REACTIONS OF DICHLOROZIRCONOCENE WITH NITROGEN CONTAINING HETEROCYCLES AND RELATED COMPOUNDS

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ABSTRACT

In this study the reaction of 16 e^- system, dichlorobiscyclopentadienylzirconium(IV) with N-containing, S-containing and thioamide containing ligands were studied.

In the presence of a non-coordinating solvent, CH_2Cl_2, thioacetamide coordinated to Cp_2ZrCl_2 through C=S unit with participation of the NH group. This complexation was proved by the new bands appearing in Zr-N and Zr-S stretching region, also by the blue shift of thioamide band I and the red shift of thioamide band IV of thioacetamide.

Deprotonated ethanethiol with Cp_2ZrCl_2 gave a dimeric complex with the formula $(Cp_2ZrClSCH_2CH_3)_2$. Without deprotonation ethanethiol did not coordinate to Cp_2ZrCl_2.

ÖZET

Bu çalışmada asıl olarak 16 elektron sistemine sahip bulunan diklorodisiklopentadienilzirkon'un yapılarında azot, kükürt ve tiyoamid grubu içeren ligandlarla olan reaksiyonları çalısılmıştır.

CH_2Cl_2 gibi koordine etme özelliği olmayan çözücülerde, tiyoasetamid diklorozirkonosin ile tiyokarbonil grubuna ek olarak amino grubundan bağlanmaktadır. Bu koordinasyon oluşumu Zr-N ve Zr-S titreşim bandlarının belirmesi ve tiyoamid I. bandının yüksek frekansa aynı zamanda tiyoamide IV. bandının daha düşük frekansa kaymasıyla kanıtlanmıştır.

Deprotone olmuş ethantiyol ile diklorozirkonosinin reaksiyonu dimerik $(Cp_2ZrClSCH_2CH_3)_2$ kompleksini vermektedir. Deprotone olmamış ethantiyol'un Cp_2ZrCl_2 ile reaksiyona girmediği gözlemlenmiştir.

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Cp = Cyclopentadienyl, η^5-C_5H_5

Cp_2ZrCl_2 = Dichlorobis(cyclopentadienyl)zirconium(IV)

THF = Tetrahydrofuran

n-BuLi = n-butyllithium

FAB = Fast Atom Bombardment

EI = Electron Impact

CI = Chemical Ionization

Dp = Decomposition Point

Mp = Melting Point

I. INTRODUCTION

Since the discovery of the Ziegler-Natta catalyst in polymerization of olefins, considerable importance has been attached to the chemistry of organo Group IV transition metals. Because of their increasing applications as catalysts in the field of olefin polymerization and organic synthesis, the complexation of the organo derivatives of zirconium with various ligands has also become a topic of interest [1].

The most commonly studied organozirconium compounds are dichlorobis(η^5-cyclopentadienyl)zirconium(IV) (Figure1.1), dimethylbis(η^5-cyclopentadienyl)zirconium (IV) (Figure 1.2) and chlorobis(η^5-cyclopentadienyl)zirconiumhydride, the so called Schwartz reagent (Figure1.3).

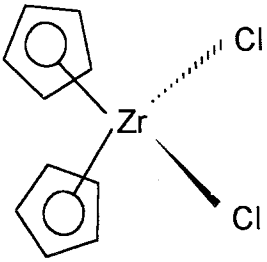


FIGURE 1.1. Dichlorobis(η^5-cyclopentadienyl)zirconium(IV)

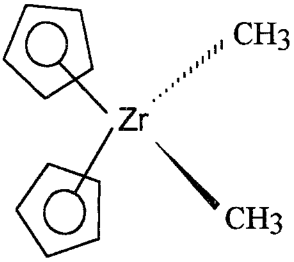


FIGURE 1.2. Dimethylbis(η^5-cyclopentadienyl)zirconium(IV)

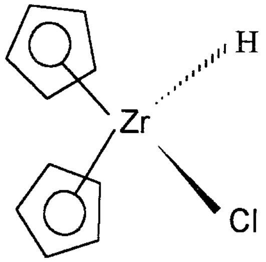


FIGURE 1.3. Chlorobis(η^5-cyclopentadienyl)zirconium(IV)hydride

In literature, there are various studies about the complexation chemistry of the above stated organozirconium compounds with various heteroatom contaning ligands.

In 1985, Srivastava and co-workers studied the reactions of dichlorozirconocene with two important series of heterocylic thiones, in the presence of a base (Figure 1.4).

R = C_6H_5 , $C_6H_4CH_3$,

R = $C_6H_4NO_2$

FIGURE 1.4. The Structures of a) 5-substituted 1,3,4-oxadiazole-2-thione,
b) 1-aryl-2-thiohydantoin

According to infrared and NMR studies, it was reported that, these compounds act as bidentate chelating ligands, coordinating through thiocarbonyl sulphur and amino nitrogen to zirconium atom. The proposed structures for these zirconium complexes for 1:1 and 1:3 adducts are shown in figure 1.5 [1].

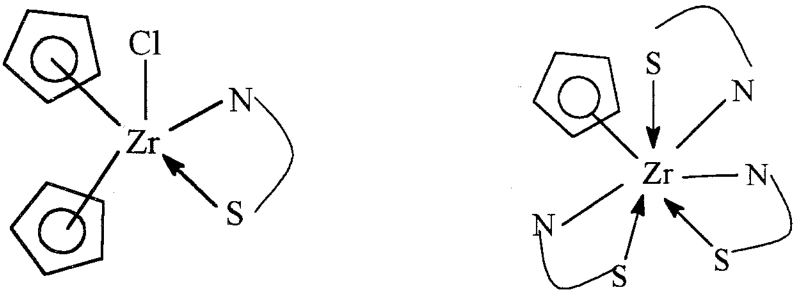


FIGURE 1.5. Proposed Structures for [$Cp_2Zr(L)Cl$] and [$Cp_2Zr(L)_3$] Complexes

In 1985 Hartmut Köpf and co-workers studied the reactions of dichloro-zirconocene with S,Ndilithium salt of o-aminothiophenol and N,N'dilithiumo-phenylenediamide. According to the IR and NMR data, the complexation of Cp_2ZrCl_2 with these ligands through elimination of LiCl was observed (Figure 1.6) [2].

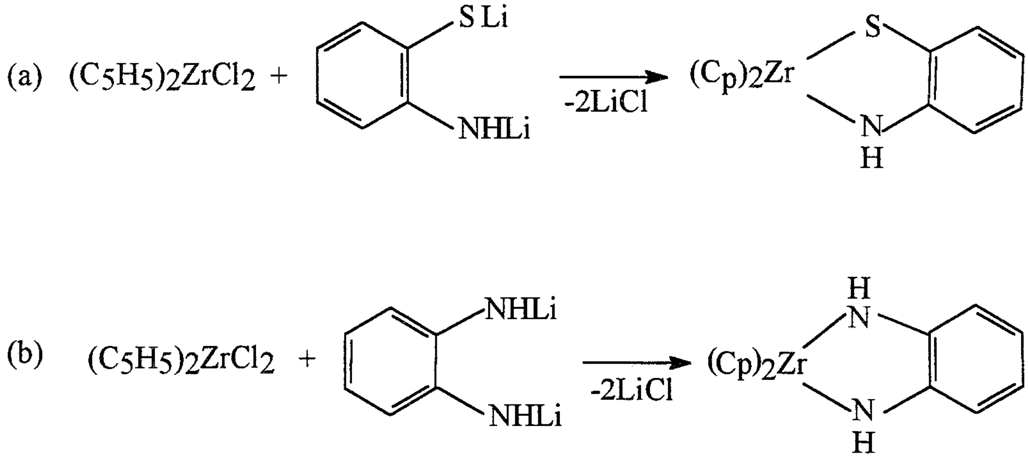


FIGURE 1.6. a) The Reaction of $(C_5H_5)_2ZrCl_2$ with S,Ndilithium Salt of o-aminothiophenol giving (biscyclopentadienyl) (o-aminothio-phenyldiate S,N)zirconium(IV),

b) The Reaction of $(C_5H_5)_2ZrCl_2$ with N,N'dilithium o-phenylenediamide Giving (biscyclopentadienyl)(o-phenylenediaminediate-N,N') zirconium(IV)

In 1992, Stephan and co-workers studied the reactions of dichlorotitanocene with dithiols in the presense of imidazole and ended up with a dimeric product with poor solubility (Figure 1.7.)[3].

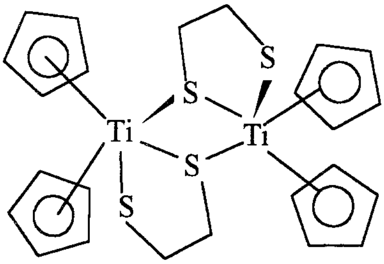


FIGURE 1.7. The Structure of Dimeric Titanocenedithiolate Complex

In 1993, Gau and co-workers studied the structures of group IV metallocene complexes of heterodifunctional ligands containing oxygen and sulphur donor atoms. They found that, the interaction of difunctional ligand (1R,2S,3R)-3mercapto-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol with group IV metallocenes, in the presence of triethylamine, affords the product $Cp_2M(OC_{10}H_{16}S)$ (M=Ti or Zr) (Figure 1.8) [4].

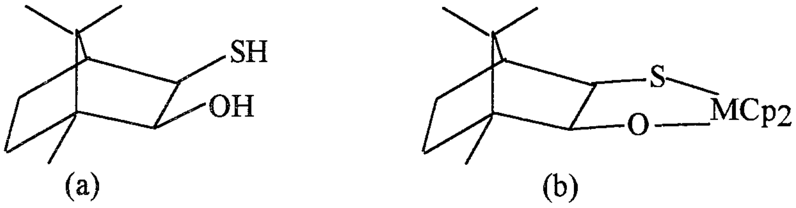


FIGURE 1.8. The Structures of a) (1R,2S,3R)-3mercapto-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, b) $Cp_2M(OC_{10}H_{16}S)$.

In 1988, Erker and co-workers studied the preparation and characterization of (benzylideneamido)zirconium complex $Cp_2Zr(N{=}CPh_2)_2$. This complex has been synthesized by reacting dichlorozirconocene with $LiN{=}CPh_2$, shown in figure 1.9, as follows :

$$Cp_2ZrCl_2 \;+\; 2\,LiN{=}CPh_2 \longrightarrow Cp_2Zr(N{=}CPh_2)_2$$

FIGURE 1.9. The Preparation Reaction of (benzylideneamido)zirconium Complex

The molecular structure of the (benzylideneamido) zirconium complex was determined by spectroscopic methods and X-ray crystallography. The proposed structure of the complex is shown in figure 1.10 [5].

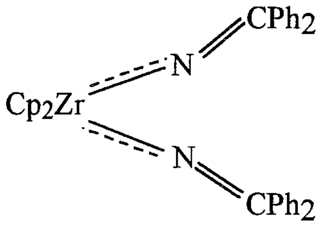


FIGURE 1.10. The Proposed Structure of (benzylideneamido)zirconium Complex

In 1991, Veya and co-workers studied the deprotonation of N,Ndiphenyl acetamide by the use of diisopropyl lithiumamide and the reaction of dichlorozirconocene with the lithiated amide. The coordination took place through the oxygen atom. The product was identified by ^{1}H-NMR and X-Ray crystallography (Figure 1.11) [6].

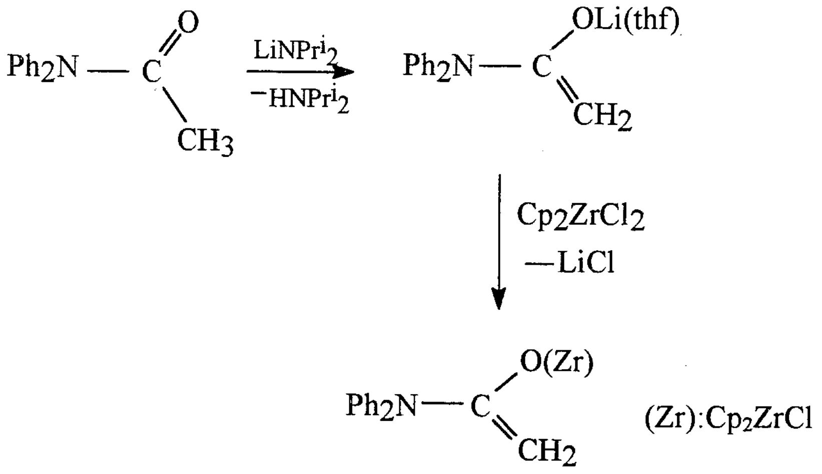


FIGURE 1.11. The Deprotonation of N,Ndihenylacetamide with Diisopropyl lithiumamide Followed by the Reaction with Dichlorozirconocene

In 1994, Erker and co-workers studied the reactions of chloro methylzirconocene with lithiated N-containing ligands such as N-pyrrolyllithium, lithium diethyl-amide and N-piperidyl lithium, shown in figure 1.12.

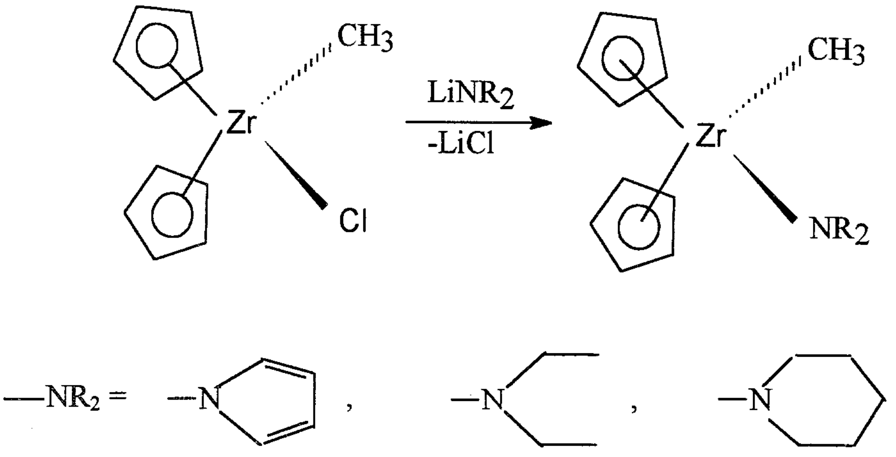


FIGURE 1.12. The Reaction of Chloro methylzirconocene with Lithiated N-Contaning Ligands Giving (N-pyrroyl)zirconocene methyl Complex and its Aliphatic Amidozirconocene methyl Complex Counterparts

Also they studied the reaction of (N-pyrollyl)zirconocene methyl complex with tris(pentafluorophenyl) borane, acting as a Lewis acid, and obtained the salt of methyl-zirconocene cation which acts as a moderate active catalyst in polymerizing ethylene (Figure 1.13) [7].

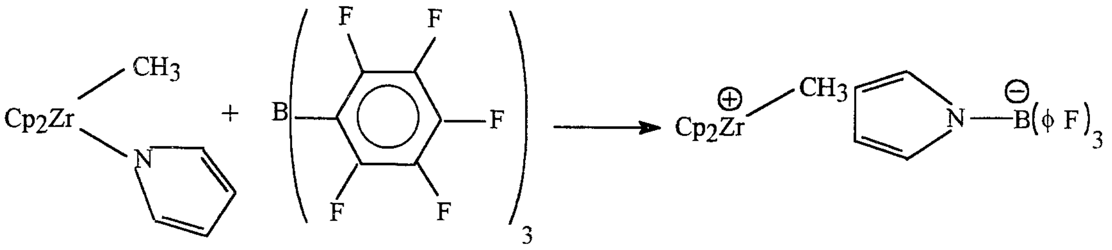
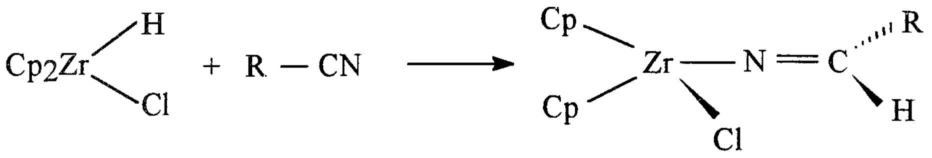


FIGURE 1.13. The Reaction of (N-pyrroyl)zirconocene methyl Complex with Tris(pentafluorophenyl) borane Giving Methylzirconocene Cation

One of the other organozirconium compound that is under study is hydridozirconocene chloride which can go through 1,2 insertion reactions with double or triple bonds.

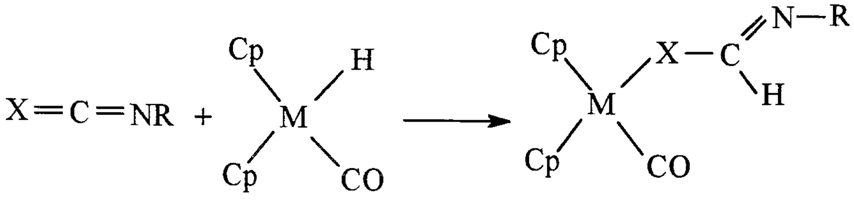
Erker and co-workers also studied hydrozirconation of acetonitrile and benzonitrile. In addition to the typical absorptions of the bent metallocene, the presence of an intense (C=N) streching frequency in the IR spectra has proven that an insertion reaction took place. This result was also supported by the NMR and X-Ray data (Figure 1.14) [8].



[R=Ph ; R=Me]

FIGURE 1.14. Hydrozirconation Reaction of Nitriles and the Proposed Structure of (methyleneamido)zirconocene chlorides.

In 1987, Leboeuf and Moise found out that various heterocumulenes insert readily into the M-H bound of d^2 complexes $[Cp_2M(CO)H]$ to give the O-, S- or N- metallated derivatives $[Cp_2M(CO)(\eta^1\text{-}XCH{=}NR)]$ (Figure 1.15) .



X = O, S, NR ; R = Ar ; M = Ta, Nb

FIGURE 1.15. The Formation of $Cp_2M(L)(\eta^1\text{-}XCH{=}NR)$ Complexes

They also studied the insertion reaction with carbondisulfide and metalhydrides. The proposed structures for these metal complexes are shown in figure 1.16.

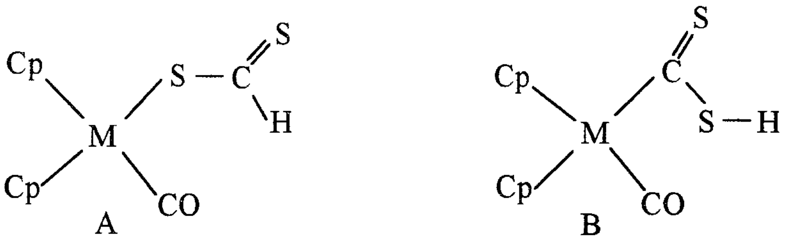


FIGURE 1.16. The Proposed Structures for $Cp_2M(CO)(CS_2H)$ Complexes

In the IR spectrum of the complex the bands of (S-H) streching frequencies were not observed, indicating that the structure of the complex was A. This result was also supported by NMR [9].

In 1991, Qui-Yun Ye and co-workers worked on the the complexation of dithiooxamides with Group 10 elements: Ni, Pd and Pt. Dithiooxamides are polyfunctional molecules that can act as chelating ligands in a variety of different ways. Ni(II) in one to one reaction with the ligand in neutral or weakly acidic media gave insoluble 1:1 polymeric product. In this material each ligand is believed to bridge between two nickel atoms through N and S atoms, forming a five membered chelate ring. It had been assumed that the chain terminates with the final dithiooxamide ligand coordinated in a bidentate S_2, rather than N,S fashion (Figure 1.17) [10].

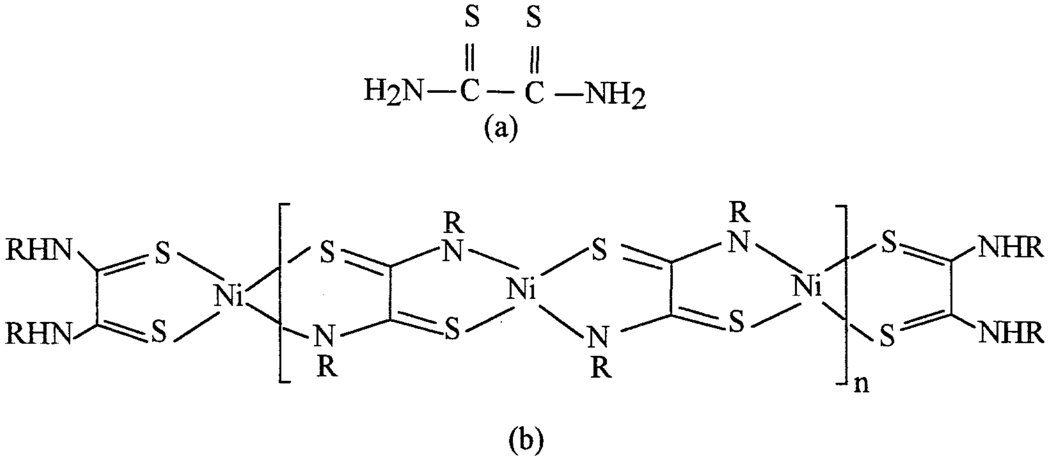


FIGURE 1.17. The Structures of a) Dithiooxamide, b) 1:1 Polymeric Ni(II) DTO Complex

In 1997, Şadiye Bayram, at Boğaziçi University, studied the THF reactions of dichlorozirconocene with compounds like thioacetamide and rhodanines which have more than one donor site. The red shift observed for the C=S stretching frequency of the thioacetamide in the IR spectrum of the product was taken as an evidence for the coordination through S atom as shown in figure 1.18. This result was supported by the ^{1}H-NMR and elemental analysis[11], as well as the theoretical study done by Şadiye Bayram under the supervision of Prof.Dr.Viktorya Aviyente [12].

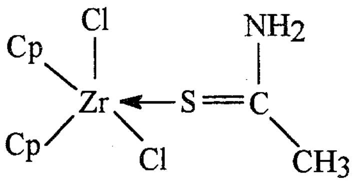


FIGURE 1.18. The Possible Structure of Thioacetamide-Zirconocene Complex

The THF reactions with rhodanines at room temprature did not lead to isolable stable complexes.

As partly being the extension of Şadiye Bayram's work, the purpose of this study was to observe the reactions of dichlorobis(η^5-cyclopentadienyl)zirconium(IV) with various N-, S- or thioamide group containing ligands and to observe the coordination sites of the latter to the metal atom.

The N-contaning ligands that were studied are shown in figure 1.19. In order to activate these ligands toward complexation, they were metallated by n-BuLi or by Na-naphtalide before reacting with dichlorozirconocene.

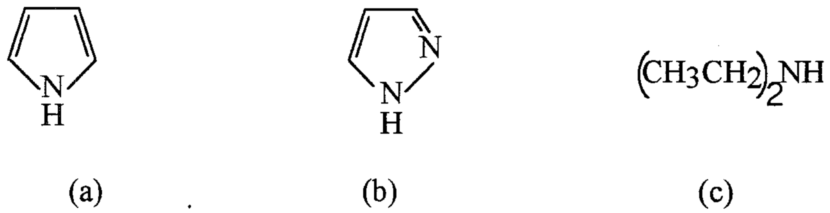
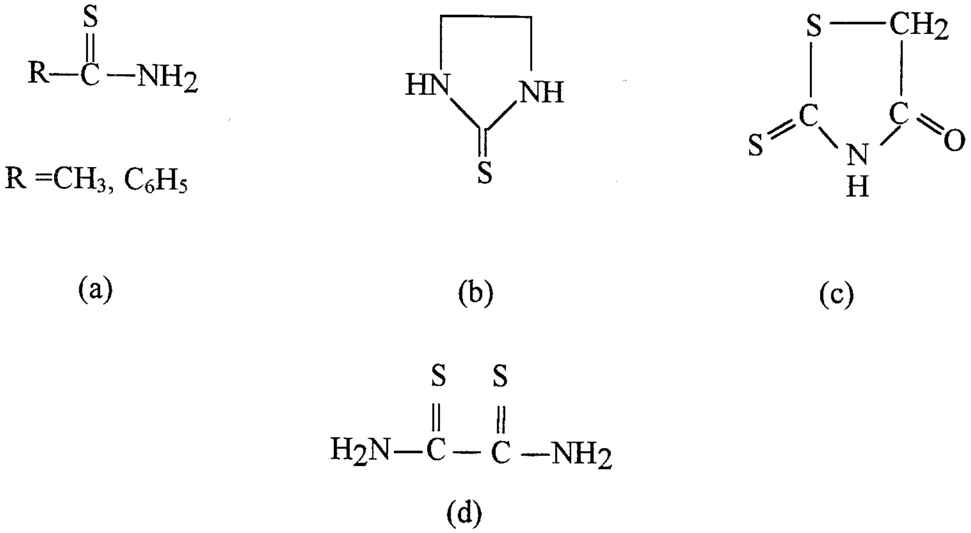


FIGURE 1.19. The N-contaning Ligands Used a)pyrolle, b) Imidazole, c)Diethylamine

The S-containing ligand that was studied is ethanethiol, CH_3CH_2SH, which was deprotonated by Na metal prior to use.

The thioamide contaning ligands, which were studied, are shown in figure 1.20. In the reaction of thioacetamide the effect of the solvent change from THF to CH_2Cl_2 was also observed.



(a) (b) (c)

(d)

FIGURE 1.20. The Ligands a) Thioacetamide, Thiobenzamide, b) Imidazolidine-2-thione, c) Rhodanine, d)Dithiooxamide.

The insertion reaction of hydridozirconocene chloride with carbondisulphide was also studied.

II. THEORY

2.1. Dichlorobis(cyclopentadienyl)zirconium(IV)

$(\eta^5\text{-}C_5H_5)_2ZrCl_2$

2.1.1. Metallocenes

A metallocene consists of a metal atom lying between two planar pentahapto cyclopentadienyl rings. The cyclopentadienyl group is perhaps the most important of the polyenyls because it is inert to both nucleophilic and electrophilic reagents.

Hapticity, η, of a ligand is the number of its carbon atoms that are within bonding distance of the metal atom.

Normal [bis(η5–cyclopentadienyl)] transition metal complexes such as ferrocene are highly symmetric molecules with parallel cyclopentadienyl rings. Their symmetry is D_5h if the two rings are eclipsed, or D_5d if the rings are staggered.

In bent [bis(η5–cyclopentadienyl)] transition metal complexes the rings are not parallel, that is the angle between the normals to the planes of the cyclopentadienyl ligands is less than 180°. One to three additional ligands can bind to the metal.(Figure 2.1).

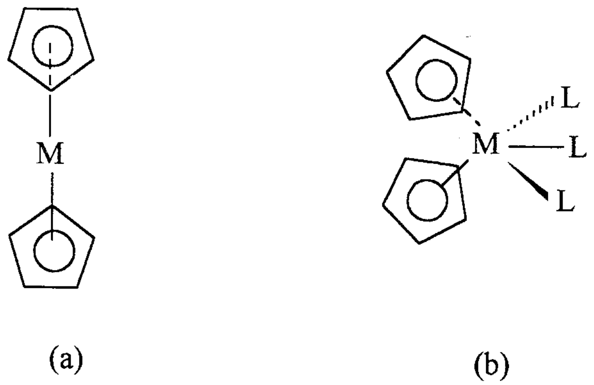


FIGURE 2.1. a) Normal Metallocene Structure, b) Bent Metallocene Structure

A bent Cp_2M fragment has C_2v symmetry if the Cp ligands are eclipsed, and only C_s symmetry if the rings are staggered [13].

Metallocenes, Cp_2M, of group IV (Ti, Zr, Hf) are capable of binding up to three ligands in addition to the two cyclopentadienyl rings. When additional ligands coordinate to the metal, the $C_5H_5^-$ ligands bent back. $(\eta5-C_5H_5)_2ZrCl_2$ has the type of bent metallocene. This bending rehybridizes the metal d orbitals, labeled dz^2, dx^2-y^2, dxy so that they point out of the open side of metallocene away from the rings and toward the additional ligands. These empty orbitals can house non-bonding electrons of the ligands.The occupancy of these orbitals depends on how many electrons the metal provides.In ferrocene itself, these are all filled. $(\eta5-C_5H_5)_2ZrCl_2$ is a 16 e- compound with an empty orbital, so that this orbital can act as Lewis Acid and tend to bind π-basic ligands, such as OR (Figure 2.2) [14].

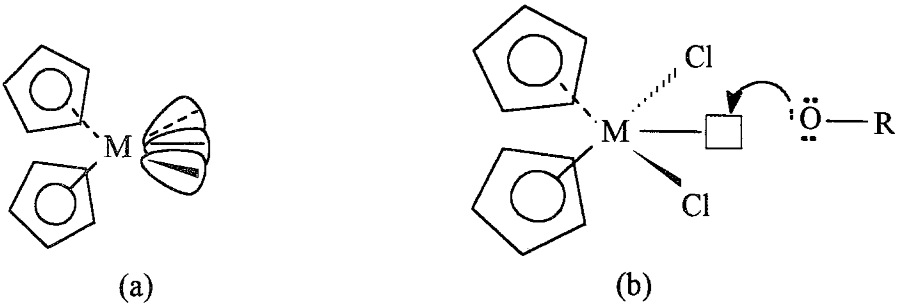


FIGURE 2.2. a) Empty orbitals of Cp_2M, b) Orbital Filling of $Cp_2M(IV)$

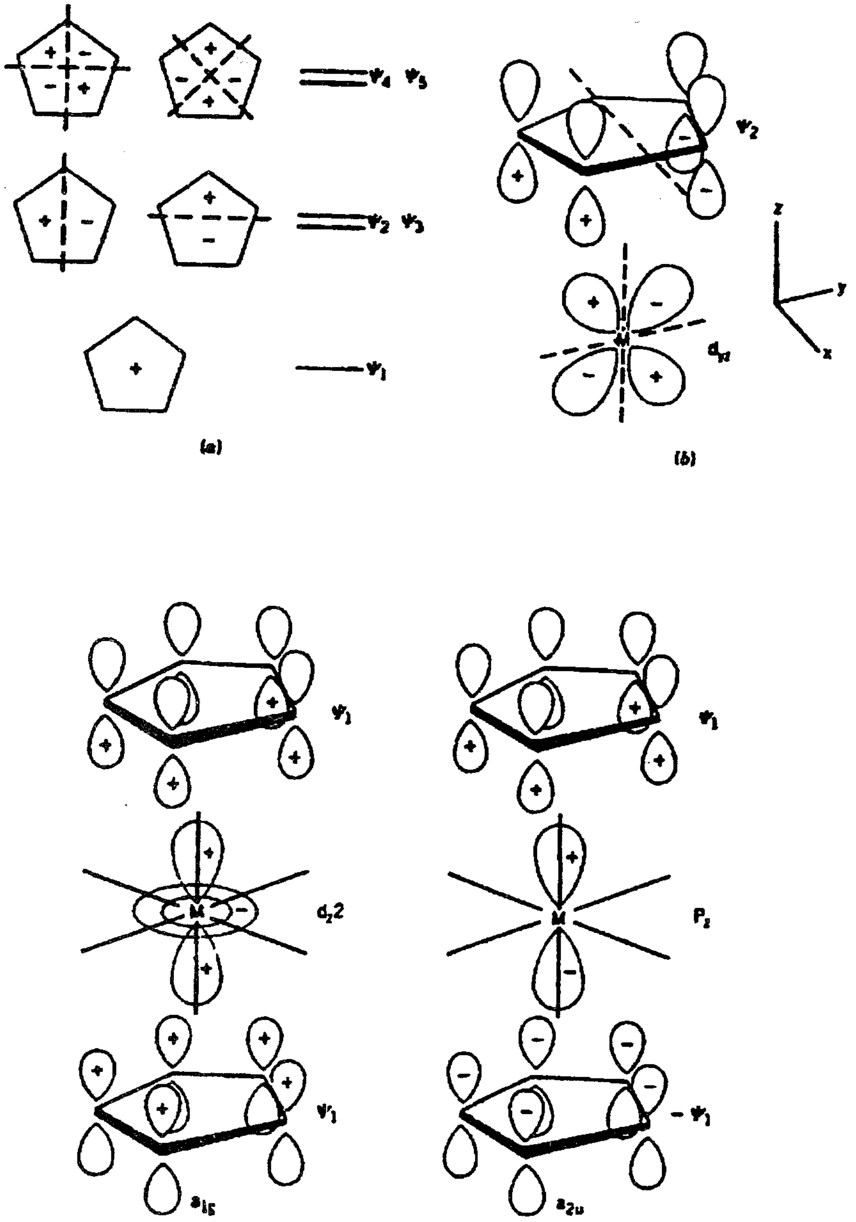


FIGURE 2.3. The Molecular Orbital Scheme for C_5H_5 Group

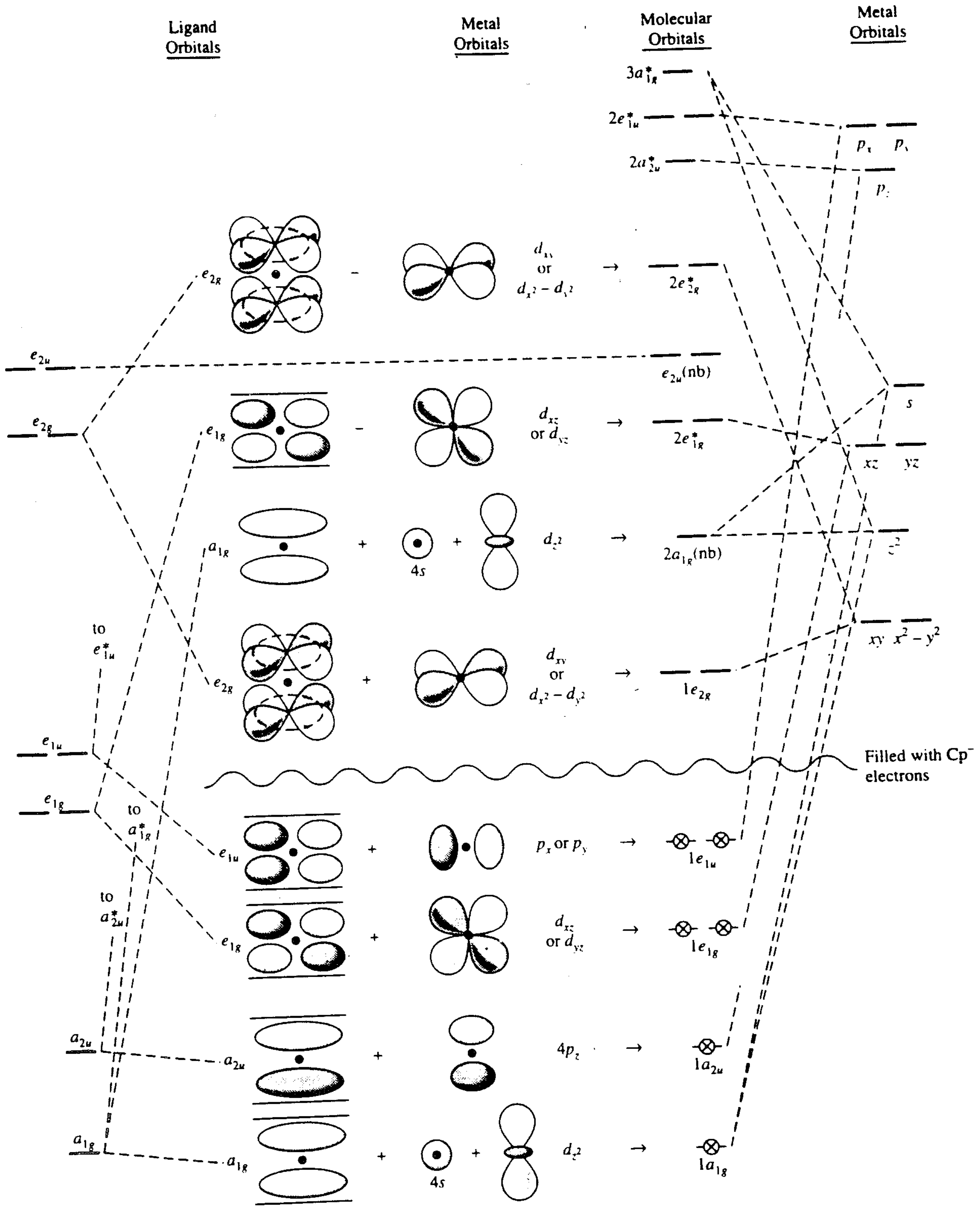


FIGURE 2.4. Molecular Orbital Energy Level Diagram for Metallocene

2.1.2. Bonding between the C_5H_5 ligand and metal

The molecular orbital scheme for C_5H_5 group is shown in figure 2.3 and 2.4. The five p orbitals on carbons give rise to five m.o.'s for the C_5H_5 group. In figure 2.3a, only the nodes are shown for simplicity. The most important overlaps are ψ_1 with the metal s, ψ_2,ψ_3 with the d_{xz} and d_{yz} orbitals; the latter is shown in figure 2.3b. ψ_4 and ψ_5 do not interact very strongly with metal orbitals and the Cp group is therefore not a particularly good π acceptor. So three orbitals are occupied with one Cp ligand. The bond between the so-called π–cyclopentadienyl group and a metal, therefore, involves six electrons, and the ligand can be regarded as occupying three coordination sites on the metal [14,15].

2.1.3. Physical Properties

The configuration of Cp_2ZrCl_2 is tetrahedral, and the Cp's are staggered (Figure 2.5). The bond angles and the bond lengths are tabulated in table 2.1[16]. Dichlorozirconocene is relatively stable compared to other organozirconium compounds.

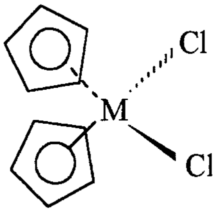


FIGURE 2.5. Structure of Dichlorobis(cyclopentadienyl)Zirconium(IV)

TABLE 2.1. Bond Lengths and Bond Angles of Cp_2ZrCl_2

Bond Lengths (A°)		**Bond Angles (degrees)**	
Zr-halide	2.31	Halide-Zr-halide	104
Zr-C (mean)	2.52	Cp-Zr-Cp	134
Zr-Cp (⊥)	2.21		
C-C (mean)	1.42		

IV B transition metal Zr (Zr ^{40}= [Kr]**4d^2** 5s^2) has empty d orbitals, therefore it is a oxophilic and halophilic metal.

2.1.4. The Spectroscopic Properties of Cp_2ZrCl_2

The identification of cyclopentadienyl derivatives of metals is facilitated by the characteristic peaks of their ^{1}H-NMR, infrared and mass spectra. ^{1}H-NMR chemical shifts (δ) of the C_5H_5 protons of some zirconium compounds are tabulated in table 2.2 [16].

TABLE 2.2. ^{1}H-NMR chemical shifts (δ) of the C_5H_5 protons of zirconium derivatives

Zirconium derivatives	$CDCl_3$	C_6D_6
Cp_2ZrCl_2	6.52(s)*	5.83(s)
$Cp_2Zr(CH_3)Cl$	6.27(s)	5.73(s)
$(Cp_2ZrCl)_2O$	6.28(s)	5.89(s)

* singlet

The protons of Cp give a singlet between 5-7 ppm which proves the aromatic character of Cp and the rapid rotation of the ring about the Metal-ring axis.

The Assignments for the IR bands associated with the C_5H_5 ring are listed in table 2.3 [17].

TABLE 2.3. The IR Spectrum of Cp_2ZrCl_2

Assignments for modes of vibration	Frequencies (cm^{-1})	Relative* intensity
ν(C-H) Symmetric inplane stretch	3108	s
ν(C-C) Symmetric inplane skeletal stretch	1443	s
ν(C-C) Asymmetric inplane skeletal stretch	1368	w
Symmetric ring breathing	1125	vw
δ(C-H) Asymmetric inplane deformation	1013	s
γ(C-H) Asymmetric out-of-plane deformation	851;840	s-s
δ(C-H) Symmetric out-of-plane deformation	811	vs

*s : strong, m : medium, w : weak, v : very

The mass spectrum of bis(cyclopentadienyl)zirconium and hafnium dihalide have been measured [17]. The breakdown pattern of these compounds proceeds via the preferential removal and fragmentation of the cyclopentadienyl ligands (Figure 2.6).

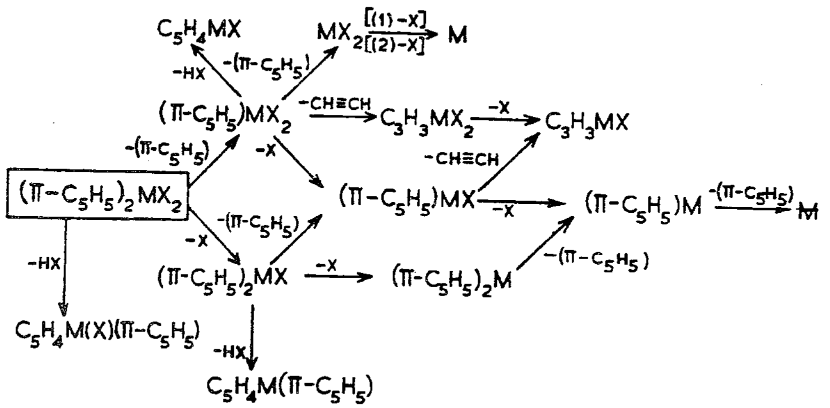
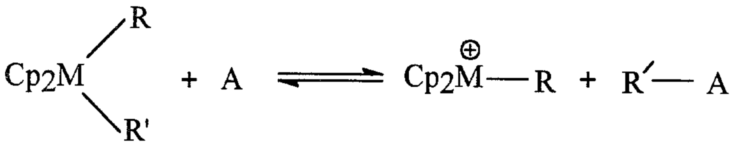


FIGURE 2.6. Fragmentation Pattern for Dichloro Metallocenes

This was thought to be indicative of the greater bond strength and higher ionic character of the M-Cl bonds in these complexes.

2.2. Cationic Metal-Alkyl Comlexes in Polymerization of Olefins

Homogeneous Ziegler catalysts based on Group IV metallocenes are used extensively in polymerization of several olefins. It is widely agreed that Cp_2ZrR^+ cation is one of the active species of these new catalyst systems. Commonly the generation of the active catalyst system is carried out by reacting the respective metallocene with Lewis acidic co-catalysts such as methylalumoxane (MAO), alkylaluminum halides. The role of these co-catalysts are thought to be facilitating the formation of electron deficient and coordinatively unsaturated 'cationic' metallocene alkyl species (Figure 2.7) [18].



M= Ti, Zr, Hf ; R= alkyl ; R'= alkyl or halide ; A= co-catalyst

FIGURE 2.7. Cationic Metallocene-alkyl Species

The cationic d° alkyl complexes Cp_2MR^+ also can be obtained by the following mechanism (Figure 2.8) [19]:

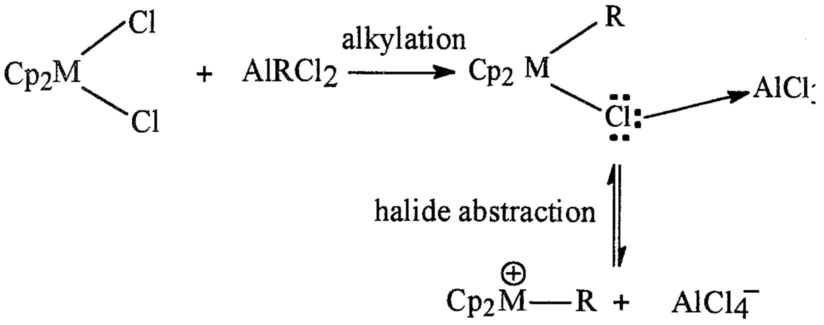


FIGURE 2.8. Formation of $Cp_2M(R)^+$ in a Soluble Ziegler-Natta System

The 14-electron cationic zirconocene complexes can easily insert olefins into the M-R bond.

Olefin polymerization by these cationic species is believed to involve a number of important reactions including (1) generation of an active metal-alkyl site, (2) repetitive insertion of olefin into the metal-alkyl bond, (3) chain termination / transfer by β-H elimination or by hydrogenolysis with added H_2 (Figure 2.9) [19].

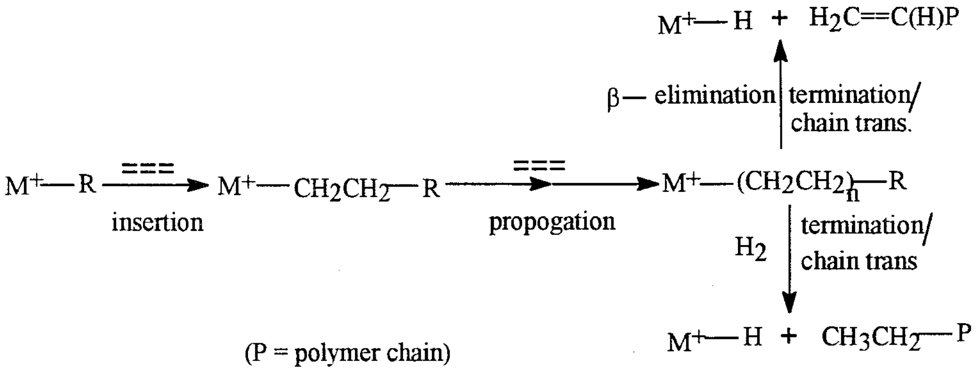


FIGURE 2.9. Key steps in Catalytic Etylene Polymerization

2.3. Hdyrozirconation

2.3.1. 1,2 Insertion and β-elimination Reactions

Once a ligand is attached to a metal, several reactions may occur, such as insertion and deinsertion or elimination reactions.

Insertion reactions that can take place are 1,1 insertion or 1,2 insertion reactions. Hyrozirconation is a typical example of 1,2 insertion reaction.

The conversion of an unactivated alkene or alkyne into a transition metal alkyl or alkenyl is supplied by 1,2 insertion reaction into M-H bond. This type of reactions involves two steps:

(1) Coordination of the olefin or acetylene to the transition metal atom

(2) β-M-H addition to the coordinated unsaturated molecule

as shown in figure 2.10 [20], [21].

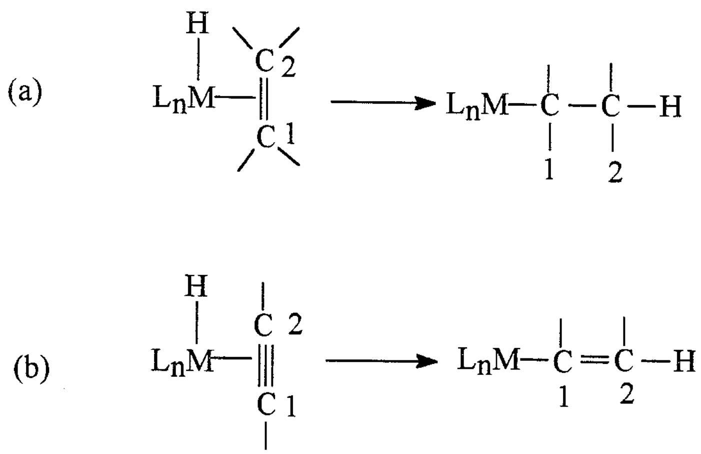


FIGURE 2.10. (a) 1,2 Insertion Reaction of Alkene into M-H Bond, (b) 1,2 Insertion Reaction of Alkyne into M-H Bond

The reverse of 1,2 insertion is called 1,2- or β-elimination. Figure 2.11 details the insertion-elimination reaction that yields a vacant site for coordination in the forward direction, 1,2 insertion and requires a vacant site for the reverse direction, β-elimination.

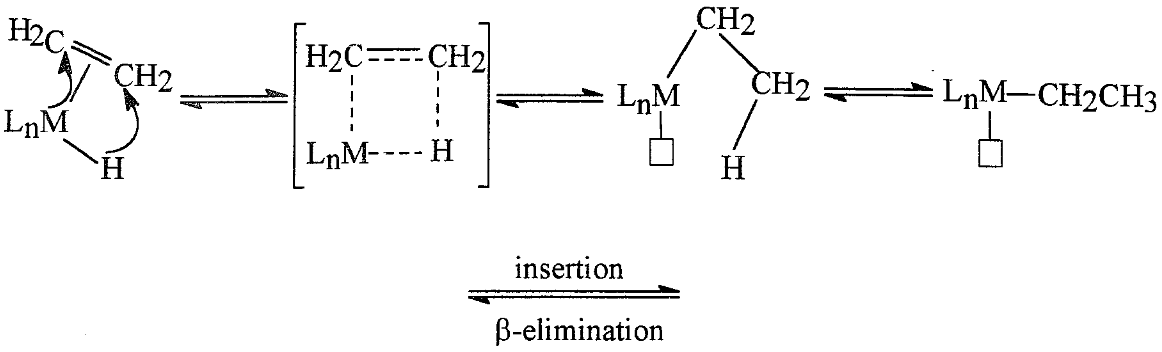


FIGURE 2.11. General Mechanism of 1,2 Insertion and β-Elimination Reactions

The hapticity of the organic ligand decreases by one with insertion, η^2 to η^1, and inreases by one with β-elimination, η^1 to η^2. Coordinatively saturated metal-alkyl complexes tend not to undergo β-elimination, especially if ligands bound to the complex such as Cp or bidentate phosphines [21].

2.3.2. Hydrozirconation and Schwartz Reagent

One of the most synthetically useful 1,2 insertion reaction is hydrozirconation which is the common name of the reactions of $Cp_2Zr(H)Cl$, known as Schwartz reagent,with several olefins and alkynes. The reaction of $Cp_2Zr(H)Cl$ with a variety of unsaturated organic molecules is summarized in figure 2.12.

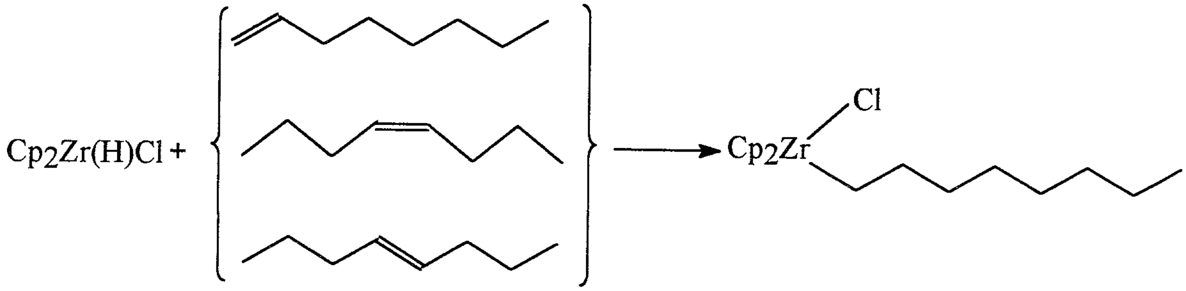


FIGURE 2.12. The Reaction of $Cp_2Zr(H)Cl$ with Olefins

As it is seen in figure 2.12, regardless of the initial position of the double bond, the Zr end up at the sterically least hindered position of the olefin chain. This rearrangment of the zirconium to the terminal position occurs by a Zr-H elimination, followed by a readdition that places Zr at the less-hindered position of the alkyl chain in each instance. This migration proceeds because of the steric congestion about Zr caused by the two cyclopentadienyl rings.

With hydride complexes of the transition metals in low formal oxidation states, the 1,2 insertion reaction in figure 2.11 lies very far to the left, because olefin (π-acceptor) complexes of electron rich metals are more stable than the corresponding alkyl (σ-donor) complexes. Because of the same reason electron poor transition metals in high formal oxidation states prefers the σ-alkyl complexes, the reaction lies to the right. $Cp_2Zr(H)Cl$, which has no d electrons to donate, reacts with a number of alkenes and alkynes to give stable, isolable alkyl complexes of the type $Cp_2Zr(R)Cl$.

Alkynes also react with $Cp_2Zr(H)Cl$, adding Zr-H in a cis manner. With unsymmetric alkynes, addition of Zr-H gives mixtures of vinyl Zr complexes with the less hindered complex predominantly (Figure 2.13) [21].

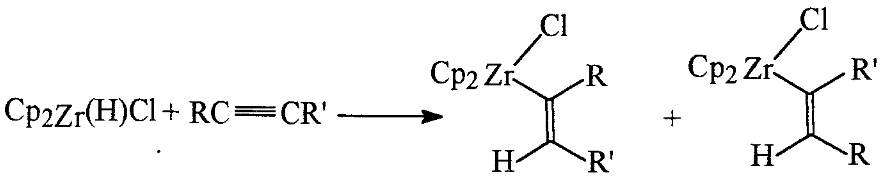


FIGURE 2.13. The Reaction of $Cp_2Zr(H)Cl$ with Alkynes

2.3.3. Physical and Spectroscopic Properties of $Cp_2Zr(H)Cl$

$Cp_2Zr(H)Cl$ is oxophilic, like Cp_2ZrCl_2, because of empty d orbitals in its structure.It is also light-sensitive, changing from white to pink on exposure to daylight.

Zr-H streching frequency appears at 1390 cm^{-1} indicative of Zr-H-Zr bridging [15].

The extreme insolubility of this compound indicates that the bridging hydrogens form a polymeric network. The attemps to obtain PMR spectrum were not succesful because of this insolubility [22].

2.4 Thioamide Bands

Organic compounds containing a thioamide group (HNC=S) are capable of undergoing thione-thiol (HNC=S ⇔ N=C-SH) tautomerism. Since the ligands contain a thiocarbonyl (C=S) group and an adjacent imino group as potential donors, they become interesting because of different coordination possibilities. Coordination can occur through either (a) both nitrogen and sulfur, or (b) through nitrogen only, or (c) through sulfur only.

Such ligands give rise to four characteristic infrared bands which are known as "thioamide bands" as listed in table 2.4.

TABLE 2.4. Thioamide Bands

Thioamide Bands	**Frequencies (cm^{-1})**	**Vibration Modes**
Band I	1500	δ (C-H) + δ (N–H) + ν (C=N)
Band II	1300 - 1200	ν (C=S) + ν (C=N) + δ (C-H)
Band III	1000	ν (C-N) + ν (C=S)
Band IV	700 - 850	ν (C=S)

These bands are expected to be affected differently by different modes of coordination after complexation with metal ions.

In 1974, Singh and Thakur studied the coordination chemistry of a number of thioamide containing ligands with Co(II) and Ni(II) ions. They observed the coordination sites by examining the thioamide bands I, II, III, IV after complexation.

Simultaneous metal-nitrogen and metal-sulfur bonding result in a decrease in the frequency of thioamide band IV by 40-100 cm^{-1}. Band II experiences a blue shift of

10 cm^{-1}. Band III is either considerably lowered in intensity and/or experiences a slight blue shift. The thioamide band I is red shifted to the extent of 30-70 cm^{-1}. Since band I is composed of contributions from δ (C-H) + δ (N–H) + ν (C=N), coordination through imino-nitrogen should result in a red shift of band I and coordination through thiocarbonyl sulfur should result a red shift of band IV which is mainly because of ν (C=S). Since band III is contributions from ν (C-N) + ν (C=S), a slight red shift of it also seems reasonable with a lowering in intensity during simultaneous metal-nitrogen and metal-sulfur bonding.

In case of only metal-sulfur bonding bands III and IV are likely to be red shifted because these have major contributions from ν (C=S). The other two bands are likely to be much less affected.

In case of only metal-nitrogen bonding bands I and II are likely to be red shifted because these have major contributions from δ (N–H) + ν (C=N) + ν (C=S) whereas band III and IV are shifted in opposite direction [23].

It has been reported by several workers that the thioamide band IV, ν (C=S), can be used as diagnostic of metal–nitrogen or metal-sulfur bonding. A red shift of 25-55 cm^{-1} in band IV indicates bonding through sulfur, a red shift of about 80-100 cm^{-1} indicates bridging sulfur ligand and a blue shift of 40-90 cm^{-1} indicates bonding through nitrogen [24].

However in 1977, Singh and co-workers reported that thioamide band IV alone can not be used in diagnosis of metal-ligand bonding according to their results on the study of the chealating behaviour of 2-mercaptoquinzole-4-one with Hg(II) (Figure 2.14).

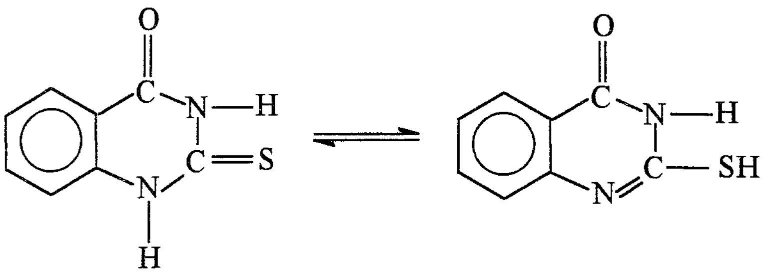


FIGURE 2.14. The Structure of 2-Mercaptoquinazole-4-one

It appeared that simultaneous coordination through nitrogen and sulfur has resulted in the red shift of band I, blue shift of band II and lowering of the intensity of band III and IV but no change in their positions. Thus they concluded that shifting of bands III and IV is dependent on the nature of the ligand. A ligand which can form metal-nitrogen and metal-sulfur bond such that red shifting because of the latter mode is compensated by the blue shifting because of the former mode, then bands III and IV remain unchanged in position. If there is more red shifting because of the coordination through sulfur and less blue shifting because of coordination through nitrogen then red shift of bands III and IV observed. Thus, only on the basis band IV, it is not possible to distinguish between metal-nitrogen, metal-sulfur and simultaneous metal-nitrogen and metal-sulfur bondings. Only for monodentate nitrogen sulfur ligands band IV can be used for diagnosis of nature of bonding [25].

In 1979, Singh and co-workers studied the thioamide bands and nature of bonding in complexes of non-transition metals with imidazolidine-2-thione. They had come to the conclusion that one should consider the nature of shifting of all the four thioamide bands as well as changes in their intensities in order to decide the coordination site. The thioamide bands of imidazolidine-2-thione and changes occuring after complexation with Hg(II) are given in table 2.5.

TABLE 2.5. Thioamide bands of imidazolidine-2-thione and its Hg(II) complex

Assignments	Ligand	Complex of imidazolidine-2-thione with Hg(II)	Changes in position	Changes in intensity
Thioamide band I ν (C-N) + δ (N–H)	1530s 1505s	1544sh 1512s	Blue shift	No change
Thioamide band II ν (C=S)+ν(C-N)+δ (N-H)	1200m	1208w	No cahnge	Decrease in intensity
Thioamide band III ν (CH_2-N) + ν (C-C) + ν (C=S)	1040s 919s	1032vw 908vw	Red shift	Decrease in intensity
Thioamide band IV ν (C-N) + ν (C=S)	685m	650vw	Red shift	Decrease in intensity

*s : strong , sh : shoulder, m : medium , w : weak, vw : very weak

Thioamide bands II, III, IV which have contributions from C=S stretching have undergone either red shift or decreased in intensity considerably or both have happened indicating the coordination through sulfur. Also the blue shift of Band I indicates that there had been no coordination through nitrogen. These results also supported by the far-IR spectrum of the complex [26].

2.5. The Ligands

A ligand is a molecule, ion, or molecular fragment bound to a central atom, usually a metal atom. Ligands may be classified according to the number of donor atoms that they have in their structure such as monodentate, bidentate etc.

In this work N-containing monodentate ligands such as pyrrole, imidazole, diethylamine are used. S-containing monodentate ligand that is used is ethanethiol. The compounds that can act as bidentate, tridentate, tetradentate ligands are the thioamide containing compounds whose structures were given in figure 1.19.

Main infrared absorption frequencies of the ligands and their Assignments are summarized in tables 2.6 - 2.12. Also the ^{1}H-NMR data are discussed in detail.

TABLE 2.6. Infrared Absorption Frequencies of Pyrrole and Their Assignments

Frequency (cm $^{-1}$)	Relative Intensity*	Assignments
~ 3400	s	N-H stretching
3129 , 3101	m	C-H stretching
1529	s	Ring stretching
1468 , 1418	m	Ring streching
1141	w	N-H inplane deformation

1074 , 1047 ,1014	s	C-H inplane and out of plane deformations
839	w	Ring out of plane deformation
732	s	C-H out of plane deformation
652	s	N-H out of plane deformation

* s : strong , m : medium , w : weak

In $CDCl_3$ the ^{1}H-NMR of pyrrole gives peaks at 6.73 and 6.17 ppm for α-CH and β-CH, respectively. In benzene these peaks appear at 5.85 and 5.80 ppm. In the absence of a solvent, a broad low field signal at 7.2 ppm is attributed to the imino proton [27].

TABLE 2.7. Infrared Absorption Frequencies of Imidazole and Their Assignments [28]

Frequency (cm^{-1})	Relative Intensity*	Assignments
3128 , 3110	s	C-H stretching
3025	s	N-H stretching
1662	m	C=N strecthing
1540	s	C-N stretching
1495 , 1478	m	C-N stretching and N-H deform.
1445	s	N-H in-plane deformation
1325	s	Ring breathing
1260 , 1144 , 1098, 1050	s	C-H in-plane deformation
930 , 895	s	N-H out of plane deformation
838	s	C-H in-plane deformation
753 , 735	s	C-H and N-H out of plane deform.
655 ,620	s	C-H and N-H out of plane deform.

* s : strong , m : medium , w : weak

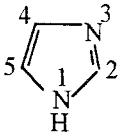


FIGURE 2.15. Structure of Imidazole

In the ^{1}H-NMR spectrum of imidazole, one proton triplet present at 7.64 ppm is assigned to second H, two proton doublet at 7.01 ppm assigned to fourth and fifth hydrogen atoms. Because of rapid exchange of N-H proton, the fourth and the fifth protons become magnetically equivalent as shown in figure 2.15 [29].

TABLE 2.8. Infrared Absorption Frequencies of Ethanethiol and Their Assignments

Frequency (cm $^{-1}$)	Relative Intensity*	Assignments
2964	s	CH_3 and CH_2 asymmetric stretching
2868	s	CH_3 and CH_2 symmetric stretching
2557	s	S-H stretching
1519	w	CH_3 asymmetric deformation
1448	s	CH_3 and CH_2 asymmetric deformation
1376 , 1269	s	CH_3 and CH_2 symmetric deformations
777 , 737	m	CH_2 in-plane rocking vibrations
657	s	C-S stretching

* s : strong , m : medium , w : weak

^{1}H-NMR of ethanethiol in $CDCl_3$ shows a triplet at 1.5 ppm for CH_3 protons and a quartet at 2.6 ppm for the CH_2 protons[30].

TABLE 2.9. Infrared Absorption Frequencies of Thioacetamide and Their Assignments

Frequency (cm $^{-1}$)	Relative Intensity*	Assignments
3520	s	N-H_2 asymmetric stretching
3300	s	N-H_2 symmetric stretching
2963 , 2920	w	CH_3 asymmetric stretchings
2850	w	CH_3 symmetric stretchings
1650	s	C=N stretching + δ NH_2
1483	m	δ (C-H)+δ (N–H) ,thioamide band I
1363	s	ν (C=S)+ν(C=N)+δ (C-H),thioamide band II
974	s	ν (C-N) + ν (C=S), thioamide band III
718	s	ν (C=S), thioamide band IV

* s : strong , m : medium , w : weak

In the ^{1}H-NMR spectrum (d-acetone) of thioacetamide, a singlet at 2.25 ppm observed for the protons of CH_3, no peak is observed for the NH_2 protons [11].

TABLE 2.10. Infrared Absorption Frequencies of Rhodanine and Their Assignments

Frequency (cm^{-1})	Relative Intensity*	Assignments
3405	w	N-H free stretching
3084	m	N-H bonded stretching
2962	m	C-H asymmetric stretching
2867	m	C-H symmetric stretching
1712	s	C=O stretching
1442	s	C-H and N-H bending

1082	s	ν (C-N) + ν (C=S), thioamide band III
784	s	ν (C=S), thioamide band IV
680	s	C-S stretching

*s strong , m : medium , w : weak

^{1}H-NMR of rhodanine (d-benzene) shows a singlet at 2.5 ppm for the CH_2 protons.

TABLE 2.11. Infrared Absorption Frequencies of Imidazolidine-2-thione and Their Assignments [26]

Frequency (cm $^{-1}$)	Relative Intensity*	Assignments
3240	s	N-H symmetric and asymmetric stretching
2878	w	C-H symmetric stretching
1520 ,1498	s	ν (C-N) + δ (N–H) , thioamide band I
1456	s	δ CH_2
1362	m	δ (N-H)
1275	s	CH_2 symmetric wagging + ν (C-C)
1203	s	ν (C=S)+ν(C=N)+δ (N-H),thioamide band II
1000 , 919	s	ν (CH_2-N) + ν (C-C) + ν (C=S) , thioamide band III
678	s	ν (C-N) + ν (C=S), thioamide band IV

*s strong , m : medium , w : weak

^{1}H-NMR of imidazolidine-2-thione in DMSO shows a singlet at 4.5 ppm for the CH_2 protons and a singlet at 8 ppm for NH_2 protons[30].

TABLE 2.12. Infrared Absorption Frequencies of Dithiooxâmide and Their Assignments [31]

Frequency (cm $^{-1}$)	Relative Intensity*	Assignments
3290	m	N-H asymmetric stretching
3206	m	N-H asymmetric stretching
3134	m	N-H symmetric stretching
1581	s	NH_2 in-plane deformation
1427	s	C-N stretching
1194	S	ρ NH_2
834	s	C=S stretching
702	m	NH_2 out of plane deformation
622	s	δ NCS

*s strong , m : medium , w : weak

In the ^{1}H-NMR spectrum of dithiooxamide in DMSO, a singlet at 9.6 ppm observed for the NH_2 protons [30].

III. EXPERIMENTAL

3.1. General Procedure

All the reactions were carried out under anhydrous conditions using Schlenk-type apparatus. All flasks were evacuated and filled with 99.998 per cent pure N_2 which was passed through molecular sieves prior to use.

All solvents and reagents were purchased from commercial sources (Table 3.1). The solvents, tetrahydrofuran and toluene were distilled from sodium benzophenone over moleculer sieves. Dichloromethane and hexane were distilled and stored over molecular sieves.

Dichlorozirconocene and $LiAlH_4$ were kept under dry N_2. All the other reagents were used directly after evacuating the possible O_2 and H_2O vapor present.

3.2. Reaction of Cp_2ZrCl_2 with Pyrrole

3.2.1. Preparation of Na-pyrrole

Naphtalene was purified by sublimation, pyrrole was distilled under N_2 prior to use. All weighing operations were carried out in glove-bag under a pre-purified dinitrogen atmosphere.

Solid Na metal (0.7187g, 31.200 mmole) and naphtalene (0.9065g, 7.08 mmole) were dissolved in THF (70 ml) in a schlenk-type flask in glove bag. The resulting dark green solution was filtered in order to get rid of excess Na. To this solution pyrrole (0.3400 ml, 5 mmole) was added and the solution turned light green. The resulting solution was stirred at room temperature, the color of the solution turned dark green during stirring.

3.2.2. Reaction of Cp_2ZrCl_2 with Na-pyrrole (in 1:1 ratio)

To a solution of Cp_2ZrCl_2 (0.5844g, 2 mmole) in 10 ml of THF, the solution of metallated pyrrole (26.5 ml, 2.5 mmole) in THF was added dropwise. The color of the solution turned yellow with the first drop and slowly orange and then brown during stirring. The resulting brown solution was stirred for 12 hours. Upon leaving the reaction mixture at –30°C, the formation of two layers were observed. As these two layers were miscible above this temperature, it was not possible to separate them either by filtration or by syringing out. After evaporating the solvent by N_2 a brown solid product mixture was obtained, which decomposed at 204°C. Further purification could not be succeded.

IR Spectrum :

The N-H stretching band of pyrrole appearing at 3400 cm^{-1} shifts to 3433 cm^{-1} in the IR spectrum of the product and a new band appears at 1629 cm^{-1}. All the other bands of pyrrole have disappeared. The C-H stretching band of dichlorozirconocene at 3100 cm^{-1} shifts to 3088 cm^{-1} and the C-H symmetric out of plane deformation band appearing at 811 cm^{-1} shifts to 794 cm^{-1}. No other change is observed in the bands of dichlorozirconocene.

NMR Spectrum :

A singlet at 6.2 ppm is observed for the protons of Cp, the peaks for pyrrole protons are not observed. (solvent : $CDCl_3$)

3.2.3. Reaction of Cp_2ZrCl_2 with Na-pyrrole (in 1:2 ratio)

To a solution of Cp_2ZrCl_2 (0.26g, 0.89 mmole) in 10 ml of THF, a solution of metallated pyrrole (19 ml, 1.79 mmole) in THF was added dropwise. The resulting solution was stirred for six hours. The color of the metallated pyrrole was dark brown and no color change was observed during addition and stirring. Upon leaving the reaction mixture at –30°C the formation of two layers was observed which were miscible at room temperature. The upper layer was separated by syringe to which three ml of toluene was added to precipitate a possible product and left at –30°C for three days. The resulting suspension was filtered at – 30 °C giving a pink residue which will be referred as 2A. The brown filtrate was left at –30°C, layer formation was observed again with some brown solid. The brown residue was filtered and the filtrate was left at –30°C again for 25 days and layer formation observed with some residue in it. After filtering the solution light brown residue (2B) was obtained. When the solvent was removed from the filtrate yellow crystals remained (2C).

2A

dp : 149 °C

Solubility : Soluble in acetone, chloroform, acetonitrile ; insoluble in water, toluene, hexane

IR Spectrum :

The N-H stretching band of pyrrole appearing at 3400 cm^{-1} shifts to 3386 cm^{-1} in the IR spectrum of 2A and a new broad band appears between 1708-1650 cm^{-1}. A new small band appears at 770 cm^{-1} and C-H out of plane deformation appearing at 732 cm^{-1} shifts to 739 cm^{-1}. All the other bands of pyrrole have disappeared. The C-H stretching band of dichlorozirconocene at 3100 cm^{-1} shifts to 3091 cm^{-1} and the C-H symmetric out of plane deformation band appearing at 811 cm^{-1} shifts to 807 cm^{-1}. No other change is observed in the bands of dichlorozirconocene.

NMR Spectrum :

A singlet appearing at 6.2 ppm is observed for Cp protons. The peaks of pyrrole are not observed. (solvent : $CDCl_3$)

2B

dp ~ 238 °C

IR Spectrum :

The N-H stretching band of pyrrole appearing at 3400 cm^{-1} shifts to 3339 cm^{-1} in the IR spectrum of 2B and a new broad band, whose center is 1655 cm^{-1} appears. C-H out of plane deformation appearing at 732 cm^{-1} shifts to 736 cm^{-1}. All the other bands of pyrrole have disappeared. No change is observed in the bands of dichlorozirconocene.

2C

mp ~ 237 °C

IR Spectrum :

No bands of pyrrole is observed in the IR spectrum of 2C and no change is observed in the bands of dichlorozirconocene except new bands appearing at 745 and 702 cm^{-1} . These peaks probably belong to the $[Cp_2ZrCl]_2O$.

NMR Spectrum :

A singlet at 6.4 ppm is observed for excess Cp_2ZrCl_2 and a peak at 6.2 ppm which must be of $[Cp_2ZrO]_2$. No peaks are observed for the protons of pyrrole.

3.3. Reaction of Cp_2ZrCl_2 with Lithiated Imidazole

A solution of imidazole (0.0068g, 10mmole) in 30 ml of THF in a schlenk-type flask under N_2 atmosphere was cooled to –78 °C and n-butyllitium (8ml of 15 per cent n-hexane solution) was added dropwise. The resulting milky suspension was stirred at –78 °C for half an hour, then warmed up to –25 °C and stirred for another half an hour. After cooling down to –78 °C, dichlorozirconocene (11mmole, 3.2142g) in THF was added and the resulting yellow reaction mixture was stirred at -78 °C for three hours. The reaction mixture was brought to –25 °C and toluene was added to precipitate LiCl and left at –30 °C for 14 hours. No precipitate formation was observed. The solution is cooled down to -78 °C and slowly warmed up to room temperature. Meanwhile the color of the solution darkened slowly and became brown. After the solvent was removed by vacuum distilation, a brown residue was left. To the resulting residue 50 ml of toluene was added and stirred for 2 hours. The resulting brown solution was left at -30 °C for 14 hours. A heavy precipitate was observed and separated by filtration. The residue (3A) obtained was brown and the filtrate was yellow. After the solvent of the filtrate was removed a yellow oily product (3B) was left.

3A

IR Spectrum :

New bands appear at 3452 cm^{-1} and 1637 cm^{-1} probably for the N-H and C=N stretching bands of imidazole respectively. All the other bands are same with the bands of dichlorozirconocene.

NMR Spectrum :

Because of the insolubility of 3A in common solvents its NMR spectrum could not be run.

3B

IR Spectrum :

No change has occurred at the bands of N-H and C-N stretching as well as at the bands of N-H bending. The bands of dichlorozirconocene remain unchanged. The bands of solvent (toluene) are also present in the spectrum.

NMR Spectrum :

A singlet appears at 2.4 ppm for the protons of CH_3. A broad singlet appears at 6.2 ppm (10H) and 7.1 ppm (13H). The former one is for the protons of Cp where as the latter one is for the protons of toluene, imidazole (solvent:C_6D_6)

Since N-H stretching and bending bands of imidazole have not disappeared, metallation through imino nitrogen did not take place. Several attemps to metalate imidazole were tried but could not be succeded.

3.4. Reaction of Cp_2ZrCl_2 with Litiumdiethylamide

Dichlorozirconocene (0.6202g, 2.12mmole) and litiumdiethylamide (0.1968g, 2.7mmole) were mixed as solids; then THF (30ml) was added and the mixture was strirred for 4 hours at room temperature. The color of the solution turned milky white. After removing the solvent in vacuum, a yellow residue remained to which 30 ml of toluene was added and the resulting precipitate was filtered. The solvent of the filtrate was removed leading a yellow solid product. The IR and NMR spectra of this product give the decomposition product of lithiumdiethylamide and unreacted dichlorozirconocene.

3.5. Reaction of Cp_2ZrCl_2 with Ethanethiol

3.5.1. Reaction of Cp_2ZrCl_2 with Ethanethiol

To a solution of dichlorozirconocene (0.6183g, 2.11mmole) in 15 ml of CH_2Cl_2, a solution of ethanethiol (0.2ml,) in 5 ml CH_2Cl_2 was added dropwise. The resulting solution was stirred for 8 hours at room temperature. The solvent was then removed in vacuo leading a white residue. The IR spectrum of the residue gave peaks of unreacted dichlorozirconocene and ethanethiol. The wide melting point of this residue also shows that no reaction has taken place.

3.5.2. Reaction of Cp_2ZrCl_2 with Metallated Ethanethiol

To a solution of ethanethiol (0.2ml, 2.7mmole) in 2 ml THF, solid Na metal (0.0459gr, 2mmole) was added and stirred. The H_2 gas was evolved through a bubler. The reaction continued until no more H_2 evolution was observed. To the metallated ehtanethiol solution dichlorozirconocene (0.79g, 2.7mmole) was added as solid. The color of the solution turned yellow after the addition of dichlorozirconocene. To this solution 18ml of THF was added and stirred for four hours. The resulting solution was seperated into two parts.

First Part : The solution was stirred at room temperature for 48 hours and left at –30 °C for eight hours. It was filtered to remove yellow residue 5A. The solvent of the filtrate was removed in vacuo and dark yellow residue 5B was left. Although 5B was tried to be recrystallized by stirring it with toluene for one hour at room temperature and leaving at -30 °C for 4 days, the resulting yellow solid 5C was not different than 5A and 5B in terms of IR spectrum.

Second Part: The solution was brought down to dryness under N_2 to leave a yellow residue 5D which could not be recrystallized by addition of toluene.

All the yellow products, 5A, 5B, 5C, 5D have almost the same IR and NMR spectra and decomposition points.

dp : 129°C

IR Spectrum :

No change is observed in the bands of dichlorozirconocene. In all the bands of ethanethiol an intensity decrease is observed. The CH_2 rocking vibration bands at 777 and 737 cm^{-1} appear at 774 and 749 cm^{-1}. C-S stretching band at 657 cm^{-1} shifts to 604 cm^{-1} and the intensity decreases which may be assignable to coordination through sulfur.

NMR Spectrum :

A singlet appears at 5.84 ppm for the protons of Cp. A quartet appears at 3.4 ppm for the protons of CH_2 and a triplet appears at 1.35 ppm for the protons of CH_3 with unrelated ratio. (solvent:C_6D_6)

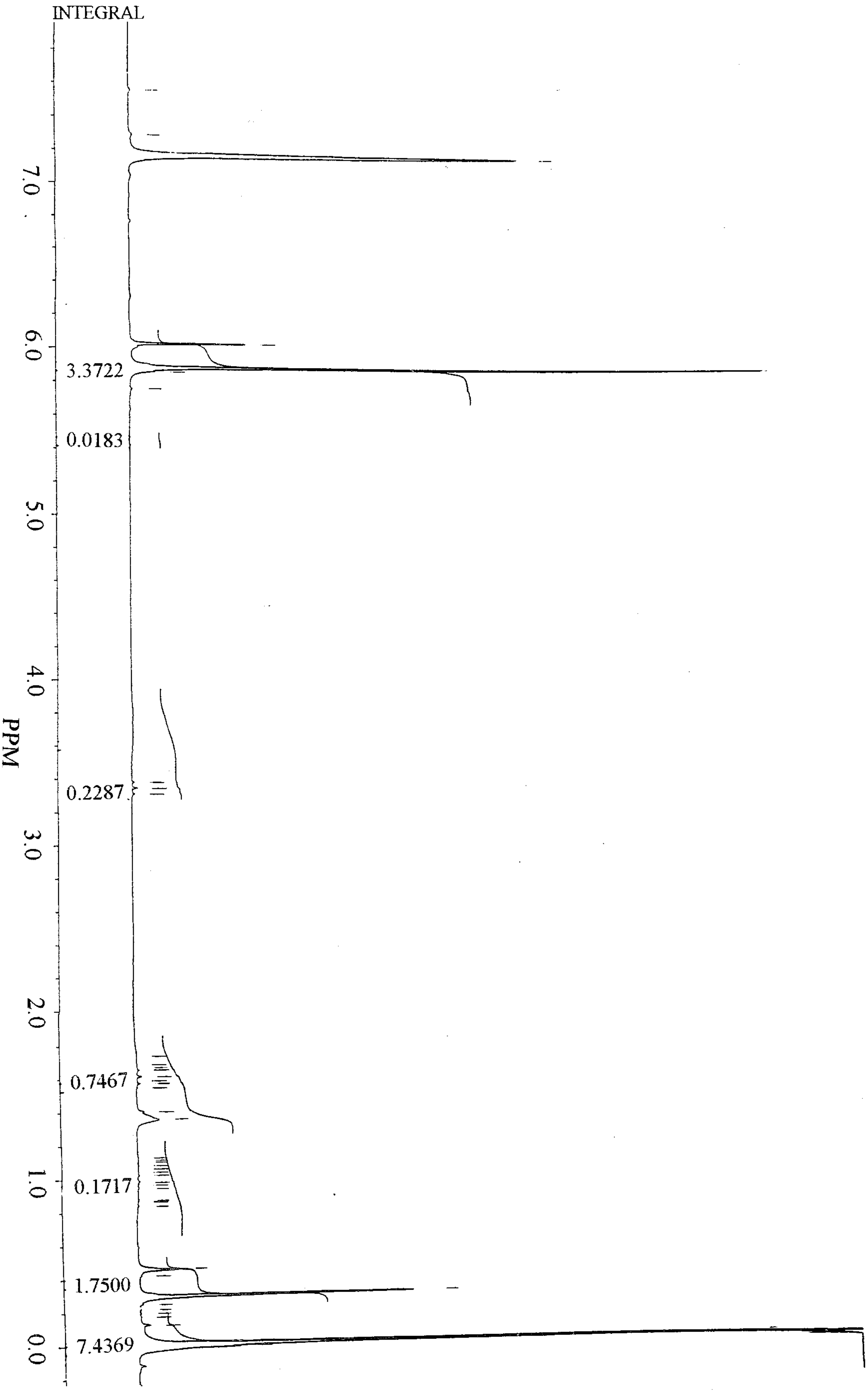


FIGURE 3.1. The ^{1}H-NMR Spectrum of $(Cp_2ZrClSCH_2CH_3)_2$ Complex

Mass Spectrum (FAB) : (per cent)

634.9 (0.5) : $M^+ = [\,Cp_2Zr(Cl)SC_2H_5\,]_2^+$
571.8 (5.0) : $M^+ - SCH_2CH_3 - 2H^+$
285.8 (23) : $M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - + 2H^+$
254.8 (5.0) : $M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - C_2H_5 + H^+$
220 (3.0) : $M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - C_2H_5 - Cl + H^+$
156 (5.0) : $M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - C_2H_5 - Cl - Cp$
132.8 (100) : $M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - C_2H_5 - Cl - Cp - C_2H_2 - 2H^+$

Elemental Analysis : (per cent)

Found : C, 39.13 ; H, 3.80
Calculated : C, 45.36 ; H, 4.72 [$C_{24}H_{30}S_2Cl_2Zr_2$]

3.6. Reaction of $Cp_2Zr(H)Cl$ with CS_2

3.6.1. Preparation of $Cp_2Zr(H)Cl$, Schwartz Reagent

3.6.1.1. Preparation of Ethereal Solution of $LiAlH_4$

1.0814g of $LiAlH_4$ with 40 ml of previously dried diethylether was refluxed for 1 hour in an atmosphere of N_2 in a round bottom flask fitted with a double surface reflux condenser protected with $CaCl_2$ tube. The resulting gray suspension was cooled to room temperature and filtered to remove excess $LiAlH_4$. The filtrate was milky and the gray residue was disposed by ethyl acetate.

3.6.1.2. Standardization of Ethereal Solution of $LiAlH_4$

0.2 M iodine solution in benzene was used to standardize the ethereal solution of $LiAlH_4$. Upon the addition of the first drops of iodine to a 5 ml of ethereal solution of $LiAlH_4$ the disappereance of the dark color of iodine and gas evolution were observed. When excess amout of iodine was added, the solution became dark in color as expected. The solution was shaken gently and allowed to stand for 5 minutes. 50 ml of distilled water and 2 ml of glacial acetic acid were added. The excess iodine was titrated with a previously standardized (0.2N) solution of sodiumthiosulfate three times. Starch indicator was added in the final stages of titration to determine the end point. The molarity of the solution $LiAlH_4$ was calculated to be 3.63 M. Standardization of sodiumthiosulfate was done by the following procedure :

25 g of $Na_2S_2O_3$ was dissolved in 500 ml of distilled water. A solution of 1.6667g of $KBrO_3$ in 250 ml distilled water was prepared and pipetted 25 ml of it. To the 25 ml of $KBrO_3$ / H_2O solution 1 g of KI and a few ml of 6 N H_2SO_4 were added. After 10 minutes the color of the solution turned brown. The $KBrO_3$ solution was titrated with $Na_2S_2O_3$ for 3 times. Starch solution was used as indicator. And the molarity of $Na_2S_2O_3$ solution was calculated to be 0.2 M.

3.6.1.3. Preparation of $Cp_2Zr(H)Cl$ with standardized $LiAlH_4$

Dichlorozirconocene (0.74g, 2.5mmole) was dissolved in THF (10ml) in a schlenk flask covered with aluminium foil under N_2. To this solution 0.18 ml of $LiAlH_4$/diethyl ether (3.63M) solution was added dropwise. The resulting solution was stirred at room temperature for two hours and at the end of this period it was left at –30°C for 48 hours but still no precipitate formation was observed. Removing the solvent from this solution in vacuo a white residue remained. It was recrystallized from THF/toluene mixture at –30°C. The filtered white recrystallized solid showed a new band at 1399 cm^{-1} referring to Zr-H stretching. This new band can be taken as an evidence for the formation of Schwartz reagent. [22].

NMR Spectrum : ($CDCl_3$)

A singlet appears at 6.4 ppm referring to protons of Cp_2ZrCl_2. It is reported in literature that $Cp_2Zr(H)Cl$ in the chlorinated solvents can turn into Cp_2ZrCl_2, therefore this peak can be from $Cp_2Zr(H)Cl$ reacting with $CDCl_3$.

3.6.2. Reaction of $Cp_2Zr(H)Cl$ with CS_2

To a solution of $Cp_2Zr(H)Cl$ ($9.3{*}10^{-3}$g, $3.6{*}10^{-5}$ mole) in 10 ml of toluene, CS_2 (0.1 ml, $1.65{*}10^{-4}$ mole) was added. The solution was stirred at room temperature for 6 hours and refluxed for 6 hours resulting in a milky solution. After toluene was removed in vacuo a green oily product remained. It was recrystallized –30°C in toluene. Green crystals were dried under vacuum. A proper recrystallization could not be done by THF/toluene mixture.

dp:250°C

IR Spectrum :

No change is observed in the bands of $Cp_2Zr(H)Cl$. The presence of the Zr-H band at 1404 cm^{-1} indicates that an insertion reaction did not take place. No new band is peresent for S-H stretching or C-H stretching indicating an insertion takes place. Also the bands of CS_2 do not exist.

NMR Spectrum :(C_6D_6)

A singlet appears at 5.86 ppm referring to Cp-H. No peak appears for the C-H or S-H indicating a possible insertion product.

Mass Spectrum(CI with methane): (per cent)

309.9 (10) ; 291.9(13) ; 254.9(38) ; 238.9(8) ; 191.9 (0.2) ; 151.1(5) ; 137.1(10) ; 123.1(15) ; 109.1(20) ; 95.1(100) ; 79(77)

3.7. Reaction of Cp_2ZrCl_2 with Thiobenzamide

To a solution of Cp_2ZrCl_2 (0.4079 g, 1.3900 mmole) in 15 ml of CH_2Cl_2, a solution of thiobenzamide (0.1900 g, 1.3800 mmole) in 15 ml of CH_2Cl_2 was added dropwise. After stirring for three hours at room temperature, there was no change in the color of the solution and no residue observed. The reaction mixture was refluxed at 40°C for two hours. After removal of the solvent, a yellow residue remained which gave no change in the bands of thiobenzamide and dichlorozirconocene.

3.8. Reaction of Cp_2ZrCl_2 with Thioacetamide

To a solution of Cp_2ZrCl_2 (0.6000 g, 2.100 mmole) in 20 ml of CH_2Cl_2, a solution of thioacetamide (0.2059 g, 2.7400 mmole) in 20 ml of CH_2Cl_2 was added dropwise. After stirring for one and a half hours at room temperature, the solution was colorless. When the solvent was removed a white residue remained, which was recrystallized with CH_2Cl_2/toluene mixture at –30°C. The product obtained was a white solid melting at 159 °C.

IR spectrum :

An intensity decrease in the N-H stretching bands of thioacetamide is observed. C=N stretching band appearing at 1650 cm^{-1} in the spectrum of thioacetamide shifts to 1642 cm^{-1} and is lowered in intensity. Thioamide band I, δ (C-H) + δ (N–H) appearing at 1483 cm^{-1} shifts to 1473 cm^{-1} and an intensity decrease has been observed. No change is observed in band II. These changes can be taken as an evidence for a coordination through nitrogen.

A slight red shift at band III, ν (C-N) + ν (C=S), and a red shift of band IV ν(C=S), from 718 cm^{-1} to 696 cm^{-1} indicate a coordination through sulfur which is confirmed by the appearance of new bands at 397 cm^{-1} and 379 cm^{-1}, assignable to ν (Zr-S), in the far-IR spectrum of the product. The band appearing at 471 cm^{-1} can be assigned either to ν(Zr-N) or δ (CCN) which are observed in the same region in far-IR spectrum.

NMR Spectrum : ($CDCl_3$)

In the ^{1}H-NMR spectrum ($CDCl_3$) of the product, a singlet at 2.5 ppm for the protons of CH_3 and a singlet at 6.48 ppm for the protons of Cp with an integral ratio of 1:3.6 are observed.

Mass Spectrum (CI with methane) : (per cent)

368 (1) : $[Cp_2ZrCl_2\text{-}SC(NH_2)(CH_3)]^+$; 255 (82) : $[Cp_2ZrCl]^+$; 76 (100) $[SC(NH_2)(CH_3)]^+$

3.9. Reaction of Cp_2ZrCl_2 with Imidazolidine-2-thione

3.9.1. Reaction of Cp_2ZrCl_2 with Imidazolidine-2-thione (without lithiation)

To a solution of Cp_2ZrCl_2 (0.3076g, 1.05 mmole) in THF, a solution of imidazolidine-2-thione (0.1941g, 1.9 mmole) in THF was added dropwise and stirred for 80 hours at room temperature and then refluxed for 8 hours. After filtration a brown residue (9A) and yellow filtrate were separated. The solvent was removed from the filtrate by vacuum distillation leading to a yellow residue (9B).

9A

IR Spectrum :

The N-H stretching band of imidazolidine-2-thione appearing at 3240 cm^{-1} splits into two broad bands at 3421 and at 3212 cm^{-1}. A new band appears at 1631 cm^{-1} in the region of C=N stretching.

The thioamide band I of imidazolidine-2-thione which has components at 1520 and 1498 cm^{-1} shows a blue shift to 1591 and 1540 cm^{-1} respectively in the IR spectrum of the product. The band at 1275 cm^{-1} refering to ω (CH2) and ν (C-C) shifts to 1242 cm^{-1}. A red shift and splitting is observed in the thioamide band II [ν(C=S) +ν (C-N) +δ (N-H)] from 1203 cm^{-1} to 1186 and 1153 cm^{-1}. A blue shift of the band III [ν(C=S) +ν (CH_2-N) +ν (C-C)] is observed from 1000 and 919 cm^{-1} to 1008 and 949 cm^{-1} respectively. And a red shift is observed at band IV refering to ν(C=S) from 678 cm^{-1} to 661 cm^{-1}.

The bands of dichlorozirconocene mostly lie under the bands of imidazolidine-2-thione except the bands at 851 and 806 cm^{-1}, they appear as a broad band at 824 cm^{-1}.

NMR Spectrum : (C_6D_6)

A singlet appearing at 3.5 ppm refers to the protons of unreacted imidazolidine-2-thione. Also singlet appearing at 2.4 ppm may refer to the shifted protons of imidazolidine-2-thione. A little singlet appear at 6.8 ppm for the very low field protons of dichlorozirconocene. Because of the poor solubility of the product the integral ratio of the protons could not be taken.

UV Spectrum :

Imidazolidine-2-thione shows a very intense peak at 248 nm in CH_2Cl_2, which is probably a π -> π* transition of the =N-CS-N= chromophore [31], is red shifted to 260 nm in the UV spectrum of product 9A in CH_2Cl_2.

Mass Spectrum (CI with methane) : (per cent)

256.1 (100) : $[Cp_2ZrCl]^+$; 100 (53) : $[SC\overline{NHCH_2CH_2N}H]^+$

9B

From the IR spectrum of 9B it is found out to be a mixture of imidazolidine-2-thione and dichlorozirconocene.

3.9.2. Reaction of Cp_2ZrCl_2 with Lithiated Imidazolidine-2-thione

A solution of imidazolidine-2-thione (0.5114g, 5mmole) in THF in a schlenk-type flask under N_2 atmosphere was cooled down to –78 °C and n-butyllitium (3.6 ml of 15 per cent n-hexane solution, 6 mmole) was added dropwise. The resulting mixture was stirred at –78 °C for half an hour, then warmed up to –25 °C and stirred for another half an hour. After cooling down to –78 °C, dichlorozirconocene (4mmole) in THF was added and the resulting mixture was stirred at -78 °C for three hours then warmed up to room temperature. A heavy milky white precipitate formation was observed. Upon filtration a good amount of dirty white residue was (9/2A) obtained. The yellow filtrate was vacuum distilled giving a yellow oily residue (9/2B).

9/2A :

dp : 140°C

Solubility : insoluble in acetone, CH_2Cl_2, $CHCl_3$, toluene, benzene, hexane and slightly soluble in THF and water.

IR Spectrum :

N-H stretching band of imidazolidine-2-thione appearing at 3240 cm^{-1} shifts to higher frequency and splits into 3380 and 3253 cm^{-1} and broaden which may indicate formation of two different N-H groups. A new band appears at 1654 cm^{-1} in the region of C=N stretching. No change occurs in the thioamide band I. N-H bending band appearing at 1362 cm^{-1} shifts to 1370 cm^{-1} and its intensity decreases. Thioamide band II appearing at 1203 cm^{-1} shifts to 1207 cm^{-1}. Thioamide band III appearing at 1000 and 919 cm^{-1} appears at 993 and 920 cm^{-1} and an intensity decrease is observed. Thioamide band IV at 678 cm^{-1} red shifted to 669 cm^{-1}.

The bands of dichlorozirconocene stay under the bands of imidazolidine-2-thione or do not exist.

Mass Spectrum (EI) : (per cent)
102 (100) : $[\mathrm{SC}\overline{\mathrm{NHCH_2CH_2N}}\mathrm{H}]^+$;
331(0.2) ; 172(5) ; 102(100) ; 86(20) ; 73(16) ; 57(4)

Elemental Analysis :
Calculated(%) : C(41.5) ; H(4.64) ; N(8.07)
Found (%) : C(23.60) ; H(4.64) ; N(7.59)

9/2B :

Solubility: Insoluble in all common solvents.

IR spectrum :

N-H stretching band of imidazolidine-2-thione appearing at 3240 cm^{-1} shifts to 3400 cm^{-1} and broaden. A new band appears at 1636 cm^{-1} in the region of C=N stretching.

No change is observed in the thioamide bands of imidazolidine-2-thione except a slight red shift is observed in thioamide band IV, from 678 cm^{-1} to 673 cm^{-1}. No change is observed in the bands of dichlorozirconocene.

3.9.3. Reaction of Imidazolidine-2-thione without Cp_2ZrCl_2 in THF

Imidazolidine-2-thione (2mmole) was dissolved in THF and stirred for 72 hours and refluxed for 8 hours. The resulting brown residue (9/3) was filtered. After the solvent was removed from filtrate in vacuum, a white residue remained which is found to be unreacted imidazolidine-2-thione by IR.

9/3

IR Spectrum :

N-H stretching band of imidazolidine-2-thione appearing at 3240 cm^{-1} shifts to higher frequency and splits into 3436 and 3242 cm^{-1} and broaden which may indicate formation of two different N-H groups. A new band appears at 1634 cm^{-1} in the region of C=N stretching. A blue shift is observed in the thioamide band I of imidazolidine-2-thione which appear at 1520 and 1498 cm^{-1} in the IR spectrum of imidazolidine-2-thione and shift to 1557 and 1536 cm^{-1} respectively in the IR spectrum of the product. A red shift observed in the thioamide band II [ν(C=S) +ν (C-N) +δ (N-H)] from 1203 cm^{-1} to 1197cm^{-1}. A blue shift is observed for band III [ν(C=S) +ν (CH_2-N) +ν (C-C)] from 1000 and 919 cm^{-1} to 1039 cm^{-1} respectively. A red shift is observed at band IV refering to ν(C=S) from 678 cm^{-1} to 601 cm^{-1}.

3.10. Reaction of Cp_2ZrCl_2 with Rhodanine

To a solution of Cp_2ZrCl_2 (0.4384g, 1.5 mmole) in CH_2Cl_2, a solution of rhodanine (0.2113g, 1.5 mmole) in CH_2Cl_2 was added dropwise. After refluxing for 8 hours and stirring for 48 hours at room temperature a yellow solution was obtained. After removal of the solvent a yellow residue remained. It was recrystallized from CH_2Cl_2/toluene mixture at –40°C for 48 hours giving a yellowish solid which turned out to be unreacted rhodanine by its IR and NMR spectra. The remaining yellow filtrate was precipitated with toluene at –40°C. After 6 days the formed orange-brown crystals (10B) were seperated by filtration and the remaining filtrate was left at –40°C for another 6 days but no crystal formation was observed. After evaporation of the solvent in vacuo a yellow residue was obtained (10C).

10B

mp : 159-230°C

IR Spectrum :

Because the C-H and N-H stretching bands of dichlorozirconocene and rhodanine (respectively) appear around 3100 cm^{-1} changes occuring in these band can not be detected well but it is observed that broadening decreases which indicates that H bonding through nitrogen does not take place any more. No other change is observed in the bands of rhodanine. The band at 777 refering to C=S stretching stay under the C-H symmetric out of plane deformationof dichlorozirconocene . No change is observed in the bands of dichlorozirconocene .

NMR Spectrum :(C_6D_6)

A singlet appears at 5.87(18.8) ppm for the protons of Cp ring. Another singlet at 2.5(1) ppm for the protons of rhodanine.

Mass Spectrum (EI) :(per cent)
294(97) : $[Cp_2ZrCl_2]^+$; 255(80) : $[Cp_2ZrCl]^+$; 133(60) : $[HN\text{-}COCH_2SCS]^+$

10C

mp : 170-245°C

IR Spectrum :

N-H free stretching disappears. The band appearing at 3094 cm^{-1} can be either C-H stretching of dichlorozirconocene or N-H stretching of rhodanine. The band at 1077 cm^{-1} which has contributions from C-N and C=S stretching shifts to 1053 cm^{-1} showing a possible coordination through sulfur. The band appearing at 777 cm^{-1} for C=S stretching of rhodanine stays under the C-H symmetric out of plane deformation of dichlorozirconocene. No change is observed in the bands of dichlorozirconocene .

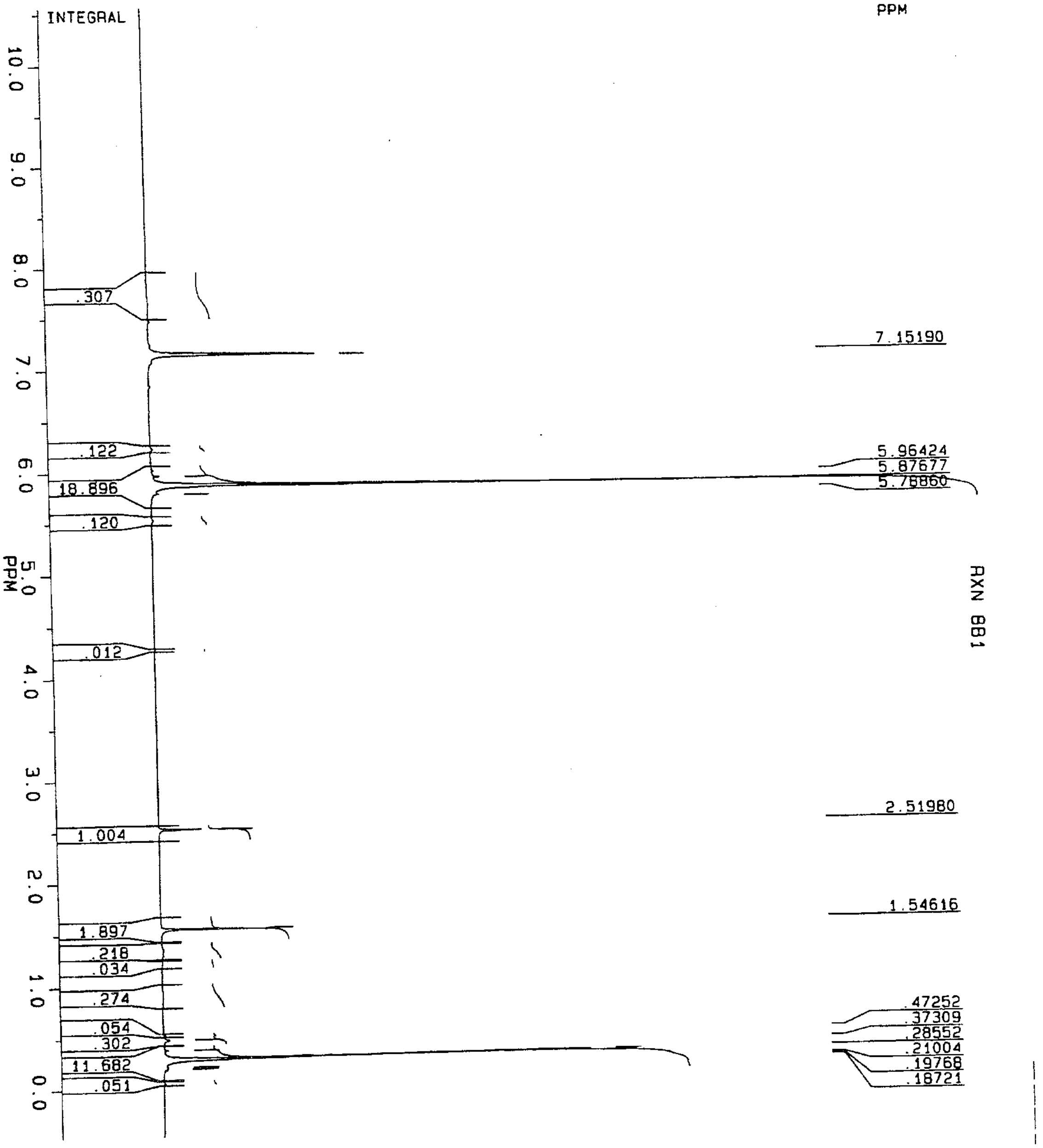


FIGURE 3.2. The ^{1}H-NMR Spectrum of the Rhodanine –Cp_2ZrCl_2 mixture (10B)

NMR Spectrum : (C_6D_6)

A singlet at 5.86 ppm for the protons of Cp, a small singlet at 2.5 ppm for the protons of rhodanine with unrelated integral ratio was observed.

Mass Spectrum (EI) :(per cent)

294(100) : $[Cp_2ZrCl_2]^+$; 255(85) : $[Cp_2ZrCl]^+$; 133(45) : $[HN\text{-}COCH_2SCS]^+$

3.11. Reaction of Cp_2ZrCl_2 with Dithiooxamide

To a solution of Cp_2ZrCl_2 (0.526g, 1.8 mmole) in CH_2Cl_2, a solution dithiooxamide (0.1803g, 1.5 mmole) in CH_2Cl_2 added dropwise and stirred for four days at room temperature. The solution was filtered to remove the orange residue which is found to be pure dithiooxamide by IR and NMR and melting point.

The resulting brown filtrate was vacuum distilled leading to a light brown residue which decomposes above 200°C. In the IR spectrum just the bands of dichlorozirconocene are present without any change. A singlet is observed at 5.9 ppm (C_6D_6) for the protons of Cp in the NMR spectrum.

3.12. Materials and Instruments

List of the chemicals used in this work, together with the names of the suppliers are briefly described in table 3.1.

The list of instruments used in the studies are briefly described below :

3.12.1. Instrumentation

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR (KBr pellet) and Nicolet 5 DXB (CsI).

^{1}H NMR were recorded on a Varian T-60A spectrometer (60 MHz, T= 24°C) and Bruker AC-200 (200MHz).

Elemental Analysis were performed on Carlo Erba 1100.

The Mass Specrea were recorded on VG ZABSPEC instrument (1000 resolution)

Melting Points were recorded using Electrothermal 9100 melting point apparatus.

3.12.2. List of Chemicals

TABLE 3.1. Chemicals Used in This Work

Name	**Formula**	**Supplier**
Tetrahydrofuran	C_4H_8O	Merck
Toluene	$CH_3C_6H_5$	Fluka
Dichloromethane	CH_2Cl_2	Merck
Hexane	C_6H_{14}	Merck
Pyrrole	C_4H_5N	Merck
Imidazole	$C_3H_4N_2$	Merck
Ethanethiol	C_2H_5SH	Merck
Thiobenzamide	$C_6H_5CSNH_2$	Aldrich
Thioacetamide	CH_3CS NH_2	Merck
Imidazolidine-2-thione	$C_2H_4N_2H_2CS$	Merck
Dithiooxamide	$NH_2CSCSNH_2$	Merck
Rhodanine	$C_3H_3NOS_2$	Merck
Carbondisulfide	CS_2	Merck
Lithiumaluminumhydride	$LiAlH_4$	Merck
N-butyllithium	C_4H_9Li	Merck
Sodium Metal	Na	Merck
Benzophenone	$C_6H_5COC_6H_5$	Eastman
Zirconocene	$(C_5H_5)_2ZrCl_2$	Fluka
Nitrogen Gas	N_2	BOS

IV. RESULTS & DISCUSSION

4.1. Reactions with N-containing Heterocycles

4.1.1. Reaction with Pyrrole

The reactions of Cp_2ZrCl_2 with Na-napthalide treated pyrrole in 1:1 ratio and 1:2 ratio lead to brown solid products. Unfortunately the identification of the product could not be done by the help of IR and NMR spectra. However, the presence of the NH stretching band in the IR spectrum of the products indicates that deprotonation did not take place through nitrogen. The new band appearing at 1629 cm^{-1} indicates C=N bond formation. The possible metallation products of pyrrole are shown in figure 4.1.

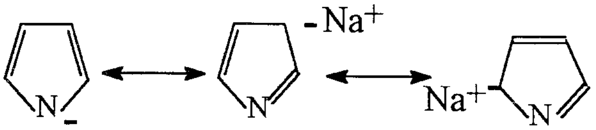


FIGURE 4.1. Metallated Pyrrole Ring

Although tautomers of pyrrole can explain the C=N formation, the presence of the NH stretching band at 3433 cm^{-1} still can not be explained. The ^1H NMR spectra of the obtained solid fractions do not support the coordination to zirconocene.

The products are thought to be mixtures of dichlorozirconocene and a decomposition product of pyrrole which can not be identified in different ratios.

One minor fraction of this reaction that was separated as (2C) is proven to be a mixture of Cp_2ZrCl_2 and $[Cp_2ZrCl]_2O$ by the NMR and IR spectra. The presence of $[Cp_2ZrCl]_2O$ can be taken as an evidence for abstraction of one Cl from Cp_2ZrCl_2 by the sodium salt of pyrrole. In solution the left fragment Cp_2ZrCl being a 15 é system can be stabilized by THF and when the solvent is removed it becomes very sensitive to O_2 which may lead to the formation of the $[Cp_2ZrCl]_2O$ dimer during the IR measurement

4.1.2. Reaction with Imidazole

The reactions of Cp_2ZrCl_2 with imidazole, which is treated with n-butyllithium prior to use, lead to brown oily products. As in the case of pyrrole, in the IR spectrum of the products broad NH stretching band is observed. The C=N stretching band of imidazole gets sharper and broadens.

The change in the C=N stretching band can be explained by the tautomers of deprotonated imidazole whereas the presence of the NH stretching band can not be explained. However the Cl abstraction can not be detected by the Zr-O-Zr band in the IR spectrum as in the case of pyrrole because Zr-O-Zr stretching band and the C-H and N-H deformation bands of imidazole appear in the same region.

4.2. Reaction with Ethanethiol

The reactions of Cp_2ZrCl_2 with ethanethiol takes place only after the removal of the RSH proton by metallation with Na. The resulting product is a dimer evidenced by the molecular ion peak appearing at 634.9 m/z in the mass spectrum of the product. Suggested fragmentations for the most abundant peaks in the mass spectrum of the product are listed in table 4.1. The elemental analysis also supports the formation of the product.

In the IR spectrum of the product the C-S stretching band appearing at 657 cm^{-1} in ethanethiol shifts to lower frequency, to 604 cm^{-1}, with an intensity decrease which indicates a coordination through sulfur. The disappearence of the symmetric C-C and C-H stretching and bending bands of ethanethiol can be explained by the formation of a highly symmetric product, where these bands become IR inactive.

TABLE 4.1. The Most Abundant Peaks of the Product Obtained from the Reaction of Cp_2ZrCl_2 with Metallated Ethanethiol

m/z	ion
634.9	$M^+ = [Cp_2Zr(Cl)SC_2H_5]_2^+$
571.8	$M^+ - SCH_2CH_3 - 2H^+$
285.8	$M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - + 2H^+$
254.8	$M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - C_2H_5 + H^+$
220	$M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - C_2H_5 - Cl + H^+$
156	$M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - C_2H_5 - Cl - Cp$
132.8	$M^+ - SCH_2CH_3 - Cp_2Zr(Cl)S - C_2H_5 - Cl - Cp - C_2H_2 - 2H^+$

The proposed structure of the dimer complex is given in figure 4.2.

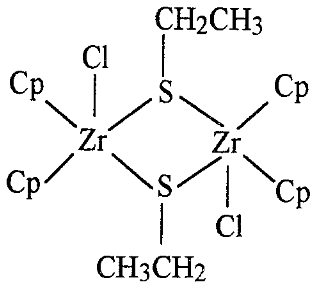


FIGURE 4.2. The Proposed Structure of the Dimer Complex Formed from the Reaction of Dichlorozirconocene with Metallated Ethanethiol

Because of the poor solubility of the product NMR spectrum was not proper to identify the peaks.

In literature it is reported that dichlorozirconocene with sulfur containig ligands forms monomers when freshly prepared, but in solution or on aging in the solid state, they tend to polymerize with subsequent loss of solubility. These compounds are all yellow in color [16].

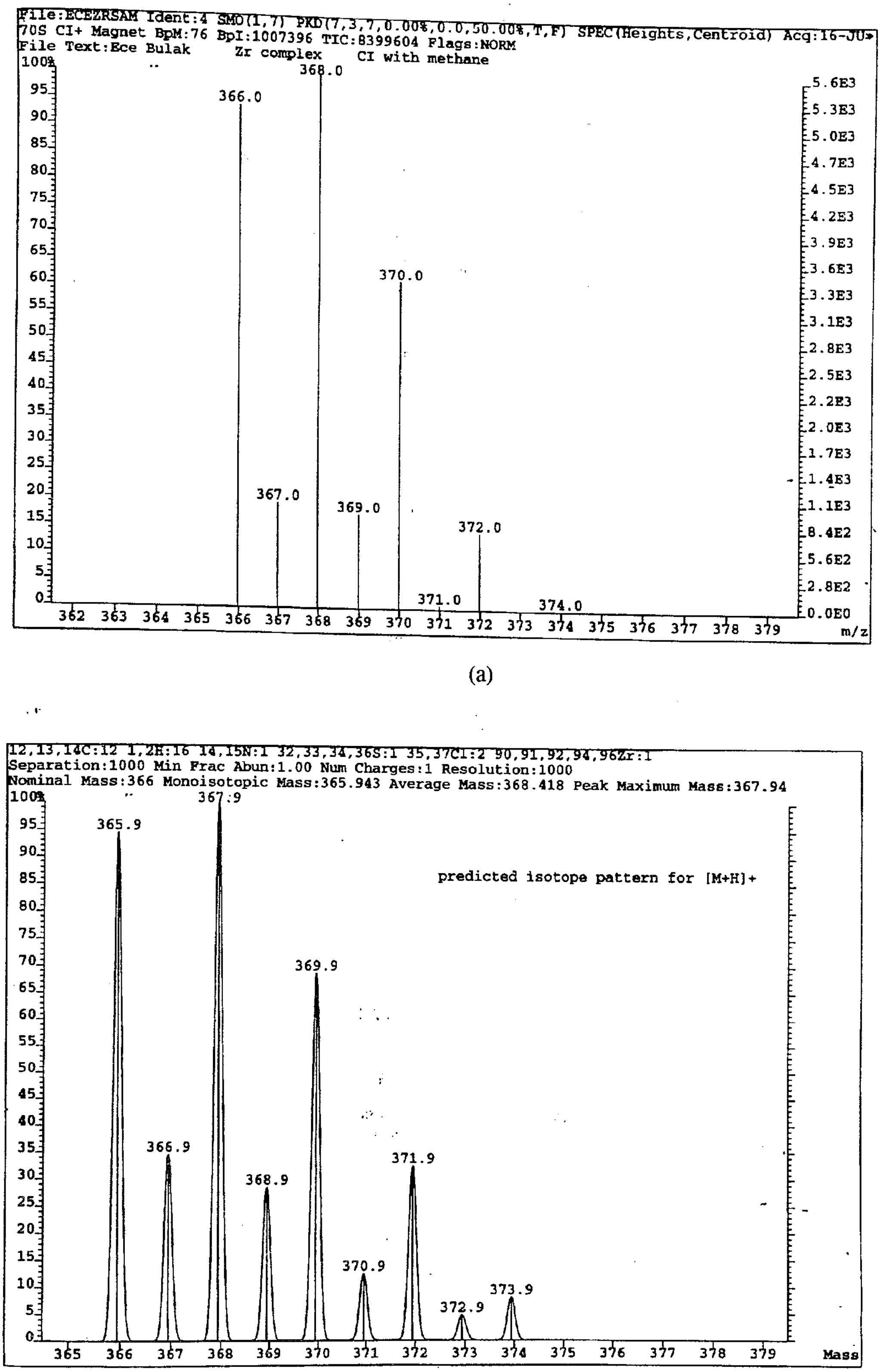
The reaction of dichlorozirconocene with ethanethiol alone does not result in any product evidenced by the IR spectrum,

4.3. Reaction with Thioacetamide

The reaction of Cp_2ZrCl_2 with thioacetamide in CH_2Cl_2 gives the monomeric product $Cp_2ZrCl_2(CH_3CSNH_2)$ evidenced by the mass spectrum which has the molecular ion peak at 368 m/z. This experimental molecular isotope pattern is in accordance with the theoretically predicted isotope pattern for the molecular ion peak as shown in figure 4.3.

In the infrared spectrum of the product, the red shift of band IV, ν (C=S), from 718 cm^{-1} to 696 cm^{-1} and the slight red shift of band III, ν (C-N) + ν (C=S), from 974 to 972 cm^{-1} indicates the coordination of thioacetamide to zirconium atom through thiocarbonyl sulfur atom. This result is also confirmed by the appearance of new bands at 397 cm^{-1} and 379 cm^{-1}, assignable to ν(Zr-S)[1], in the far IR spectrum of the product (Figure 4.4).

The red shift of C=N stretching band from 1650 cm^{-1} to 1642 cm^{-1} and the red shift of thioamide band I, δ (C-H) + δ (N-H) from 1483 cm^{-1} to 1473 cm^{-1} as well as the decrease in the intensity of these bands can be taken as evidences for participation of the NH group of thioacetamide in the bond formation with zirconium. The band appearing at 471 cm^{-1} in the far IR Spectrum of the product can be assigned either to ν (Zr-N)[1] or to δ (CCN) of thioacetamide[32] which is observed in the same region. But the band assigned to δ (CCN) is weak, whereas the band appearing in the far IR spectrum of the product is medium and broad therefore it can be still be accepted as Zr-N stretching (Figure 4.4).



(a)

(b)

FIGURE 4.3. a) Experimental Molecular Ion Isotope Pattern of $Cp_2ZrCl_2(CH_3CSNH_2)$ Complex; b) Predicted Molecular Ion Isotope Pattern of $Cp_2ZrCl_2(CH_3CSNH_2)$ Complex

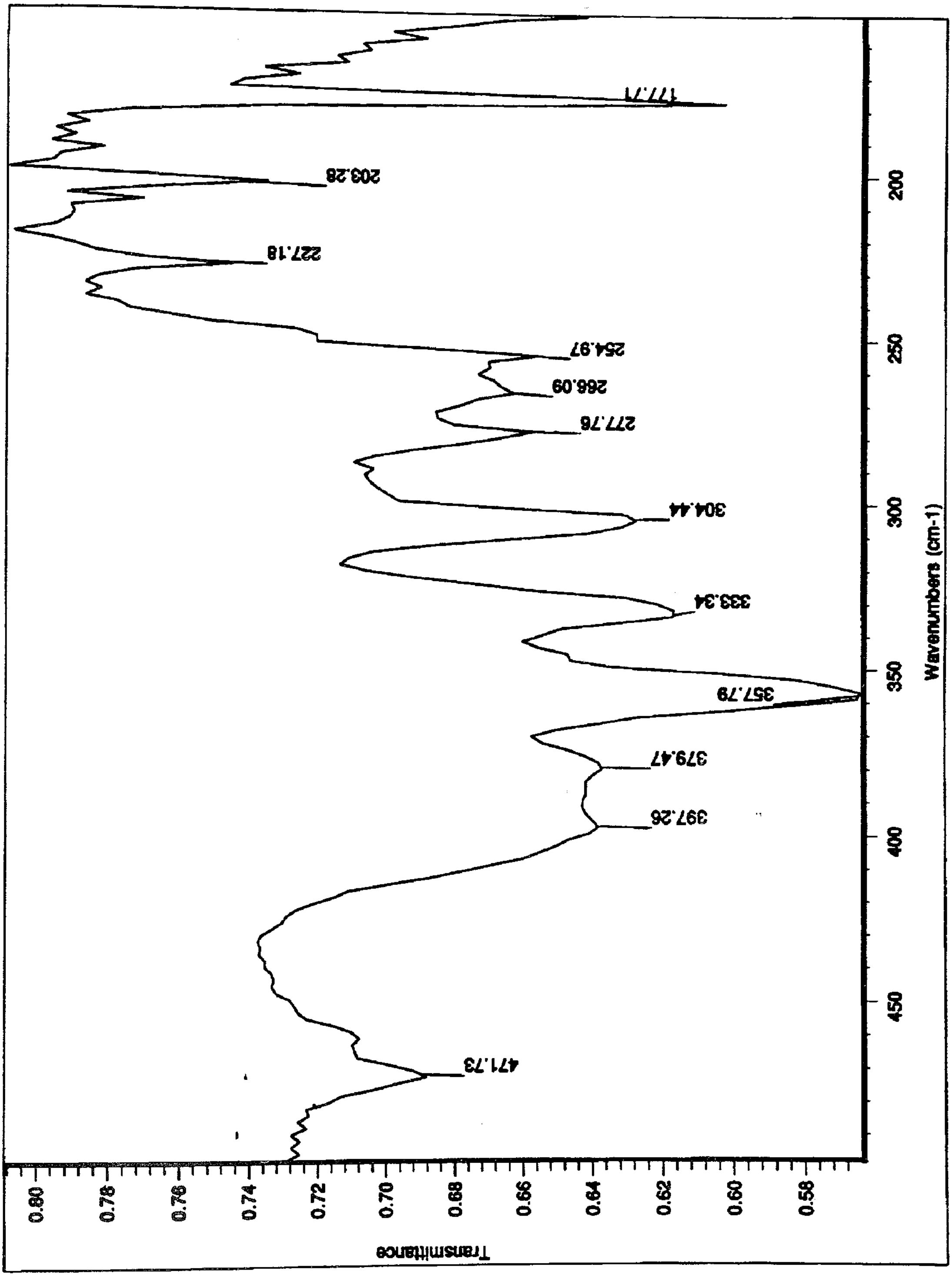


FIGURE 4.4. Far-IR Spectrum of $Cp_2ZrCl_2(CH_3CSNH_2)$ Complex

In the proton NMR spectrum of the product a slight high field shift for the Cp protons is observed which is expected in the case of an electronically richer environment of Cp's upon coordination to an electron donor ligand like thioacetamide. The shift of NH_2 protons of thioacetamide can not be observed as it probably lies under the Cp peak of dichlorozirconocene which also explains the higher integral ratio of the 6.48 ppm peak to 2.5 ppm peak than expected for the product.

When the same reaction is carried out in the presence of THF a red shift of band IV is observed indicating a coordination through S but no change is observed for C=N stretching band and thioamide band I which excludes coordination through N [11], however when CH_2Cl_2 is used as the reaction solvent, coordination seems to take place through S and N. The proposed structures of the complexes in THF and CH_2Cl_2 are shown in figure 4.5.

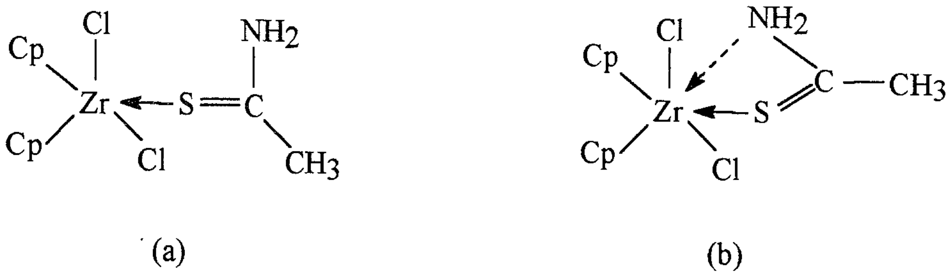


FIGURE 4.5. The Proposed Structures of the a) Thioacetamide-Zirconocene complex in THF, b) Thioacetamide-Zirconocene Complex in CH_2Cl_2

This result can be explained by the solvent effect. THF being an effective coordinating solvent prevents a possible coordination through N so coordination takes place only through S. However, because CH_2Cl_2 does not have such an effect coordination can take place through N as well as through S.

4.4. Reaction of Imidazolidine-2-thione

4.4.1. Reaction of Imidazolidine-2-thione (without lithiation)

The reaction of dichlorozirconocene with imidazolidine-2-thione in THF via refluxing leads to a brown product with poor solubility. However refluxing imidazolidine-2-thione in THF also leads to a brown product with poor solubility. Because of the resemblance of both products in their physical properties and as well as their IR spectra it seems reasonable that a self reaction of imidazolidine-2-thione took place rather than a coordination to Cp_2ZrCl_2.

In the IR spectrum of the product(s), the NH strecthing band of imidazolidine-2-thione splits into two which shows the presence of two different types of NH groups in the product. The band appearing at higher frequency is because of the free NH streching, whereas the broad absorption appearing at lower frequency is NH strecthing with H bonding (the presence of the bonded NH stretching band may be because of unreacted imidazolidine-2-thione existing in the product) [33].

While the free ligand exhibits typical thione character, when refluxed in THF (with dichlorozirconocene or alone) it can be found in its tautomeric thiolate form (Figure 4.6) which leads to a new band appearing in the region of C=N stretching. It is known that zwitterionic forms give a very high contribution, evaluated for imidazolidine-2-thione in the solid state of *ca.* 80 per cent [33].

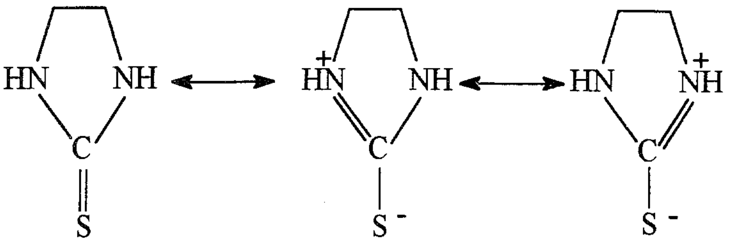


FIGURE 4.6. Tautomers of Imidazolidine-2-thione

The red shift of thioamide band IV, from 678 cm^{-1} to 661 cm^{-1}, which has main contribution from ν (C=S) indicates a lowering in the bond strength of thiocarbonyl group. The blue shift of thioamide band I from 1520 and 1498 cm^{-1} to 1591 and 1540 cm^{-1} indicates an increase in the C-N bond strength. This is further supported by the new band appearing at 1631 cm^{-1} indicating C=N formation.

From the changes in the IR spectrum it can be concluded that refluxing imidazolidine-2-thione in THF leads to a product dominant in its thiolate form. And the poor solubility of the product (precipitates in THF and other common solvents) can be taken as an evidence for the oligomeric structure. The following reaction can be suggested to have taken place but further analysis like mass spectrum are needed to strengthen this suggestion (Figure 4.7).

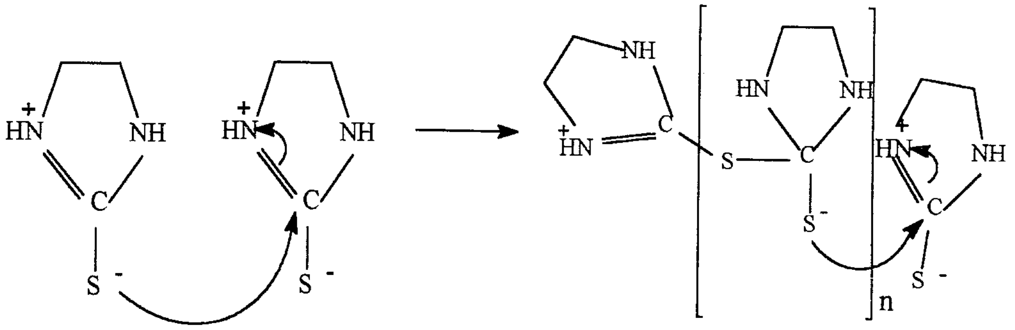


FIGURE 4.7. The Proposed Reaction of Imidazolidine-2-thione

Also the red shift of π -> π* transition of the =N-CS-N= chromophore in the product can be taken as an evidence for the increasing thiolate character in the complex.

In the mass spectrum of the product with dichlorozirconocene the peaks of $[Cp_2ZrCl]^+$ and $[SCNHCH_2CH_2NH]^+$ appear with high intensity. The fragmentations of a possible complex are not observed.

4.4.2. Reaction of Lithiated Imidazolidine-2-thione

The reaction of Cp_2ZrCl_2 with lithiated imidazolidine-2-thione gives dirty white and yellow solid products.

In the mass spectrum of dirty white product, the absence of Cp_2ZrCl_2 as well as any possible fragmentations of it indicate that dichlorozirconocene is not present. The low percentage of C in the elemental analysis of the dirty white product also indicates the absence of dichlorozirconocene. However if the product is just imidazolidine-2-thione or its lithiated form the C percentage is not expected to be that low. This can be explained by the formation of a product without any carbon in its composition, like LiCl so that overall mixture would have a low percentage of C. The slight solubility of the product in THF and water can be indicative of a mixture of LiCl and a decomposition product of imidazolidine-2-thione. It is thought to be a decomposition product because imidazolidine-2-thione or its lithiated salt should be soluble in most of the common polar solvents. In the IR spectrum of the dirty white product the bands at 3380cm^{-1} and 3254cm^{-1} show that free NH groups occur after the reaction. The new band appearing at 1645 cm^{-1} indicates formation of C=N. The slight red shift of thioamide band IV from 678 cm^{-1} to 669cm^{-1} indicates a weakening of the C=S. These two changes show that the thiolate character is dominant in the product. Also its insolubility in common solvents like toluene,chloroform etc can be taken as an evidence for an oligomeric product. However its structure can not be predicted with this information.

Although in the dirty white product LiCl seems to be present (indicating a Cl abstraction), in the IR spectrum of the yellow solid no significant change is observed either in the bands of dichlorozirconocene or in the thioamide bands of imidazolidine-2-thione indicating a possible coordination. Only a slight red shift of thioamide band IV from 678 cm^{-1} to 673cm^{-1} is observed which can indicate a possible coordination through S. New band appearing at 1636 cm^{-1} shows the formation of C=N. Therefore the slight red shift of thioamide band IV can be either because of a possible coordination through S or because of appeareance of thiolate form after the reaction. The shift of the NH stretching band to higher frequency indicates the presence of free NH groups.

4.5. Reaction with Rhodanine

The reaction of Cp_2ZrCl_2 with rhodanine in CH_2Cl_2 gives a yellow and orange solid mixture. The wide melting point range of this solid also supports the formation of a mixture.

The IR spectrum of the solid does not give much information as both the C-H and N-H stretching bands of dichlorozirconocene and rhodanine appear around 3100 cm^{-1}. Also the band at 777 cm^{-1} of rhodanine which belongs to the C=S stretching overlaps with the C-H symmetric out of plane deformation band of dichlorozirconocene. Any change that will happen in these bands can not be detected well. However the sharpening of the 3100 cm^{-1} band in the obtained solid can be taken as evidences for the loss of H bonding but occupation of the NH group of rhodanine by other groups. No change is observed in the non-overlapping bands of dichlorozirconocene.

Unfortunately any coordination of rhodanine to zirconocene can not be observed by the ^1H NMR and Mass spectra of the solid. In the ^1H NMR two singlets due to the Cp protons of dichlorozirconocene and CH_2 protons of rhodanine without any change can be seen. In the mass spectrum of the solid the molecular ion peaks of rhodanine and Cp_2ZrCl_2 can be detected with high intensities.

Even in the presence of a non-coordinating solvent rhodanine does not coordinate to zirconocene which can be explained by the steric hindarance of dichlorozirconocene. Without a Cl abstraction cyclic systems can not approach the tetrahedral dichlorozirconocene .

4.6. Reaction with Dithiooxamide

The reaction of Cp_2ZrCl_2 with dithiooxamide in CH_2Cl_2 gives dithiooxamide and the unreacted Cp_2ZrCl_2 as evidenced by the IR and NMR spectra.

In literature, it is reported that planar dithiooxamides form planar $Cu(LH_2)X_2$ complexes where X=Cl,Br and LH_2= dithiooxamide, without deprotonation of the ligand. Coordination takes place through both sulfur atoms, forming a five-membered chealate ring [34]. However in the case of dichlorozirconocene , compared to $CuCl_2$, the presence of the two cyclopentadienyl rings in addition to the Cl atoms can prevent formation of such a five-membered chelate ring because of steric crowdness. Coordination through only one sulfur or nitrogen can disturb the planarity of the ligand therefore, dithiooxamide can not approach to the tetrahedral structure of dichlorozirconocene.

4.7. Reaction of $Cp_2Zr(H)Cl$ with Carbondisulfide

The reaction of CS_2 with $Cp_2Zr(H)Cl$ in toluene gives a green unstable solid product. In the IR spectrum of the product the presence of the Zr-H stretching band at 1404 cm^{-1} and the absence of new bands for S-H and C-H stretching indicates that the expected insertion reaction into the Zr-H bond does not take place.

In the NMR spectrum of the product a singlet appearing at 5.86 ppm belonging to the Cp group is seen. No new peak is observed for the protons of S-H or C-H, which excludes the possibility of the insertion reaction.

It is possible to think that CS_2 behaves as a π donor ligand to the $Cp_2Zr(H)Cl$. In that case Zr-H stretching band is expected to appear at a higher frequency in the IR spectrum (which shifts from1399 to 1404 cm^{-1}) and no C-H or S-H stretching band is to be observed. In the ^1H NMR spectrum again no C-H or S-H peak is expected. The Zr-H proton shift is expected to be seen at very high field (between 0- -8 ppm). This region of the NMR could not be covered with the NMR instrument available.

The white color of Schwartz reagent turning into green in the product indicates that a new compound has formed which is unstable. Indeed, during Mass Spectroscopic analysis the color of the product becomes yellow which shows a decomposition. These color changes usually happen in π complexes. Although the molecular ion peak (332 m/z) can not be observed in the mass spectrum of the product, the presence of the peaks over 291 m/z like 309 m/z can be accepted as an evidence for the formation of a π complex between $Cp_2Zr(H)Cl$ and CS_2. The following peaks can be attributed to the fragmentation of the formed complex :

291.9(13) : $[Cp_2Zr(H)(Cl)S]^+$ 254.9(35.4): $[Cp_2Zr(H)S]^+$; 191.1(0.8): $[Cp_2Zr(H)S]^+$-Cp+$2H^+$; 123.1(14.4): $[Cp_2ZrS]^+$-Cp-Cp. Also the presence of the peak at 79(77) can be attributed to the formation of $[CSCl]^+$ which is caused by the fragmentation of the possible complex.

In the mass spectrum, the parent peak at 95 m/z can be explained by the presence of $[ZrH_4]^+$ from the fragmentation of $Cp_2Zr(H)AlH_4$ (Figure 4.8) which may have formed during the reduction of Cp_2ZrCl_2 with $LiAlH_4$. The peak at 254.9 (38) also explains the presence of $Cp_2Zr(H)AlH_4$ which can give the following fragmentation :

254.9(35.4): $M^+ = [Cp_2Zr(H)AlH_4]^+$; 191.1(0.8): M^+-Cp+$2H^+$; 123.1(14.4): M^+-Cp-Cp; 95.1(100): M^+-Cp-Cp-Al

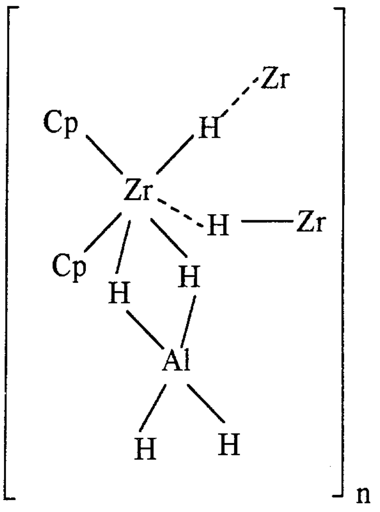


FIGURE 4.8. The Structure of $Cp_2Zr(H)AlH_4$

In the ^1H NMR spectrum of the product only one Cp signal is observed. It is reported in literature that although $Cp_2Zr(H)AlH_4$ is more soluble than the other hydrido derivatives attempts to obtain a PMR spectrum were not succesful. It is to be expected that rapid exchange of all the hydridic protons can occur, and this apparently destroys any resolution in the PMR spectrum [22]. Therefore the presence of $Cp_2Zr(H)AlH_4$ can not be observed by NMR. Also this impurity can not be detected in the IR spectrum as the bands of this compound stay under those of $Cp_2Zr(H)Cl$.

V. CONCLUSION

The following conclusions can be drawn from this study.

The reactions of pyrrole, imidazole and imidazolidine-2-thione, which were treated with n-BuLi or Na-naphtalide prior to use, with Cp_2ZrCl_2 gave unidentified products with poor solubility. Metal-ligand coordinations through N could not be observed. Instead the presence of the broad NH stretching band in the IR spectrum of the products shows that deprotonation did not take place through NH groups. Na-naphtalide or n-BuLi being very strong bases can cause deprotonation to take place from different sites, even at -78°C, and can lead to mixture of unidentified products. It can be suggested to use weaker bases for deprotonation and Cl abstraction. Also the reactions should be carried out at –78°C for a longer time with non-polar solvents in order to separate the resulting salt more easily.

The reaction of deprotonated ethanethiol with Cp_2ZrCl_2 gives a dimeric complex $(Cp_2ZrClSCH_2CH_3)_2$. The same reaction without deprotonation does not take place.

It was found that, thioacetamide can make a complex with Cp_2ZrCl_2 via C=S unit in THF which is a coordinating solvent. In this study it is observed that in the presence of a non-coordinating solvent, CH_2Cl_2, thioacetamide coordinates to Cp_2ZrCl_2 through C=S unit with the participation of the NH group.

In case of rhodanine and thiobenzamide using a non-coordinating solvent, CH_2Cl_2, does not lead to possible coordination. It seems that coordination is hindered because of steric reasons in rhodanine. But in thiobenzamide the electron donation to zirconium is hindered by the presence of an electron withdrawing phenyl ring. Therefore in order to coordinate thioamides, which have complex structures than thioacetamide, to Cp_2ZrCl_2 abstraction of one of the Cl is needed. It is suggested that, Cl abstraction should be done with weaker bases in the presence of a non-coordinating solvent.

In case of imidazolidine-2-thione, it is found that a self reaction of imidazolidine-2-thione took place rather than a coordination to Cp_2ZrCl_2. It can be suggested that the reaction should be carried out by using another solvent than THF without refluxing.

It seems that the coordination of dithiooxamide to Cp_2ZrCl_2 did not take place because of steric reasons. It can be suggested that for a possible coordination of dithiooxamide to dichlorozirconocene one of the Cl atom should be abstracted in order to provide avaliable steric conditions for the formation of a five-membered chelate ring.

The reaction of CS_2 with $Cp_2Zr(H)Cl$ did not lead to a possible insertion product as expected. Although no significant change occurred in the IR spectrum of the product, the color change to green and the mass spectral data indicate the possibility of coordination of CS_2 to $Cp_2Zr(H)Cl$ without insertion but forming a π-complex. It is suggested to synthesize $Cp_2Zr(H)Cl$ in major amounts so that seperation of it from the possible side-products like $Cp_2Zr(H)AlH_4$ become easier.

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