

accessible at the reaction conditions. Furthermore, in Case 3, where the **ID-1** can migrate either toward a second ID or toward the TiCl_4 , the calculated barriers are 20.9 kcal/mol and 15.4 kcal/mol for migration towards TiCl_4 . The corresponding migration barriers of **ID-1** toward a second ID are 21.1 kcal/mol and 14.2 kcal/mol.

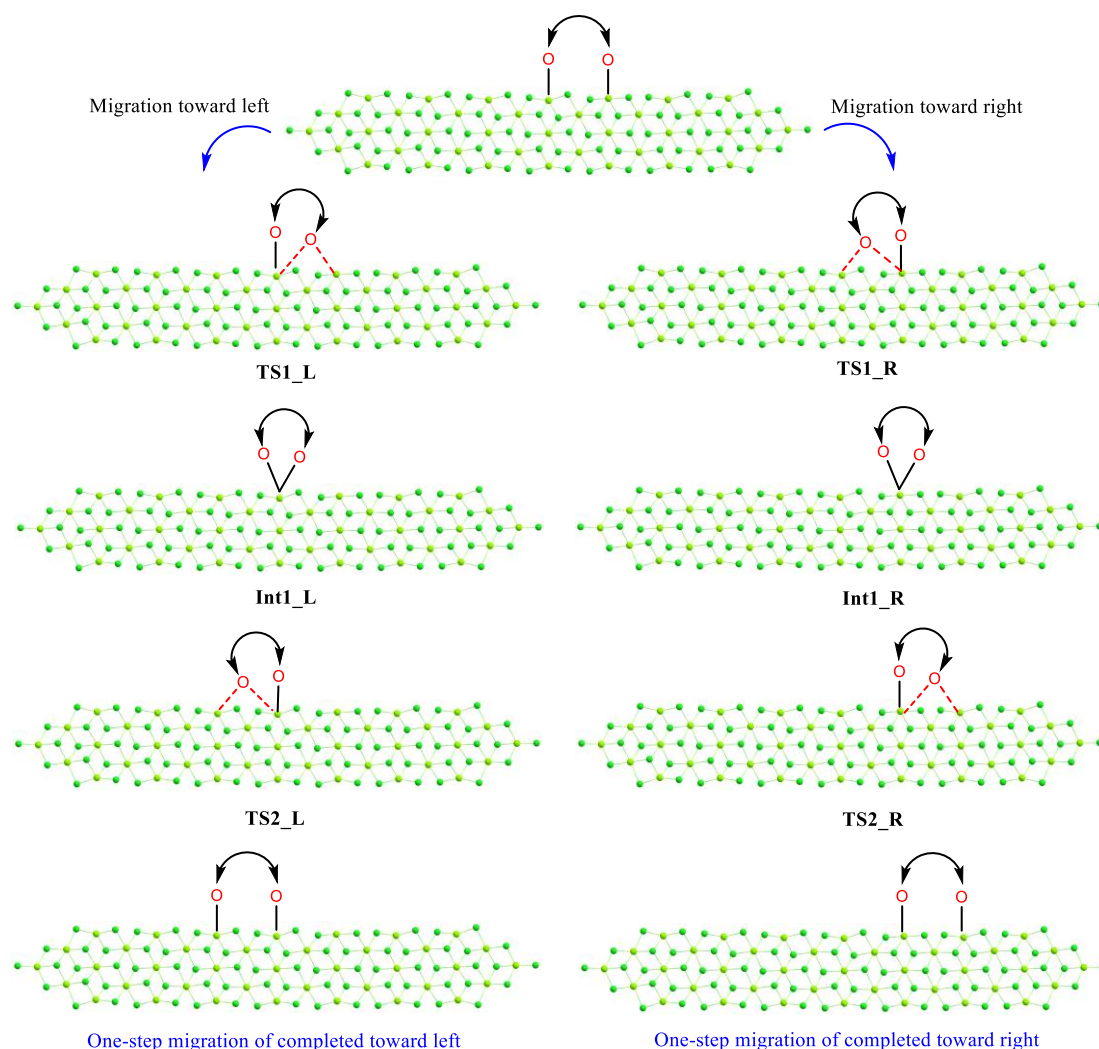


Figure 6.5. Schematic representation of an ID migration (via two transition states and one intermediate) towards left or right on the bare (110) MgCl_2 facet.

Therefore, the results suggest that even though the migration barriers do not show a clear directionality towards or away from the TiCl_4 , the obtained barriers suggest that the migration of **ID-1** on bare (110) MgCl_2 facet and the migration even in the presence of another coordinated species (both in the presence of TiCl_4 and the second ID) would be favorable under the reaction conditions.

6.4. Conclusions

Achieving directionality at the molecular level is one of the most exciting areas in chemistry today. Even though there are many known examples of molecular movements in a particular direction, the directional migration of molecules in catalytic systems, known for decades, is less explored. We have selected three well-known internal donors (IDs) in the Z-N catalytic systems in this study: dimethyl succinate (**ID-1**), dimethyl phthalate (**ID-2**), and 1,3-dimethoxy-2,2-dimethylpropane (**ID-3**). DFT calculations suggest that **ID-1** and **ID-2** prefer to migrate toward the TiCl_4 . However, this migration preference is only when they are coordinated at a one-step distance from the TiCl_4 . Intriguingly, this one-step migration preference increases in the presence of a second ID. On the contrary, **ID-3** does not show a similar trend in migration.

Furthermore, we have also explored the three steps migration of an ID towards TiCl_4 . There is no thermodynamic gradient toward TiCl_4 observed for the three ID cases considered, but there is a clear migrational preference toward the TiCl_4 for **ID-1** and **ID-2** in the presence of a second ID, which is closer to the experimental observations vis-à-vis the stereochemical influence of the three donors. Finally, we have calculated the barriers to the migration of **ID-1** in various cases. Our calculated values suggest that barriers are easily accessible at the Z-N reaction conditions. So, in a nutshell, we have shown that short range directional migration already exists in Z-N catalytic systems.

6.5. References

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Chapter 7

Conclusions and Future Outlook

Chapter 7

Conclusions and Future Outlook

7.1. Focus of this Thesis

Undoubtedly, Ziegler-Natta (Z-N) catalysis is one of the most important heterogeneous catalytic processes. Z-N catalysts were discovered in the 1950s, and since then, several significant improvements have been made, which enhanced the activity and selectivity of the polymerization reaction. Z-N catalysts consist of four components: MgCl_2 (support), TiCl_4 (pre-catalyst), alkyl aluminum species (co-catalyst), and donors. Donors are Lewis basic species, which can donate electrons to the system. Donors are classified into internal donors (ID) if they are added to the system during catalyst preparation, and external donors (ED) if they are added along with the co-catalyst. A suitable pair of ID and ED can significantly improve the performance of the catalyst. However, the understanding of Z-N catalysts at the molecular level is still not entirely clear. This lack of understanding arises due to the multi-component and multi-site nature of the heterogeneous system. This thesis focuses on the various unexplored roles of donors and how the interaction of the donors influences the properties of the Z-N reaction. The main conclusions from the DFT studies are summarized below.

(I) Reactor fouling is an undesirable phenomenon that can happen inside the reactor due to an uncontrollable rise in the temperature. Recent patents have put forward a solution to this problem. The use of self-extinguishing external donors can suppress the reaction and control the temperature inside the reactor. DFT studies on two external donors, **D1** (2,2,2-trifluoroethyl myristate) and **D2** (2,2,2-trifluoroethyl palmitate) reveal that the reason for the self-extinguishing property is their ability to undergo decomposition reactions with Lewis acidic species such as aluminum and titanium in the Z-N system. Such decomposition reactions lead to the formation of an aldehyde and a ketone, considered poisons for the Z-N system. Furthermore, both donors prefer to coordinate with titanium than aluminum and prefer the ketone pathway over the aldehyde pathway. Interestingly, the alkyl chain length of the external donor plays a vital role in the coordinating ability. An external donor with a higher alkyl chain length

has higher binding energy for coordinating with the active titanium site on the MgCl_2 surface. This is due to the favorable non-covalent interaction of the alkyl chain with the MgCl_2 surface.

(II) Stereoselectivity is an appealing property of heterogeneous Z-N catalysts, leading to the production of isotactic polypropylene. A pair of donors (internal and external) has been used to enhance the stereoselectivity. The role of external donors is to occupy the vacant sites produced by the removal of internal donors by the alkyl aluminum species. However, there is a considerable bite difference between alkoxysilanes (EDs) and phthalates (IDs), which immediately raises the question of how alkoxysilanes coordinate to the same vacant sites previously occupied by phthalates. DFT studies provide an answer to this intriguing question. Alkoxysilanes can form stable Lewis acid-base adducts with AlEt_3 and AlEt_2Cl species. Furthermore, such adducts prefer to coordinate in the vicinity of the active site, while only alkoxysilane donors prefer to coordinate away from the active site. Then, the coordinated adducts in the vicinity influence the relative stabilities of *re*- and *si*-insertion transition states, enhancing the stereoselectivity. Hence, the Lewis acid-base adducts are the real players in enhancing the stereoselectivity of the Z-N catalysis, not the alkoxysilane donor.

(III) Z-N catalysis is also a regioselective reaction. Regioselectivity is less explored than stereoselectivity because experimental studies suggest that Z-N catalysts are highly stereoselective. We have further explored the role of adducts in the regioselectivity of the Z-N catalysts. DFT studies indicate that the bare site (without any adjacent donors/adducts) is highly regioselective, and the active sites with adduct on one side and phthalate on another also exhibit similar regioselectivity. In other words, the Lewis acid-base adducts improve the stereoselectivity of the reaction without compromising the regioselectivity.

(IV) Achieving directionality at the molecular level is one of the most challenging problems in chemistry. Even though many examples are known, the directional migration of molecules in the chemical system known to us for decades is less explored. We have selected three IDs known in the Z-N systems: dimethyl succinate (**ID-1**), dimethyl phthalate (**ID-2**), and 1,3-dimethoxy-2,2-dimethylpropane (**ID-3**). DFT studies suggest that **ID-1** and **ID-2** show a thermodynamic preference to migrate toward the TiCl_4 , and that such preference can be enhanced in the presence of a second ID in

the vicinity. Furthermore, the calculated barriers for **ID-1** indicate that all the barriers to migration are accessible at the reaction conditions. Hence, we have shown that directional migration of IDs takes place, which explains how the IDs and the catalyst find each other on a vast MgCl_2 surface.

7.2. Future Outlook

As explained in the introduction of this thesis, Z-N catalysis is a complex chemical system to study. Without proper understanding at the molecular level, it is not easy to improve the various aspects of the reaction. Our DFT studies on the self-extinguishing property, stereoselectivity, and regioselectivity shed light on vital factors that can further be exploited by experimental chemists to make better Z-N catalytic systems. Moreover, our results on donor migration on the (110) MgCl_2 facet show the need to revisit chemical systems known to us for decades to explore some fundamental research areas like directionality.

However, despite all these studies, Z-N catalysts remain elusive. Many aspects of these systems can be further explored. An important aspect of polymers is their molecular weight, which depends upon the relative energy difference between the propagation and termination transition states. What would be the effect of Lewis acid-base adducts on the molecular weight of the polymer? Furthermore, the stereoselectivity in Z-N catalysts is a complex phenomenon because it depends on many factors, such as the prochiral nature of the active site, the chirality of the active site, the orientation of the growing polymer chain and the presence of donors. What would be the effect of employing a chiral donor on the stereoselectivity of the reaction?

Moreover, one exciting area in chemical research is the catalysis of reactions in an external electric field. Some examples show that internal electric fields can also enhance the reaction rate. MgCl_2 is a vital component consisting of Mg^{2+} cations and Cl^- anions, which can produce an internal electric field in the system. What would be the effect of such an internal electric field on the activity and selectivity of the Z-N catalysts? Furthermore, a very pertinent question is why some combinations of internal and external donors work, and others do not. In general, experimentalists try trial-and-error methods to find suitable combinations. Can we use machine learning techniques to come up with the factors to decide the best pair of internal and external donors?

The list of challenging questions continues. However, one must see these challenging questions as opportunities for seeking answers through computational chemistry, which will not only help experimentalists working in the area of Z-N chemistry, but which will also allow the application of those insights to the vast area of heterogeneous catalysis.

ABSTRACT

Name of the Student: Vipin Raj K Faculty of Study: Chemical Science AcSIR academic centre/CSIR Lab: CSIR-NCL Title of the thesis: Computational Studies into Ziegler-Natta Catalysis	Registration No.: 10CC18A26017 Year of Submission: 2022 Name of the Supervisor: Dr. Kumar Vanka
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Ziegler-Natta (Z-N) catalysis is one of the most important heterogeneous catalysis processes that produces more than 150 million metric tons of polyolefins. Despite numerous experimental and computational studies in Z-N catalysis, the understanding at the atomic level is still inadequate. This is because of the multi-component and multi-site nature of the Z-N catalysts. Innumerable possibilities of interactions between the components make the Z-N catalysts challenging to study using any experimental or computational techniques alone. Generally, a combination of internal and external donors is used in Z-N catalysts to increase the performance of the catalyst in terms of activity and selectivity. It needs to be better understood why some specific combination of donors works perfectly while others do not. One of the active research areas in the Z-N catalysts is to understand the role of donors so that such insights would help to synthesize new donors that can improve the performance of the catalyst further.

In this regard, **Chapter 3** sheds light on the self-extinguishing nature of the new external donors patented by the research and development (R & D) wing of Reliance Industries Limited (RIL). Self-extinguishing is a property that reduces the polymerization reaction in case there is an uncontrollable temperature rise in the reactor, which helps to prevent reactor fouling. The DFT studies of the two donors, **D1** (2,2,2-trifluoroethyl myristate) and **D2** (2,2,2-trifluoroethyl palmitate), reveal that **D1** and **D2** undergo decomposition reactions with the aluminum and titanium species present in the system and lead to the production of aldehyde or ketone, which are considered as poisons for the system. Furthermore, **D1** and **D2** prefer to coordinate with titanium rather than aluminum, and the alkyl chain length plays a vital role in such coordination. An external donor with a higher alkyl chain coordinates more strongly with the titanium due to the additional non-covalent interaction between the alkyl chain and the MgCl_2 surface. Our calculations corroborate with the experimental observations. **Chapter 4** addresses how the alkoxysilane donors effectively act as suitable external donors for phthalates, despite the considerable difference in their bite distance. Our DFT study reveals that alkoxysilane donors can form stable adducts with alkyl aluminum species in the Z-N system and that such adducts prefer to coordinate in the vicinity of the active site. However, an alkoxysilane donor prefers to coordinate away from the active site. Moreover, such adducts can significantly enhance the stereoselectivity of propylene polymerization. In other words, it is not the alkoxysilane donors; it is the alkoxysilane- AlEt_2Cl adduct that is the key player in enhancing the stereoselectivity of the polymerization. **Chapter 5** further explores the effect of Lewis acid-base adducts on the regioselectivity of the reaction. DFT studies indicate that the adducts coordinating in the vicinity of the active site can enhance the stereoselectivity without compromising the regioselectivity. Furthermore, 2,1-insertion is seen to be more stereoselective than 1,2-insertion. **Chapter 6** illustrates that internal donors such as phthalates and succinates have a directional preference to migrate towards the TiCl_4 on the (110) MgCl_2 facet. Moreover, the presence of a second donor increases the directionality. Furthermore, our barrier calculations for the succinate donor reveal that all the barriers are accessible under the reaction conditions.

Details of the Publications Emanating from the Thesis Work

1) List of publication(s) in SCI Journal(s) (published & accepted) emanating from the thesis work, with complete bibliographic details.

(i) **K. Vipin Raj**, Jugal Kumawat, Sunil Dhamaniya, Murugan Subaramanian, Ekambaram Balaraman, Virendra Kumar Gupta, Kumar Vanka, and Robert H. Grubbs. Insights into the Nature of Self-Extinguishing External Donors for Ziegler-Natta Catalysis: A Combined Experimental and DFT Study. *ChemCatChem* **2021**, *13*, 674-681.

DOI: 10.1002/cctc.202001493

2) List of Papers with abstract presented (oral/poster) at national/international conferences/seminars with complete details.

(i) Presented a poster entitled “A New Class of Self-extinguishing External Donors for Ziegler-Natta Catalysis: A Combined Experimental and DFT Study” at the International Conference on Recent Trends in Catalysis, RTC 2020 during 26-29 February 2020 at NIT Calicut.

Abstract: Developing donors for Ziegler-Natta (Z-N) catalysis to control the polymerization reaction and produce polymers with desirable properties has always been challenging due to the multi-component nature of the catalytic systems. Here, we have developed a new synthetic protocol for making two external donors, **D1** (2,2,2-trifluoroethyl myristate) and **D2** (2,2,2-trifluoroethyl palmitate), that show self-extinguishing properties, followed by a systematic DFT study to understand this peculiar property of these donors. **D1** and **D2** can undergo parallel reactions with aluminum and titanium species present in the system to produce ketones and aldehydes, which are poisons for Z-N catalytic systems, thus explaining their self-extinguishing nature. The non-covalent interaction between the long alkyl chain of the donors with the surface plays a vital role in determining the donors’ self-extinguishing nature. There is a significant thermodynamic preference for the binding of the donor with the longer alkyl chain at the titanium center. The current work, therefore, provides interesting insights into how self-extinguishing donors function in Z-N catalytic systems.

2022-Ph.D. Thesis: Vipin Raj K, (CSIR-NCL), AcSIR

(ii) Presented a poster entitled “*Insights into the Nature of Self-Extinguishing External Donors for Ziegler-Natta Catalysis: A Combined Experimental and DFT Study*” at the #LatinXChem Twitter Conference 2020 on Sept 7th, 2020.

Abstract: See the abstract for entry (i).

(iii) Presented a poster entitled “*Insights into the Nature of Self-Extinguishing External Donors for Ziegler-Natta Catalysis: A Combined Experimental and DFT Study*” during National Science Day Celebrations at CSIR-National Chemical Laboratory, Pune, India, February 2021.

Abstract: See the abstract for entry (i).

(iv) Presented an oral talk entitled “*The Hidden Role of Lewis Acid-Base Adducts in Enhancing the Stereoselectivity of Ziegler-Natta Catalysis: A DFT Study*” at the Annual Students’ Conference 2021, organized by NCL Research Foundation & CSIR-NCL, Pune. **(Received best oral presentation award).**

Abstract: Ziegler-Natta (Z-N) catalyst is the most crucial heterogeneous catalyst that produces isotactic polypropylene and polyethylene. The use of Lewis base donors, a combination of internal and external donors, in the Z-N system significantly improved the stereoselectivity of the polymerization. Even though there is a consensus that the primary role of external donors is to coordinate to the vacant site created by the extraction of internal donors and thus maintain the stereoselectivity, the bite difference between the internal donor (phthalate or succinate) and external alkoxysilane donor raises a question that how alkoxysilane donors overcome this. In this work, we have chosen four external alkoxysilane donors; (1) diisopropyl dimethoxysilane (DIPDMS), (2) dicyclopentyl dimethoxysilane (DCPDMS), (3) disec-butyl dimethoxysilane (DSBDMS), and (4) sec-butyl(methyl) dimethoxysilane (SBMDMS), and the DFT calculations reveal that it is not the alkoxysilane, but the Lewis acid-base adducts (alkoxysilane-AlEt₂Cl) that are majorly responsible for the stereoselectivity.

Insights into the Nature of Self-Extinguishing External Donors for Ziegler-Natta Catalysis: A Combined Experimental and DFT Study

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Developing donors for Ziegler-Natta (ZN) catalysis to control the polymerization reaction and produce polymers with desirable properties has always been challenging due to the multi-component nature of the catalytic systems. Here, we have developed a new synthetic protocol for making two external donors, **D**₁ (2,2,2-trifluoroethyl myristate) and **D**₂ (2,2,2-trifluoroethyl palmitate) that show self-extinguishing properties, followed by a systematic DFT study to understand this peculiar property of these donors. **D**₁ and **D**₂ can undergo parallel reactions with aluminum and titanium species present in the

system to produce ketones and aldehydes, which are poisons for ZN catalytic systems, thus explaining their self-extinguishing nature. The non-covalent interaction between the long alkyl chain of the donors with the surface plays a vital role in determining the donors' self-extinguishing nature. There is a significant thermodynamic preference for the binding of the donor with the longer alkyl chain at the titanium center. The current work, therefore, provides interesting insights into how self-extinguishing donors function in ZN catalytic systems.

Introduction

Ziegler-Natta (ZN) catalysis is one of the most important catalytic processes, which produces around 150 million tons of polyolefins/year, and has a billion dollar market.^[1] Since its discovery in the 1950s by Karl Ziegler and Giulio Natta, for which they received the Nobel prize in 1963,^[2,3] continuous efforts to improve the performance of the ZN systems, concerning their activity and the selectivity, have been undertaken, along with understanding at the molecular level, by employing various experimental^[4–11] and computational

tools.^[12–34] The main components of the ZN system are (i) MgCl₂ as a catalyst support, (ii) TiCl₄ as precatalyst, (iii) triethylaluminum (*teal*) as an alkylating agent, and (iv) Lewis base donors (e.g. oxygen-containing molecules and nitrogen-containing polymers^[35]). Donors are generally classified into (i) internal donors (**D**_i) that are added during the catalyst preparation, such as ethyl benzoate,^[26,36–41] diethers,^[13,27,38,42–44] phthalates,^[13,22,38,45,46] tetrahydrofuran,^[29,47] and succinates,^[27,38,48] and (ii) external donors (**D**_e) that are added along with the alkylating agent, such as alkoxysilanes^[38,46,49] and *p*-ethoxyethylbenzoate.^[38]

Donors are vital components of the ZN polymerization process that can enhance the stereo- and regioselectivity of the product by coordinating in the vicinity of the active titanium center.^[9,42,43,46] It can influence the kinetics of the activation, insertion and termination steps in the polymerization reaction, and can also help the titanium to coordinate to the (104) MgCl₂ surface, which is otherwise unutilized.^[30,31,33] It is interesting to note that tuning the structure of existing donors and developing new donors has always been challenging and a prominent area of research in ZN catalysis, because of their potential to produce polyolefins with desirable properties.

Olefin polymerization is an exothermic process that releases heat, and an increase in the temperature inside the reactor results in increase in the rate of the polymerization reaction, and vice versa. The reaction temperature is a crucial factor for polymerization as the heat generation causes polymer melting, which leads to the agglomeration of polymer particles that further causes lump formation. Such situations are detrimental to the continuous production of polymer resin. There is, therefore, considerable incentive to develop new ways over the existing ones to overcome this problem without affecting the desirable properties of the polymerization reaction. One of the

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promising ideas is to use one of the components itself to “self-extinguish” the process at a higher temperature. There are several patents regarding the use of long-chain fatty acid external donors as activity limiting agents and bringing self-extinguishing behavior in the catalyst system.^[50–55] However, to the best of our knowledge, there are no detailed studies available about such systems that can shed light into the underlying reasons leading to the self-extinguishing of the donors, which can help to modify them to eliminate reactor fouling.

In the current work, we report the synthesis, polymerization studies, and a systematic density functional theory study (DFT) of a new class of self-extinguishing molecules **D**₁ and **D**₂ (see Figure 1) that can be used as self-extinguishing donors in ZN polymerization. **D**₁ and **D**₂ are fluorine-containing ester derivatives of myristic acid and palmitic acid, respectively. These compounds, when employed as donors (as **D**_Es), reduce the activity at elevated temperatures. The most probable reason for the lowering of the activity is parallel reactions in the ZN system. In 2014, the parallel reactions of various ester donors with Al₂Et₆ and TiCl₂Et on the MgCl₂ surface was investigated.^[34] We have now performed a systematic study using DFT to develop an understanding of this peculiar behavior of these **D**_Es.

Results and Discussion

(A) Synthesis of **D**₁ and **D**₂

The synthesis of 2,2,2-trifluoroethyl fatty esters has been done by an entirely new strategy, which is significantly superior to the methods reported in the literature (see Scheme 1). Our approach involves only a single step, which is free from a base and chlorinated solvent, and, additionally, also occurs without the formation of any by-product. The eco-benign and economically favourable synthesis of such donors for ZN systems opens up a new area for deep exploration.

In 1993, Liu *et al.* reported the synthesis of the trifluoromethylated ester of fatty acids.^[56] The synthesis involved conversion of fatty acids into the corresponding acid chlorides, followed by treatment with trifluoroethanol in the presence of base. However, a purification method was required and yielded the desired product up to 89% yield. Monteiro *et al.* reported the synthesis of the trifluoromethylated ester of fatty acids using a similar strategy (*via* acid chloride method) and employed reusable acylating agents in the enzyme-catalyzed transacylation reactions.^[57]

(B) Polymerization Studies

Slurry phase propylene polymerization studies have been done using non/fluorinate myristic and palmitic derivatives as external donors. During the polymerization, the MgCl₂ supported TiCl₄ catalyst and triethyl aluminium were used as catalyst and co-catalyst respectively. In a preheated, 4 L CSTR moisture free stainless-steel jacketed reactor having a stirrer, 2 L n-hexane was added as a medium. During polymerization, a molar ratio of 250 of cocatalyst and precatalyst were maintained. 300 ml of hydrogen used as a chain transfer agent was added into the reactor under ambient conditions. The polymerization was carried out at 5.0–5.5 kg/cm² pressure and 70 °C temperature. During polymerization, the reactor temperature increased to a maximum temperature due to the exothermicity of the reaction and then subside depending on the catalyst system. After 2 hours, propylene supply was cut off and the reactor was degassed slowly to atmospheric pressure. The hexane was removed and the polymer resin was collected and dried. A free-flowing polymer resin was found without lump formation, which indicated the absence of runaway reactions and the polymerization was self-extinguished in the presence of different catalyst systems. The self-limiting temperature for the isopropyl myristate (**D**₃), 2,2,2-trifluoroethyl myristate (**D**₁) and 2,2,2-trifluoroethyl palmitate (**D**₂) were observed to be 87.1 °C, 81.9 °C and 77.5 °C respectively. These polymerization results suggest that the fluorinated donor showed a good self-extinguishing property in comparison to the non-fluorinated one (see Figure 2). The results also show that the length alkyl chain is an important factor, because **D**₂, having the longest alkyl chain, has the lowest self-extinguishing temperature.

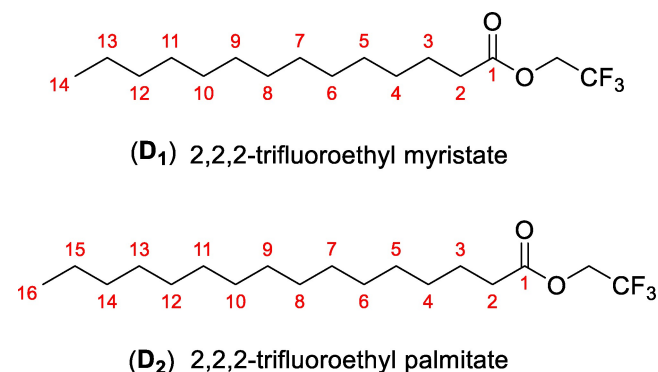
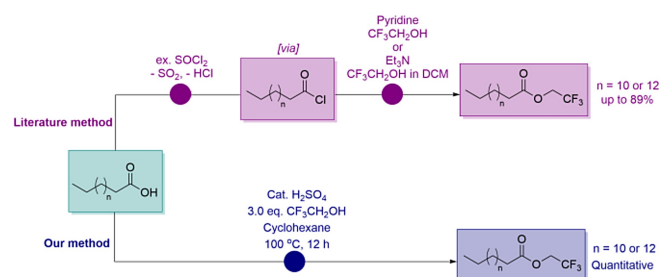


Figure 1. Structures of the two self-extinguishing donors **D**₁ and **D**₂.



Scheme 1. Synthesis of **D**₁ and **D**₂.

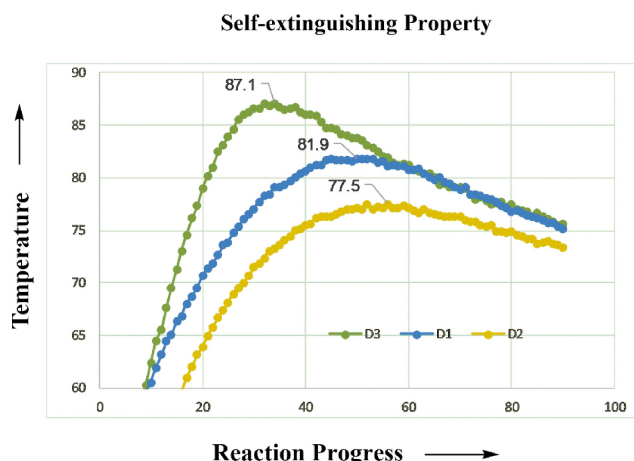


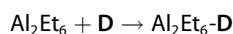
Figure 2. The self-extinguishing temperature for D_1 , D_2 , and D_3 .

(C) DFT Studies

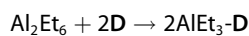
In order to understand the reason for the difference in the self-extinguishing property of D_1 and D_2 , we have performed a systematic full quantum mechanical study at the PBE-D3/TZVP//PBE0-D3/TZVP level of theory using density functional theory (for further information, please see the Computational Details section). Since D_1 and D_2 both have a long alkyl chain attached to the carbonyl carbon (see Figure 1), they can exist in different conformations. Before starting the study of the interaction of these D_1 s with aluminum and titanium, we have performed a conformational analysis using the HyperChem software package.^[58] Our calculations indicate that the linear chain conformation of the alkyl chain is preferable among the other possible structures, and therefore, these most stable conformations of D_1 and D_2 have been used for further computational studies.

(i) Decomposition reaction of D_1 and D_2 with Al_2Et_6

D_1 and D_2 can react with Al_2Et_6 , and lead to two different products. It can either form a dimer-donor adduct ($Al_2Et_6 \cdot D_1/D_2$) or two monomer-donor adducts ($2AlEt_3 \cdot D_1/D_2$). Our calculations indicate that the formation of two monomer-donor adducts is more favorable than the formation of a dimer-donor adduct (see below). We have taken the monomer-donor adduct ($AlEt_3 \cdot D_1/D_2$) as the reference energy for further calculations of the formation of ketone and aldehyde.



$$\Delta G = -2.0 \text{ kcal/mol } (D_1), -1.9 \text{ kcal/mol } (D_2)$$



$$\Delta G = -4.4 \text{ kcal/mol } (D_1), -5.1 \text{ kcal/mol } (D_2)$$

(a) Ketone pathway (KP)

Once the monomer-donor adduct formation takes place, it can pass through a six-membered transition state with the help of one more molecule of $AlEt_3$ (TS_{1KPM} and TS_{1KPP} for D_1 and D_2 respectively), in which one ethyl group from aluminum is transferred into the carbonyl carbon of the donor (see Figures 3 and 4). The barriers are 23.6 kcal/mol and 23.7 kcal/mol for D_1 and D_2 , respectively. The second transition state is also six-membered, which involves the transfer of one ethyl group from $AlEt_3$ to $AlEt_2$, which is already bonded with the carbonyl O of the donor, along with the breakage of the C–O bond and the formation of the Al–O bond, leading to the formation of the ketone. The corresponding barriers are minimal for D_1 (5.0 kcal/mol) and D_2 (4.9 kcal/mol). Our calculations therefore suggest that the formation of ketone by the reaction of D_1 and D_2 with Al_2Et_6 is thermodynamically and kinetically favourable. It should also be noted that since the corresponding barriers for the D_1 and D_2 cases are almost the same, the results also indicate that there is no difference in the reactivity of D_1 and D_2 in this particular reaction.

(b) Aldehyde pathway (AP)

Another possible pathway for the donor- $AlEt_3$ adduct to proceed is the AP, in which the first transition state (TS_{1APM} and TS_{1APP}) is the rate-determining one for both D_1 and D_2 . The

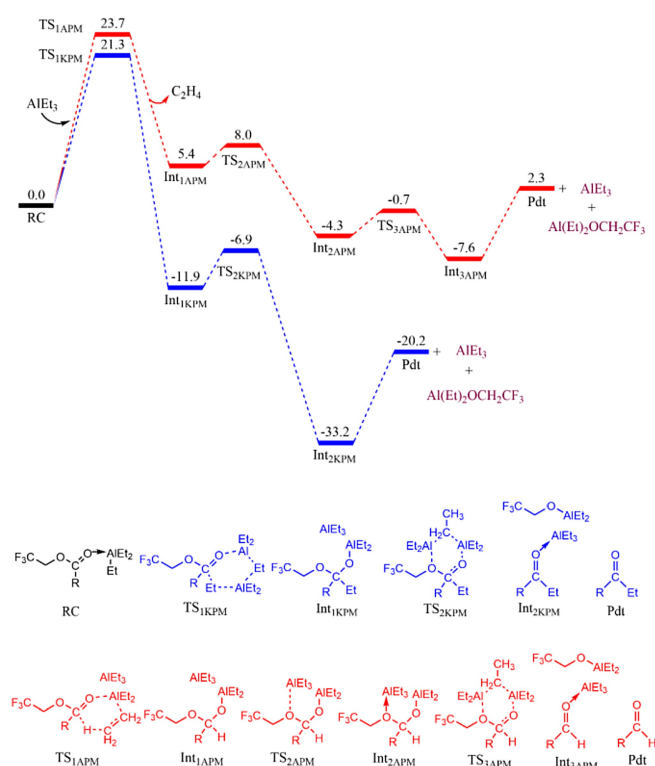


Figure 3. The free energy profile for the decomposition reaction of D_1 ($R = (CH_2)_{12}CH_3$) with Al_2Et_6 . The values are in kcal/mol. Blue indicates the ketone pathway (KP) and red indicates the aldehyde pathway (AP).

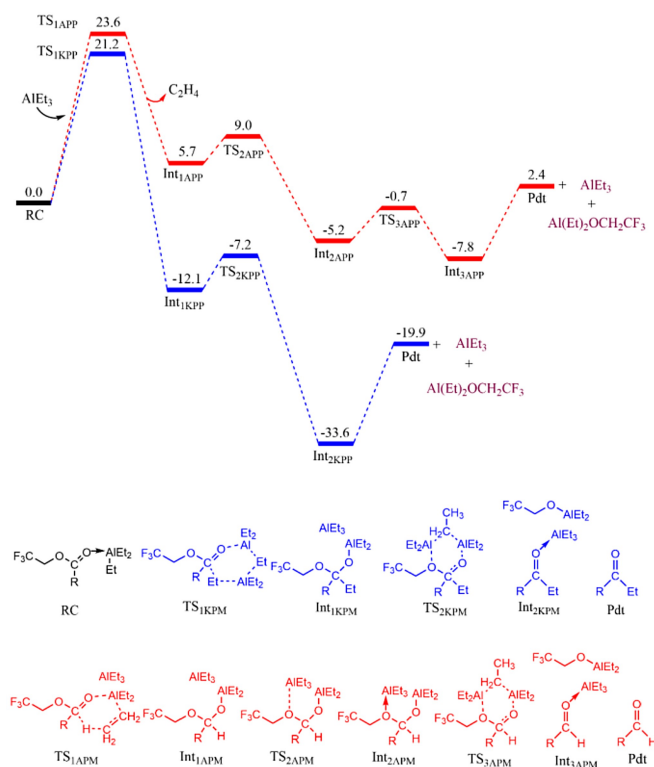


Figure 4. The free energy profile for the decomposition reaction of D_2 ($R = (CH_2)_{14}CH_3$) with Al_2Et_6 . The values are in kcal/mol. Blue indicates the ketone pathway (KP) and red indicates the aldehyde pathway (AP).

transition state involves the transfer of a hydride ion and the elimination of an ethylene molecule in the presence of one more molecule of $AlEt_3$, with a barrier of 21.2 kcal/mol for D_1 and 21.3 kcal/mol for D_2 (see Figure 3 and 4). It is interesting to note that the extra $AlEt_3$ molecule is not covalently interacting like in the case of KP. The second transition state is different from KP because the AP has a new stable intermediate (Int_{2APM} and Int_{2APP} for D_1 and D_2 , respectively). We were not able to optimize such an intermediate for KP, probably due to the electron-donating effects of the ethyl group, which facilitates the C–O bond breakage and leads to the formation of the final product. The second transition state involves the formation of the Al–O bond alone, with a barrier of 2.6 kcal/mol for D_1 and 3.3 kcal/mol for D_2 . Subsequent to this, the intermediate surmounts a barrier of 3.6 kcal/mol for D_1 and 4.5 kcal/mol for D_2 , which leads to the formation of aldehyde.

Our calculations therefore suggest that the AP is less favorable compared to the KP, thermodynamically and kinetically, which corroborates with NMR studies. However, like KP, D_1 and D_2 do not show any considerable difference for the AP as well.

(c) The effect of the $-CF_3$ group and the length of alkyl chain on the decomposition with Al_2Et_6

In order to understand the effect of the $-CF_3$ group and the length of the alkyl chain in the decomposition reactions, we have chosen three donors; D_3 , D_4 , and D_5 (see Figure 5 below). Experimental studies with D_3 (where trifluoroethyl group is replaced with isopropyl group), as reported above, indicate that it is less reactive than D_1 and D_2 . On the other hand, D_4 and D_5 are two model donors that we considered here for computational purposes, in which the $-CF_3$ group has been replaced with $-CH_3$, and a long alkyl chain has been replaced with a $-CH_3$ group, respectively. Since the rate of the reaction depends on the slowest step in a reaction profile, we have calculated barriers for only the rate-determining steps for both KP and AP and compared the same with the barriers of D_1 (see Figure 6). It was found that the alkyl chain has a small effect on the barriers (for D_5 , the barriers were 21.7 kcal/mol and 23.8 kcal/mol for KP and AP, respectively), but replacing the $-CF_3$ group with other alkyl groups had a significant impact on the barriers (the barriers increased by around 2.1 to 3.2 kcal/mol in both D_3 and D_4 , see Figure 6). These calculated values indicate that a long alkyl chain would not help significantly to facilitate the decomposition reaction of a donor with Al_2Et_6 , but having an electron-withdrawing group attached to it (such as $-CF_3$) can increase the rate of decomposition reactions with Al_2Et_6 .

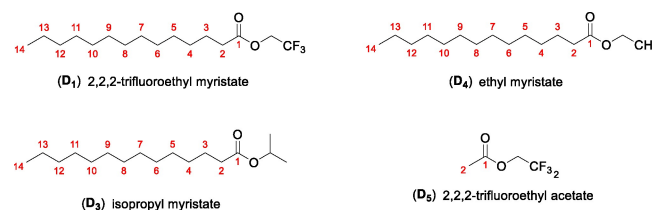


Figure 5. Structures of D_1 and D_3 , and the two model donors D_4 and D_5 .

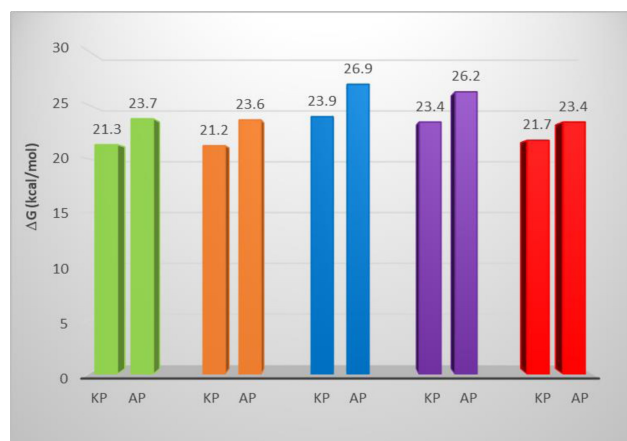


Figure 6. Barriers (values in kcal/mol) for the rate determining step for the decomposition reaction with Al_2Et_6 .

It is interesting to note that D_1 and D_2 did not show any considerable difference in their reactivity towards Al_2Et_6 , either thermodynamically or kinetically. However, there is a difference in their self-extinguishing properties, according to experimental observations.

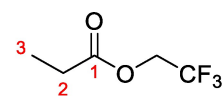
(ii) Decomposition reaction of D_1 and D_2 with titanium on the (110) $MgCl_2$ surface

As mentioned in the Introduction, a donor can interact with titanium as well. We have calculated the binding energy of D_1 with titanium on the (110) $MgCl_2$ surface, where the choice of $MgCl_2$ model is based on work reported earlier (for further information, please see the Computational Details section).^[34] Here, one important thing to be noted is the orientation of the alkyl chain concerning the (110) $MgCl_2$ surface. We have considered two extreme cases: (i) the alkyl chain oriented away from the $MgCl_2$ surface and (ii) the alkyl chain oriented just above the $MgCl_2$ surface (see Figure 7). The calculated values indicate that the structure in which the alkyl chain is oriented just above the $MgCl_2$ surface is more stable than the other possibility by 21.0 kcal/mol. This vast difference in the binding energy is due to the favorable non-covalent interactions between the alkyl chain and the $MgCl_2$ surface. In other words, the long alkyl chain helps the donor to bind to the titanium more strongly. If the above hypothesis is correct, then there should be a considerable difference in the binding energies of D_1 and D_2 with titanium on the (110) $MgCl_2$ surface, because there is a difference of the alkyl chain length (by two carbon units) among these D_i s. However, our results do not show any significant difference in the binding energies, due to the limitation of our chosen small $MgCl_2$ surface model. The use of a sizeable $MgCl_2$ surface model that can completely interact with the long alkyl chain of D_1 and D_2 can provide the exact difference between the binding energies of D_1 and D_2 , but such a computationally expensive approach is beyond the scope of the current work. However, another way to proceed forward is to use the same $MgCl_2$ surface model but choose new donors in such a way that the difference between them is the same as between D_1 and D_2 . We have chosen three model donors D_6 ,

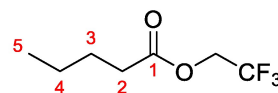
D_7 , and D_8 (see Figure 8) with small alkyl chains so that complete interaction is possible between the alkyl chain and the (110) $MgCl_2$ surface. The binding energy values obtained (−11.5 kcal/mol for D_6 , −14.5 kcal/mol for D_7 and −16.6 kcal/mol for D_8) for these new model donors clearly show an increase in the binding energy around 2.0 to 3.0 kcal/mol per addition of an extra CH_2CH_3 group in the structure of the donor. It is reasonable to assume that the same would be true for the case of D_1 and D_2 , which means that D_2 has a thermodynamic preference over D_1 to bind with titanium on the (110) $MgCl_2$ surface.

In order to obtain more insights into the interaction between the alkyl chain and the (110) $MgCl_2$ surface, we have done non-covalent interaction (NCI) plots^[59] for the binding of D_6 , D_7 , and D_8 . The NCI plots indicate that there is a weak attractive interaction (the area colored in green between the alkyl chain and the $MgCl_2$ surface, see Figure 9) between the alkyl chain and the (110) $MgCl_2$ surface and, more importantly, the area of attraction increases with increase in the length of the alkyl chain.

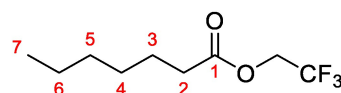
Once the donor binds with titanium, it can undergo decomposition through KP and AP. It is already reported that the first step, involving ethyl transfer in KP and hydride transfer in AP, are the rate-determining transition states. We have, therefore, calculated the barriers for both D_1 and D_2 (see



(D_6) 2,2,2-trifluoroethyl propionate



(D_7) 2,2,2-trifluoroethyl pentanoate



(D_8) 2,2,2-trifluoroethyl heptanoate

Figure 8. Structures of new model donors D_6 , D_7 , and D_8 with small alkyl chains compared to D_1 and D_2 .

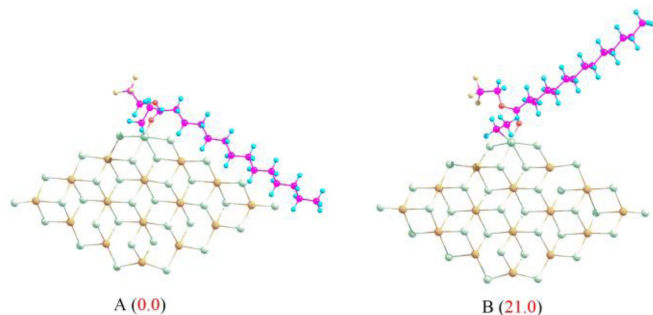


Figure 7. The relative binding energies (for D_1) of two possible orientations of the alkyl chain concerning the $MgCl_2$ surface (values are in kcal/mol); (A) the alkyl chain is oriented just above the (110) $MgCl_2$ surface, and (B) the alkyl chain is oriented away from the (110) $MgCl_2$ surface.

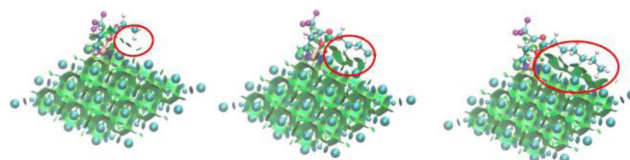


Figure 9. The non-covalent interaction (NCI) plots for D_6 , D_7 , and D_8 binding to titanium, with the alkyl chain interacting with the $MgCl_2$ surface (the area of interest encircled in red). The color code for the NCI plots is as follows: blue – strongly attractive, green – weakly attractive, and red – strongly repulsive.

Figure 10), and our calculations suggest that KP is much more favorable than AP, both in cases of D_1 and D_2 . However, the alkyl chain length does not have any influence on the barriers. It is important to note here that for D_1 and D_2 , the alkyl chain does not entirely interact with the (110) $MgCl_2$ surface. Therefore, in order to make sure that the alkyl chain length is not affecting the barriers, we have calculated the barriers for AP for D_6 (29.0 kcal/mol), D_7 (29.1 kcal/mol), and D_8 (29.3 kcal/mol), and found that there is no difference in the barriers. Our study also indicates that among various possibilities of decomposition reactions of D_1 and D_2 with Al_2Et_6 and titanium, the KP with the help of titanium is the most preferred pathway for both D_1 and D_2 .

Our calculations indicate that difference in the reactivity of D_1 and D_2 is due to the difference in the chain length. However, in the slurry phase polymerization, there could be a competition between the alkyl chain of the donor and the n-hexane molecules for the $MgCl_2$ surface. We have calculated the free energy required to displace the alkyl chain from the $MgCl_2$ surface by the n-hexane molecule (we have used an n-hexane molecule explicitly; see Figure S1 in ESI). For D_1 and D_2 , the values are found to be the same (17.6 kcal/mol and 17.4 kcal/mol, respectively), which is due to the reason discussed earlier: our surface model is not big enough to quantify the complete

interaction of alkyl chain with the $MgCl_2$ surface. Hence, we have calculated the corresponding free energy for D_6 (−4.7 kcal/mol), D_7 (−3.1 kcal/mol), and D_8 (−0.9 kcal/mol). Results indicate that with an increase in the alkyl chain length, it is difficult for the n-hexane molecule to displace the alkyl chain from the $MgCl_2$ surface, which is applicable for the case of D_1 and D_2 donors as well.

Conclusion

Reactor fouling is a significant issue in ZN catalyst systems, caused by overheating of the reactor vessel during the exothermic polymerization process. An interesting means of avoiding this problem is to employ donors with the ability to stop the polymerization process if the temperature were to exceed a certain value. In the current work, we report the synthesis and performance of two new donors and demonstrate their ability to self-extinguish under polymerization conditions. The two donors, D_1 (2,2,2-trifluoroethyl myristate) and D_2 (2,2,2-trifluoroethyl palmitate), have been made with an entirely new synthetic strategy, which is both eco-benign and economical. These donors can be employed as self-extinguishing in ZN catalyst systems, and polymerization studies that we have conducted show that D_2 self-extinguishes the reaction progress at 77.5 °C, while D_1 does the same at 81.9 °C. We have further explored the reason behind this difference in the self-extinguishing property between the two donors using density functional theory (DFT). A systematic study of the decomposition reaction of D_1 and D_2 with Al_2Et_6 and titanium attached on the (110) $MgCl_2$ surface has been done. With Al_2Et_6 , both D_1 and D_2 show a tendency to form monomer-donor adducts, and these adducts can undergo decomposition reactions with the help of another $AlEt_3$ molecule, either through the ketone pathway (KP) or the aldehyde pathway (AP), leading to the formation of a ketone or an aldehyde respectively. Such species are known to act as poisons in ZN systems, thereby explaining why D_1 and D_2 have the self-extinguishing property. Both donors have similar barriers for KP and AP, and among the two possible pathways, KP is more favorable, which corroborates with experimental observations. With titanium, both D_1 and D_2 bind strongly compared to Al_2Et_6 , and KP is a significantly more facile pathway. It is also interesting to note that the alkyl chain plays a significant role in making the binding stronger through non-covalent interactions. Even though the barriers are similar for both D_1 and D_2 for the decomposition reactions (both KP and AP) with titanium, the thermodynamic binding preference of D_2 over D_1 makes D_2 a better self-extinguishing donor, which agrees with the polymerization studies.

In summary, our work encompasses novel donor synthesis, polymerization studies that demonstrate their peculiar ability to self-extinguish during ZN catalysis, and careful and comprehensive computational studies that provide insight into how the donors interact with Al_2Et_6 , $TiCl_4$ and, importantly, also the $MgCl_2$ surface in order to undergo the self-extinguishing process.

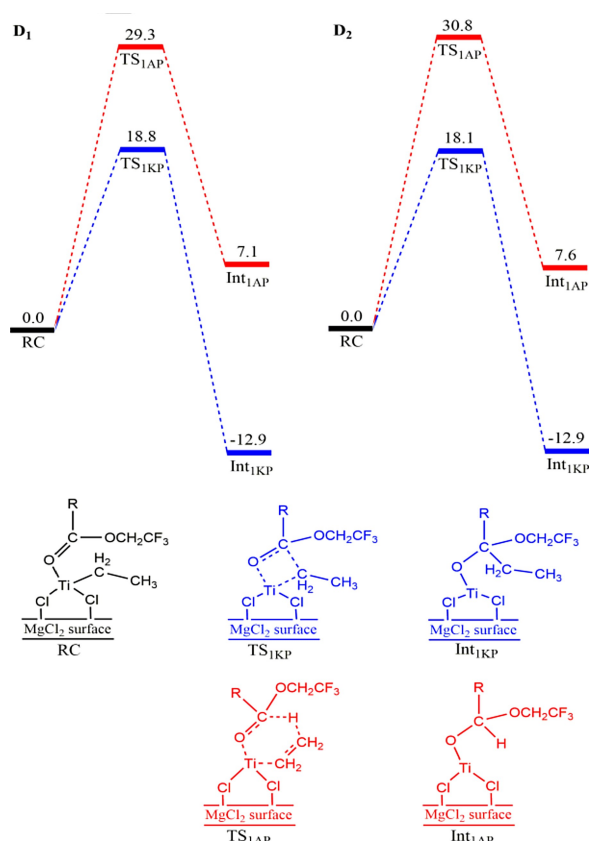


Figure 10. The free energy profile for the rate determining steps for the decomposition reaction of D_1 ($R = (CH_2)_{12}CH_3$) and D_2 ($R = (CH_2)_{14}CH_3$) with titanium. The values are in kcal/mol. Blue indicates the ketone pathway (KP) and red indicates the aldehyde pathway (AP).

Experimental Section

Computational Details

The Turbomole 7.0 suite of program^[60] has been employed to optimize all the structures including intermediates and transition states using density functional theory (DFT). Geometry optimizations have been performed using the Perdew, Burke, and Ernzerhof (PBE) functional^[61] and TZVP basis set.^[62] The dispersion correction (DFT-D3) developed by Grimme et al. has been used to increase the accuracy of the calculations.^[63] The resolution of identity (RI)^[64] and the multipole accelerated resolution of identity (marij)^[65] approximations were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations. Closed-shell calculations were done for the Al_2Et_6 -donor model system cases, while open-shell calculations have been considered for the TiCl_3Et -donor model system cases. For better accuracy, we have performed single point calculations using PBE0 functional,^[66] TZVP basis set,^[62] and dispersion correction (DFT-D3).^[63] Our choice of the PBE-D3/TZVP//PBE0-D3/TZVP level of theory is based on benchmarking and computational studies.^[67,68,34] For the calculations that we have performed, the energy convergence criteria was 10^{-6} H, and the norm for the cartesian gradients was 10^{-3} . And the second-order derivatives of the potential energy obtained numerically. Further, to check whether our chosen level of theory is adequate to address the interactions in the system, especially in alkyl aluminum species (many functionals are known to underestimate the dimerization energy of bridged alkyl aluminum species),^[69] we have calculated the dimerization energy of AlEt_3 . Our calculations indicate that dimeric Al_2Et_6 is more favorable by 8.7 kcal/mol over monomeric AlEt_3 , suggesting that the chosen level of theory is sufficient to address the interactions. We have employed a 15 molecule MgCl_2 cluster (see Figure S2 in ESI) and have not employed any periodic boundary conditions. This model is chopped from the MgCl_2 model proposed by Cavallo and co-workers.^[27] The values reported are ΔG values, with zero point energy, internal energy, and entropic contributions (including translational, rotational, and vibrational entropy contributions) included through frequency calculations on the optimized minima and transition state structures, with the temperature taken to be 298.15 K. This was done in order to ensure that all of the reported transition state structures contained only one imaginary frequency corresponding to the correct normal mode. IRC calculations have been considered for the confirmation of the transition states. In every case, the IRC calculations have yielded the correct reactant and product structures.

General information for synthesis

^1H , ^{13}C , and ^{19}F NMR spectra were recorded either with JEOL 400 MHz, or BRUKER 500 MHz. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CHCl_3 at 7.27 ppm, integration, multiplicities (s=singlet, d=doublet, q=quartet, t=triplet, m=multiplet), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77.0 ppm. $\text{CF}_3\text{CO}_2\text{H}$ used as external standards for ^{19}F NMR. Myristic acid, Palmitic acid and Trifluoroethanol was purchased from Sigma-Aldrich and used without further purification. HPLC grade cyclohexane was purchased from Merck and used as received. Other organic solvents and conc. H_2SO_4 was purchased from local suppliers and used as received.

Procedure for preparation of D_1

To a solution of myristic acid (50.0 mmol, 1.0 equiv., 11.4 gm,) and 2,2,2-trifluoroethanol (50.0 mmol, 1.0 equiv., 5.0 gm) in 50 mL cyclohexane, was added conc. H_2SO_4 (30.0 mol%) at ambient temperature and heated to reflux (at 100°C) for 12 h. The mixture was cooled to room temperature, added saturated NaHCO_3 solution to neutralize excess H_2SO_4 , and then was extracted three times with CH_2Cl_2 (100 mL each time). The combined organic phases were washed with brine solution, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo* to give the desired 2,2,2-trifluoroethyl myristate.

Colourless liquid at 300 K. Isolated Yield: 15.3 gm, 99.0%. ^1H NMR (500 MHz, CDCl_3): δ = 4.46 (q, J = 8.5 Hz, 2H), 2.41 (t, J = 7.6 Hz, 2H), 1.66 (quin, J = 7.4 Hz, 2H), 1.35–1.24 (m, 20H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ = 172.11, 126.33, 124.12, 121.92, 119.72, 60.51, 60.22, 59.93, 59.64, 33.61, 31.93, 29.68, 29.64, 29.57, 29.42, 29.37, 29.18, 28.97, 24.69, 22.69, 14.06. ^{19}F NMR (376 MHz, CDCl_3): δ = –74.02. GC data (Rt): 8.356 min (GC Programme: Column HP 5; Method: 80°C hold 1 min; 20°C ramp up to 280°C ; at 280°C Hold for 10 min; Inlet temp. 300°C , Detector temp. 300°C , H_2 Flow 40 mL, Air Flow 400 mL, N_2 Flow 25 mL per minute, Constant Flow mode).

Procedure for preparation of D_2

To a solution of palmitic acid (50.0 mmol, 1.0 equiv., 12.82 gm,) and 2,2,2-trifluoroethanol (50.0 mmol, 1.0 equiv., 5.0 gm) in 50 mL cyclohexane was added conc. H_2SO_4 (30 mol%) at ambient temperature and heated to reflux (at 100°C) for 12 h. The mixture was cooled to room temperature, added saturated NaHCO_3 solution to neutralize excess H_2SO_4 , and then was extracted three times with CH_2Cl_2 (100 mL each time). The combined organic phases were washed with brine solution, dried over anhydrous Na_2SO_4 , and concentrated in *vacuum* to give the desired 2,2,2-trifluoroethyl palmitate.

Colourless solid at 300 K. Isolated Yield: 16.5 gm, 98%. ^1H NMR (500 MHz, CDCl_3): δ = 4.46 (q, J = 8.5 Hz, 2H), 2.41 (t, J = 7.8 Hz, 2H), 1.66 (quin, J = 7.4 Hz, 2H), 1.35–1.22 (m, 24H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ = 172.11, 126.32, 124.12, 121.92, 119.71, 60.51, 60.23, 59.93, 59.64, 33.61, 31.94, 29.70, 29.67, 29.64, 29.57, 29.42, 29.38, 29.18, 28.97, 24.68, 22.70, 14.07. ^{19}F NMR (376 MHz, CDCl_3): δ = –73.99. GC data (Rt): 9.359 min (GC Programme: Column HP 5; Method: 80°C hold 1 min; 20°C ramp up to 280°C ; at 280°C Hold for 10 min; Inlet temp. 300°C , Detector temp. 300°C , H_2 Flow 40 mL, Air Flow 400 mL, N_2 Flow 25 mL per minute, Constant Flow mode).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Ziegler-Natta catalysis • self-extinguishing • donors • non-covalent interactions • DFT

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