CHAPTER 4

RESULTS

4.1 Optimized Structure of Zirconocene using QM and ONIOM

Structural parameters such as bond distance, bond angle and torsion angle of 5 neutrally charged zirconocene obtained from QM and ONIOM calculations were presented in Tables 4.1 – 4.5.

4.1.1 $(Me_2C)_2(4\text{-}tBu\text{-}C_5H_3)_2ZrCl_2$

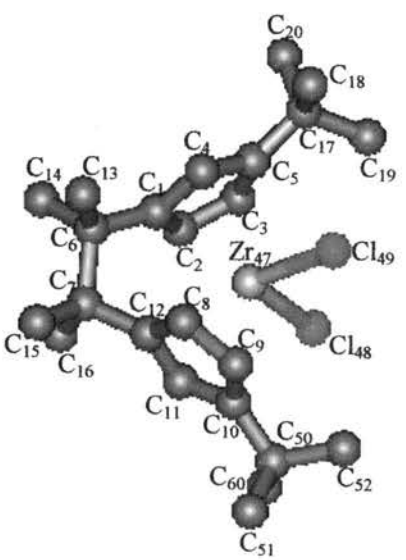


Figure 4.1 Zirconocene **structure 1** with atomic numbering.

Table 4.1 Structural parameters of $(Me_2C)_2(4\text{-}t\text{Bu-}C_5H_3)_2ZrCl_2$ obtained at various levels of theory.

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_1-C_2	1.429	1.431	1.436
C_2-C_3	1.422	1.422	1.416
C_3-C_5	1.415	1.416	1.416
C_5-C_4	1.432	1.432	1.432
C_4-C_1	1.428	1.428	1.434
C_1-C_6	1.533	1.532	1.548
C_6-C_7	1.604	1.605	1.661
C_7-C_{12}	1.533	1.533	1.550
C_{12}-C_{11}	1.428	1.429	1.439
C_{11}-C_{10}	1.432	1.433	1.441
C_{10}-C_9	1.415	1.416	1.416
C_9-C_8	1.422	1.424	1.416
C_8-C_{12}	1.429	1.429	1.429
C_6-C_{13}	1.548	1.547	1.542
C_6-C_{14}	1.552	1.551	1.538
C_7-C_{15}	1.552	1.551	1.540
C_7-C_{16}	1.548	1.548	1.542
C_5-C_{17}	1.529	1.529	1.525
C_{17}-C_{18}	1.542	1.542	1.543
C_{17}-C_{19}	1.544	1.545	1.541
C_{17}-C_{20}	1.553	1.552	1.542
Zr_{47}-Cl_{48}	2.479	2.510	2.473
Zr_{47}-Cl_{49}	2.479	2.515	2.481
C_{10}-C_{50}	1.529	1.529	1.530

Table 4.1 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_{50}-C_{51}	1.553	1.553	1.544
C_{50}-C_{52}	1.544	1.544	1.545
C_{50}-C_{60}	1.542	1.542	1.545
Angle (°)			
$C_1\hat{C}_2C_3$	108.7	108.7	109.3
$C_2\hat{C}_3C_5$	109.1	109.1	108.6
$C_3\hat{C}_5C_4$	106.2	106.2	106.9
$C_5\hat{C}_4C_1$	110.1	110.1	109.6
$C_4\hat{C}_1C_2$	105.9	105.9	105.5
$C_4\hat{C}_1C_6$	127.0	127.0	128.5
$C_2\hat{C}_1C_6$	127.0	126.9	125.7
$C_1\hat{C}_6C_7$	110.1	110.0	110.0
$C_1\hat{C}_6C_{14}$	107.5	107.5	107.4
$C_1\hat{C}_6C_{13}$	109.3	109.3	108.8
$C_6\hat{C}_7C_{12}$	110.1	110.0	110.0
$C_6\hat{C}_7C_{16}$	112.2	112.3	112.6
$C_6\hat{C}_7C_{15}$	111.9	111.9	112.2
$C_7\hat{C}_{12}C_8$	127.0	126.9	125.0
$C_7\hat{C}_{12}C_{11}$	127.0	127.0	129.4
$C_{12}\hat{C}_{11}C_{10}$	110.1	110.0	109.6
$C_{11}\hat{C}_{10}C_9$	106.2	106.2	106.3
$C_{10}\hat{C}_9C_8$	109.1	109.1	109.0
$C_9\hat{C}_8C_{12}$	108.7	108.7	109.4
$C_8\hat{C}_{12}C_{11}$	105.9	105.9	105.5
$C_3\hat{C}_5C_{17}$	125.6	125.5	124.4

Table 4.1 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Angle (°)			
$C_4\hat{C}_5C_{17}$	127.3	127.5	128.1
$C_5\hat{C}_{17}C_{18}$	111.8	111.7	111.5
$C_5\hat{C}_{17}C_{19}$	111.8	111.7	110.2
$C_5\hat{C}_{17}C_{20}$	106.6	106.7	108.7
$C_{11}\hat{C}_{10}C_{50}$	127.3	127.3	127.6
$C_9\hat{C}_{10}C_{50}$	125.6	125.5	124.3
$C_{10}\hat{C}_{50}C_{51}$	106.6	106.4	107.2
$C_{10}\hat{C}_{50}C_{52}$	111.8	111.8	111.9
$C_{10}\hat{C}_{50}C_{60}$	111.8	111.9	112.1
$Cl_{48}\hat{Z}r_{47}Cl_{49}$	101.0	102.8	99.8
Torsion (°)			
$C_1C_2C_3C_5$	0.5	0.4	1.4
$C_2C_3C_5C_4$	1.5	1.2	0.2
$C_3C_5C_4C_1$	-2.9	-2.5	-1.7
$C_5C_4C_1C_2$	3.2	2.8	2.5
$C_4C_1C_6C_7$	-123.7	-124.7	-125.1
$C_2C_1C_6C_7$	61.5	60.5	61.3
$C_1C_6C_7C_{12}$	35.2	35.1	31.3
$C_8C_{12}C_7C_6$	61.5	62.6	68.9
$C_{11}C_{12}C_7C_6$	-123.7	-122.3	-115.5
$C_{12}C_{11}C_{10}C_9$	-2.9	-3.1	-0.7
$C_{11}C_{10}C_9C_8$	1.5	1.7	-1.7
$C_{10}C_9C_8C_{12}$	0.5	0.3	3.4
$C_9C_8C_{12}C_{11}$	-2.2	-2.1	-3.7

4.1.2 $Me_2Si(4\text{-}tBu\text{-}C_5H_3)_2ZrCl_2$

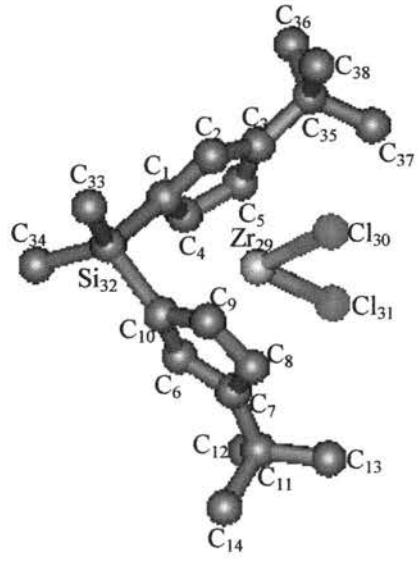


Figure 4.2 Zirconocene **structure 2** with atomic numbering.

Table 4.2 Structural parameters of $Me_2Si(4\text{-}tBu\text{-}C_5H_3)_2ZrCl_2$ obtained at various levels of theory.

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_1-C_2	1.439	1.441	1.440
C_2-C_3	1.429	1.430	1.434
C_3-C_5	1.420	1.420	1.425
C_5-C_4	1.423	1.424	1.422
C_4-C_1	1.426	1.427	1.430
C_{10}-C_9	1.437	1.439	1.438
C_9-C_8	1.418	1.419	1.417

Table 4.2 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_8-C_7	1.420	1.420	1.420
C_7-C_6	1.430	1.430	1.433
C_6-C_{10}	1.430	1.432	1.431
C_7-C_{11}	1.529	1.528	1.526
C_{11}-C_{12}	1.542	1.542	1.543
C_{11}-C_{13}	1.545	1.545	1.541
C_{11}-C_{14}	1.552	1.551	1.542
C_3-C_{35}	1.527	1.526	1.531
C_{35}-C_{36}	1.553	1.554	1.541
C_{35}-C_{37}	1.544	1.543	1.544
C_{35}-C_{38}	1.543	1.543	1.544
Zr_{29}-Cl_{30}	2.469	2.500	2.456
Zr_{29}-Cl_{31}	2.478	2.511	2.436
C_1-Si_{32}	1.881	1.573	1.895
Si_{32}-C_{10}	1.880	1.873	1.878
Si_{32}-C_{33}	1.880	1.866	1.881
Si_{32}-C_{34}	1.879	1.865	1.880
Angle (°)			
$C_1\hat{C}_2C_3$	110.0	110.1	110.0
$C_2\hat{C}_3C_5$	106.2	106.2	106.4
$C_3\hat{C}_5C_4$	108.9	108.8	108.7
$C_5\hat{C}_4C_1$	109.1	109.3	109.4
$C_4\hat{C}_1C_2$	105.6	105.4	105.5
$C_1\hat{Si}_{32}C_{10}$	95.3	95.3	96.1
$C_1\hat{Si}_{32}C_{33}$	112.4	112.4	112.7

Table 4.2 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Angle (°)			
$C_1\hat{S}i_{32}C_{34}$	111.8	111.8	112.7
$C_{33}\hat{S}i_{32}C_{34}$	111.9	112.0	111.8
$C_{10}\hat{S}i_{32}C_{33}$	112.2	112.1	112.9
$C_9\hat{C}_{10}Si_{32}$	123.2	123.3	123.4
$C_6\hat{C}_{10}Si_{32}$	127.3	127.4	126.4
$C_{10}\hat{C}_6C_7$	110.3	110.4	109.3
$C_6\hat{C}_7C_8$	106.2	106.2	107.1
$C_7\hat{C}_8C_9$	109.1	109.0	108.5
$C_8\hat{C}_9C_{10}$	108.9	109.0	109.0
$C_2\hat{C}_3C_{35}$	126.6	126.7	125.8
$C_5\hat{C}_3C_{35}$	126.2	126.2	125.5
$C_3\hat{C}_{35}C_{36}$	106.1	106.0	107.8
$C_3\hat{C}_{35}C_{37}$	111.8	111.8	111.4
$C_3\hat{C}_{35}C_{38}$	112.1	112.1	111.5
$C_6\hat{C}_7C_{11}$	127.8	127.9	128.1
$C_8\hat{C}_7C_{11}$	125.4	125.5	124.4
$C_7\hat{C}_{11}C_{12}$	111.5	111.4	111.5
$C_7\hat{C}_{11}C_{13}$	111.5	111.4	110.2
$C_7\hat{C}_{11}C_{14}$	107.1	107.1	108.7
$Cl_{30}\hat{Z}r_{29}Cl_{31}$	100.1	101.4	99.1
Torsion (°)			
$C_1C_4C_5C_3$	-1.2	-1.4	1.4
$C_4C_5C_3C_2$	3.6	3.8	-0.8
$C_5C_3C_2C_1$	-4.8	-4.8	-0.1

Table 4.2 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Torsion (°)			
$C_2C_1Si_{32}C_{10}$	-69.4	-69.0	-66.7
$C_4C_1Si_{32}C_{10}$	84.4	84.5	84.8
$C_2C_1Si_{32}C_{33}$	47.2	47.6	51.3
$C_2C_1Si_{32}C_{34}$	174.1	174.5	179.1
$C_6C_{10}Si_{32}C_{33}$	155.7	156.0	154.4
$C_9C_{10}Si_{32}C_{33}$	-49.9	-49.8	-52.0
$C_6C_{10}Si_{32}C_{34}$	28.6	29.0	29.0
$C_9C_{10}Si_{32}C_{34}$	-177.0	-176.8	-177.3
$C_{10}C_6C_7C_8$	-2.2	-2.0	-1.6
$C_6C_7C_8C_9$	1.0	0.9	0.0
$C_7C_8C_9C_{10}$	0.6	0.5	1.6
$C_8C_9C_{10}C_6$	-2.0	-1.7	-2.5
$C_8C_7C_{11}C_{13}$	-55.6	-56.9	-59.8
$C_6C_7C_{11}C_{13}$	134.1	132.0	128.3
$C_6C_7C_{11}C_{14}$	-106.9	-108.9	-112.4
$C_8C_7C_{11}C_{14}$	63.4	62.2	59.5
$C_6C_7C_{11}C_{12}$	11.5	9.5	7.0
$C_8C_7C_{11}C_{12}$	-178.2	-179.3	178.9
$C_2C_3C_{35}C_{36}$	-86.1	-86.6	-81.3
$C_5C_3C_{35}C_{36}$	81.3	81.2	79.0
$C_2C_3C_{35}C_{37}$	155.7	155.3	160.0
$C_5C_3C_{35}C_{37}$	-36.9	-36.9	-39.7
$C_2C_3C_{35}C_{38}$	32.0	31.6	37.5
$C_5C_3C_{35}C_{38}$	-160.5	-160.6	-162.3

4.1.3 $Me_2Si(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2ZrCl_2$

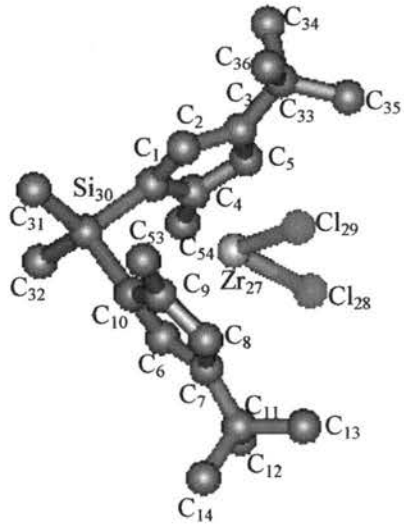


Figure 4.3 Zirconocene **structure 3** with atomic numbering.

Table 4.3 Structural parameters of $Me_2Si(2\text{-}Me\text{-}4\text{-}tBu\text{-}C_5H_2)_2ZrCl_2$ obtained at various levels of theory.

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_1-C_2	1.439	1.441	1.438
C_2-C_3	1.428	1.428	1.430
C_3-C_5	1.416	1.417	1.422
C_5-C_4	1.427	1.427	1.426
C_4-C_1	1.436	1.437	1.436
C_{10}-C_9	1.436	1.437	1.434

Table 4.3 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_9-C_8	1.427	1.427	1.424
C_8-C_7	1.416	1.417	1.417
C_7-C_6	1.428	1.428	1.435
C_6-C_{10}	1.439	1.441	1.441
C_7-C_{11}	1.528	1.528	1.527
C_{11}-C_{12}	1.542	1.542	1.544
C_{11}-C_{13}	1.544	1.544	1.543
C_{11}-C_{14}	1.553	1.553	1.541
C_1-Si_{30}	1.884	1.876	1.904
Si_{30}-C_{10}	1.884	1.876	1.900
Si_{30}-C_{31}	1.884	1.871	1.899
Si_{30}-C_{32}	1.884	1.871	1.865
C_3-C_{33}	1.528	1.528	1.522
C_{33}-C_{34}	1.553	1.553	1.547
C_{33}-C_{35}	1.544	1.544	1.548
C_{33}-C_{36}	1.542	1.542	1.549
C_4-C_{54}	1.509	1.508	1.495
C_9-C_{53}	1.509	1.508	1.496
Zr_{27}-Cl_{28}	2.476	2.507	2.530
Zr_{27}-Cl_{29}	2.476	2.507	2.548
Angle (°)			
$C_1\hat{C}_2C_3$	110.1	110.2	110.4
$C_2\hat{C}_3C_5$	105.9	105.9	106.6
$C_3\hat{C}_5C_4$	110.0	110.0	108.3
$C_5\hat{C}_4C_1$	107.7	107.9	109.6

Table 4.3 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Angle (°)			
$C_4\hat{C}_1C_2$	106.1	105.9	105.0
$C_2\hat{C}_1Si_{30}$	121.1	120.9	117.3
$C_4\hat{C}_1Si_{30}$	129.1	129.3	132.5
$C_1\hat{S}i_{30}C_{10}$	95.0	95.1	93.7
$C_1\hat{S}i_{30}C_{31}$	111.5	111.4	111.7
$C_1\hat{S}i_{30}C_{32}$	115.4	115.4	119.5
$C_{10}\hat{S}i_{30}C_{31}$	115.4	115.4	116.7
$C_{10}\hat{S}i_{30}C_{32}$	111.5	111.3	109.0
$C_6\hat{C}_{10}Si_{30}$	121.1	121.0	120.4
$C_9\hat{C}_{10}Si_{30}$	129.0	129.3	130.9
$C_{10}\hat{C}_6C_7$	110.1	110.2	109.9
$C_6\hat{C}_7C_8$	105.9	105.9	106.8
$C_7\hat{C}_8C_9$	110.0	110.0	108.5
$C_8\hat{C}_9C_{10}$	107.7	107.9	109.6
$C_9\hat{C}_{10}C_6$	106.1	105.9	105.2
$C_6\hat{C}_7C_{11}$	127.5	127.6	126.9
$C_8\hat{C}_7C_{11}$	125.6	125.6	124.6
$C_7\hat{C}_{11}C_{12}$	111.8	111.8	111.4
$C_7\hat{C}_{11}C_{13}$	112.0	111.9	110.8
$C_7\hat{C}_{11}C_{14}$	106.3	106.2	108.3
$C_2\hat{C}_3C_{33}$	127.5	127.6	125.6
$C_5\hat{C}_3C_{33}$	125.7	125.6	125.8
$C_3\hat{C}_{33}C_{34}$	106.3	106.2	106.3
$C_3\hat{C}_{33}C_{35}$	112.0	111.9	122.3
$C_3\hat{C}_{33}C_{36}$	111.8	111.8	113.4

Table 4.3 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Angle (°)			
$C_1\hat{C}_4C_{54}$	128.5	128.6	126.0
$C_5\hat{C}_4C_{54}$	123.5	123.3	124.4
$C_8\hat{C}_9C_{53}$	123.5	123.3	124.0
$C_{10}\hat{C}_9C_{53}$	128.5	128.6	126.3
$Cl_{28}\hat{Z}r_{27}Cl_{29}$	99.7	101.6	99.4
Torsion (°)			
$C_1C_2C_3C_5$	-4.2	-4.3	1.1
$C_2C_3C_5C_4$	3.0	3.2	-2.6
$C_3C_5C_4C_1$	-0.8	-1.0	3.3
$C_5C_4C_1C_2$	-1.8	-1.6	-2.5
$C_2C_1C_4C_{54}$	-176.1	-176.1	179.7
$C_3C_5C_4C_{54}$	173.9	173.9	-178.9
$C_2C_1Si_{30}C_{10}$	-77.3	-76.9	-75.7
$C_4C_1Si_{30}C_{10}$	77.8	77.7	74.7
$C_2C_1Si_{30}C_{31}$	42.6	42.9	45.0
$C_2C_1Si_{30}C_{32}$	166.1	166.5	170.1
$C_4C_1Si_{30}C_{31}$	-162.4	-162.4	-164.6
$C_4C_1Si_{30}C_{32}$	-38.9	-38.8	-39.6
$C_6C_{10}Si_{30}C_{31}$	166.0	166.4	166.3
$C_6C_{10}Si_{30}C_{32}$	42.4	42.8	45.7
$C_9C_{10}Si_{30}C_{31}$	-39.0	-38.9	-38.5
$C_9C_{10}Si_{30}C_{32}$	-162.5	-162.5	-159.0
$C_{10}C_6C_7C_8$	-4.1	-4.3	-2.1
$C_6C_7C_8C_9$	3.0	3.2	0.3

Table 4.3 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Torsion (°)			
$C_7C_8C_9C_{10}$	-0.8	-1.0	1.7
$C_7C_8C_9C_{53}$	173.9	173.9	178.2
$C_6C_{10}C_9C_{53}$	-176.1	-176.1	-179.4
$C_6C_7C_{11}C_{12}$	22.3	21.0	23.3
$C_6C_7C_{11}C_{13}$	145.9	144.6	145.1
$C_6C_7C_{11}C_{14}$	-95.7	-97.0	-95.9
$C_8C_7C_{11}C_{12}$	-170.6	-171.4	-173.4
$C_8C_7C_{11}C_{13}$	-47.0	-47.8	-51.7
$C_8C_7C_{11}C_{14}$	71.4	70.6	67.3
$C_2C_3C_{33}C_{34}$	-95.6	-96.9	-92.5
$C_2C_3C_{33}C_{35}$	146.0	144.7	151.4
$C_2C_3C_{33}C_{36}$	22.4	21.1	24.1
$C_5C_3C_{33}C_{34}$	71.5	70.7	69.4
$C_5C_3C_{33}C_{35}$	-46.9	-47.7	-46.7
$C_5C_3C_{33}C_{36}$	-170.5	-171.3	-174.1

4.1.4 $Me_2Si(2\text{-}Me\text{-}4\text{-}i\text{Pr-}C_5H_2)_2ZrCl_2$

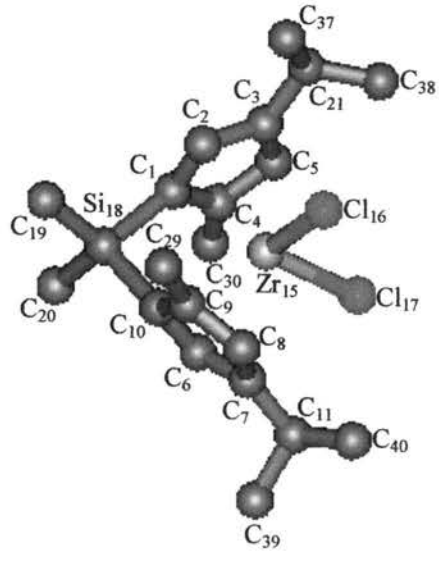


Figure 4.4 Zirconocene **structure 4** with atomic numbering.

Table 4.4 Structural parameters of $Me_2Si(2\text{-}Me\text{-}4\text{-}i\text{Pr-}C_5H_2)_2ZrCl_2$ obtained at various levels of theory.

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_1-C_2	1.439	1.441	1.435
C_2-C_3	1.427	1.427	1.419
C_3-C_5	1.417	1.417	1.419
C_5-C_4	1.425	1.426	1.466
C_4-C_1	1.438	1.439	1.446
C_{10}-C_9	1.435	1.436	1.452
C_9-C_8	1.429	1.429	1.425
C_8-C_7	1.414	1.414	1.414

Table 4.4 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_7-C_6	1.427	1.427	1.419
C_6-C_{10}	1.439	1.442	1.436
C_7-C_{11}	1.513	1.513	1.512
C_{11}-C_{39}	1.546	1.546	1.532
C_{11}-C_{40}	1.536	1.536	1.534
C_1-Si_{18}	1.886	1.877	1.888
Si_{18}-C_{10}	1.886	1.878	1.879
Si_{18}-C_{19}	1.884	1.870	1.880
Si_{18}-C_{20}	1.884	1.871	1.879
C_3-C_{21}	1.521	1.521	1.520
C_{21}-C_{37}	1.538	1.537	1.535
C_{21}-C_{38}	1.541	1.541	1.535
C_4-C_{30}	1.509	1.508	1.519
C_9-C_{29}	1.508	1.508	1.510
Zr_{15}-Cl_{16}	2.477	2.509	2.438
Zr_{15}-Cl_{17}	2.474	2.507	2.441
Angle (°)			
$C_1\hat{C}_2C_3$	110.1	110.2	109.4
$C_2\hat{C}_3C_5$	106.0	106.0	109.0
$C_3\hat{C}_5C_4$	110.0	110.0	106.8
$C_5\hat{C}_4C_1$	107.8	107.9	108.2
$C_4\hat{C}_1C_2$	106.0	105.9	106.3
$C_2\hat{C}_1Si_{18}$	121.6	121.4	113.5
$C_4\hat{C}_1Si_{18}$	128.5	128.7	138.6
$C_1\hat{Si}_{18}C_{10}$	95.0	95.1	98.1

Table 4.4 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Angle (°)			
$C_1\hat{S}i_{18}C_{19}$	111.4	111.3	112.0
$C_1\hat{S}i_{18}C_{20}$	115.3	115.4	113.6
$C_{10}\hat{S}i_{18}C_{19}$	115.4	115.5	112.3
$C_{10}\hat{S}i_{18}C_{20}$	111.5	111.2	111.4
$C_6\hat{C}_{10}Si_{18}$	120.6	120.4	114.8
$C_9\hat{C}_{10}Si_{18}$	129.4	129.7	134.7
$C_{10}\hat{C}_6C_7$	110.0	110.1	110.1
$C_6\hat{C}_7C_8$	106.2	106.2	107.4
$C_7\hat{C}_8C_9$	109.8	109.8	108.7
$C_8\hat{C}_9C_{10}$	107.9	108.0	108.5
$C_6\hat{C}_7C_{11}$	125.8	125.9	124.3
$C_8\hat{C}_7C_{11}$	127.8	127.8	128.3
$C_7\hat{C}_{11}C_{39}$	109.6	109.5	110.2
$C_7\hat{C}_{11}C_{40}$	113.2	113.2	112.4
$C_2\hat{C}_3C_{21}$	128.0	128.0	126.7
$C_5\hat{C}_3C_{21}$	125.4	125.4	123.4
$C_3\hat{C}_{21}C_{37}$	113.6	113.6	112.8
$C_3\hat{C}_{21}C_{38}$	113.6	113.6	112.2
$C_1\hat{C}_4C_{30}$	128.6	128.7	123.0
$C_5\hat{C}_4C_{30}$	123.3	123.1	128.8
$C_8\hat{C}_9C_{29}$	123.6	123.4	122.0
$C_{10}\hat{C}_9C_{29}$	128.3	128.4	129.6
$Cl_{16}\hat{Z}r_{15}Cl_{17}$	101.2	103.3	99.6

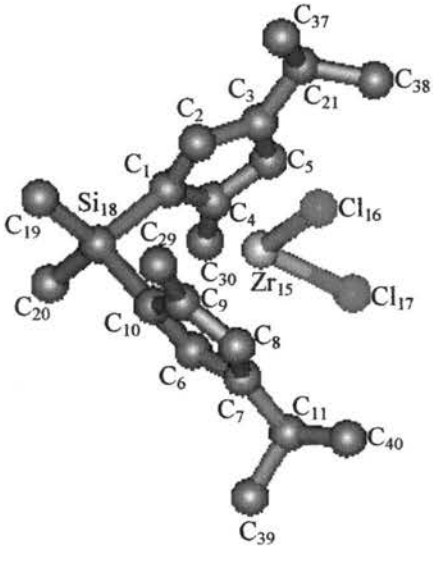
Table 4.4 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Torsion (°)			
$C_1C_2C_3C_5$	-3.3	-3.5	-2.3
$C_2C_3C_5C_4$	2.3	2.6	-1.1
$C_3C_5C_4C_1$	-0.6	-0.8	4.0
$C_5C_4C_1C_2$	-1.4	-1.4	-5.3
$C_2C_1C_4C_{30}$	-175.4	-175.6	175.1
$C_3C_5C_4C_{30}$	173.8	173.9	-176.4
$C_2C_1Si_{18}C_{10}$	-79.9	-79.3	-75.2
$C_4C_1Si_{18}C_{10}$	74.8	75.0	87.4
$C_2C_1Si_{18}C_{19}$	39.9	40.6	42.9
$C_2C_1Si_{18}C_{20}$	163.4	164.3	167.1
$C_4C_1Si_{18}C_{19}$	-165.4	-165.0	-154.5
$C_4C_1Si_{18}C_{20}$	-41.9	-41.3	-30.3
$C_6C_{10}Si_{18}C_{19}$	170.5	170.5	157.4
$C_6C_{10}Si_{18}C_{20}$	46.8	46.8	34.7
$C_9C_{10}Si_{18}C_{19}$	-35.4	-35.6	-52.6
$C_9C_{10}Si_{18}C_{20}$	-159.0	-159.3	-175.3
$C_{10}C_6C_7C_8$	-3.6	-3.7	-1.4
$C_6C_7C_8C_9$	2.4	2.7	-0.2
$C_7C_8C_9C_{10}$	-0.4	-0.6	1.7
$C_7C_8C_9C_{29}$	174.6	174.5	-178.1
$C_6C_{10}C_9C_{29}$	-176.5	-176.5	177.3
$C_6C_7C_{11}C_{39}$	-71.1	-72.8	-64.4
$C_6C_7C_{11}C_{40}$	164.7	163.0	172.1
$C_8C_7C_{11}C_{39}$	103.0	101.7	112.5
$C_8C_7C_{11}C_{40}$	-21.3	-22.6	-11.0

Table 4.4 (continue)

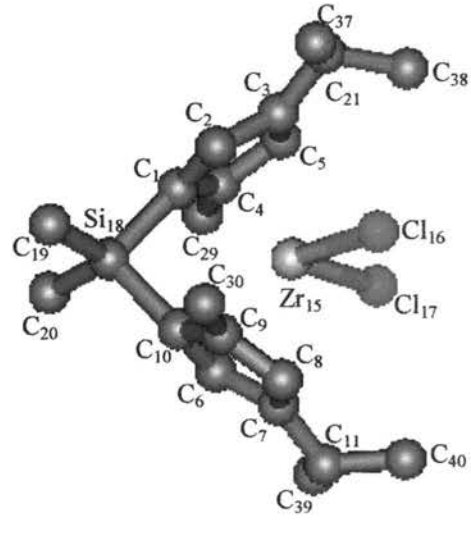
	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Torsion (°)			
$C_2C_3C_{21}C_{37}$	14.7	13.7	7.5
$C_2C_3C_{21}C_{38}$	143.6	142.6	132.3
$C_5C_3C_{21}C_{37}$	-176.4	-176.8	175.7
$C_5C_3C_{21}C_{38}$	-47.5	-47.8	-59.5

There are 2 conformers, conformer I and conformer II, for **structure 4**. The geometry as given in Table 4.4, is that of conformer I. These 2 conformers are different in the orientation of *i*Pr group as shown below. Conformer I has C_1 symmetry (*i*Pr's C pointing in the same direction) and conformer II has C_2 symmetry (*i*Pr's C pointing in the different direction). At B3LYP/DZVP, Conformer I is 2.96 kcal/mol more stable than conformer II.



Conformer I

C_1 symmetry



Conformer II

C_2 symmetry

4.1.5 $(CH_2)_2$(tetrahydroindenyl)$_2ZrCl_2$

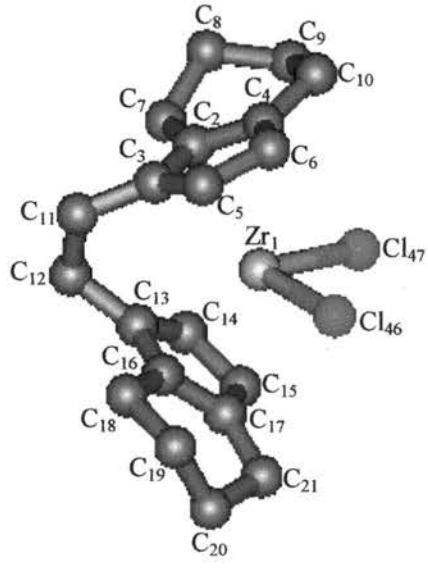


Figure 4.5 Zirconocene **structure 5** with atomic numbering.

Table 4.5 Structural parameters of $(CH_2)_2$(tetrahydroindenyl)$_2ZrCl_2$ obtained at various levels of theory.

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_3-C_2	1.432	1.433	1.439
C_2-C_4	1.429	1.430	1.422
C_4-C_6	1.416	1.416	1.411
C_6-C_5	1.425	1.426	1.428
C_5-C_3	1.424	1.424	1.429
C_2-C_7	1.514	1.513	1.502
C_7-C_8	1.542	1.542	1.538

Table 4.5 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Distance (Å)			
C_8-C_9	1.537	1.537	1.539
C_9-C_{10}	1.542	1.542	1.543
C_{10}-C_4	1.507	1.507	1.502
C_3-C_{11}	1.510	1.510	1.460
C_{11}-C_{12}	1.546	1.547	1.256
C_{12}-C_{13}	1.512	1.512	1.451
C_{13}-C_{14}	1.426	1.426	1.436
C_{14}-C_{15}	1.425	1.425	1.421
C_{15}-C_{17}	1.414	1.414	1.414
C_{17}-C_{16}	1.432	1.433	1.421
C_{16}-C_{13}	1.431	1.431	1.438
C_{16}-C_{18}	1.512	1.512	1.504
C_{18}-C_{19}	1.542	1.541	1.542
C_{19}-C_{20}	1.537	1.537	1.538
C_{20}-C_{21}	1.542	1.542	1.539
C_{21}-C_{17}	1.507	1.507	1.500
Zr_1-Cl_{46}	2.475	2.507	2.439
Zr_1-Cl_{47}	2.475	2.507	2.434
Angle (°)			
$C_3\hat{C}_5C_6$	108.6	108.6	108.6
$C_5\hat{C}_6C_4$	108.0	108.0	107.7
$C_6\hat{C}_4C_2$	108.0	108.0	108.8
$C_4\hat{C}_2C_3$	108.2	108.1	107.9
$C_2\hat{C}_3C_5$	107.2	107.2	106.9
$C_2\hat{C}_3C_{11}$	126.9	126.9	125.4

Table 4.5 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Angle (°)			
$C_5\hat{C}_3C_{11}$	125.9	125.9	125.1
$C_3\hat{C}_{11}C_{12}$	112.0	112.0	120.8
$C_{11}\hat{C}_{12}C_{13}$	112.5	112.5	126.4
$C_{12}\hat{C}_{13}C_{14}$	125.4	125.3	125.1
$C_{12}\hat{C}_{13}C_{16}$	127.5	127.5	127.1
$C_{13}\hat{C}_{14}C_{15}$	108.6	108.6	109.4
$C_{14}\hat{C}_{15}C_{17}$	108.1	108.1	107.1
$C_{15}\hat{C}_{17}C_{16}$	108.0	108.0	109.2
$C_{17}\hat{C}_{16}C_{13}$	108.2	108.1	108.1
$C_3\hat{C}_2C_7$	129.1	129.1	127.6
$C_2\hat{C}_7C_8$	110.2	110.2	110.7
$C_7\hat{C}_8C_9$	111.3	111.3	111.4
$C_8\hat{C}_9C_{10}$	112.1	112.1	112.3
$C_9\hat{C}_{10}C_4$	112.2	112.2	111.8
$C_{10}\hat{C}_4C_6$	128.3	128.3	127.1
$C_{13}\hat{C}_{16}C_{18}$	128.8	128.8	128.1
$C_{16}\hat{C}_{18}C_{19}$	111.9	111.9	111.8
$C_{18}\hat{C}_{19}C_{20}$	111.9	111.9	112.4
$C_{19}\hat{C}_{20}C_{21}$	111.5	111.5	111.9
$C_{20}\hat{C}_{21}C_{17}$	110.7	110.6	110.8
$C_{21}\hat{C}_{17}C_{15}$	128.7	128.7	127.0
Torsion (°)			
$C_3C_2C_4C_6$	2.0	2.1	4.4
$C_2C_4C_6C_5$	-1.6	-1.6	-2.9

Table 4.5 (continue)

	QM		ONIOM
Parameter	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Torsion (°)			
$C_4C_6C_5C_3$	0.5	0.5	0.3
$C_6C_5C_3C_2$	0.8	0.8	2.3
$C_5C_3C_{11}C_{12}$	-118.8	-118.4	-109.9
$C_2C_3C_{11}C_{12}$	60.7	60.9	49.3
$C_3C_{11}C_{12}C_{13}$	39.9	39.1	45.7
$C_{11}C_{12}C_{13}C_{14}$	-115.9	-115.7	-113.3
$C_{11}C_{12}C_{13}C_{16}$	64.5	64.7	50.0
$C_{13}C_{14}C_{15}C_{17}$	0.0	0.1	-1.8
$C_{14}C_{15}C_{17}C_{16}$	-1.5	-1.6	-0.3
$C_{15}C_{17}C_{16}C_{13}$	2.5	2.4	2.3
$C_{17}C_{16}C_{13}C_{14}$	-2.4	-2.3	-3.3
$C_{13}C_{16}C_{18}C_{19}$	-176.9	-177.0	179.9
$C_{16}C_{18}C_{19}C_{20}$	-43.8	-43.8	-40.5
$C_{18}C_{19}C_{20}C_{21}$	62.8	62.8	61.4
$C_{19}C_{20}C_{21}C_{17}$	-48.0	-48.0	-46.8
$C_{20}C_{21}C_{17}C_{15}$	-155.5	-155.4	-153.9

4.1.6 Comparison with X-ray data [39]

The comparison between the X-ray structure [39] and B3LYP/DZVP optimized structure of **structure 3** ($Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_2)_2ZrCl_2$) was made. Only important geometrical parameters were listed in Table 4.6.

Table 4.6 Comparison between X-ray structure and B3LYP/DZVP optimized structure of **structure 3**.

Bond distance (Å)			Bond angle (°)		
parameter	B3LYP/DZVP	X-ray	parameter	B3LYP/DZVP	X-ray
Zr_{27}-Cl_{29}	2.476	2.420	Cl_{28}-Zr-Cl_{29}	99.7	97.6
Zr_{27}-C_1	2.511	2.470	CR_1-Zr-CR_{1A}[a]	125.7	126.7
Zr_{27}-C_2	2.541	2.484	C_1-Si-C_{10}	95.0	94.3
Zr_{27}-C_3	2.703	2.629	C_{31}-Si-C_{32}	107.9	109.4
Zr_{27}-C_4	2.546	2.504	PL_1-PL_{1A}[a]	61.0	62.6
Zr_{27}-C_5	2.644	2.586			
Si_{30}-C_1	1.884	1.876			
Si_{30}-C_{31}	1.884	1.847			
Zr-Centriod	2.287	2.231			

[a] CR = centroid, PL = mean plane of η^5- C_5 ring

4.1.7 Comparison between computation techniques

The average differences between structural parameters of 5 zirconocenes such as bond distances, bond angles and torsion angles obtained using B3LYP/DZVP and other methods were computed as a mean to compare geometries obtained at various levels of theory. These values were given in Table 4.7. The average difference (mean error) of 5 zirconocene structures was determined using

$$\bar{x} = \frac{\sum_{i}^{N} |x - x_i|}{N} \tag{4.1}$$

where $\bar{x}$ is the mean error of zirconocene structural parameters

x is the reference structural parameter (obtained using B3LYP/DZVP)

x_i is the structural parameter obtained at various levels of theory

N is the numbering of structural parameters

Table 4.7 The average difference of bond distances, bond angles and torsion angles of 5 zirconocene structures.

Parameter	average difference	
	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
Bond distance (Å)	0.0065	0.0114
Bond angle(°)	0.1184	1.3621
Torsion angle(°)	0.4353	26.6086

4.2 Geometrical parameters and their relation to catalytic properties

4.2.1 Distance and angle between Cp planes

The distance and angle between Cp planes which deciphered from structures of zirconocene optimized at the QM and ONIOM levels of theory were given in Table 4.8 and Table 4.9, respectively. Figure 4.6 and 4.7 showed the plot of distance between Cp planes and angle between Cp planes obtained at various levels of theory versus % isotacticity respectively, whereas Figure 4.8 and 4.9 showed the plot of these values versus productivity respectively. The numbering appeared in all plots given in this thesis refers to structure number in Table 4.8.

Table 4.8 The distance between Cp planes (Å) of 5 zirconocene structures from QM and ONIOM calculations.

Structure	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
1	4.019	4.005	4.013
2	4.059	4.045	4.042
3	4.070	4.054	4.002
4	4.053(4.064)[a]	4.036(4.046)[a]	4.262
5	4.030	4.015	4.228

[a]Values in parentheses are the distance between Cp planes of zirconocene structure 4 which has C_2 symmetric.

Table 4.9 The angle between Cp planes (°) of 5 zirconocene structures from QM and ONIOM calculations.

Structure	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
1	58.71	58.36	56.84
2	62.08	61.84	61.02
3	60.99	60.66	57.51
4	60.42(60.96)[a]	60.09(60.57)[a]	68.61
5	56.49	56.03	53.62

[a]Values in parentheses are the angle between Cp planes of zirconocene structure 4 which has C_2 symmetric.

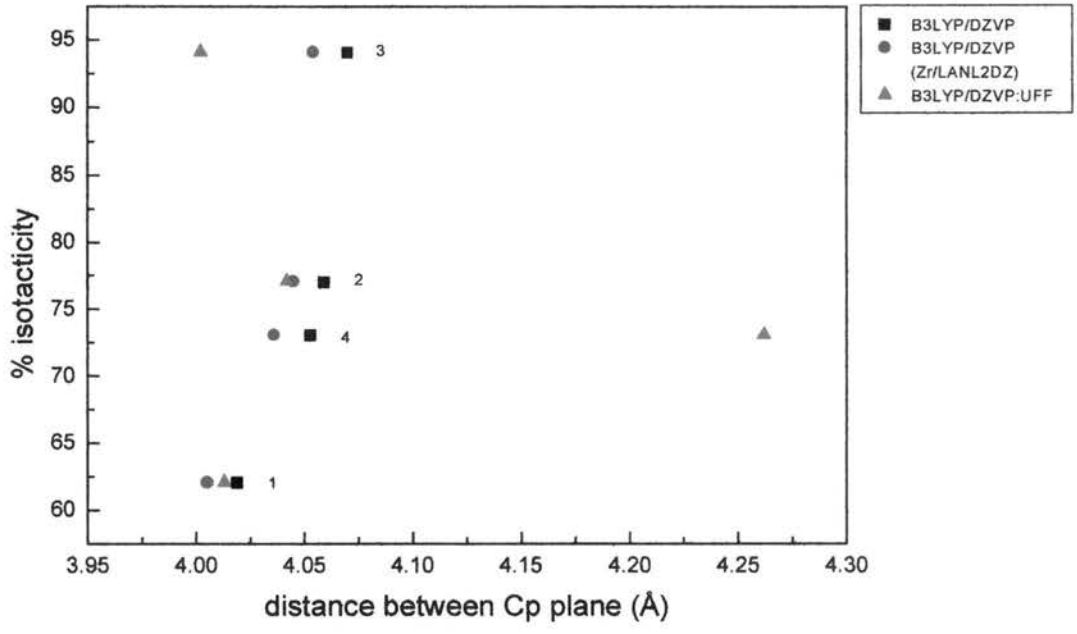


Figure 4.6 Plot of distance between Cp planes obtained at various levels of theory versus % isotacticity.

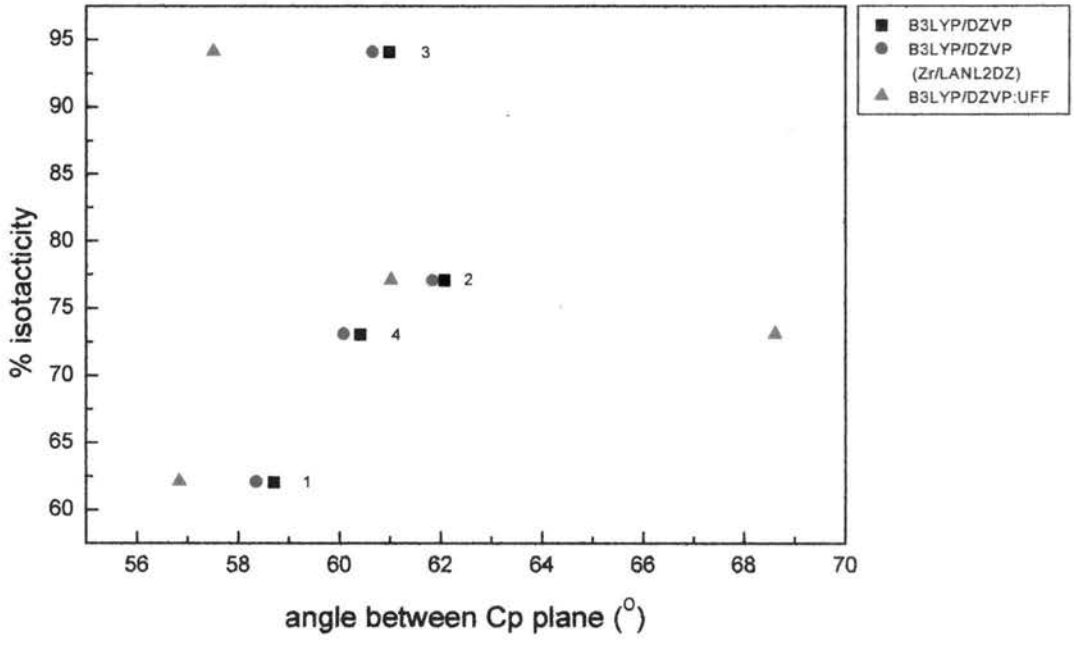


Figure 4.7 Plot of angle between Cp planes obtained at various levels of theory versus % isotacticity.

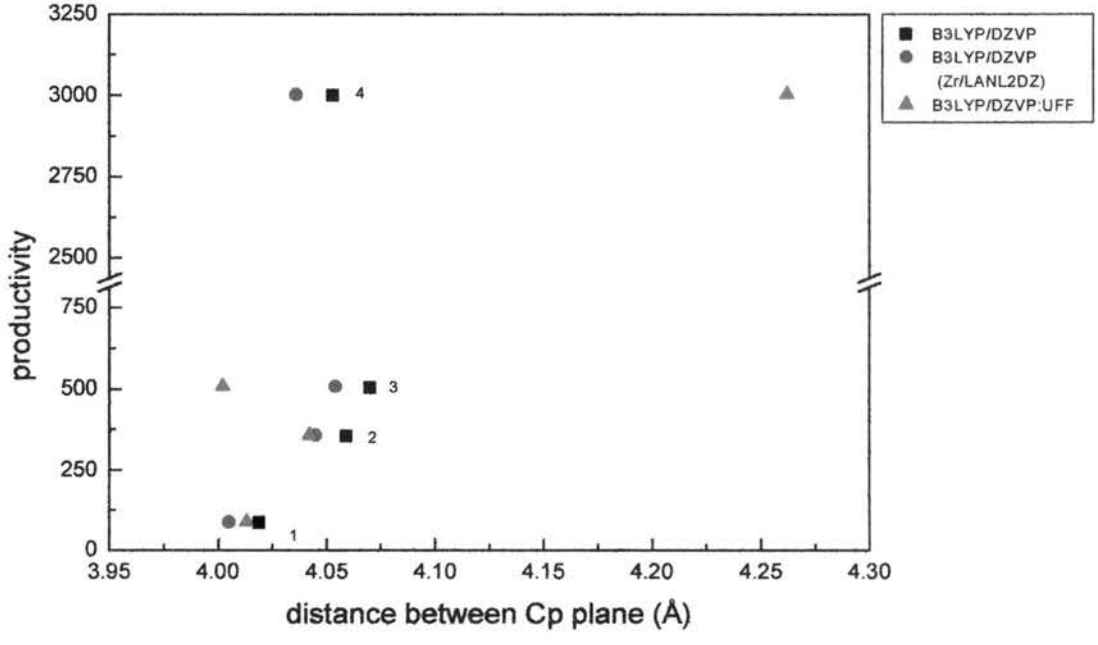


Figure 4.8 Plot of distance between Cp planes obtained at various levels of theory versus productivity.

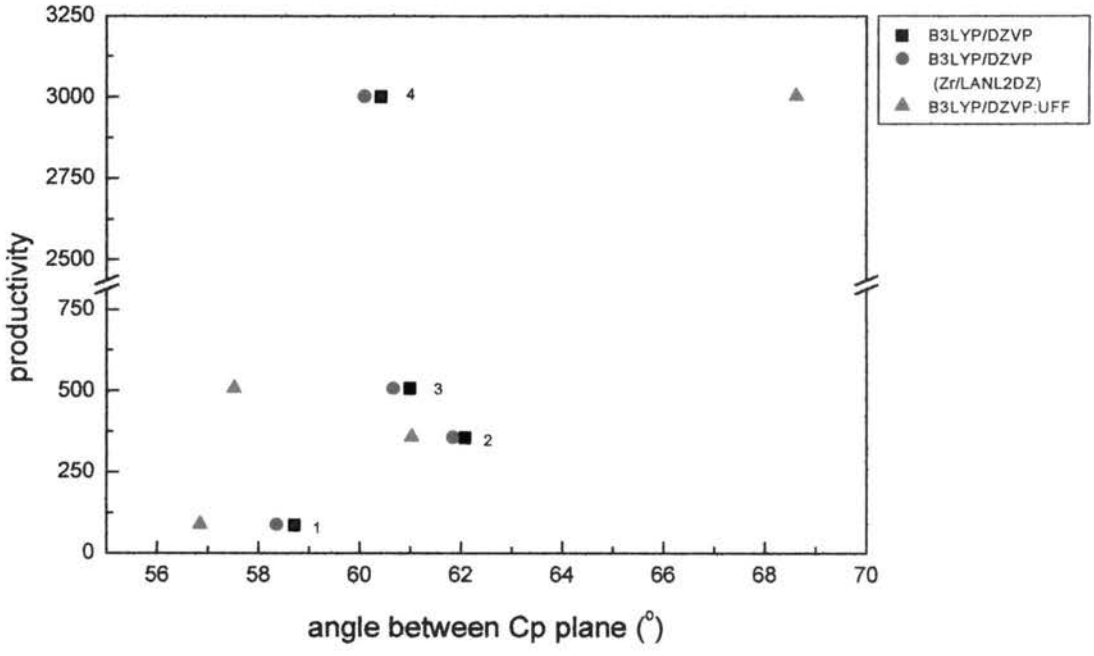


Figure 4.9 Plot of angle between Cp planes obtained at various levels of theory versus productivity.

4.2.2 Gap aperture and Obliquity

The gap aperture and obliquity of zirconocenes computed from their optimized geometries at various levels of theory were given in Table 4.10 and Table 4.11, respectively. The plot of gap aperture versus % isotacticity and productivity were shown in Figure 4.10 and Figure 4.12, respectively. While, plot of obliquity versus % isotacticity and productivity show in Figure 4.11 and Figure 4.13, respectively.

Table 4.10 The gap aperture (°) of 5 zirconocene structures from QM and ONIOM calculations.

Structure	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
1	31	30	23
2	42	40	36
3	60	58	50
4	62(62)[a]	60(60)[a]	81
5	63	63	67

[a]Values in parentheses are the gap aperture of zirconocene structure 4 which has C_2 symmetric.

Table 4.11 The obliquity (°) of 5 zirconocene structures from QM and ONIOM calculations.

Structure	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
1	-33	-32	-31
2	-34	-34	-33
3	-16	-16	-14
4	-17(-17)[a]	-16(-16)[a]	-16
5	-23	-22	-22

[a]Values in parentheses are the obliquity of zirconocene structure 4 which has C_2 symmetric.

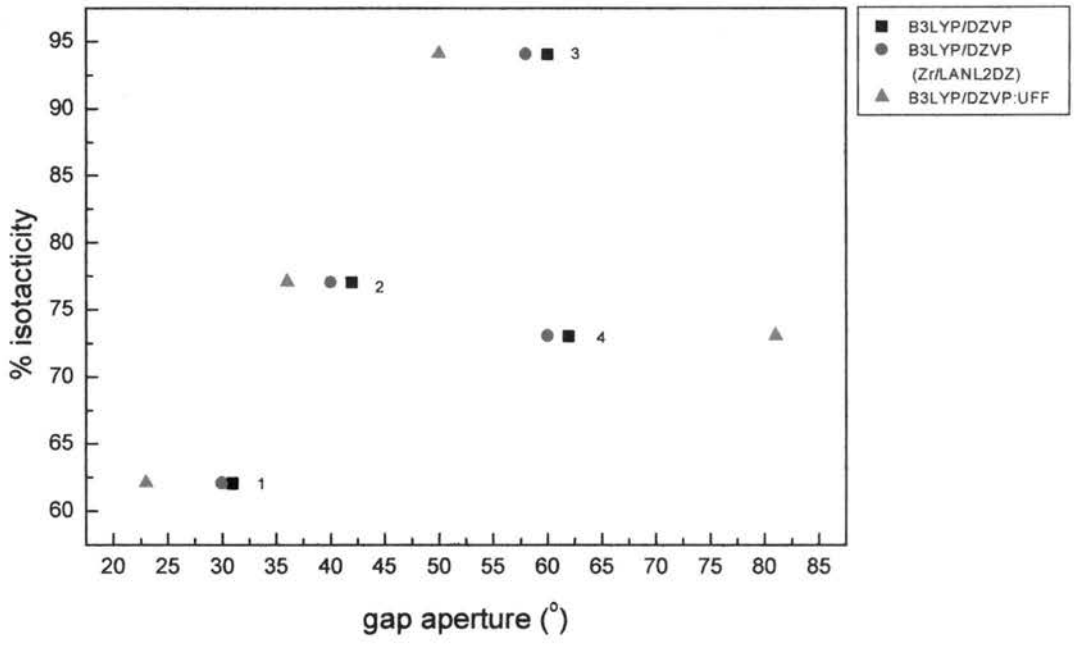


Figure 4.10 Plot of gap aperture obtained at various levels of theory versus % isotacticity.

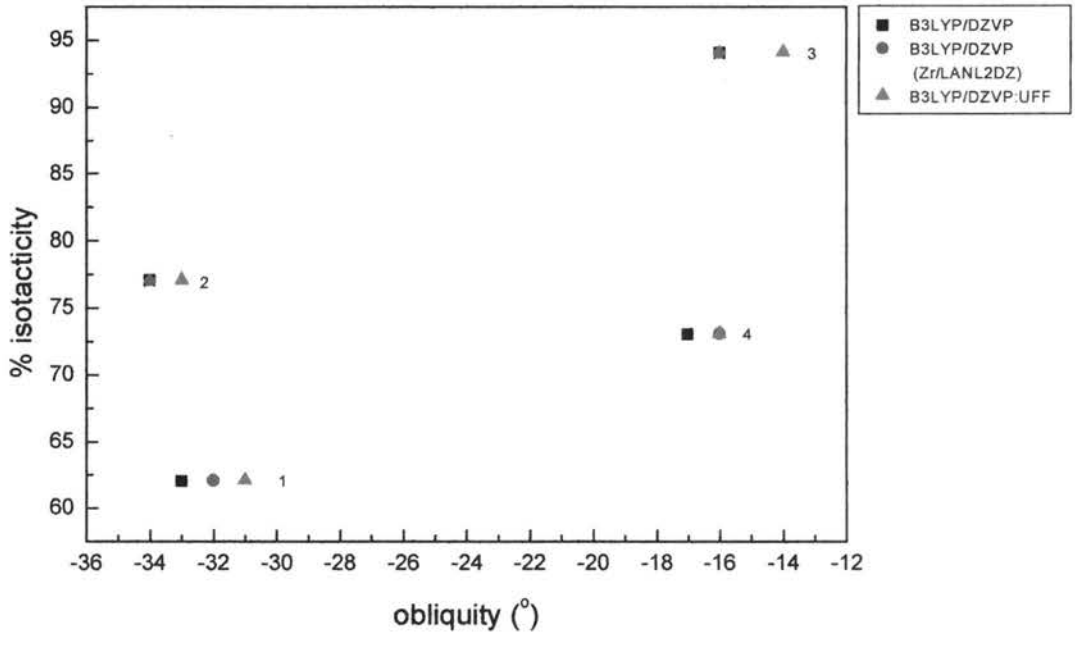


Figure 4.11 Plot of obliquity obtained at various levels of theory versus % isotacticity.

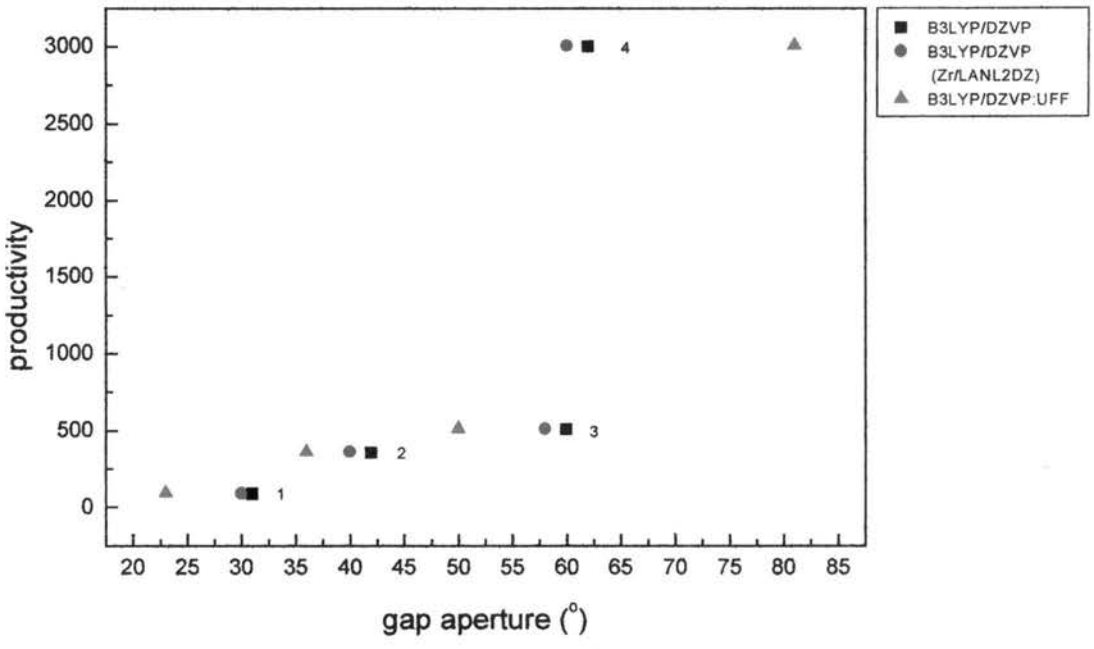


Figure 4.12 Plot of gap aperture obtained at various levels of theory versus productivity.

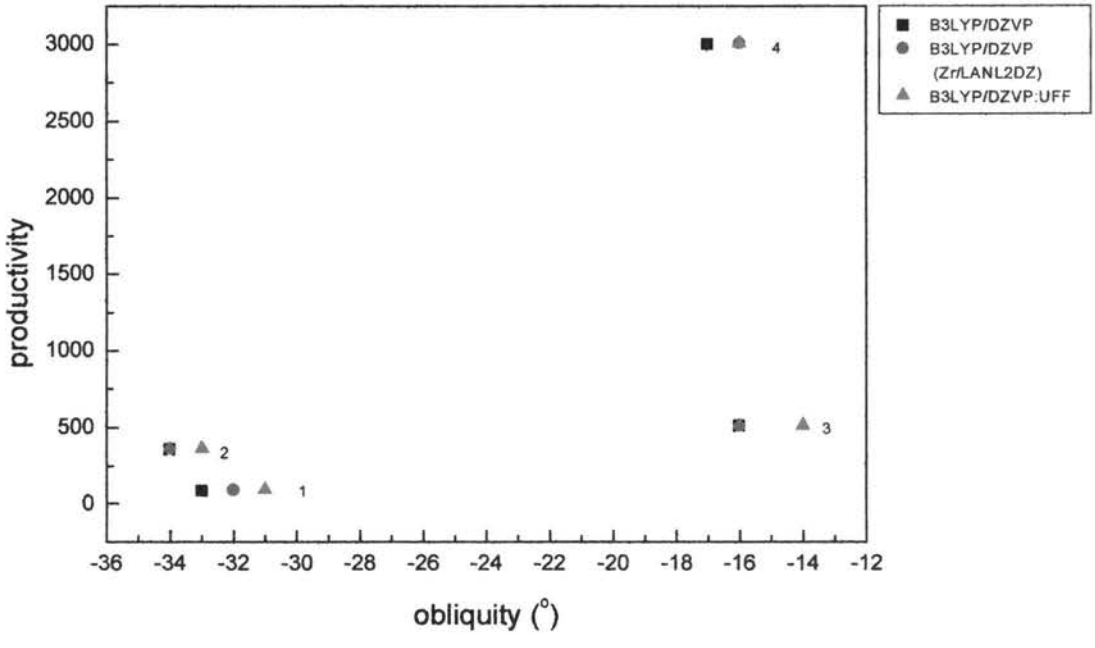


Figure 4.13 Plot of obliquity obtained at various levels of theory versus productivity.

4.2.3 Twisted angle

The twisted angle describes the distortion of the alignment of 2 cyclopentadienyl rings of zirconocene from the overlapped position. This distortion depends on the steric of bulky groups on the cyclopentadienyl ring. The twisted angle obtained from optimized geometries of 5 zirconocenes at various levels of theory were displayed in Table 4.12. While, plot of twisted angle versus %isotacticity and productivity showed in Figure 4.14, and 4.15, respectively.

Table 4.12 The twisted angle (°) of 5 zirconocene structures from QM and ONIOM.

Structure	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
1	22.24	22.23	24.65
2	0.10	0.28	-0.33
3	-9.98	-10.24	-14.04
4	-9.24(-10.37)[a]	-9.70(-10.52)[a]	-28.80
5	20.62	20.10	10.52

[a]Values in parentheses are the twisted angle of zirconocene structure 4 which has C_2 symmetric.

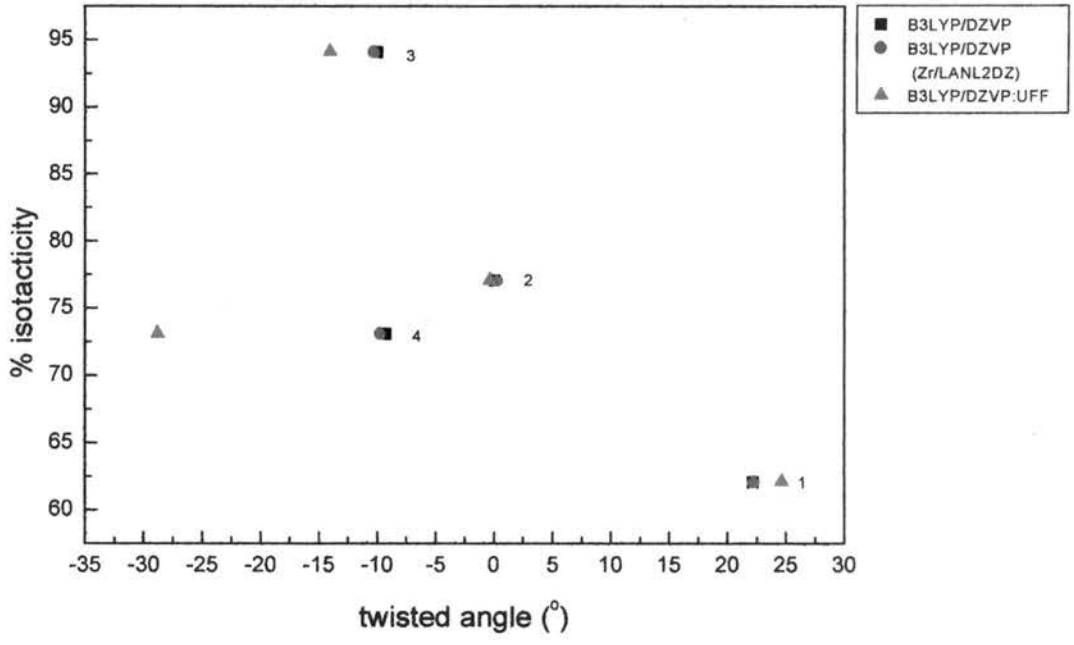


Figure 4.14 Plot of twisted angle obtained at various levels of theory versus % isotacticity.

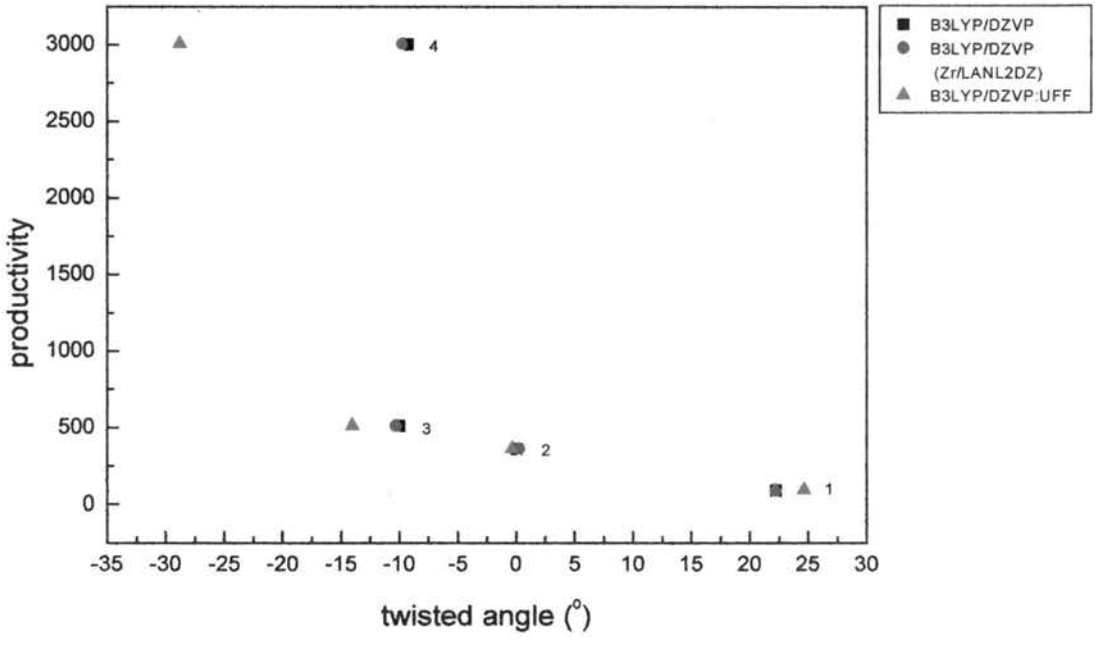


Figure 4.15 Plot of twisted angle obtained at various levels of theory versus productivity.

4.2.4 Cavity distance and cavity angle

The cavity distance and cavity angle were measured from the optimized structures of 5 zirconocenes at various levels of theory and were given in Table 4.13 and Table 4.14, respectively. The plot of cavity distance and cavity angle versus % isotacticity as shown in Figure 4.16 and 4.17. The plot of cavity distance and cavity angle versus productivity were shown in Figure 4.18 and 4.19.

Table 4.13 The cavity distance (Å) of 5 zirconocene structures from QM and ONIOM calculations.

Complex	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
1	5.126	5.029	4.623
2	5.563	5.467	5.208
3	5.713	5.638	5.303
4	5.665(5.738)[a]	5.572(5.647)[a]	6.370
5	6.834	6.778	6.664

[a]Values in parentheses are the cavity distance of zirconocene structure 4 which has C_2 symmetric.

Table 4.14 The cavity angle (°) of 5 zirconocene structures from QM and ONIOM calculations.

Complex	B3LYP/DZVP	B3LYP/LANL2DZ	B3LYP/DZVP:UFF
1	87.80	86.34	82.41
2	94.79	93.49	91.77
3	96.91	95.84	93.29
4	95.01(96.16)	93.59(94.94)	105.55
5	132.59	131.31	129.65

[a]Values in parentheses are the cavity angle of zirconocene structure 4 which has C_2 symmetric.

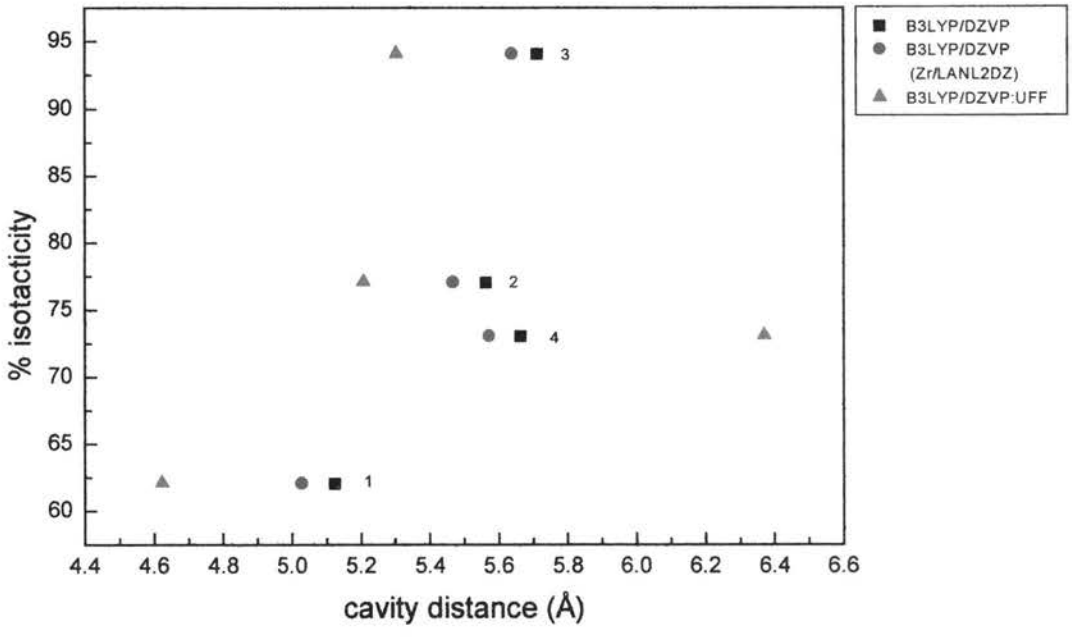


Figure 4.16 Plot of cavity distance obtained at various levels of theory versus % isotacticity.

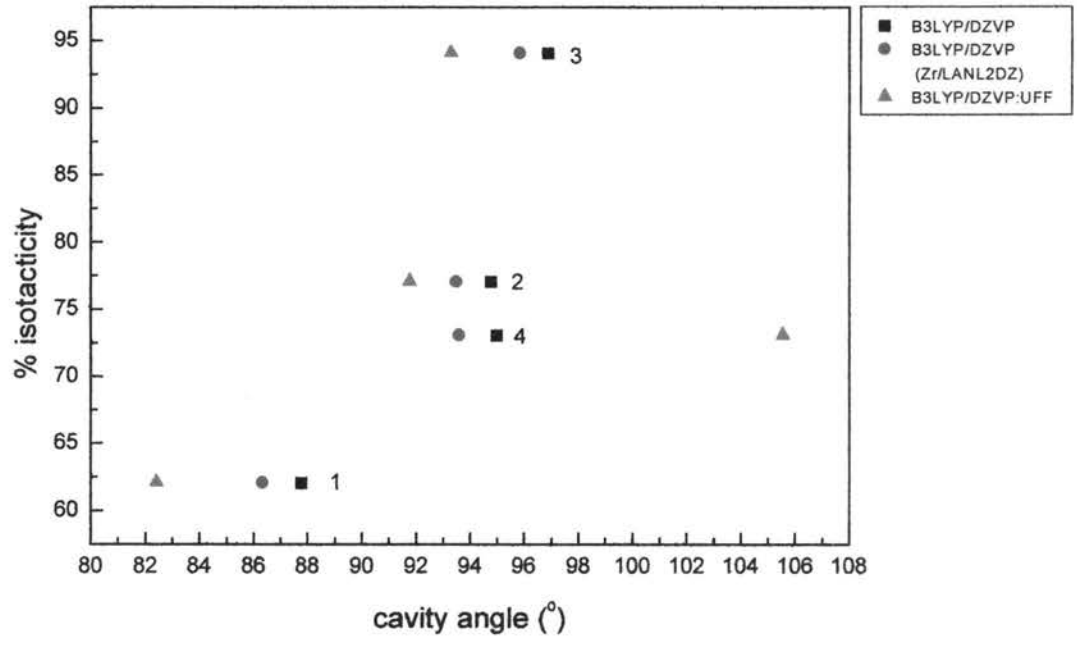


Figure 4.17 Plot of cavity angle obtained at various levels of theory versus % isotacticity.

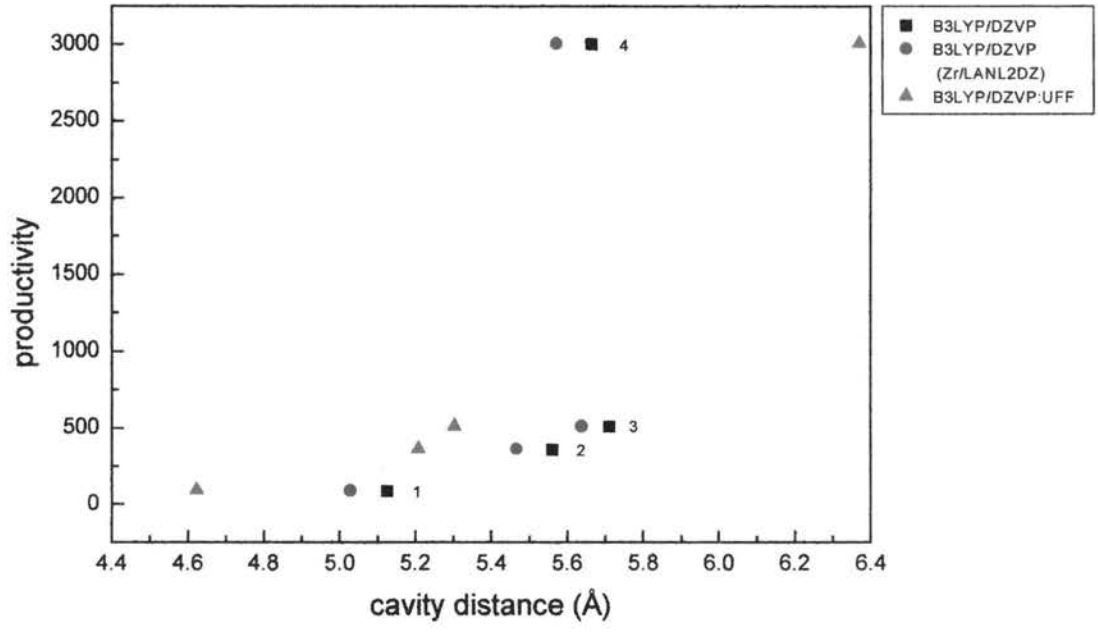


Figure 4.18 Plot of cavity distance obtained at various levels of theory versus productivity.

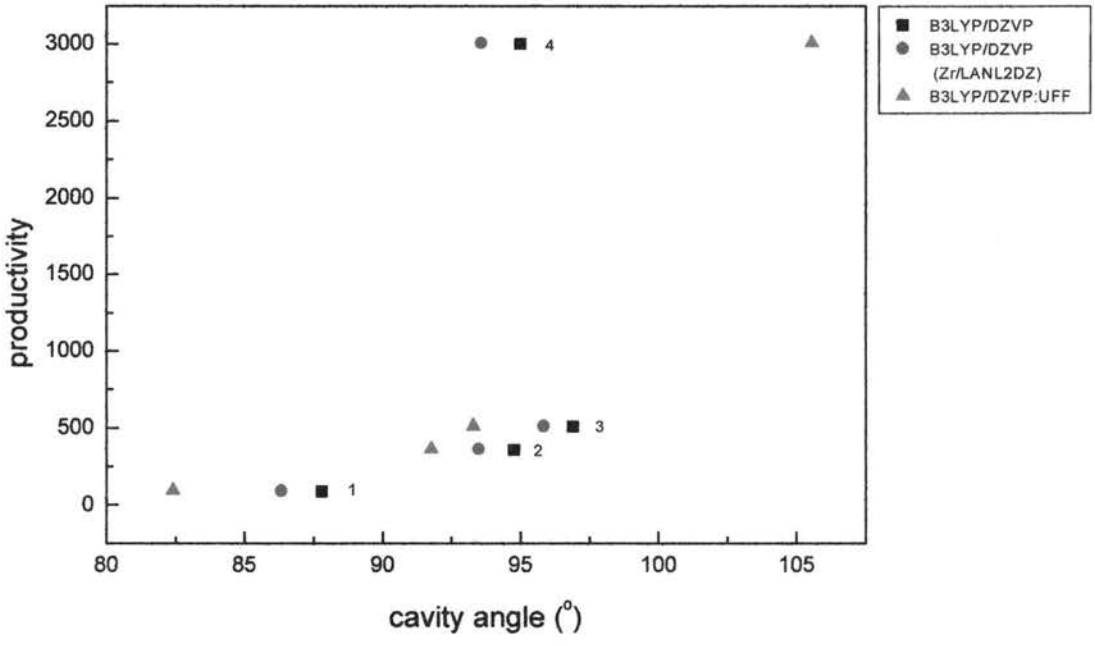


Figure 4.19 Plot of cavity angle obtained at various levels of theory versus productivity.

4.2.5 Atomic charges

Taken the atomic charges form the Figure 3.1, the mulliken's charges of atoms and group atoms of 5 zirconocene structures both neutral and ion forms were given in the Table 4.15 and Table 4.16, respectively. The plots of net charges on Cp ring, and on Zr of both neutral and ion form of 5 zirconocene structures versus productivity were shown in Figure 4.20., and 4.21, respectively.

Table 4.15 The net charges of various atoms and group atoms (R^1, R^2, and μ-x) of 5 zirconocene structures in neutral form obtained using B3LYP/DZVP.

	Charges				
	Structure 1	Structure 2	Structure 3	Structure 4	Structure 5
C_1	0.261	-0.063	-0.116	-0.123	0.146
C_2	-0.514	-0.450	-0.466	-0.462	-0.393
C_3	0.262	0.263	0.268	0.247	-0.368
C_4	-0.398	-0.353	0.092	0.101	0.000
C_5	-0.391	-0.361	-0.433	-0.423	0.141
Total Charges of Cp ring	-0.780	-0.964	-0.655	-0.660	-0.474
R^1	0.006	0.020	0.008	0.024	0.000
R^2	0.000	0.000	0.001	-0.004	0.017
μ-x	-0.024	0.365	0.316	0.331	-0.329
Cl	-0.394	-0.384	-0.386	-0.382	-0.378
Zr	0.677	0.649	0.672	0.628	0.638

Table 4.16 The net charges of various atoms and group atoms (R^1, R^2, and μ-x) of 5 zirconocene structures in ion form obtained using B3LYP/DZVP.

	Charges				
	Structure 1	Structure 2	Structure 3	Structure 4	Structure 5
C_1	0.326	0.003	-0.064	-0.071	0.220
C_2	-0.502	-0.402	-0.427	-0.411	-0.341
C_3	0.237	0.219	0.222	0.220	-0.357
C_4	-0.377	-0.312	0.100	0.105	-0.012
C_5	-0.369	-0.355	-0.423	-0.414	0.130
Total charges of Cp ring	-0.685	-0.847	-0.592	-0.571	-0.360
R^1	0.267	0.284	0.267	0.240	0.000
R^2	0.000	0.000	0.110	0.115	0.268
μ-x	0.211	0.562	0.514	0.530	0.100
Zr	0.645	0.621	0.627	0.642	0.775

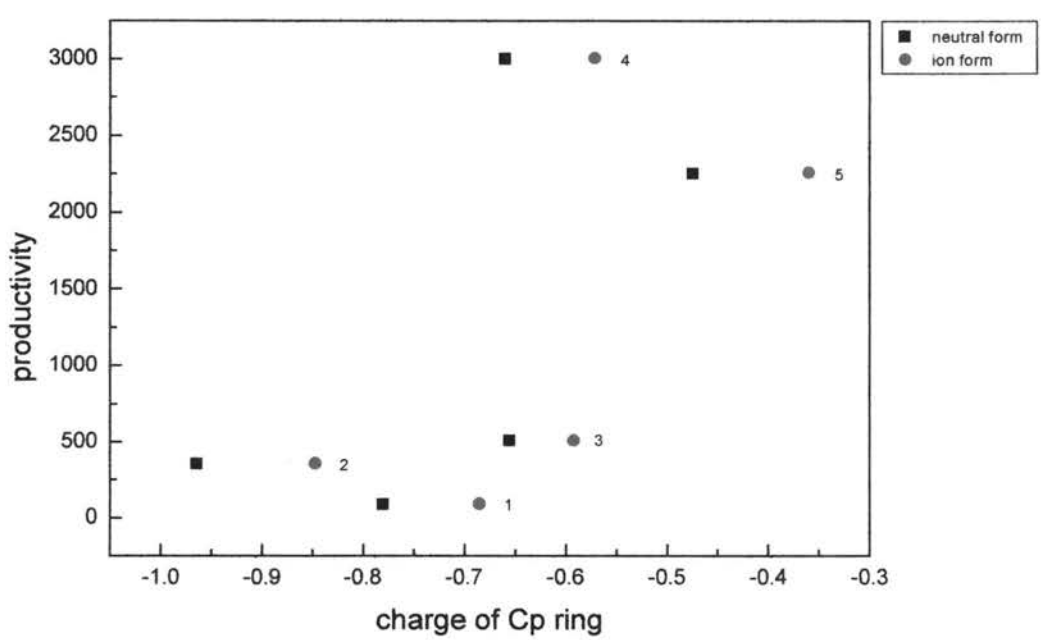


Figure 4.20 Plots of charges of cyclopentadienyl ring in neutral and ion forms obtained from B3LYP/DZVP versus productivity.

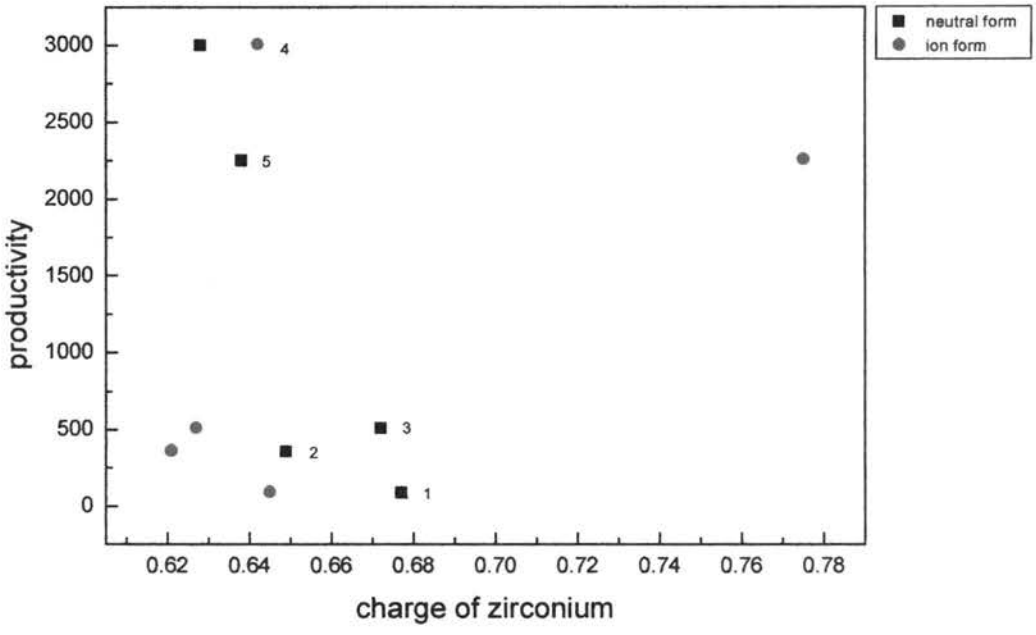


Figure 4.21 Plots of charges of zirconium in neutral and ion forms obtained from B3LYP/DZVP versus productivity.