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Theoretical Studies of d^0 Titanocene Complexes

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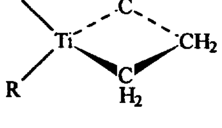
Ab initio calculations with various basis sets have been carried out to investigate the geometries and ring inversion barrier of $R_2TiC_3H_6$ and R_2TiS_3, R=Cp and Cl. Optimized geometries of $R_2TiC_3H_6$ showed the four membered ring was planar on C_s symmetry. However, R_2TiS_3 complexes were optimized to be stable in the puckered form. The smallest Basis III with STO-3G on Cp ligands gave reasonable results for the calculations of metallocene. The energy barrier for the ring inversion of metallacyclosulfanes, Cp_2TiS_3 was computed to be 8.72 kcal/mol at MP2 level. For the Cl system, we reproduced the molecular structure and ring inversion energy with Basis V.

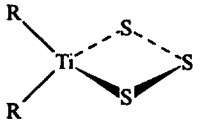
Introduction

The electronic structures and bonding properties of transition metal complexes are not as well understood as organic molecules are. The elementary reaction steps with transition metal complexes have been studied by various theoretical methods such as the semi-empirical and ab initio calculations. Quantitative ab initio calculations on transition metal complexes are only recently becoming commonplace due to the large number of electrons and poor basis sets. Several approaches are available to investigate the large transition metal complexes. For instance, effective core potentials (ECP),[1] density functional theory (DFT),[2] and model systems[3] with all electron calculations are useful methods. We have started to investigate systematically the performance of model system calculations. $Cp_2TiC_3H_6$ (**1**), $Cl_2TiC_3H_6$ (**2**), Cp_2TiS_3 (**3**), and Cl_2TiS_3 (**4**) complexes have been chosen to study the substitution effect of cyclopentadienyl (Cp) ligand by Cl ligand in theoretical viewpoint.



1 R=Cp

2 R=Cl



3 R=Cp

4 R=Cl

The Cp ligand is ubiquitous in transition metal complexes. Titanium-cyclopentadienyl complexes shows the rich structural chemistry of Cp ligand[4] and are also important in a number of synthetic applications. It is known that the geometry and properties of Cp ligand in Cp_2TiCl_2 and its derivatives are useful to cancer research.[5] Dicyclopentadienyltitanacyclobutane (**1**) is considered to be one of the important intermediates in Ziegler-Natta catalytic systems. In 1978, Green and Rooney[6] proposed a metathesis type mechanism in studies of the stereospecific Ziegler-Natta polymerization reaction of olefins. Complex **3** (metallacyclosulfane) is isoelectronic with complex **1**. We recently[7] examined the electronic structures and four-membered ring inversion motion with the extended Hückel and preliminary ab initio calculations. In this publication, molecule structures and inversion process of four-membered ring shall be examined for **1-4** complexes using all electron ab initio molecular orbital theory with various basis sets.

Table 1. Ligand Basis Sets Used in This Study

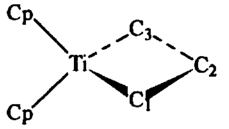
Basis Sets		No. of basis functions	
		$Cp_2TiC_3H_6$ or Cl_2TiS_3	$Cl_2TiC_3H_6$ or Cl_2TiS_3
I	C (Cp); 3-21G, H (Cp); STO-3G C, H (C_3H_6), S; 4-31G	164	
II	C (Cp); 3-21G, H (Cp); STO-3G C, H (C_3H_6), S; 4-31G*	182	
III	C, H (Cp); STO-3G C, H (C_3H_6), S; 4-31G*	142	
IV[a]	C, H (C_3H_6), Cl, S; 4-31G		90
V[a]	C, H (C_3H_6), Cl, S; 4-31G*		120

[a] Basis Sets for model systems of $Cl_2TiC_3H_6$ and Cl_2TiS_3

Computational Methods

The ab initio calculations were carried out with the GAUSSIAN 92[8] and GAMESS[9] on a Cray Y-MP C916 and an IBM, respectively. The basis set for Ti metal atom was of the form (4333/433/31) and has been described elsewhere.[10] Basically, it is of double-ξ quality for the metal d region. Table 1 shows the combinations of ligand basis sets used in this study.

Table 2. Optimized Geometries and Total Energies (a.u) of $Cp_2TiC_3H_6$ with three Basis Sets. The bond distances are in angstroms and the angles in degrees



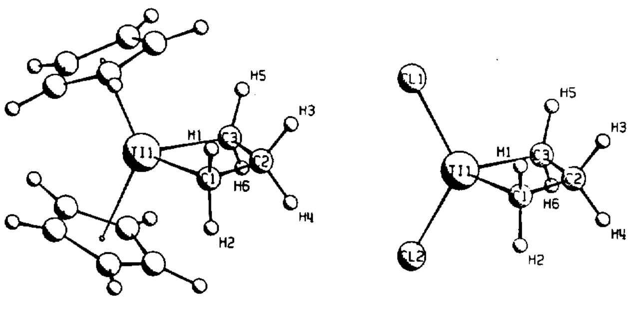
Basis Sets	I	II	III	Exp.
Ti-$C_{1,3}$	2.097	2.098	2.131	2.127
Ti-C (Cp)	2.440	2.468	2.397	2.36-2.40
C_1-C_2	1.570	1.559	1.562	1.563
C_1-H	1.079	1.080	1.083	
C-C (Cp)	1.381^a	1.411	1.418	
C-H (Cp)	0.87^a	1.079	1.079	
∠Cp-Ti-Cp	132.8	133.8	135.3	
φ^b	179.9	179.9	180.1	~180.0
∠C_1-Ti-C_3	75.4	74.5	73.8	75.3
∠C_1-C_2-C_3	109.5	109.0	109.9	112.0
SCF E.	−1346.30287	−1346.81502	−1344.41445	

^{a}C-C and C-H distances on Cp are fixed. ^{b}Dihedral angles between C_1-Ti-C_3 and C_1-C_2-C_3 planes.

The first, referred to as Basis I, was a 3-21G[11] and STO-3G basis set[12] for C and H on Cp ligand, respectively, and a 4-31G basis set[13] for S and C and H on C_3H_6 ligand. Basis II used 4-31G* polarization functions[14] for C and H on C_3H_6 ligand. Basis III used 4-31G* for S, C and H atoms, except for the atoms on Cp ring which were given a STO-3G basis. Basis IV and V were for the model systems of $Cl_2TiC_3H_6$ and Cl_2TiS_3 complexes. The geometries of **1** and **3** were optimized at the restricted Hartree-Fock (RHF) level by the energy gradient technique. Second-order Moller-Plesset perturbation (MP2) calculations were carried out at the RHF optimized geometries to obtain improved energy comparisons for the energy barrier. Model systems were also optimized at the RHF and MP2 level using the Basis IV and V. Throughout this study the systems have been assumed to retain either C_s or C_{2v} symmetry with C_{5v} local symmetry in the cyclopentadienyl ring.

Results and Discussion

$Cp_2TiC_3H_6$ (1) and $Cl_2TiC_3H_6$ (2) complexes. Metallacyclobutanes are demonstrated as intermediates in a number of olefin metathesis catalyst.[15] The molecular structures of titanacyclobutanes are pretty interesting. The metallacyclic ring is nearly planar.[16] It is compared to the puckered geometry of cyclobutane molecule which is isolobal to titanacyclobutane. Upton and Rappe[17] reported the electronic and molecular structures of titanacyclobutane to investigate the isomerization of titanacyclobutane to ethylene-titanium methylidene complex. They applied generalized valence bond (GVB) calculations using the model system. We carried out all electron ab initio calculations for $Cp_2TiC_3H_6$ and $Cl_2TiC_3H_6$ complexes using various basis sets. Geometry optimization of $Cp_2TiC_3H_6$ at C_s symmetry was carried out at the RHF level. These are reported in Table 2. The optimized molecular structures are illustrated in Figure 1.



1 **2**

Figure 1. Optimized geometries at the RHF level for $Cp_2TiC_3H_6$, **1** and $Cl_2TiC_3H_6$, **2**.

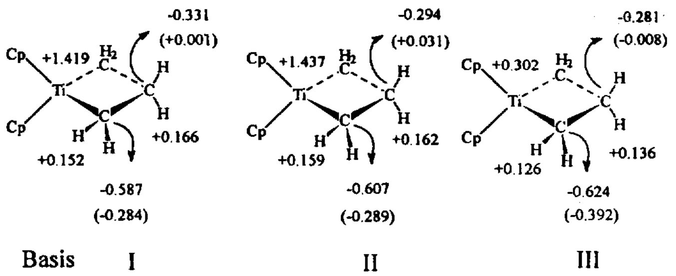
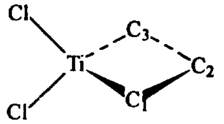


Figure 2. Mulliken charges for $Cp_2TiC_3H_6$ complex calculated by three basis sets. The values in parentheses are charges with hydrogen summed into C atoms.

With basis III, the calculated Ti-$C_{1,3}$ bond lengths of 2.131 Å were in good agreement with the experimental 2.127 Å.[16] Basis I and II also produced reasonable values of 2.097 and 2.098 Å, respectively. C_1-C_2 distances of C_3H_6 ligand were optimized within typical C-C single bond distance of 1.56 Å. The optimized Cp-Ti-Cp and C_1-Ti-C_3 angles also displayed pretty close to the one observed experimentally. Another important results are of φ angles that are the dihedral angles between C_1-Ti-C_3 and C_1-C_2-C_3 planes. All φ angles with three kinds of basis sets were optimized to be about 180.0°. These are consistent with the planar geometry of metallacyclic ring in the observed X-ray structures.[16] Generally, the optimum values with Basis III were a little closer to the experimental ones than those with other basis sets. And the number of basis functions for Basis III is 142 as indicated in Table 1. This number is much smaller than Basis I and II of 164 and 182, respectively. Basis III is quite reasonable for the calculations of metallocene complexes with respect to molecular structural view. The computed Mulliken charges for complex **1** are shown in Figure 2.

The numbers in parentheses are net charges with hydrogens summed into C atoms. The negative charges on the carbon atoms directly connected to Ti metal are partly due to electron withdrawal from the Ti and partly due to the positive charges on the hydrogens. The net charges in parentheses on the central C atoms are almost zero for all three basis sets. This indicates Ti metal does not interact with the central C atom in complex. The positive charge on Ti metal is affected by the basis sets on Cp ligands. The charge on Ti with Basis III is +0.302, which is much smaller than

Table 3. Optimized Geometries and Total Energies (a.u) of $Cl_2TiC_3H_6$. The bond distances are in angstroms and the angles in degrees



Basis Sets	IV	V	Calcd.[a]
Ti-$C_{1,3}$	1.997	2.002	2.12
C_1-C_2	1.581	1.571	1.57
Ti-Cl	2.284	2.249	2.31
C-H	1.078	1.080	1.08
∠Cl-Ti-Cl	125.2	125.0	133.5
φ^b	180.0	180.0	180.0
∠C_1-Ti-C_3	80.4	79.8	74.6
∠C_1-C_2-C_3	109.2	109.6	109.2
SCF E.	−1882.57695	−1882.67879	

[a] Reference 17. [b] Dihedral angles between C_1-Ti-C_2 and C_1-C_2-C_3 planes.

the other basis since STO-3G on Cp ligands are minimum basis sets.

It is an usual approach in calculations of metallocene complexes substituting cyclopentadienyl by Cl ligand to reduce computational complexity. The important optimized bond distances and angles for $Cl_2TiC_3H_6$ are reported in Table 3.

Calculations were also done in C_s symmetry. $\varphi=180.0°$ corresponds to a planar geometry of 4-membered ring skeleton. This is in agreement with experimental and previously calculated results given in Table 2. Also the planar geometry of **2** is same with other theoretical result.[17] Upton and Rappe used effective core potential theory for Ti and Cl atoms. Carbon-Carbon bond distances of 1.581 and 1.571 Å are comparable to typical C-C single bond distance. Ti-C bond distances for Basis IV and V are about 0.1 Å shorter than those in Table 2 because of less steric hindrance of Cl ligands. This hindrance also affected to be small Cl-Ti-Cl angles of about 125°. In general, dicyclopentadienyltitanium complexes have Cp-Ti-Cp angles around 130°.[18] Bond distance between Ti and central C atom was computed to be 2.443 Å with Basis V. This is too long to make an interaction between two atoms. The net Mulliken charge on central carbon was calculated to be +0.076.

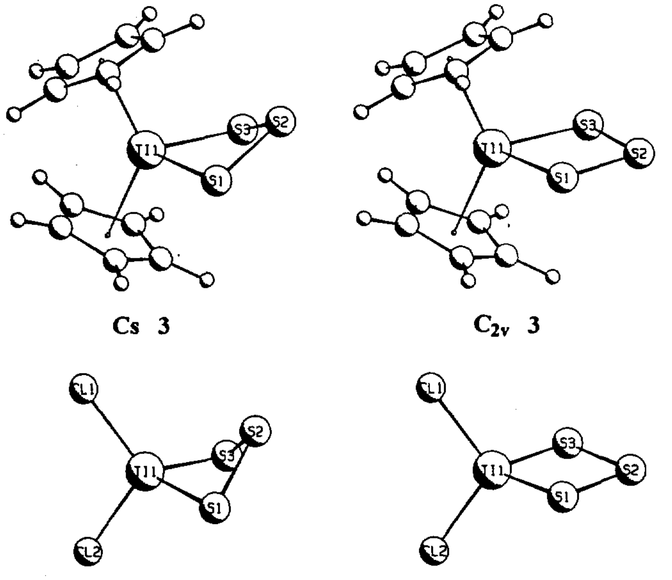
Cp_2TiS_3 (3) and Cl_2TiS_3 (4) complexes. Recently, it has been actively investigated to understand S-S and metal-S bonding both experimentally and theoretically.[19] Sulfur atom is isoelectronic with CH_2 group. Complex **3** is isoelectronic and isolobal to $Cp_2TiC_3H_6$ complex. In our previous studies,[7] geometry of Cl_2TiS_3 was puckered form like cyclobutane molecule. The important optimized bond distances and angles for the C_s and C_{2v} metallacyclosulfane Cp_2TiS_3 are listed in Table 4. MP2 energies were obtained with single point calculations at the RHF optimized geometries. The optimized molecular geometries are illustrated in Figure 3.

The optimized φ angles in C_s symmetry were around 145° for three applied basis sets. These values displayed the same trend with experimental result. The X-ray structure of $(C_5Me_5)_2TiS_3$ shows a puckered form with $\varphi=\sim 131.0°$.[20] The optimized geometries were about 14° less bent in TiS_3 unit than the observed structure since cyclopentadienyl ligand were used instead of bulky pentamethyl cyclopentadienyl ligands in ab initio calculations. Our calculated S-S bond distances of 2.108 and 2.111 Å with Basis II and III, respectively, were close to the observed one. Our S-S distances were in good agreement with other theoretical results. Quelch and Schaefer[21] studied many isomers of elemental sulfur, S_4 with high level ab initio calculations. Puckered-ring isomer of S_4 is one of isolobal to Cp_2TiS_3 complex and S-S distances are 2.141 and 2.109 Å with DZP and TZ2P basis sets, respectively. The optimized geometries within C_{2v} symmetry ($\varphi=180.0°$) were very close to Cs geometries except φ angle.

Table 4. Optimized Geometries and Total Energies (a.u) of C_s and C_{2v} Cp_2TiS_3 complexes. The bond distances are in angstroms and the angles in degrees

Basis Sets	I		II		III		Exp.[a]
Symm.	C_s	C_{2v}	C_s	C_{2v}	C_s	C_{2v}	
Ti-S	2.465	2.474	2.413	2.424	2.488	2.498	2.413
	3.153	3.215	3.019	3.134	3.110	3.190	
S-S	2.289	2.295	2.108	2.123	2.111	2.124	2.041
Ti-C (Cp)	2.403	2.401	2.443	2.440	2.380	2.378	~2.373
C-C	1.381[b]	1.381[b]	1.412	1.412	1.420	1.420	
C-H	0.870[b]	0.870[b]	1.078	1.079	1.080	1.080	
∠Cp-Ti-Cp	130.7	131.3	131.1	132.0	133.6	134.5	136.9
φ^c	146.1	180.0	143.0	180.0	145.6	180.0	~131.0
∠S-Ti-S	87.9	90.6	83.0	85.2	81.0	83.4	84.4
∠S-S-S	96.7	100.0	98.7	101.2	99.9	102.9	
SCF E.	−2420.66177	−2420.65909	−2421.23440	−2421.22884	−2418.85346	−2418.84891	
MP2 E.	−2421.83274	−2421.82664	−2422.65092	−2422.63702	−2419.98373	−2419.97433	

[a] Reference 20. Experimental data for $(C_5Me_5)_2TiS_3$ complex. [b] C-C and C-H distances on Cp are fixed. [c] Dihedral angles between S-Ti-S and S-S-S planes.



Cs 3 **C$_{2v}$ 3**

Cs 4 **C$_{2v}$ 4**

Figure 3. Optimized geometries for C_s, C_{2v} Cp_2TiS_3, **3** and C_s, C_{2v} Cl_2TiS_3, **4**.

Ti-S and S-S bond distances were a little increased. The computed Mulliken charges for complex **3** are shown in Figure 4.

The negative charges on the sulfur atoms are due to electron withdrawal from the Ti metal atom. In Basis III, the charge on Ti metal was computed only to be +0.142 in C_s symmetry. This small value was also observed in $Cp_2TiC_3H_6$ complex.

We already reported the results of ab initio calculations with RHF level for model Cl_2TiS_3 compound. Here, we optimized C_s and C_{2v} Cl_2TiS_3 complex using Basis IV at the MP2 level. The optimized geometries and total energies are given in Table 5 and the geometries are displayed in Figure 3.

At the MP2 calculations, dihedral angle for four membered ring, φ was calculated to be 121.3° in C_s geometry. The structure of four membered ring was more puckered by 6.2° than HF level calculation. The other angles and bond distances were slightly changed.

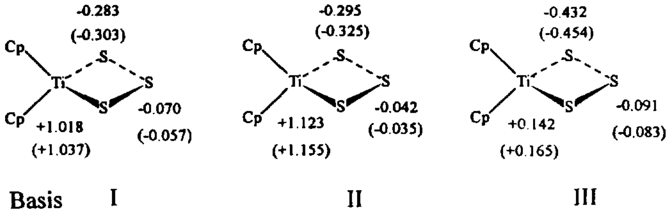


Figure 4. The computed Mulliken charges for C_s and C_{2v} Cp_2TiS_3 complex. The charges in parentheses are for C_{2v} geometries.

The ring inversion barriers in metallacyclosulfanes have been measured by variable temperature NMR studies, and the electronic structure and potential energy surface for the inversion process have been also studied by various theoretical methods.[22] The 4-membered ring flipping barrier from one side to the other in $Cp^*{}_2TiS_3$ (Cp^* = pentamethylcyclopentadienyl) has been measured to be 9.6 kcal/mol.[20] This barrier is much higher than cyclobutane of 1.5 kcal/mol.[23] We summarized the calculated ring flipping energy barriers for Cp_2TiS_3 and Cl_2TiS_3 in Table 6.

At the RHF level, the ring inversion barriers for Cp_2TiS_3 were computed to be 1.68, 3.49, and 3.36 kcal/mol with Basis I, II, and III, respectively. MP2 calculations increased it to 3.83, 8.72, and 5.90 kcal/mol. As we pointed out in the previous studies,[7] the energy barrier was sensitive to the basis sets applied. Basis II and III have the polarization function 4-31G* for sulfur atoms. Their energies were better than that of Basis I without polarization function 4-31G. Basis II most reproduced the experimental measurement of 9.6 kcal/mol. However, Basis II has the largest number of basis set functions in Table 1. Basis III also moderately reproduced the ring inversion energy and molecular structure. This has STO-3G basis sets for Cp ligands and the smallest basis

Table 5. Optimized Geometries and Total Energies (a.u) at the HF[a] and MP2 levels for Cl_2TiS_3, **4**. The bond distances are in angstroms and the angles in degrees

Basis Sets	IV				V	
symm.	C_s		C_{2v}		C_s	C_{2v}
	HF	MP2	HF	MP2		
Ti-S	2.320	2.336	2.306	2.302	2.297	2.268
	2.758	2.681	3.025	2.951	2.527	2.943
S-S	2.324	2.362	2.325	2.379	2.116	2.143
Ti-Cl	2.228	2.232	2.230	2.239	2.210	2.201
∠Cl-Ti-Cl	109.6	110.5	110.1	109.9	109.8	110.9
φ	127.5	121.3	180.0	180.0	115.9	180.0
∠S-Ti-S	97.2	99.0	99.0	104.2	90.1	92.7
∠S-S-S	97.0	97.5	97.9	99.5	100.4	100.0
SCF E.	−2956.90745		−2956.90591		−2957.09079	−2957.08407
MP2 E.[b]	−2957.33791	−2957.52249	−2957.33299	−2957.51812	−2957.88306	−2957.86966

[a] Data for HF level are from reference 7. [b] MP2 E. at HF column were obtained with frozen core single point calculation at the optimized HF geometries. MP2 optimization are full electron correlation.

Table 6. The calculated 4-membered ring flipping barriers for R_2TiS_3, R=Cp and Cl. The energies are listed in kcal/mol

R	Cp			Cl	
Basis Set	I	II	III	IV	V
RHF	1.68	3.49	3.36	0.97	4.22
MP2	3.83	8.72	5.90	3.09	8.41
MP4				3.41	8.02
Exp.			9.57		

sets applied in this studies. As noticed in Cl_2TiS_3 calculations, it is not necessary to apply the electron correlation beyond second-order Moller-Plesset perturbation theory.

Conclusions

We made a detailed computational study of d^0 titanocene complexes. Optimized structures for $Cp_2TiC_3H_6$ and Cp_2TiS_3 were obtained with SCF wavefunction. We applied three different basis sets for the ligand atoms. Among them, the smallest Basis III gave quite reasonable geometries for the calculations of metallocene complexes. Optimized geometries of $R_2TiC_3H_6$, R=Cp and Cl, showed the four membered ring was a planar form. However, R_2TiS_3 complexes were optimized to be puckered. Our best calculations of Cp_2TiS_3 complex showed an energy barrier for the ring inversion of 8.72 kcal/mol at MP2 level. This value was in reasonable agreement with the experimental 9.57 kcal/mol. For the Cl system, Basis IV and V gave good structural accuracy at HF and MP2 levels. The basis sets with the polarization function were much better to reproduce the energy barrier. And MP2 correlation was also important.

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