CHAPTER 3

CALCULATIONS

The zirconocene catalyst is a powerful catalyst in the olefin polymerization. The catalytic properties such as selectivity and reactivity of zirconocene catalyst are controlled by the structure of the catalyst. So far a design of zirconocene catalysts is based on trial and error. This procedure wastes chemical substances, is time-consuming, and creates lots of waste chemical. These problems could be reduced by molecular modeling. It was observed that there is a relation between catalytic properties and structure of the catalyst. The structure-property relationship (SPR) approach could be employed for such a system. In this study, we performed SPR study on 5 zirconocenes, with catalytic properties such as % isotacticity, and productivity and structural properties such as distance between cyclopentadienyl (Cp) planes, angle between Cp planes, gap aperture, obliquity, twisted angle, cavity distance, cavity angle as well as other parameters such as atomic charges.

3.1 Zirconocene Catalyst

Geometry optimizations of the 5 zirconocene structures (Figure 3.1) were performed. These structures were taken from Brintzinger *et al.* [17] where catalytic properties such as reaction time, productivity and % isotacticity were available as shown in Table 3.1.

1. $R^1=t$Bu,R^2=H,μ-x=Me$_2$C-CMe$_2$
2. $R^1=t$Bu,R^2=H,μ-x=Me$_2$Si
3. $R^1=t$Bu,R^2=Me,μ-x=Me$_2$Si
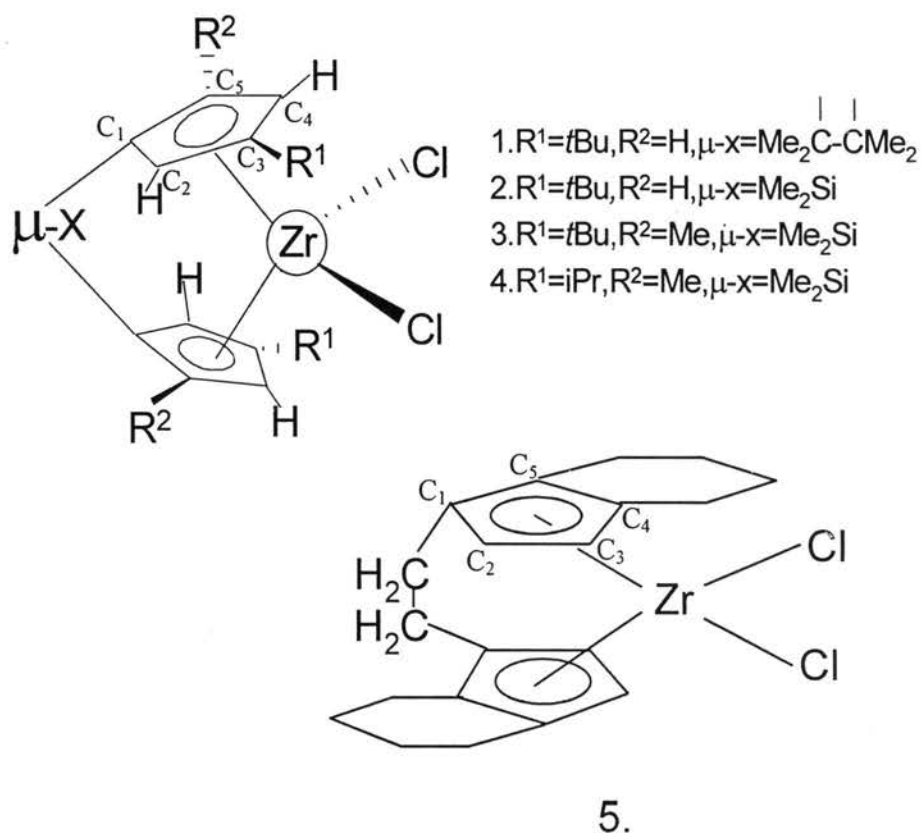4. R^1=iPr,R^2=Me,μ-x=Me$_2$Si

5.

Figure 3.1 Structures of zirconocene investigated.

The **structure 1** is the tetramethylethano-bridged zirconocene whereas **structures 2-4** are the dimethylsilano-bridged zirconocene [17], and the **structure 5** is ethano-bridged bis(tetrahydroindenyl) zirconocene [3]. The **structures 1-4** are the series of indenyl based zirconocene, which have very high reactivity and selectivity. The **structure 5** is the classical catalyst, which used as the reference structure in terms of effect of substituents position and the kind of bulky group for the study.

Table 3.1 Reaction time, productivity, and % isotacticity of 5 structure zirconocenes obtained from Brintzinger [17]

	Reaction time [min]	Productivity [kg(PP).(h mol(Zr) p]	% isotacticity [% mmmm Pentads]
1	120	85	62
2	120	355	77
3	185	505	94
4	45	3000	73
5	50	2250	49

From the experimental data (Table 3.1), the **structures 1-4** have higher yield of isotactic polypropylene than "classical" catalyst **structure 5**. The **structure 3** yielded products with the highest percentage of isotactic polypropylene. This structure has the *t*Bu group and the methyl group substitution at β and α positions, respectively. The catalyst which, yielded the highest productivity of polypropylene is the **structure 4**, which has *i*Pr group and methyl group substitution at β and α positions, respectively. The **structure 5** was taken as the reference structure that has the difference position of substituents group and excluded from the discussion since its structure does not belong to the same series as **structures 1-4**.

3.2 Geometry Optimization

Calculation techniques used in this study can be categorized into 2 types *i.e.* the full quantum mechanical calculation (QM) and the combined quantum mechanical and molecular mechanical calculation (QM/MM). All calculations were perform using the Gaussian 98 program on 16 CPU Hewlett-Packard V2250 server at Hewlett-Packard, Colorado, on SGI-powerchallenge at the High Performance Computing Center (HPCC), the National Electronics and Computer Technology

Center (NECTEC), and on PC-workstation the Austrian-Thai Center for Computer Assisted Chemical Education and Research (ATC), Chulalongkorn University.

3.2.1 QM Method

The Density Functional Theory with B3LYP functional [32] was used as the QM method of choice. Two types of basis sets, *i.e.* DZVP [29] for all atoms, which are (5s)/[2s] for hydrogen, (9s,5p,1d)/[3s,2p,1d] for carbon (12s,8p,1d)/ [4s,3p,1d] for silicon, and (18s,12p,9d)/[6s,5p,3d] for zirconium and the effective core potential basis LANL2DZ [30] for Zr and DZVP otherwise were employed. The LANL2DZ basis set for zirconium is (5s,6p,4d)/[3s,3p,2d]. The B3LYP calculation employing DZVP basis is denoted as "B3LYP/DZVP" and that employing LANL2DZ effective core basis for Zr and DZVP on other atoms is denoted "B3LYP/LANL2DZ".

3.2.2 QM/MM Method

The ONIOM was used as the QM/MM method of the choice. Here, the molecule was partitioned into 2 levels where 2 different levels of theory were treated. The partition was illustrated in Figure 3.2. The first level, the high level or the "model system", was treated using B3LYP/DZVP. The second level, the low level or "real system", was treated using Universal force field (UFF) [31] The method denoted as ONIOM (B3LYP/DZVP:UFF).
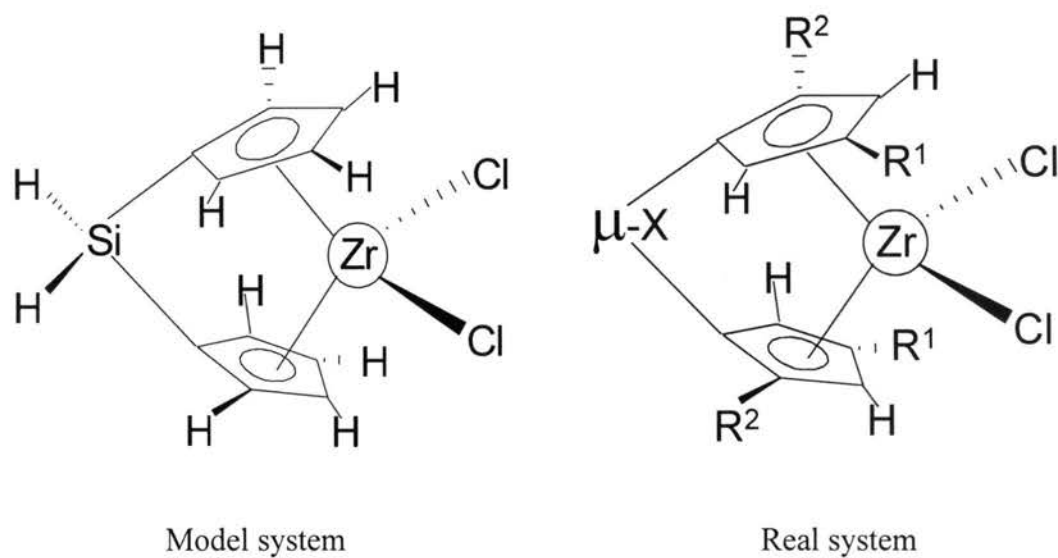
Figure 3.2 Model and real systems using for partitioning dimethylsilano bridged zirconocene complexes.
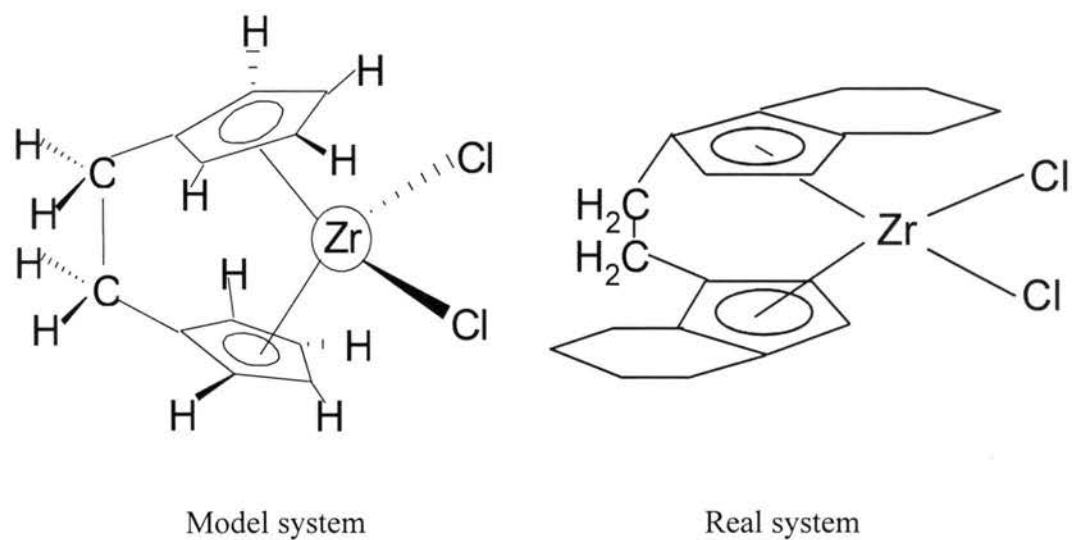

Figure 3.3 Model and real systems using for partitioning of tetramethylethano and ethano bridged zirconocene complexes.

3.3 Parameters for Predicting Catalytic Property

In this study, geometrical parameters such as the distance between Cp plane, the angle between Cp plane, the gap aperture, the obliquity, the twisted angle, the cavity distance, the cavity angle, as well as other parameters such as the atomic charge were computed and their relation with catalytic activity such as % isotacticity (selectivity) and productivity (reactivity) were sought.

3.3.1 Distance and Angle between Cp Plane

The angle between Cp planes was determined from the cross product between normal vector **N** of each Cp plane. The distance between Cp planes was determined from the distance between the center of mass of the two cyclopentadienyl rings (Figure 3.4). This distance can be computed using

$$distance = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \qquad (3.1)$$

where (x_1, y_1, z_1) and (x_2, y_2, z_2) is the Cartesian coordinate of center of mass of upper and lower Cp ring, respectively. Similarly, the angle between Cp planes can be computed using

$$\cos\theta = \frac{\vec{N}_1 \cdot \vec{N}_2}{\left\|\vec{N}_1\right\|\left\|\vec{N}_2\right\|} \qquad (3.2)$$
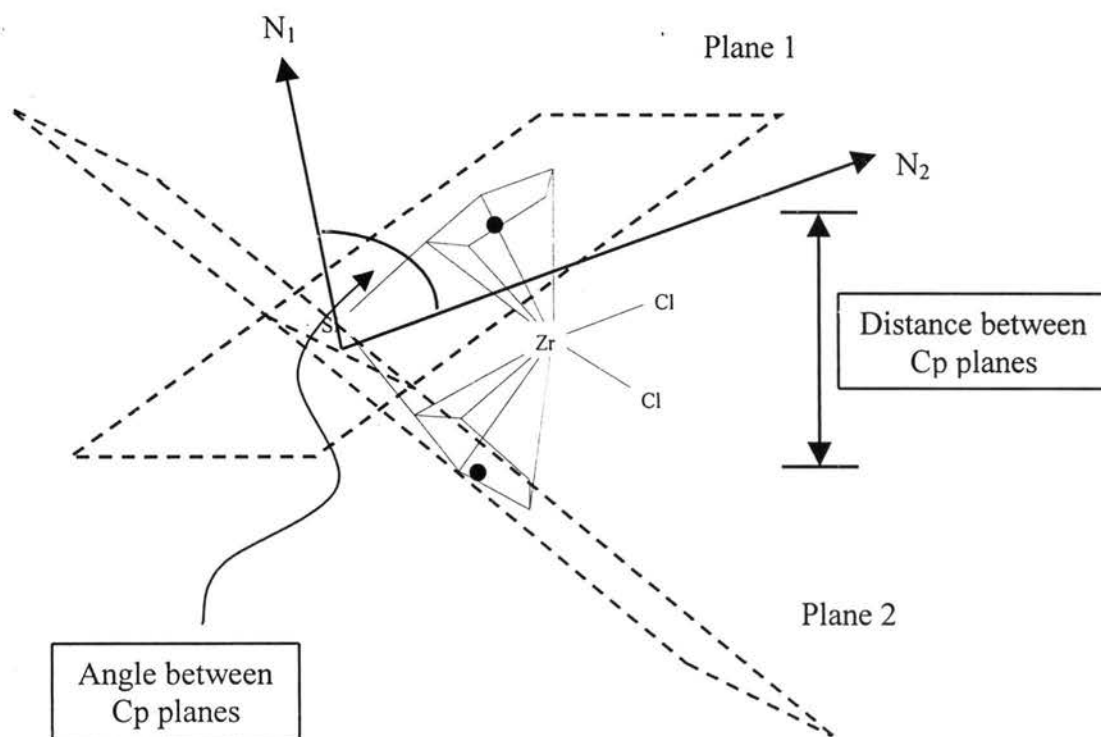
Figure 3.4 The measurement of angle and distance between Cp planes.

3.3.2 Gap aperture and Obliquity [18]

From the structure of zirconocene, it is apparent that the accessibility of its coordination sites is primarily controlled by the size of the immediately adjacent β-substituents of each Cp ring that includes van der Walls radius. This property is represented by the gap aperture, which is an angle generated from two tangential planes intersection. The largest possible size of this angle in a given complex would then provide a reasonable measure for the openness of its Zr coordination site (Figure 3.5). Another property is the obliquity, which is an angle generated by the plane bisecting the centroid-Zr-centroid angle (Figure 3.5). The gap aperture and obliquity were calculated using Aperture program of Brintzinger et al. [18].
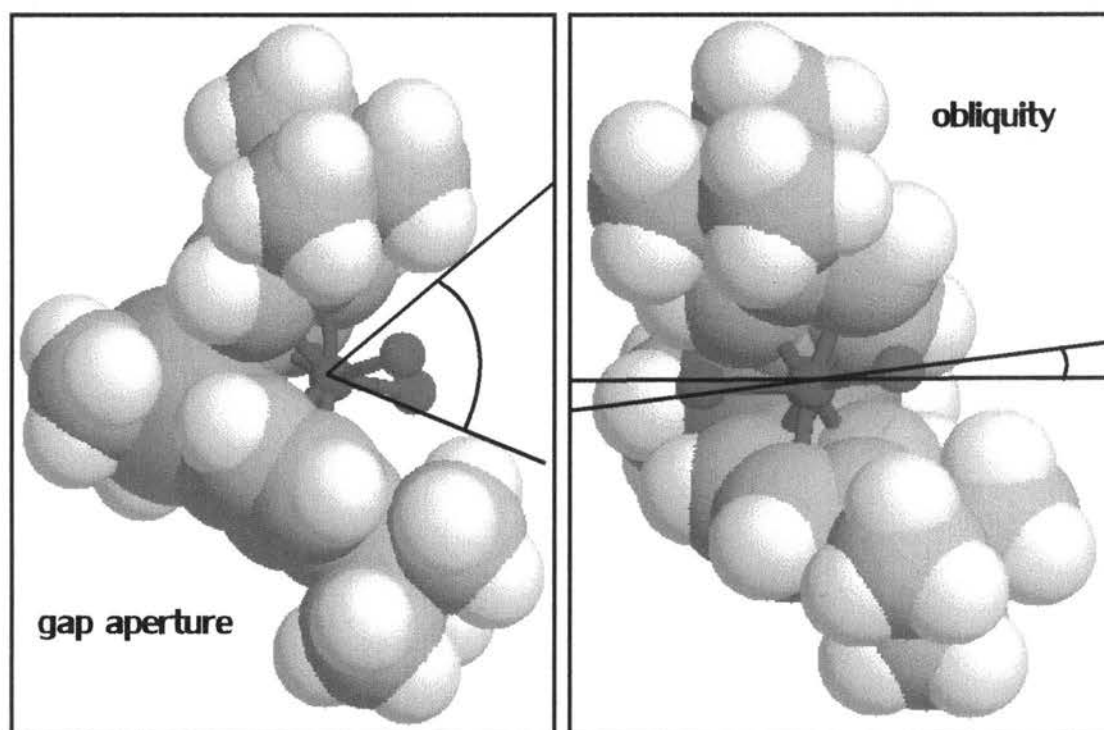
Figure 3.5 Illustrating of gap aperture and obliquity of zirconocenes.

3.3.3 Twisted angle

The twisted angle is defined as the angle between the projection of the vector pass through center of mass of the Cp ring and bisecting it as shown in Figure 3.6. This twisted angle is another indicator for the openness of zirconocene coordination site.
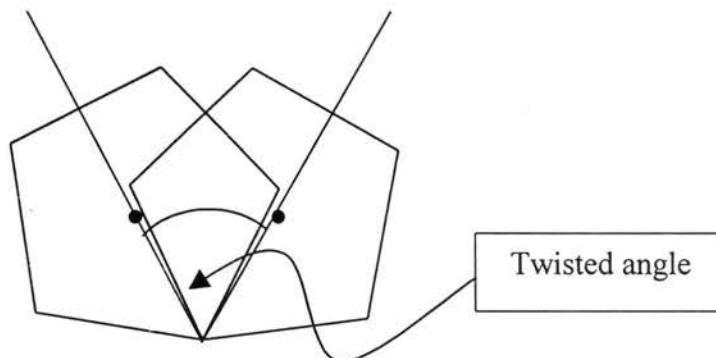
Figure 3.6 The illustration of twisted angle between two cyclopentadienyl rings of zirconocenes.

3.3.4 Cavity distance and Cavity angle

The cavity distance is the closest distance between 2 hydrogen atoms of the bulky group at β-substituents in each cyclopentadienyl rings (excluding van der Walls radius) as displayed in Figure 3.7. The cavity distance is the size of the entrance of the zirconocene cavity. The orientation as well as the % isotacticity of the elongated polypropylene should be controlled by this cavity distance. The cavity angle is the angle of H-Zr-H where as H is hydrogen atom of the bulky group at β-substituents in each cyclopentadienyl rings (excluding van der Walls radius) as displayed in Figure 3.8. Again this cavity angle represents the openness of the zirconocene cavity.
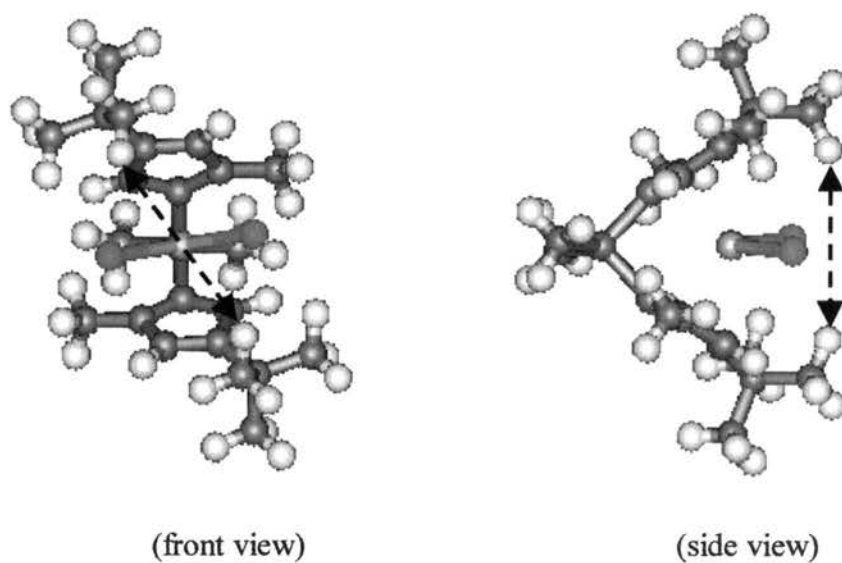
(front view)　　　　(side view)

Figure 3.7 The illustration of cavity distance of hydrogen atom at β-substituents.
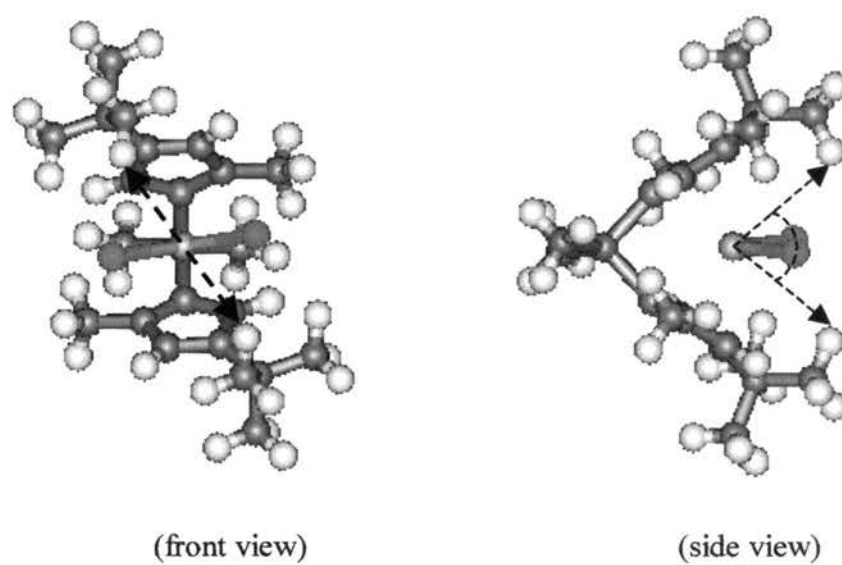

(front view)　　　　(side view)

Figure 3.8 The illustration of cavity angle of hydrogen atom at β-substituents.

3.3.5 Atomic charges

The atomic charges or net charge is the difference between nuclear charge and the charge of electrons around the nucleus. The Mulliken charge computed from quantum mechanical calculation were taken. The definition is given as

$$q_\mu = P_{\mu\mu} + \sum_{\nu \neq \mu} P_{\mu\nu} S_{\mu\nu} \qquad (3.3)$$

$P_{\mu\nu}$ are the elements of the density matrix. $S_{\mu\nu}$ is the overlap matrix over basis functions.