SYNTHESIS, SPECTROSCOPIC INVESTIGATIONS, THERMAL ANALYSIS AND DFT CALCULATIONS OF SOME PENTACARBONYL(PYRIMIDINETHIOL)METAL(0) COMPLEXES OF GROUP VI B ELEMENTS

ÖZLEM İLKİN

JANUARY 2011

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by

ÖZLEM İLKİN

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..

Approval of the Graduate School of Natural and Applied Sciences

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Çetin BOZKURT
Head of the Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

SYNTHESIS, SPECTROSCPIC INVESTIGATIONS, THERMAL ANALYSIS AND DFT CALCULATIONS OF SOME PENTACARBONYL(PYRIMIDINETHIOL)METAL(0) COMPLEXES OF GROUP VI B ELEMENTS

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The photochemical reaction of hexacarbonylmetal(0); M: Cr, Mo, W, complexes in the presence of a substituted pyrimidinethiol (mercaptopyrimidine) ligand (4,6-dimethyl-2-mercaptopyrimidine) at 10 ºC yields the corresponding pentacarbonyl-N-pyrimidinethiolmetal(0) complexes. These synthesized organometallic complexes are purified under high vacuum by recrystallization and their structures are investigated by using IR-, ^{1}H- and ^{13}C-NMR spectroscopies. The IR spectroscopy results showed three absoption bands (one in strong, the other two in medium intensities). These three absorption bands in the carbonyl region of the complexes indicates that

the pentacarbonyl metal unit of the complexes has a local C_{4v} symmetry. The ^{1}H- and ^{13}C-NMR spectroscopies showed that the pyrimidinethiol ligand bonded to metal complex through the pyrimidinethiol nitrogen atom symmetrically. Also, the ^{13}C-NMR spectroscopy results showed 1:4 ratio of peaks in the CO-region, the ratio of the peaks proved the C_{4v} symmetry of these complexes. The thermal behaviour of these organometallic complexes is investigated by using DTA/TGA methods. The results of the analysis showed that the complexes decomposed in three different temperatures. The density functional theory, DFT, calculations are made in Becke's three parameters (B32YP, B3PW91, B31PBE functionals) and Perdew/Wang 91, B3PW91 is used throughout this computation performed by Gaussian03W Software (Gaussian 03W single, CPU Serial number: PC 99997441 W-5042N) by this way all datas of experimental studies (IR, UV, NMR, TGA) are compared with the theoretical values.

Keywords: Pyrimidinethiol, Photochemical synthesis, Metal carbonyls, Thermal analysis, DFT calculations

ÖZET

GRUP VI B ELEMENTLERİNİN BAZI PENTAKARBONİL(PİRİMİDİNTİYOL)METAL(0) KOMPLEKSLERİNİN SENTEZİ, SPEKTROSKOPİK İNCELENMESİ, TERMAL DAVRANIŞI VE DFT HESAPLAMALARI

İlkin, Özlem

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. İzzet Morkan

ARALIK 2010, 55 sayfa

Hekzakarbonilmetal(0); M:Cr, Mo, W, bileşikleri ile sübstitüye pirimidintiyol(merkaptoprimidin) ligandı (4,6-dimetil-merkaptopirimidin) arasında, 10 ºC de yapılan fotokimyasal tepkimeler, pentakarbonil-N-pirimidintiyolmetal(0) bileşiklerini oluşturmaktadır. Sentezlenen bu organometalik bileşikler yüksek vakum kullanılarak yeniden kristallendirme yöntemi ile saflaştırılır ve yapıları IR-,^{1}H- ve ^{13}C-NMR spektroskopileriyle incelenir. IR spektroskopi sonuçlarında üç adet soğurma bandı (biri güçlü, diğer ikisi orta şiddette) görülmüştür. Karbonil bölgesinde görülen bu IR-bantlar doğrultusunda sentezlenen bileşiklerinin pentakarbonilmetal(0) bölümünün C_{4v} yerel simetrisinde olduğu anlaşılmıştır.^{1}H- ve ^{13}C-NMR spektrumları ligandın metal komplekse

pirimidintiyol üzerindeki azot atomundan simetrik bağlandığını göstermiştir. Ayrıca ^{13}C-NMR spektrumlarının CO-bölgesinde 1:4 şiddetindeki iki pik $M(CO)_5^-$ kısmını göstermektedir. Sentezlenen komplekslerin termal davranışı DTA/TGA metodu kullanılarak incelenmiştir ve komplekslerin üç farklı sıcaklıkta parçalandığı belirlenmiştir. Yoğunluk Fonksiyonel Teorisi, DFT, hesaplamaları Gaussian 03W Programı (Gaussian 03W single, CPU Seri numarası: PC 99997441 W-5042N) ile Becke'in üç parametreli fonksiyonları (B32YP, B3PW91, B31PBE fonksiyonları) kullanılarak hesaplanmıştır ve Perdew / Wang 91, B3PW91 fonksiyonu hesaplamalar için kullanılmıştır. Böylece deneysel verilerin teorik değerler ile kıyaslanabilmesi sağlanmıştır.

Anahtar kelimeler: Pirimidintiyol, Fotokimyasal sentez, Metal karboniller, Termal analiz, DFT hesaplamaları

to my family

ACKNOWLEDGMENTS

I express sincere appreciation to my supervisor Prof. Dr. İzzet MORKAN for his guidance, encouragement and insight throughout the research. I would like to thank the other faculty members especially Prof. Dr. Ayşe UZTETİK MORKAN for her moral support and motivation. The technical asisstance of Hasan Can YAZICI is gratefully acknowledged. I would also like to thank to all academic staff of Chemistry Department of Düzce University. I sincerely thanks to Dr. Erhan BUDAK, Canan SAPMAZ, Özge GÖZLÜKAYA, Günnur İPEK and Derya ÇELİK for their support whenever I need. I am gratefull to my family for my life, they provided me through my entire life and in particular, I must acknowledge my sisters Gül Nihal YALÇIN, Hande EMİRALİOĞLU and best friends without their patience, encouragement and editing assistance, I would not have finished this thesis.

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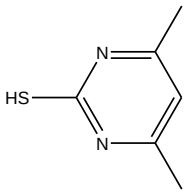
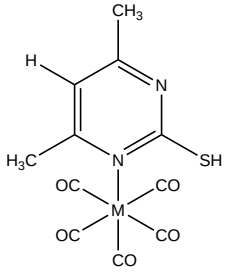
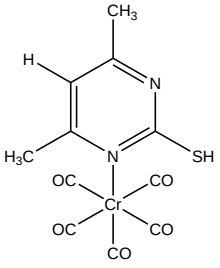
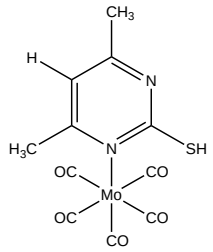
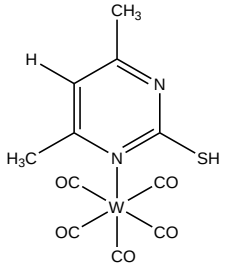
TABLE OF ABBREVIATIONS

NOMENCLATURE	FORMULA& MOLECULAR WEİGHT(g.mol^{-1})	STRUCTURE	ABBREVIATION
4,6-dimetyl-2-mercaptopyrimidine or 4,6-dimethyl-2-pyrimidinethiol	$C_6H_8N_2S$ 140.21		dmmp
Pentacarbonyl(4,6-dimethyl-2- mercaptopyrimidine)metal(0)	$C_{11}H_8MN_2O_5S$		MP(dmmp)
Pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine) chromium(0)	$C_{11}H_8CrN_2O_5S$ 332.26		CrP(dmmp)

Pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine) molibdenum(0)	$C_{11}H_8MoN_2O_5S$ 376.20		MoP(dmmp)
Pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)tungsen(0)	$C_{11}H_8WN_2O_5S$ 464.10		WP(dmmp)

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CHAPTER 1

INTRODUCTION

Organometallic chemistry generally donates compounds in which organic group linked directly to the metal through at least one carbon atom [1]. In other words, it is the chemistry of compounds containing metal carbon bonds [2].

As an interdisiplinary science, organometallic chemistry has grown at a phenomenal pace during the last three or four decades. On academic plane, efforts to elucidate the nature of bonds in the ever increasing list of exciting novel organometallic compounds have led to a clearer understanding of nature and a variety of bonds [3]. That is the reason of why organometallic chemistry is one of the most interesting and absolutely most rapidly growing area of chemical researches.

The historical development of organometallic chemistry begins with the first organometallic compound, 'Cacodyl' (tetramethyldiarsine, $As_2(CH_3)_4$), which was synthesized by a French chemist L.C. Cadet in 1760 [3]. The first olefin compound was synthesized by a Danish Pharmacist W. C. Zeise in 1827, an ethylenecomplex of platinum(II), $Na[PtCl_3C_2H_4]$, known as a Zeiss's Salt [4]. The metal carbonyl complexes are very important and common type of organometallic compounds. The first compound containing

carbonmonoxide as a ligand was synthsized by L. Mond in 1890, tetracarbonylnickel(0), $Ni(CO)_4$ [1]. That followed by reporting the synthesis of pentacarbonyliron, $Fe(CO)_5$, by Mond and Berthelot in 1891 [5]. Further progress was made 30 years later, in 1919, polyphenylchromium was synthesized by Hein from the reaction of chromium trichloride and PhMgBr [7].

The structures of d and f block organometallics are difficult or impossible to deduce by chemical means alone, fundamental advances had to await the development of X-ray diffraction for precise structural data on solid samples and of IR and NMR spectroscopy for structural information about organometallic complexes in solution. When these techniques were becoming available, the one of the most important development in this area occured by the synthesis of ferrocene, $Fe(C_5H_5)_2$, in 1951. The sandwich structure of ferrocene was correctly inferred from its IR spectrum and then determined in detail by X-ray crystallography, the X-ray analysis showed the structure to consists of an iron atom sandwiched between two paralel C_5H_5 rings [1,2]. The product was surprisingly stable ; it could be sublimed in air without decomposition and was resistant to catalytic hydrogenation and Diels-Alder reactions [2]. Conventional bonding description was defied due to the stability, structure, and bonding of ferrocene and therefore captured the imagination of chemists. That of a train of synthesizing, characterizing, and theorizing led to a rapid development of organometallic chemistry [1].

Organotransition metal chemistry is distinguished from the organometallic chemistry of the main group metals by its greater versality.

Although reactive main group organometallics generally add to carbonyl compounds and some activated carbon-carbon double bonds, transition metal compounds frequently react with unactivated, unsaturated organic compounds, often in catalytic manner. Transition metal compounds have strong tendency to make complexes with various organic and inorganic compounds by sharing more electrons in order to attain the electronic configuration of the next inert gas. An important difference between organotransition chemistry with the chemistry of main group is the low tendency of transition metals combines with oxygen or its derivatives when compared to main group metals. That's why the chemistry of transition metals is accepted as a developing seperate field in the organometallic chemistry [7].

Most of the transition metals form compunds with carbon monoxide which has an important role in organometallic chemistry. There are three main interests about carbonyl compounds. First of all, carbonyl ligand could form strong bonds with metals in coordination complexes although it is not a very strong base. Second, the oxidation state of metal in these kind of complexs is usually zero and sometimes appeared as low positive and negative oxidation states. Third, these carbonyl compounds generally obey the 18-electron rule [8].

The vibrational spectra of metal carbonyls is very informative and a good approximation for specific group frequencies. The CO strecthing bands observed in infrared spectra are sharp, sensitive to environment, and commonly intense [9]. The number and pattern of these bands are related to

the molecular symmetry and geometry while the positions of them are related to bonding [10]. The observed spectra is rich in well-resolved bands because the vibrations of individual M-CO groups strongly interact [9]. Metal carbonyl complexes which one or more CO bonded to a single metal atom show one or more intense infrared bands between 2200 and 1800 cm^{-1} [11]. Because of the polarization of carbonyl on binding metal , the dipole moment during vibration is large therefore intensity is large [12].

Transition metal carbonyl complexes are the basic starting materals for the synthesis of many organometallic compounds [13]. The octahedral complexes of hexacarbonylmetal(0) ; M: Cr, Mo, W are convenient starting materials for a variety of synthesis which are air-stable, hydrophobic white crytalline solids which are readily sublimable under vacuum and also soluble in polar solvents such as THF (tetrahydrofurane) and CH_2Cl_2 (dichloromethane) and very slightly soluble in nonpolar solvents[14].

Photochemical reactions can occur when light is absorbed by a compound. By this way, an electron is promoted and the ground state electronic configuration is changed to that of one of excited states [12]. Photochemical substitution of ligands, most commonly carbonyl groups, has been used as a versatile synthetic method for new coordination compounds[15].

Substitution reaction of carbonyls, such as $W(CO)_6$,are accelerated by light [12]. Particularly, numerous of the $M(CO)_5L$ type complexes have been prepared by using the photochemical CO substitution of Group VI

metal-carbonyls [15]. For example, on ultraviolet (UV) irradiation in THF as solvent the pentacarbonyl $W(CO)_5(THF)$ is obtained. This is a useful synthetic intermediate because it reacts with variety of ligands L to give $W(CO)_5L$ cleanly by rapid thermal substitution[12].

The synthesis of new complexes by photochemical substitution of ligands, most commonly carbonyl groups, have been studied as a familiar application of photochemistry [2]. The coordination chemistry of heterocyclic ligands is a field of increasing interest. Usually, such ligands have multiple sites available for coordination so that a wide variety of coordination modes is possible [16]. Pentacarbonyl(pyridine)metal(0) complexes of the Group VI elements have been known for a long time. Since pyridine has many properties in common with pyrimidine, acts as mainly σ-donor ligand with little π-accepting ability, the M-N bond in these low valent metal complexes is not very strong [17].

Pyrimidines are one of the main constituents of nucleic acids and play an important role in many biological systems. Substituted pyrimidines are also biologically important; pyrimidine thions were found to inhibit the synthesis of t-RNA under certain conditions [18]. Ligands of the thiopyrimidines type and their complexes are currently being investigating as antiviral, antimetabolite and antitumor drugs as well as for their interesting photochemical properties. These ligands are ubiquitous S,N donors that form a variety of complexes with different kind of metals. Their coordination chemistry has been constantly reviewed [19].

The number of studies concerning the interaction modes and reactivity of transition metal complexes containing pyridinethiolate and pyrimidinethiolate ligands is growing rapidly such ligands are especially interesting because (i) they contain functional groups common in crude oils (thiolate-S and aromatic-N), (ii) the pyrimidine group is a constituent of nucleic acids, and (iii) they have the ability to chelate and bridge transition metals, allowing access to both mononuclear and oligonuclear products [20,21].

Owing to their many field of application, mercaptopyrimidines (pyrimidinethiols) have been widely studied over the past years. The chemistry of mercaptopyrimidines that incorporate both S and N atoms in their structure is rich [22]. The ligand 4,6-dimethyl-2-mercaptopyrimidine (4,6-dimethyl-2-pyrimidinethiol) is an ambidentate ligand that can coordinate through the sulphur and the pyrimidine ring of nitrogen atom [23].

In this study, it was aimed that synthesize and characterize of the pentacarbonyl(primidinethiol)metal(0) complexes of Group VI elements for the first time for this purpose 4,6-dimethyl-2-mercaptopyrimidine (4,6-dimethyl-2-pyrimidinethiol) ligand was used as pyrimidinethiol ligand. For this reason substituted pyrimidinethiol ligand photochemically reacted with hexacarbonylmetal(0), M: Cr, Mo, W (Eq 1.1) and resulting complexes were purified by recrystallization.

$$M(CO)_6 + THF \xrightarrow[CO]{h\nu} M(CO)_5(THF) \xrightarrow[THF]{+L} M(CO)_5L \qquad \text{Eq 1.1}$$

L: 4,6-dimethyl-2-mercaptopyrimidine (dmmp) ; M: Cr, Mo,W

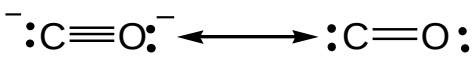
The next part of this work was the structural indentification of the synthesized complexes using IR-, ^{1}H- and ^{13}C-NMR spectroscopies. Then, by using TGA/DTA methods thermal behaviour of the complexes was investigated. Finally DFT calculations of these complexes was made by using Gaussian software.

CHAPTER 2

THEORETICAL BACKGROUND

2.1. Metal-Carbonyl Bonding

Carbon monoxide is the most common π-ligand in organometallic chemistry. Its primary mode of attachment to metal atoms is through the C atom [1]. CO has a non bonding σ-electron pair localized on carbon atom available for donation to the metal. The resonance form of carbon monoxide is shown below [2];



An important observation has guided by researchers studying these metal-CO complexes and other organometallic compounds; The effective atomic number (EAN) rule, now often reffered as the 18-electron rule, states that compounds in which the sum of the metal valence electrons plus the electrons donated by the ligands groups totals 18 are likely to be stable. Thus, the 18-electron rule predicts the stoichiometry of a number of compounds [24].

Classical ligands are lewis bases and form donor bonds to lewis acids via their lone electron pairs; they do not, however, react with zerovalent

metals [25]. On the other hand, in metal carbonyls, the zerovalent metal lacks a charge, and CO is only slightly polar [24]. In other words, CO is a weak base [25], so the features argue against ionic bonding. The best model for these species instead describes the bonding between the metal and CO as covalent. Each CO donates a C-atom lone pair to the atom to form a sigma bond (Fig. 2.1.1.a). However, carbon monoxide is a very poor donor, and this alone would not lead to these species being stable. Moreover, in conjuction with the sigma bond, the electron-rich metal donates a pair of electrons to form a π-bond formed by overlap of a d orbital of the metal and a π* antibonding orbital of CO(Fig. 2.1.1.b). The latter interaction is describes as dπ-pπ bonding. Based on this model of bonding, carbon monoxide in these compounds is best described as a σ donor and π acceptor ligand [24].

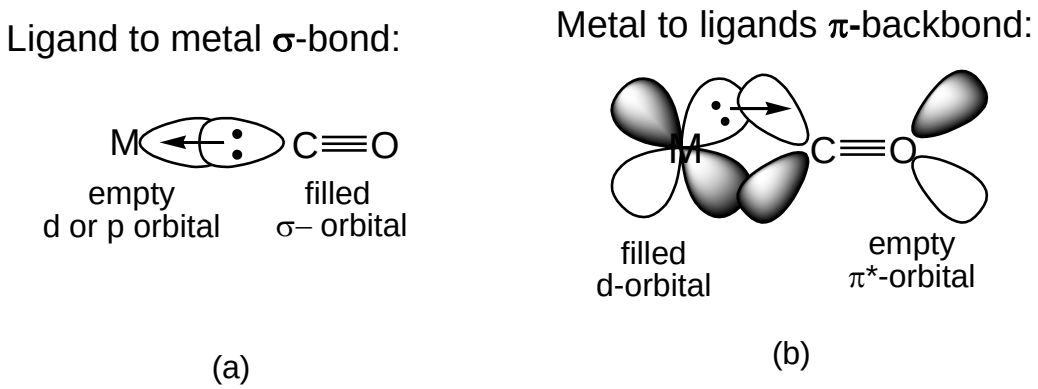


Figure.2.1.1.a. Donation of CO lone pair to empty orbital on M.

Figure.2.1.1.b.Donation of electrons from filede M d-orbital to empty π*-antibonding orbital on CO.

Bonding of metal and carbonyl ligand can be described with molecular orbital terms. Molecular orbital calculations allow to derive a molecular orbital diagram resulting from the intreaction of metal orbitals with the ligands orbitals of corresponding symmetry. The molecular orbital diagram of the complex contains bonding and antibonding molecular orbitals resulting from these interactions and non-bonding metal orbitals that do not interact with ligand orbitals. In the simplest case of an octahedral ML_6 complex, six metal orbitals, i.e. the s, p and two d orbitals interacts with the six orbitals of six ligands in the six directions of the octahedron, whereas the three other metal d orbital remain non-bonding. The π-acceptor ligand CO in a metal hexacarbonyl complex $[M(CO)_6]$ (M=Cr, Mo, W), the three non-bonding metal d orbital are those involved in the π backbonding with the CO antibonding π* orbitals. As a result, that type of bond is a combination of σ- and π-bonding as shown in Figure.2.1.2. [2,14]

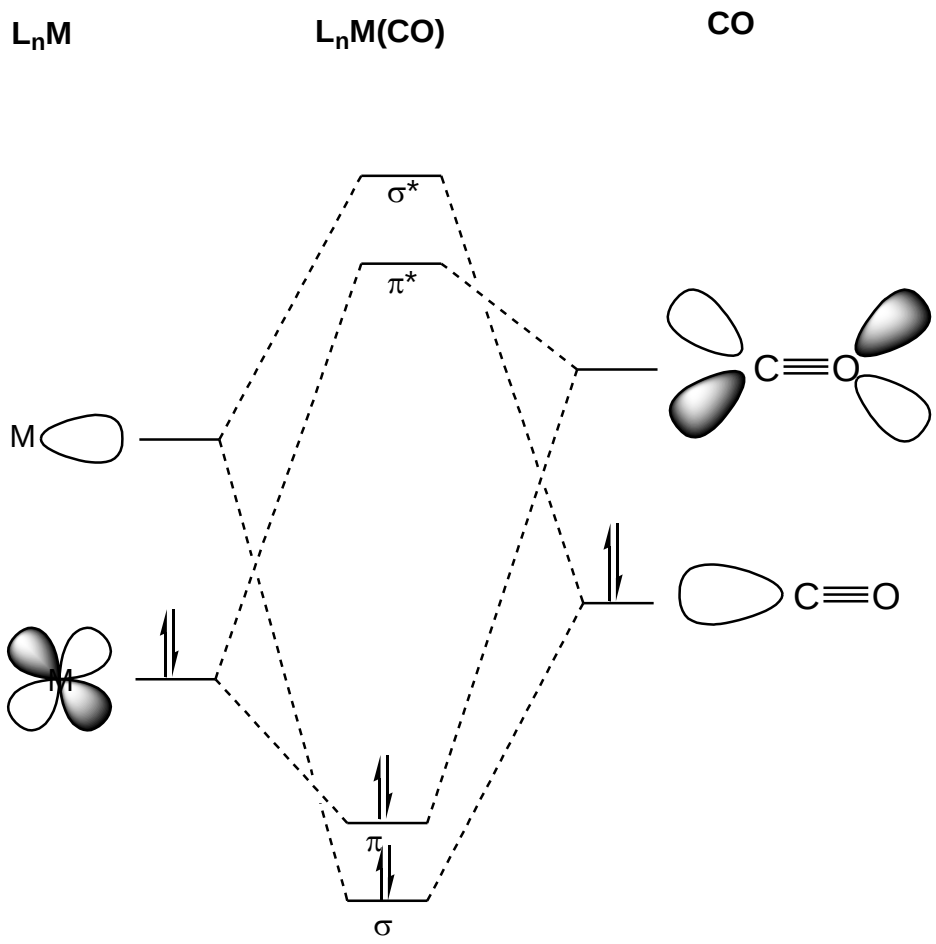


Figure.2.1.2. Molecular orbital diagram of $L_nM(CO)$

It is this backbonding that makes the big difference between inorganic and organometallic chemistry. For inorganic complexes, the backbonding cannot exist, because of the too high energy level of the antibonding N and O orbitals. The fact that there is no backbonding with O and N ligands explains, for example, why complexes such as $M(H_2O)_6$ or $M(NH_3)_6$ (M=Cr, Mo, W) do not exist even with EAN=18. These complexes would have zero oxidation state, and the metal would be too electron-rich, since backbonding would be absent [26]

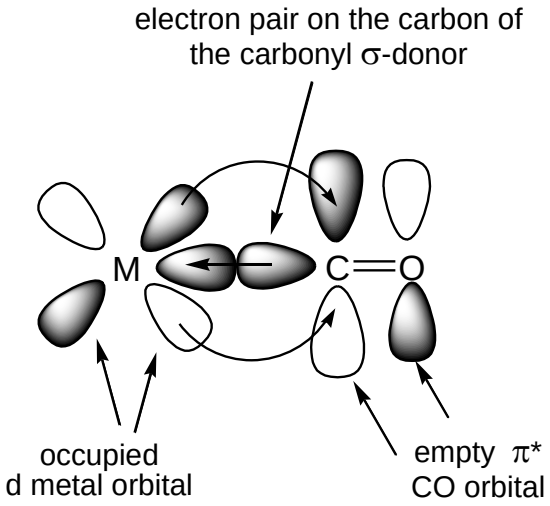


Figure.2.1.3. The synergistic effect of metal-carbonyl bonding.

The current understanding is that the CO ligand donates a lone pair of electrons to the low-valent metal to form a sigma bond. The electron rich metal then donates electrons from d-orbital to the antibonding π*-orbital of the CO. There is a “synergistic effect” ; the σ and π bonds complement each other , Fig.2.1.3. [24].

2.2. Metal-Olefin Bonding

As carbon monoxide (CO), olefin (C_2H_4) is one of the most important ligands in organometallic chemistry. The ligand, L, olefin coaxially give a pair of electrons to the metal π orbital of C_2H_4 towards a vacant d metal orbital. It is this bond that is formally taken into account in the characteristics of the complexes. There is another bond that is not considered in electron count , but also very important; it is the lateral backbonding of π type from a filled d orbital to a vacant antibonding of C_2H_4,. This π-bond is in the opposite

direction to the σ-bond, as indicated by its name. It partly compensates the σ-bond and allows the metal to give back part of its excess of electron density and therefore to exist in a low or even negative oxidation state [26].

Although the first known organometallic complex is Zeisse Salt, it was not known how ethylene bonded to platinum metal. In 1950, X-ray analyse results showed that molecular plane of ethylene is perpendicular to interaction axis of metal. Ethylene molecule bonded to metal in a way that the molecular plane is perpendicular to this bonding axis and metal is the center of two carbon atoms of ethylene. The distance between metal and carbon atoms of ethylene is short enough to make a chemical bond between them. It was said that the two carbon atoms of ethylene bonded to the metal. Upon this, three scientists Dewar, Chatt and Duncanson developed a model which is known as their names which explains metal-olefin bonding with molecular orbital theory.

According to the Dewar-Chatt-Duncanson model the metal-olefin bond, like metal-carbonyl bond, consists of two parts; σ- and π-bond. First one is interaction between filled π molecular orbital of olefin and σ orbital of metal. Here, olefin acts as σ-donor because there is an electron flow through filled orbital of ethylene to empty orbital of metal. In other words, olefin gives π-electron density to the metal (Fig.2.2.1.a). Secondly, antibonding π* orbital of olefin is in π symmetry to metal-olefin bonding axis and make a π-interaction with the d orbital of metal which is in the appropriate symmetry. There is an electron flow through filled d orbital of metal to empty

antibonding π* orbital of olefin(Fig.2.2.1.b). So olefin acts as π-acceptor. That π-interaction is a backbonding like M-CO.

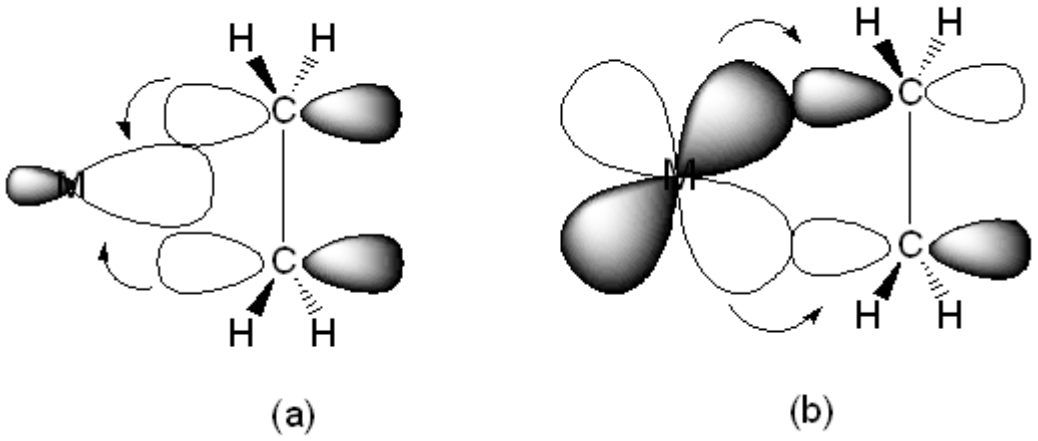


Figure 2.2.1. Dewar-Chatt-Duncanson model of metal-olefin bonding, (a) σ-interaction, (b) π-interaction

That σ- and π-interactions is synergistic (fig.II.2.2). That means in the σ-interaction, the olefin gives electrons to metal, metal gives that many electrons to olefin with π-bonding. Also olefin takes many electrons with backbonding, it gives that electron density to metal with σ-interaction. As a result, this two interactions fortify each other so there is a very strong bond formed between olefin and metal [26][27].

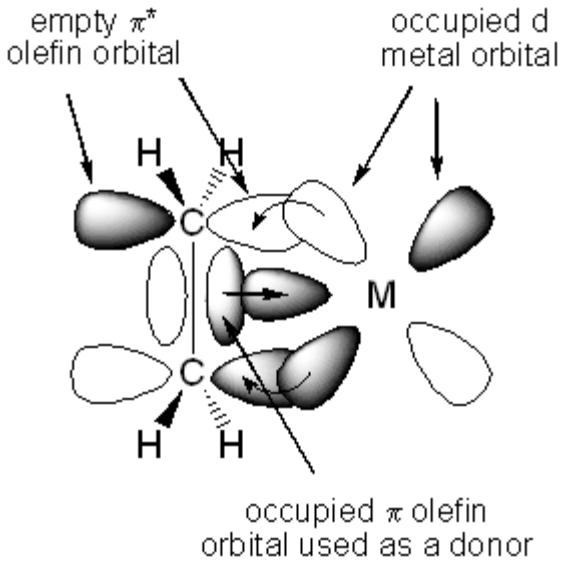
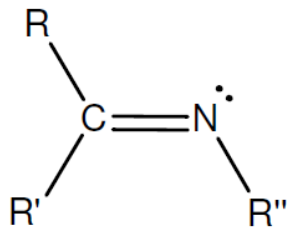


Figure 2.2.2 The synergistic effect of metal-olefin bonding.

2.3. Metal- Imine Bonding

Aldehydes or ketones react with primary amines (RNH_2) to form compounds with a carbon-nitrogen double bond called imines (RCHNR or R_2CNR) [27]. The structure of imine molecule is shown in Figure.2.3.1



R: H, alkyl or aryl group

R': H, alkyl or aryl group

R'': H, alkyl or aryl group

Figure.2.3.1 The structure of imine molecule

The carbon-nitrogen double bond in an imine molecule consists of σ-bond and π-bond. In the MO energy level diagram, (Fig.2.3.2) there will be

two σ-orbitals (bonding and antibonding) and two π-orbitals (bonding and antibonding) for C=N: moiety.

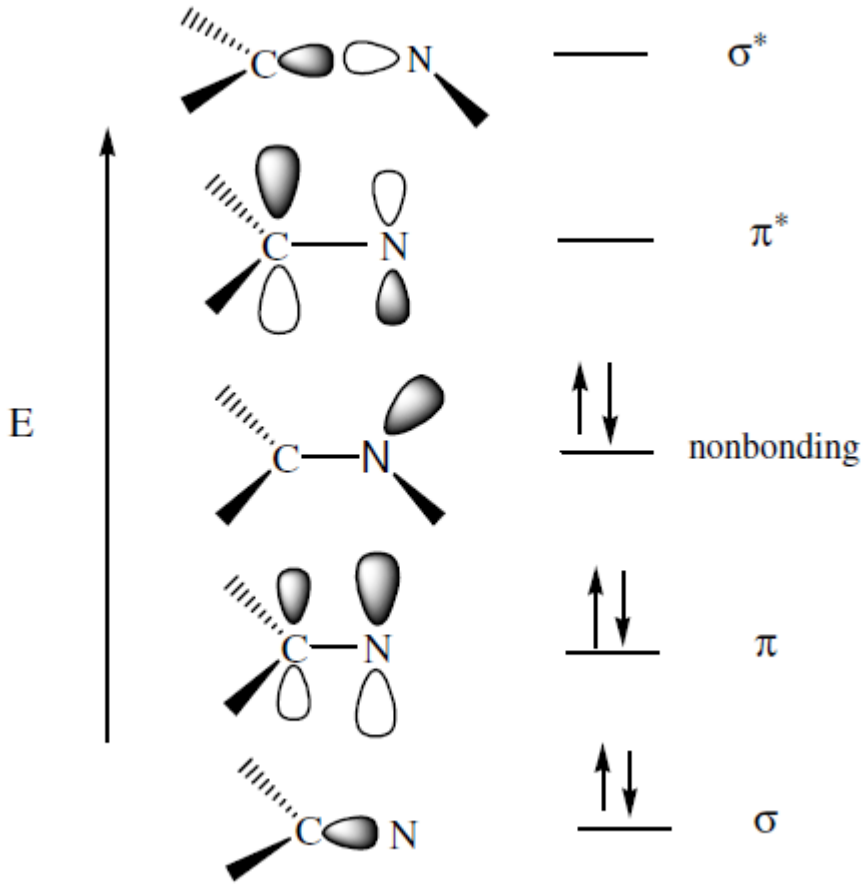


Figure.2.3.2 The molecular orbital diagram of an imine molecule

Since nitrogen is more electronegative atom than carbon, it can be deduced that the bonding orbitals are mainly localized on the nitrogen atoms whereas the antibonding orbitals belong mainly to the carbon atom. In addition, there should be one nonbonding σ orbital localized on the nitrogen atom because there are two lone-pair electrons on the nitrogen atom as

seen from the structure of the molecule. Totally six electrons (2 from the carbon and 4 from the nitrogen) are available to occupy molecular orbitals of the C=N: moiety of the imine molecule.

The HOMO of the imine molecule is the nonbonding σ orbital, and the LUMO is the antibonding π* orbital. A strong σ interaction between metal and the imine ligand should be expected because the HOMO, the sigma-symmetry orbital completely localized on the nitrogen, is directed to the dσ orbital of the metal along the bond-axis (Fig.2.3.3.a). On the other hand, the π bonding takes place to the lower extent in comparison with the σ-bonding because the π* orbital (LUMO) of imine is mainly localized on the carbon atom, that is, the LUMO has its smaller amplitude on the nitrogen (Fig.2.3.3.b)

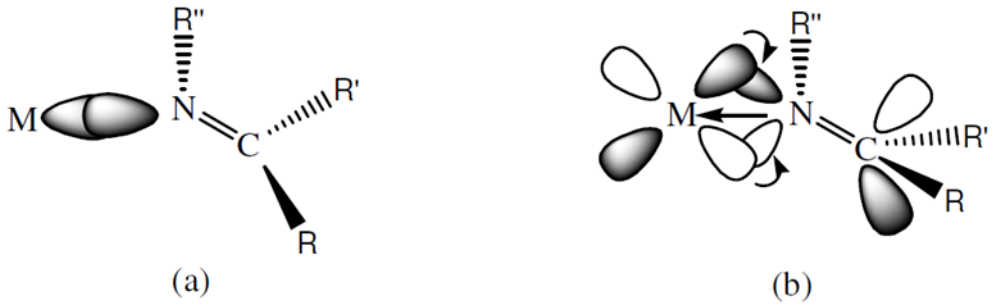


Figure.2.3.3. Molecular orbital description of the metal-imine bonding

(a) Metal ←imine σ bonding; electrons are donated from nonbonding σ orbital on the nitrogen atom to the empty σ-symmetry d orbital of the metal

(b) Metal→imine π bonding; the electrons on the dπ orbital of the metal are backdonated to the empty π* orbital of the imine.

These σ and π interactions are synergic. If the π* orbital of the imine molecule were mainly localized on the nitrogen atom, π bonding would have been much stronger; i.e. imines would have π-accepting ability as strong as the CO ligand. However, the imine ligand is a strong σ-donor and weak π-acceptor, depending on the substituents on the carbon and nitrogen atoms, transition metal and the other ligands coordinated to the metal.

In an imine molecule the more electronegative nitrogen atom strongly attracts the electrons of the σ bond and the π bond causing the C=N bond highly polarized; the carbon atom bears a partial positive charge and the nitrogen atom bears a partial negative charge. Polarization of the π-bond can be represented by the following resonance structures(Fig.2.3.4)

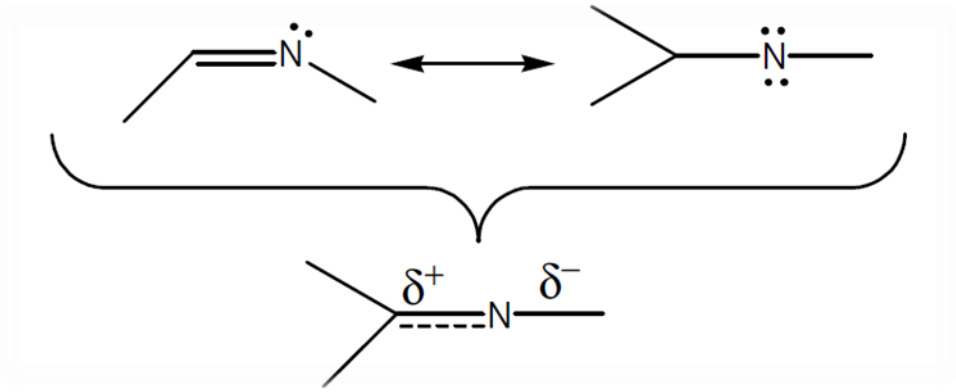


Figure.2.3.4 Polarization of the π bond in an imine molecule

The nucleophile, which is electron-rich, attacks on the carbon atom bearing a positive charge.

It is often found that imines are stabilized towards hydrolysis by coordination of the nitrogen to a π-bonding transition metal. Of course in the absence of significant π-bonding interactions, ligand polarization is expected

to have the opposite effect and activate the imine towards nucleophilic attact [27]. The polarization of C=N bond of imine is inverted in case of coordination to a transition metal. The electron density of imine is reduced by the donation of non bonding electrons through σ bonding to the metal. In addition, the electrons backdonated from the dπ orbital of the metal to the π* orbital of the imine ligand are localized on the nitrogen very little, so the nitrogen atom bears a partial positive charge; that is, the electron density on the nitrogen lost by σ-bonding cannot be compensated by back bonding. Because the π* orbital of the imine mainly belongs to the carbon atom, upon coordination to the transition metal, this π* orbital becomes more populated by electrons, the C=N bond is weakened and the electron density on the carbon atom will increase with respect to the carbon atom of an uncoordinated imine molecule. Consequently, the carbon atom bears a substantial negative charge. On account of this inversion of polarization of C=N bond, the reactivity of imines in nucleophilic addition reactions, where the nucleophile ($Nu:^-$) attacks the carbon atom of the C=N: moiety, is reduced upon coordination to a transition metal. However, they might undergo a nucleophilic attack on the nitrogen atom bearing a partial positive charge as long as the transition metal and the substituent on the nitrogen do not create a significant crowding (Fig.2.3.5) [29].

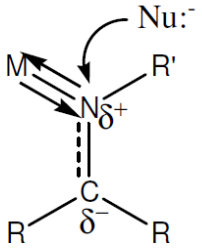


Figure.2.3.5 Nucleophile attacks the nitrogen atom of the coordinated imine

CHAPTER 3

EXPERIMENTAL STUDIES

3.1. Basic Techniques

It is known that most of the organometallic compounds are thermodynamically unstable and airsensitive. In order to overcome this difficulty, all reactions and purification of syntesized organometallic compounds were carried out under dry and deoxygenated nitrogen gas atmosphere and under vacuum as shown in Figure 3.1.1.

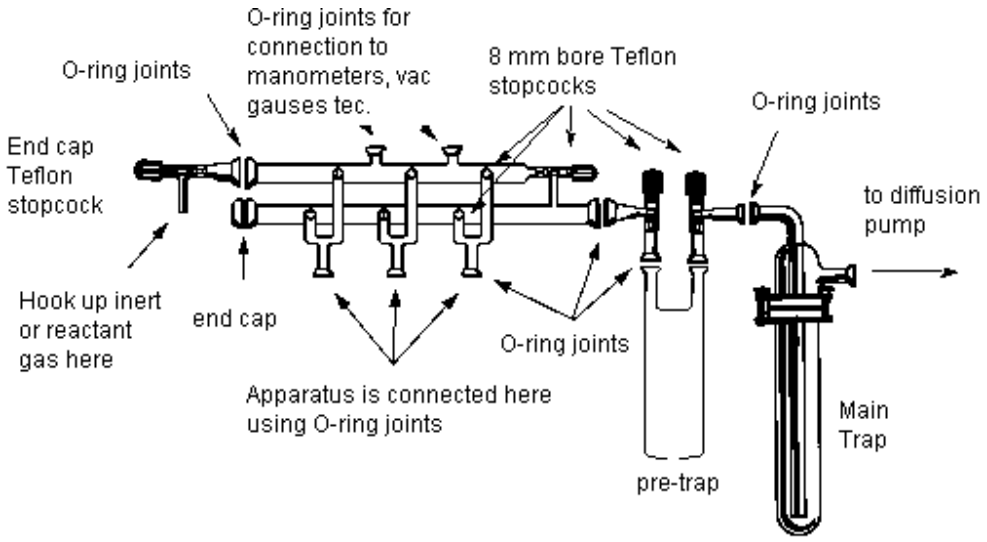


Figure.3.1.1. A typical schlenk system

Because of the airsensivity of organometallic compounds all experiments of this work carried out by using the vacuum line and schlenk

glassware. The simplest and best known technique is the “Schlenk” technique. Techniques using the vacuum line are sufficient and convenient. A Schlenk (Fig.3.1.2) is a flask which has at least one arm where inert gas can be introduced. Usually a three- or two way stopcock is fitted at the end of the arm. In use, the air in a Schlenk flask should be replaced at least three times by pumping and filling inert gas and all subsequent handling should be carried out under nitrogen flow.

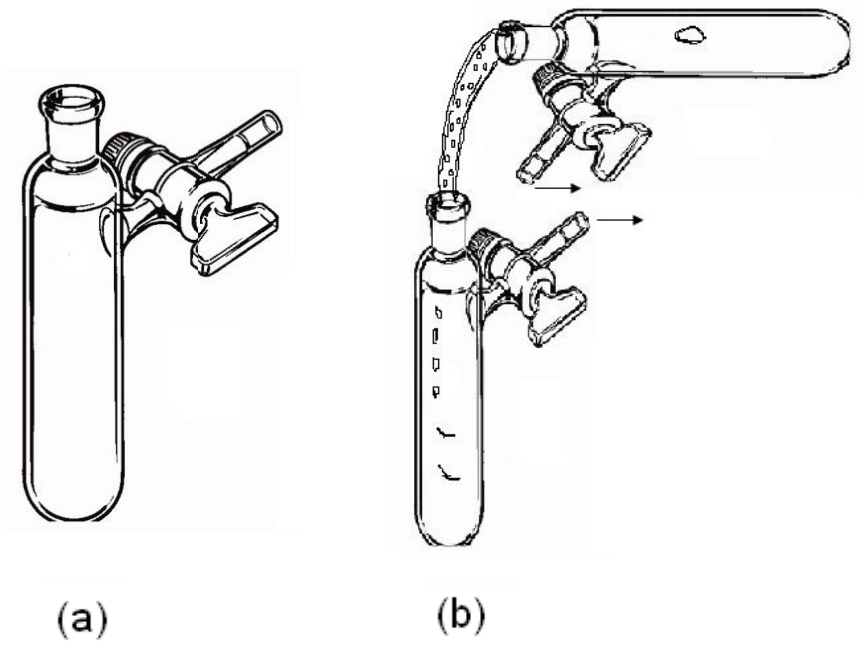


Figure.3.1.2 (a) Standard Schlenk tube and (b) transfering liquid in nitrogen atmosphere.

Transfer of a liquid sample under nitrogeen gas atmosphere can be carried out by connecting two shlenck tubes by using an adaptor (Fig.3.1.2)

Solvents were purified by refluxing over metallic sodium or unhydrous phosphoruspentaoxide under an inert atmosphere of nitrogen or argon for three or four days before using.

Hexacarbonylmetals and organic compounds that used as ligand were purchased from the Merck and Aldrich, and used without further purification.

For the photochemical reactions, a special apparatus (Fig.3.1.3) was used. The apparatus consist of three coaxial glass tubings. Into the iner part (a) a mercury lamp, (b) (Hg-Tauchlampe TQ 150 high pressure mercury lamp (Quarzlampen GmbH, Hereaus, Germany, solidex glass, λ>280 nm) is immersed. To carry out photochemical reactions, the prepared solution mixtures (consist of $M(CO)_6$, (M:Cr, Mo, W) and the ligands dissolved into the THF) is filled into the outer part (c) and cooled to room temperature by circulating tap water through the space and third tubings.

Figure.3.1.3 Apparatus used for photochemical reactions

(a) İner part

(b) Mercury lamp

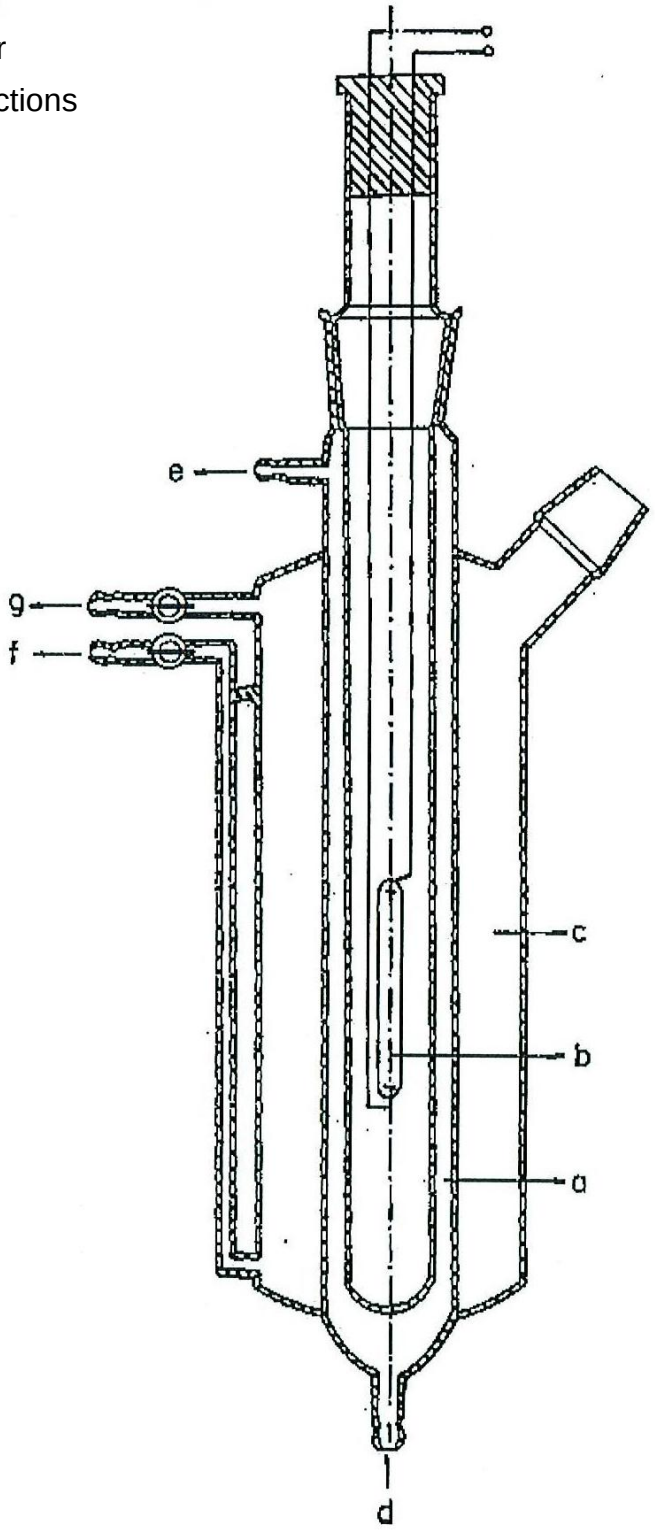
(c) Outer part

(d) Tap water inlet

(e) Tap water outlet

(f) Nitrogen gas inlet

(g) Nitrogen gas outlet



3.1.1. FT-IR (Fourier Transform Infrared)- Spectra

The synthesis of complexes and substitution reactions were followed by taking IR-spectra at intervals during the reactions. The IR spectra were recorded using Schmadzu FTIR- 8400S spectroscopy.

3.1.2. UV/VIS Spectra

The UV/Vis spectra of these complexes were recorded from their dichloromethane solutions using JASCO V-530 UV/VIS spectrophotometer.

3.1.3. ^{1}H-NMR Spectra

The ^{1}H-NMR spectra of these complexes were recorded from their d-chloroform and d-dimethylsulfoxide solutions using Brucker-Spectroscopin DPX 400 MHz spectrometer.

3.1.4. ^{13}C-NMR Spectra

The ^{13}C-NMR spectra of these complexes were recorded from their d-chloroform solutions using Brucker-Spectroscopin DPX 400 MHz spectrometer. All chemical shift values are given relative to TMS signal which has been used as an internal reference.

3.2 The Synthesis of Complexes

The proposed complexes have been synthesized using the following reactions.

$$M(CO)_6 + THF \xrightarrow[1hr]{hv/\ -CO} M(CO)_5(THF) + L \xrightarrow{hv} M(CO)_5L + THF$$

L; 4,6-dimethyl-2-mercaptopyrimidine, M; Cr, Mo, W

3.2.1.Pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0), ($M(CO)_5$(4,6-dm-2-mp); M: Cr, Mo,W

0,5 gram $M(CO)_6$ [M:Cr (2,27mmol), Mo (1,89mmol), W (1,42mmol)] was dissolved in excess amount of THF and irradiated for one hour at room temperature (using 150 W mercury lamp, λ>280 nm.). At the of reaction time a stoichiometric amount of 4,6-dimethyl-2-mercaptopyrimidine (0,318g, 0,266g, 0,148g respectively) was added to the reaction mixture and the irradiation continued until the reaction completed (135min. for Cr, 240min. for Mo, 120min. for W). The reaction process was followed by IR-spectra taken at 20 minutes intervals, during the reaction nitrogen gas passed through the reaction vessel.

At the end of the reaction, the color of solutions were yellow for $Cr(CO)_5$(4,6-dm-2-mp), red for $W(CO)_5$(4,6-dm-2-mp), and dark red for $Mo(CO)_5$(4,6-dm-2-mp). Each solution was filtered to evacuated schlenk storage tubes under nitrogen gas atmosphere. Excess solvents were removed by evaporating under high vacuum. The pure coordination compounds were then isolated by recrystallition from 1:5 mixture CH_2Cl_2 : n-hexane solution producing the solids which were then dissolved in n-hexane to remove out any $M(CO)_6$ reamin unreacted. The pure solids were then stored under nitrogen atmosphere at low temperature for analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1.IR Spectra

4.1.1. IR Spectra of $M(CO)_5L$ Complexes

The photolytic conversion of $M(CO)_6$ to $M(CO)_5L$ (L:4,6-dimethyl-2-mercaptopyrimidine) was followed by IR spectra taken at intervals during the reaction courses. The infrared spectra of the complexes, recorded from their dichloromethane solutions, showed the development of bands.

The IR spectrum of $M(CO)_5L$ (L:4,6-dimethyl-2-mercaptopyrimidine) in solution exhibits three prominent absorption bands (one in strong, the others in medium intensities) in the CO streching vibrational region. The IR-spectra of these complexes are given in Figure.4.1.1, Figure.4.1.2, Figure.4.1.3. All the IR-data of these molecules are given in Table.4.1.1.

The three-band ν(CO) pattern of these complexes indicates that the C_{4v} local symmetry of $M(CO)_5$ skeleton, commonly observed for $M(CO)_5L$ complexes with a general pattern $2A_1 + E$ [17]. The A_1 and E modes are both IR-active modes where E must be lower in frequency than one of A_1-modes as explained by Orgel [2,27].

Table.4.1.1. The CO-strecthing frequencies ν(CO) (cm^{-1}) of $M(CO)_5L$ (L:4,6-dimethyl-2-mercaptopyrimidine) ; M: Cr, Mo, W in dichloromethane..

Complex	ν(CO) (cm^{-1})		
	$A_1(2)$	E	$A_1(1)$
$Cr(CO)_5$(4,6-dm-2-mp)	2061.9(m)	1930.8(s)	1886.4(m)
$Mo(CO)_5$(4,6-dm-2-mp)	2061.9(m)	1932.7(s)	1888.3(m)
$W(CO)_5$(4,6-dm-2-mp)	2067.7(m)	1926.6(s)	1891.9(m)

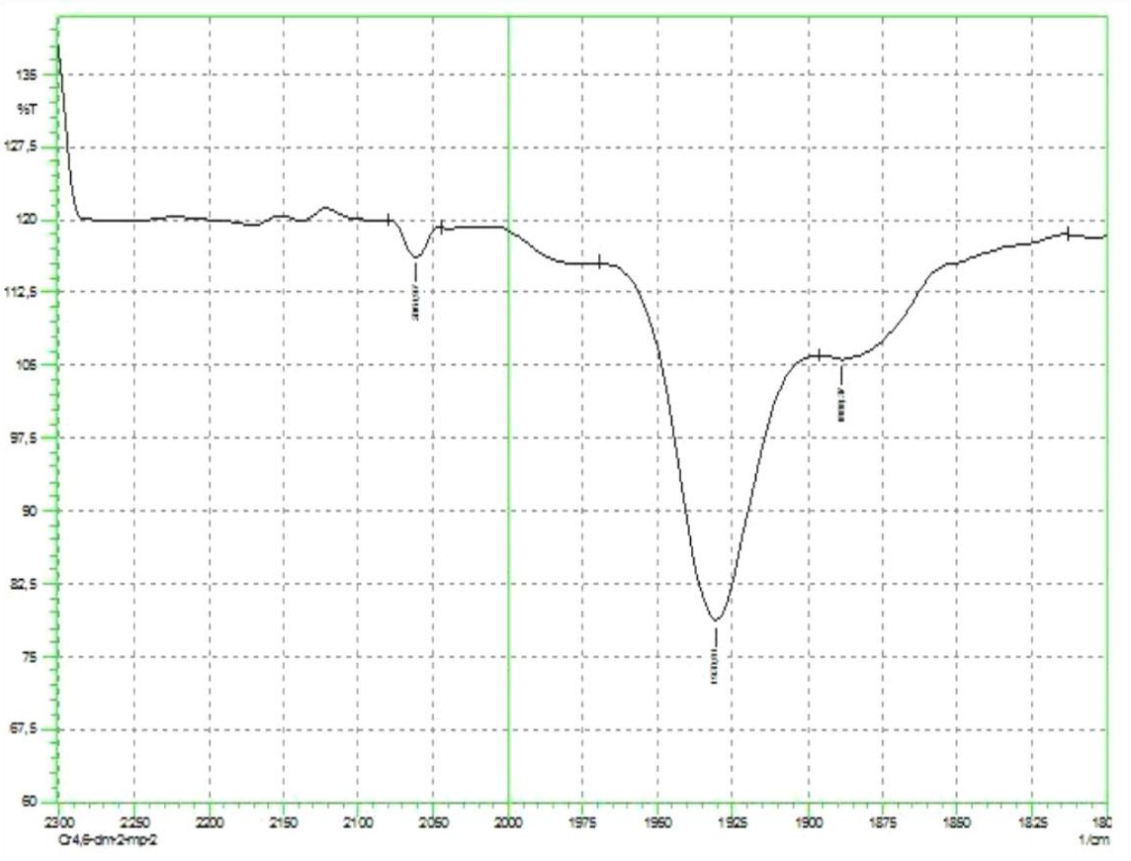


Figure.4.1.1. The IR spectrum of $Cr(CO)_5$(4,6-dimethyl-2-mercaptopyrimidine) in CH_2Cl_2 solution

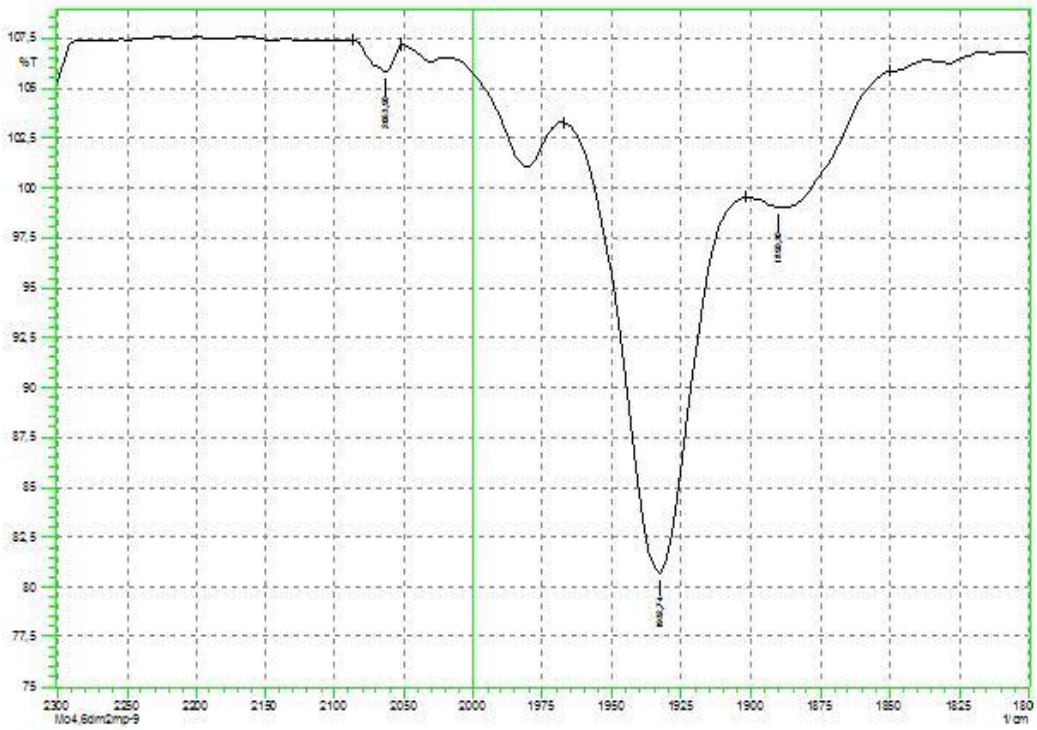


Figure.4.1.2.The IR spectrum of $Mo(CO)_5$4,6-dimethyl-2-mercaptopyrimidine) in CH_2Cl_2 solution

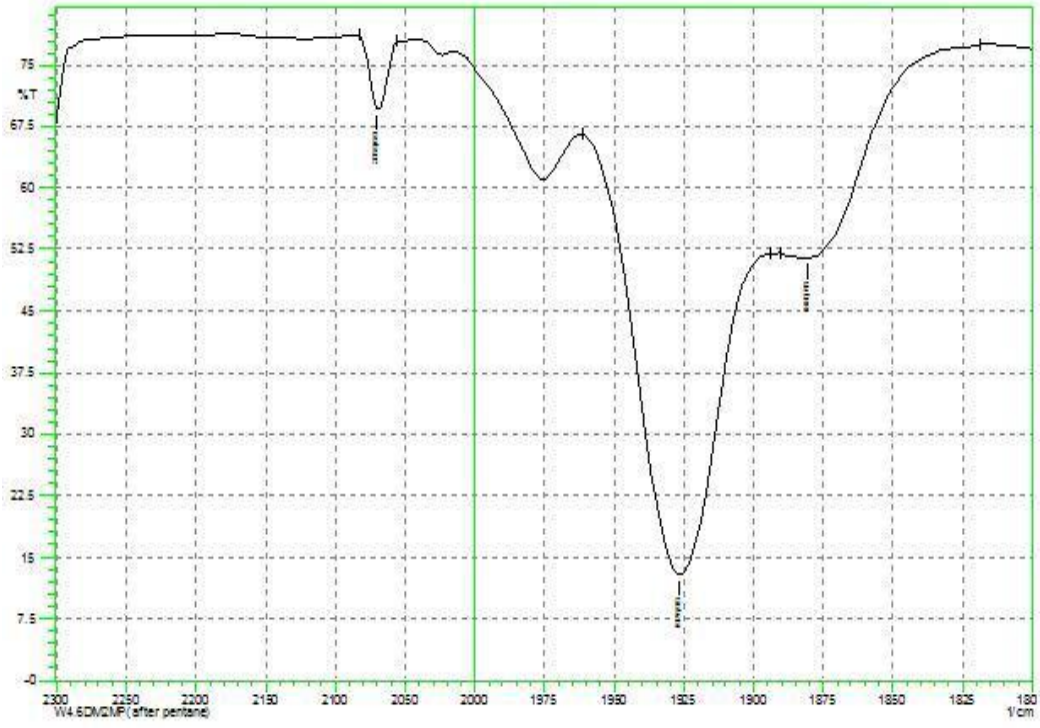


Figure.4.1.3.The IR spectrum of $W(CO)_5$(4,6-dimethyl-2-mercaptopyrimidine) in CH_2Cl_2 solution.

4.1.2 Assignment of IR Bands

The infrared spectra of MC(dmmp), M;Cr, Mo, W in n-dichloromethane solution taken in the range 400 - 4000 cm^{-1} (Fig.4.1.2.1, Fig.4.1.2.2, Fig.4.1.2.3) showed different bands. The bands at 3065 and 3053 cm^{-1} are assigned to the ν(C-H) vibration. The band at 889 cm^{-1} is attributed to ν(C-S) vibration. The ν(M-N) vibration appeared at 420.5 cm^{-1}. The other bands are associated with the aromatic ring vibrations [22].

All the experimental data of the complexes that obtained from FT-IR spectra are compared with the DFT theoretically calculated IR bands of the complexes (using Gaussian03 Software). The data are given in Table.4.1.2.1, Table.4.1.2.2, and Table.4.1.2.3.

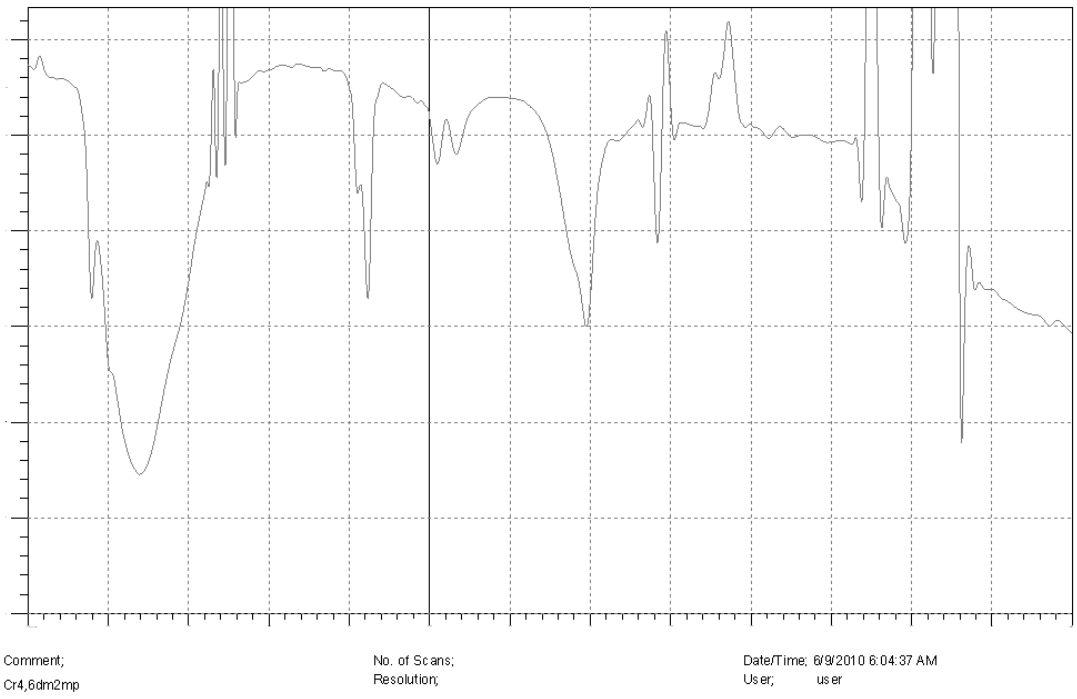


Figure.4.1.2.1. The IR spectrum of $Cr(CO)_5$(4,6-dimethyl-2-mercaptopyrimidine) in CH_2Cl_2 solution

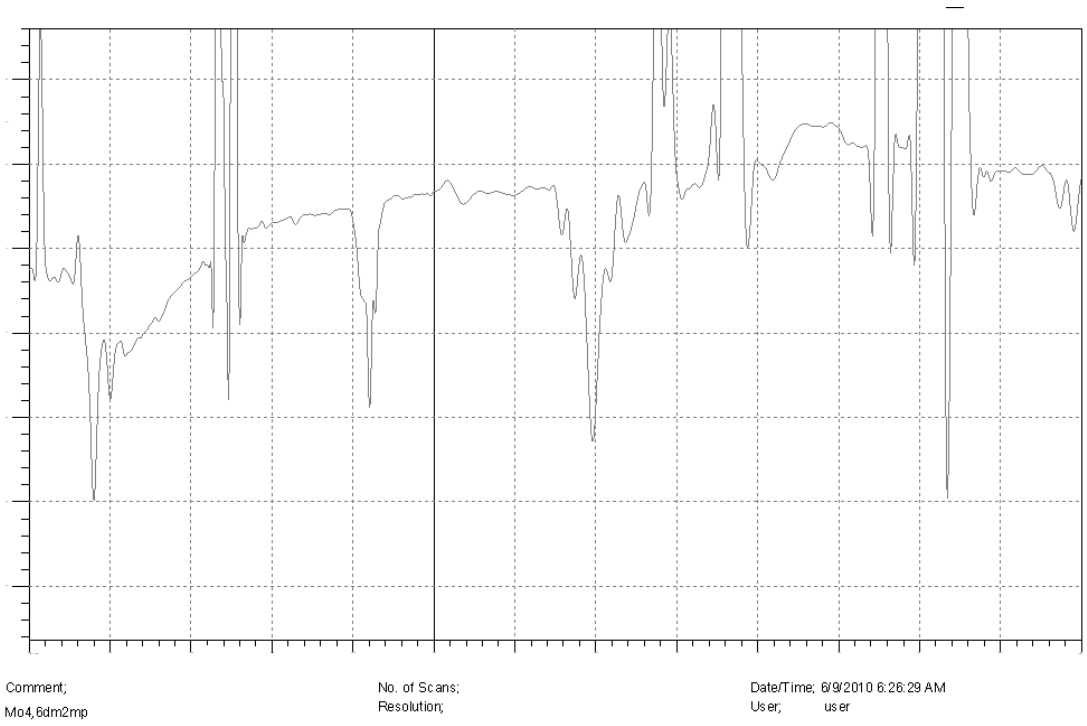


Figure.4.1.2.2.The IR spectrum of $Mo(CO)_5$(4,6-dimethyl-2-mercaptopyrimidine) in CH_2Cl_2 solution.

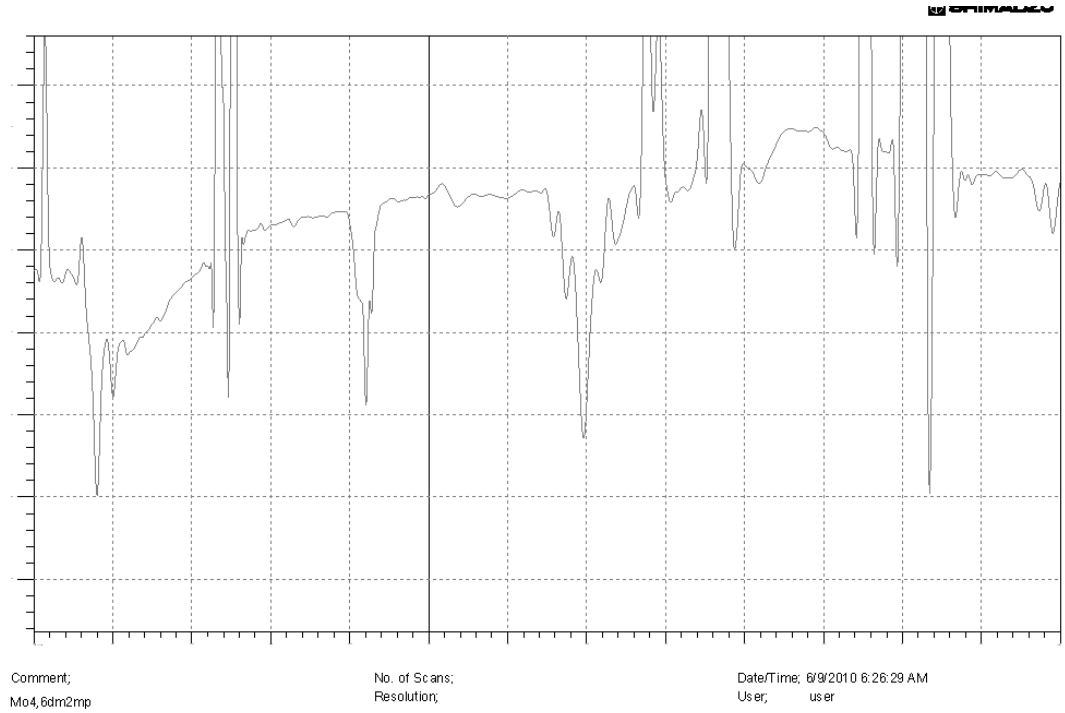


Figure.4.1.2.2 The IR spectrum of W(4,6-dimethyl-2-mercaptopyrimidine) in CH_2Cl_2 solution

Table 4.1.2.1 Experimental and DFT-Calculated vibrational frequencies of CrP(dmmp) complex

Vibration	Experimental Band, cm^{-1}	Theoretical (DFT, B3PW91) Band, cm^{-1}
ν(CO)	2061.90	2036.06
ν(CO)	1930.81	1925.70
ν(CO)	1886.44	1914.30
ν(C=C)Aromatic	1604.83	1633.76
ν(C=C)Aromatic	1535.39	1565.40
ν(M-N)	420.50	419.36
ν(C-C)	1429.30	1449.57
ν(C-C)	1425.44	1451.60
$\nu(CH_3)$	3064.99	3097.37
$\nu(CH_3)$	3053.42	3070.74
ν(C-N)	1290.42	1303.74
ν(C=N)	1411.94	1400.09
ν(C-H) Bend	794.70	795.01
ν(C-H) Bend	893.07	896.96
ν(C-S)	889.21	879.66

Table.4.1.2.2 Experimental and DFT-Calculated Streching frequencies of MoP(DMMP) complex

Vibration	Experimental Band, cm^{-1}	Theoretical (DFT, B3PW91) Band, cm^{-1}
ν(CO)	2061.97	2036.68
ν(CO)	1932.74	1917.33
ν(CO)	1888.37	1905.80
ν(C=C)Aromatic	1653.49	1634.07
ν(C=C)Aromatic	1558.91	1564.48
ν(M-N)	418.51	397.01
ν(C-C)	1437.21	1449.52
ν(C-C)	1429.46	1450.58
$\nu(CH_3)$	3080.37	3087.32
$\nu(CH_3)$	3074.61	3070.68
ν(C-N)	1290.71	1306.96
ν(C=N)	1244.48	1238.50
ν(C-H) Bend	889.23	794.98
ν(C-H) Bend	901.02	894.67
ν(C-S)	893.27	880.93

Table.4.1.2.3 Experimental and DFT-Calculated Streching frequencies of WP(dmmp) complex

Vibration	Experimental Band, cm^{-1}	Theoretical (DFT, B3PW91) Band, cm^{-1}
ν(CO)	2034.12	2067.50
ν(CO)	1926.56	1913.30
ν(CO)	1891.88	1900.18
ν(C=C)Aromatic	1653.05	1635.43
ν(C=C)Aromatic	1558.50	1563.20
ν(M-N)	418.50	402.55
ν(C-C)	1431.23	1449.74
ν(C-C)	1454.38	1451.09
$\nu(CH_3)$	3078.44	3087.46
$\nu(CH_3)$	3068.50	3070.69
ν(C-N)	1292.50	1309.34
ν(C=N)	1242.20	1236.74
ν(C-H) Bend	794.81	794.35
ν(C-H) Bend	906.41	895.68
ν(C-S)	889.31	879.55

4.2. ^{1}H-NMR Spectra

The ^{1}H-NMR spectra of the complexes pentacarbonyl(4,6-dimethyl-2-mercaptopyrimdine)metal(0) ; M: Cr, Mo, W complexes (Fig.4.2.1) were recorded from their (M: Cr, W ; d-chloroform, M: Mo ; d-dimethylsolfoxide) solutions. All chemical shifts(δ-) values are given in ppm relative to TMS as the internal reference. The spectra of these complexes show two singlets for the methyl and thiol substitutuents and one singlet for the aromatic proton of the pyrimidine ring. The ^{1}H-NMR spectrum of (pentacarbonyl(4,6-dimethyl-2-mercaptopyrimdine)metal(0) ; M: Cr, Mo, W complexes is given in

Figure.4.2.2. The chemical shifts of the free ligand and the complexes are given in Table.4.2.1.

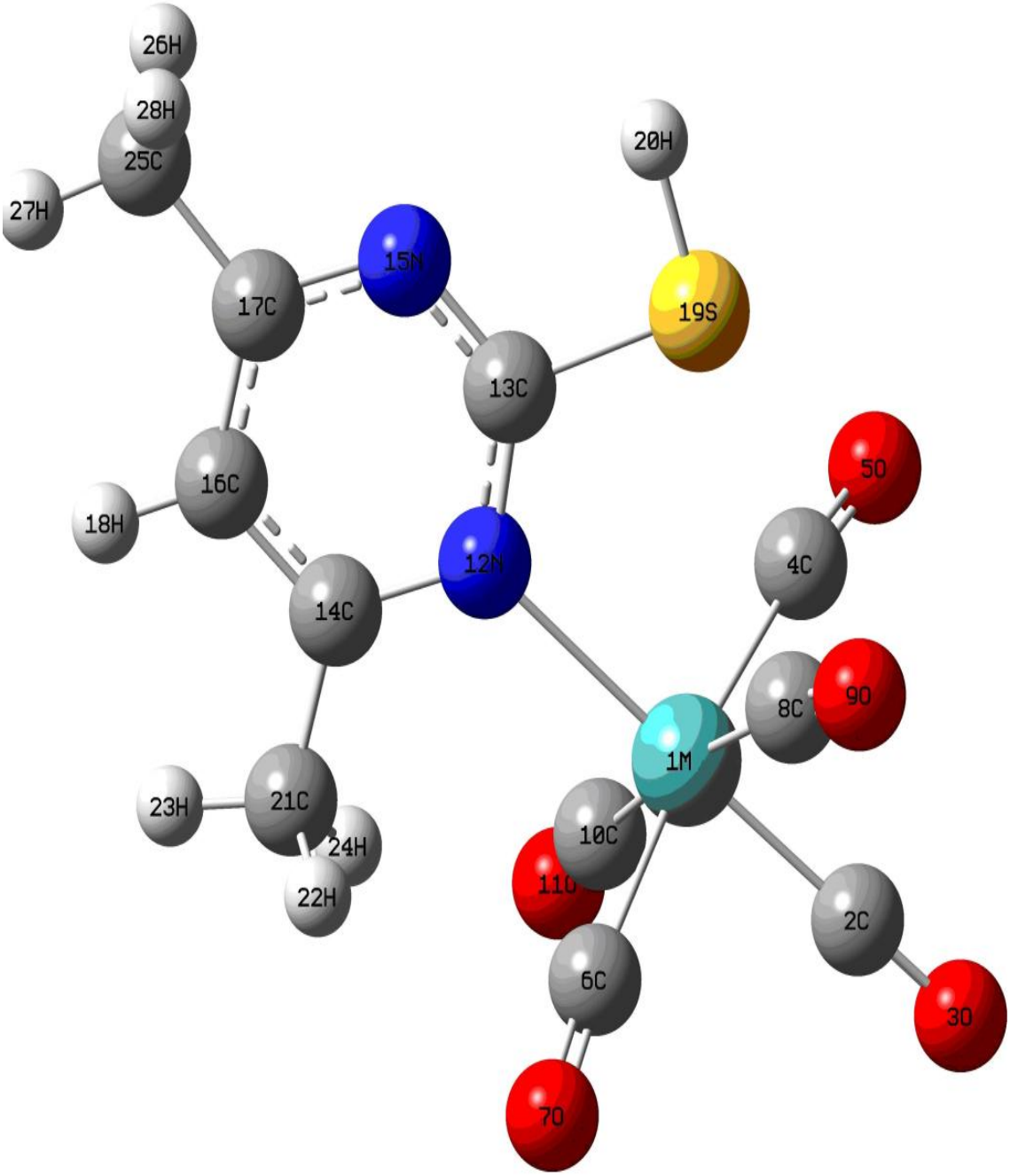


Figure.4.2.1.The structure of pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0) ; M: Cr, Mo, W.

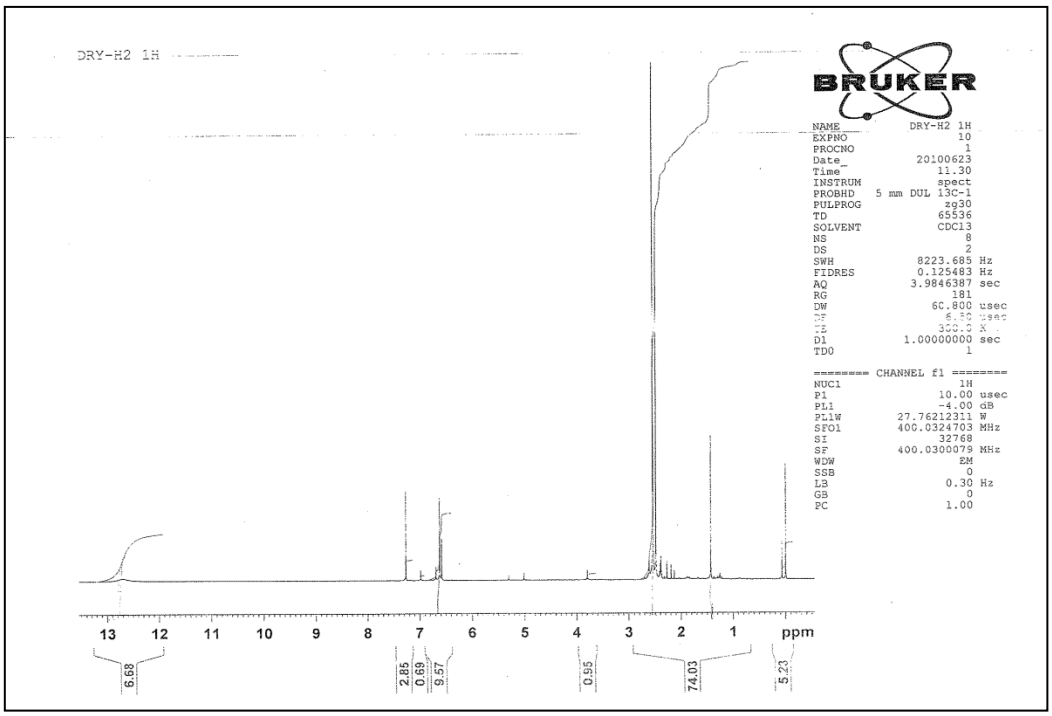


Figure.4.2.2.^{1}H-NMR spectrum of pentacarbonyl(4,6-dimethyl-2-mercaptopyrimdine)metal(0) ; M: W complex in d-chloroform.

Table.4.2.1. The ^{1}H-NMR chemical shifts (ppm, ref.TMS) of Pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0) ; M: Cr, Mo, W complexes.

	S-H, $H_{(20)}$	$CH_3(H_{(22,24)}$-$H_{(26,27)}$	$H_{(18)}$
Free ligand	12.15	2.33	6.93
CPDMMP			
Experimental	13.1	1.40	6.70
DFT(B3PW91)	4.93	2.46-1.82-1.13	6.33
MPDMMP			
Experimental	13.5	1.38	6.70
DFT(B3PW91)	4.82	2.01-2.13-1.78-1.1	6.33
WPDMMP			
Experimental	12.85	1.42	6.75
DFT(B3PW91)	4.84	1.99-2.13-1.77.1.1	6.28

The ^{1}H-NMR spectrum of free 4,6-dimethyl-2-mercaptopyrimidine (DMMP) shows three singlets with different intensities at 2.33, 6.93 and 12.15 ppm. Upon coordination to the metal atom the signal due to the SH group show no significant shift from that of free ligands. One can notice the followings,

- The appearance of only one singlet for the SH group proton which show no shift from that of the free ligand could rule out any metal-sulfure coordination.

- The appearance of only one singlet for the CH_3 groups with no significant chemical shift in an indication of the metal-nitrogen coordination through the nitrogen lone pair of the pyrimidine ring.

From these ^{1}H-NMR and previous IR-data discussed in section 4.1. , the can conclude the appearance of metal-pyrimidine coordination throught the nitrogen atom lone pair of the pyrimidine ring rather than the expected metal-thiol coordination.

4.3. ^{13}C-NMR Spectra

The ^{13}C-NMR spectra of the complexes $M(CO)_5$(4,6-dimethyl-2-mercaptopyrimidine); M: Cr, W were recorded from their d-chloroform solutions, M: Mo recorded from its d-dimethylsulfoxide solution are given in Figure 4.3.1. They show four signals in the region of 20-180 ppm for the pyrimidine ring and its substituents. The carbonyl groups give two signals

with relative intensities 1:4 in the region of 190-230 ppm as shown in the figures.

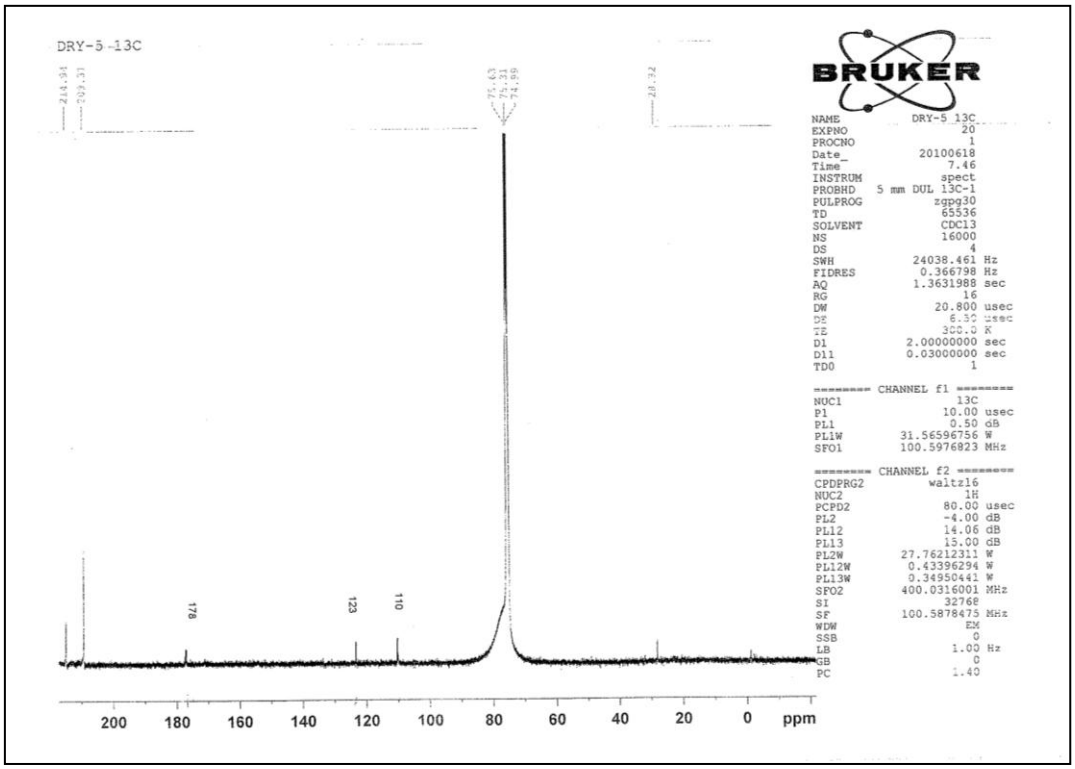


Figure.4.3.1. The ^{13}C-NMR spectrum of $M(CO)_5$(4,6-dimethyl-2-mercaptopyrimidene) ; M: Cr complex, TMS reference.

The ^{13}C-NMR chemical shifts of these complexes with the DFT calculated values are given in Table.4.3.1.

Table.4.3.1. The ^{13}C-NMR chemical shifts (δ ppm. ref.TMS) and DFT calculated chemical shift values.

	δ (ppm)							
	$C_{(13)}$	**$C_{(14)}$**	**$C_{(16)}$**	**$C_{(17)}$**	**$C_{(21)}$**	**$C_{(25)}$**	**Trans-CO**	**Cis-CO**
Free ligand	180	165.1	111.7	165.1	24.7	24.7	-	-
$Cr(CO)_5L$	179.6	168.3	112.8	168.3	29.43	28.32	214.9	209.3
$Mo(CO)_5L$	181.05	166.03	109.70	166.03	30.39	30.39	206.8	200.9
$W(CO)_5L$	180.80	165.6	111.71	166.0	30.32	30.32	198.2	190.60

The ^{13}C-{^{1}H}-NMR spectrum of the free 4,6-dimethyl-2-mercaptopyrimidine ligand (dmmp) show four signls with relative intensities at 179.9, 169, 118.7 and 23.8 ppm. Upon coordination to the metal atom, the signal belongs to $C_{(13)}$ show no significant shift comparing with that of free ligand. From the ^{13}C-NMR data of the complexes, one can notice the followings,

- The appearance of only one singlet for all the carbons of the pyrimidine ring an indication for the symmetric metal-ligand coordination through on of the ring nitrogen atoms.

- All the ^{13}C-signals of all carbons of the pyrimidine ring and substituentsshow no significant shift from these of free ligands indicates weak metal-nitrogen coordination.

- The appearance of two signals of relative intensities 1:4 in the CO-region indicates the formation of pentacarbonylmetal, $M(CO)_5$, group.

4.4. UV Spectra

The UV-Vis electronic absorption spectra of the complexes $M(CO)_5L$; (M: Cr, W ; L: 4,6-dimethyl-2-mercaptopyrimidine) were measured from their dichloromethane (CH_2Cl_2) solution where CH_2Cl_2 is the reference solution. The UV-Vis spectrum of CPDMMP complex shows one absorption band at 243 nm, 2.09557 Abs. while that of MPDMMP complex shows four absorption bands at 234 nm, 0.8893 Abs., 287nm,1.3061 Abs., 349nm, 0.3203 Abs. and 507nm, 0.1456 Abs. The WPDMMP complex shows three absorption bands at 243nm, 2.04778 Abs., 294nm, 0.5262 Abs. and 352nm, 0.3904 Abs. (Fig.4.4.1-3)

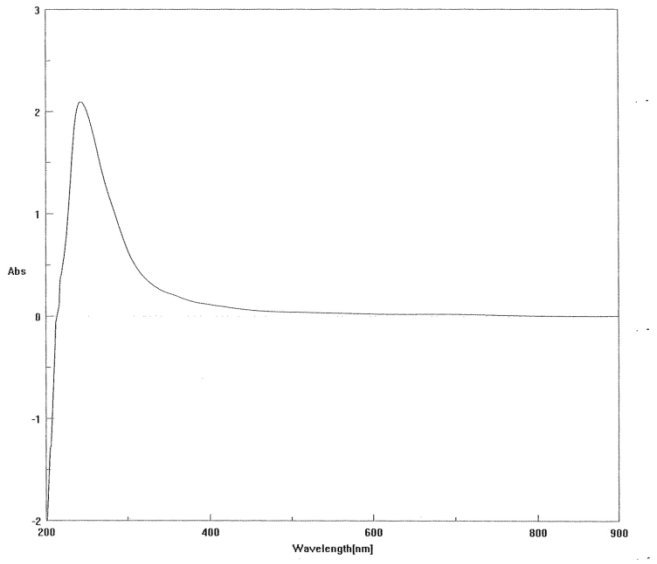


Figure.4.4.1.UV-Vis spectrum of CrP(dmmp) complex in CH_2Cl_2.

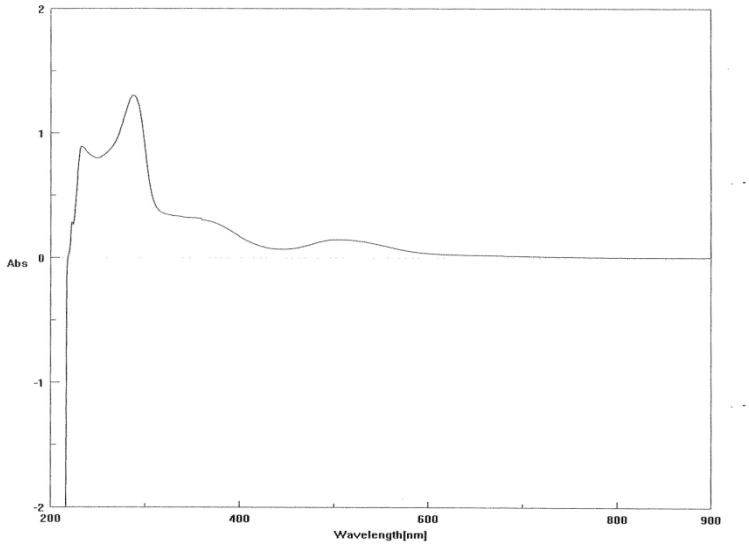


Figure.4.4.2.UV-Vis spectrum of MoP(dmmp) complex in CH_2CI_2.

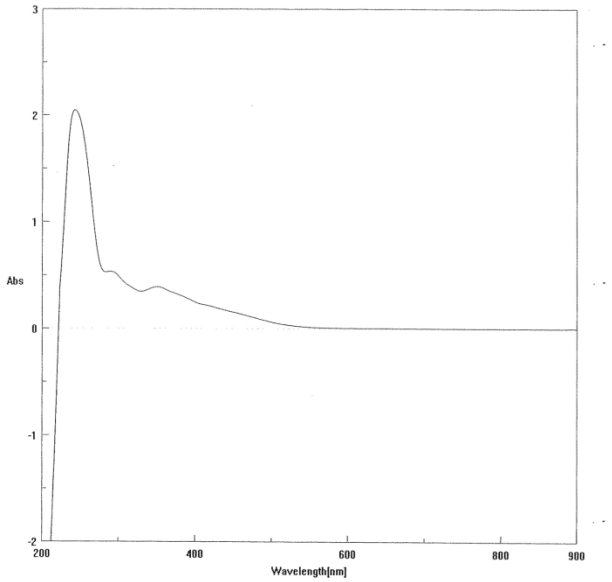


Figure.4.4.3.UV-Vis spectrum of WP(dmmp) complex in CH_2CI_2.

The transition energies of the complexes from High Occupied Molecular Orbital (HOMO) to Lowest Unoccupied Molecular Orbital (LUMO) was calculated by Gaussian molecular visualization program using Density Functional Theory, B3PW91 method as shown in Figure.4.4.4-6.

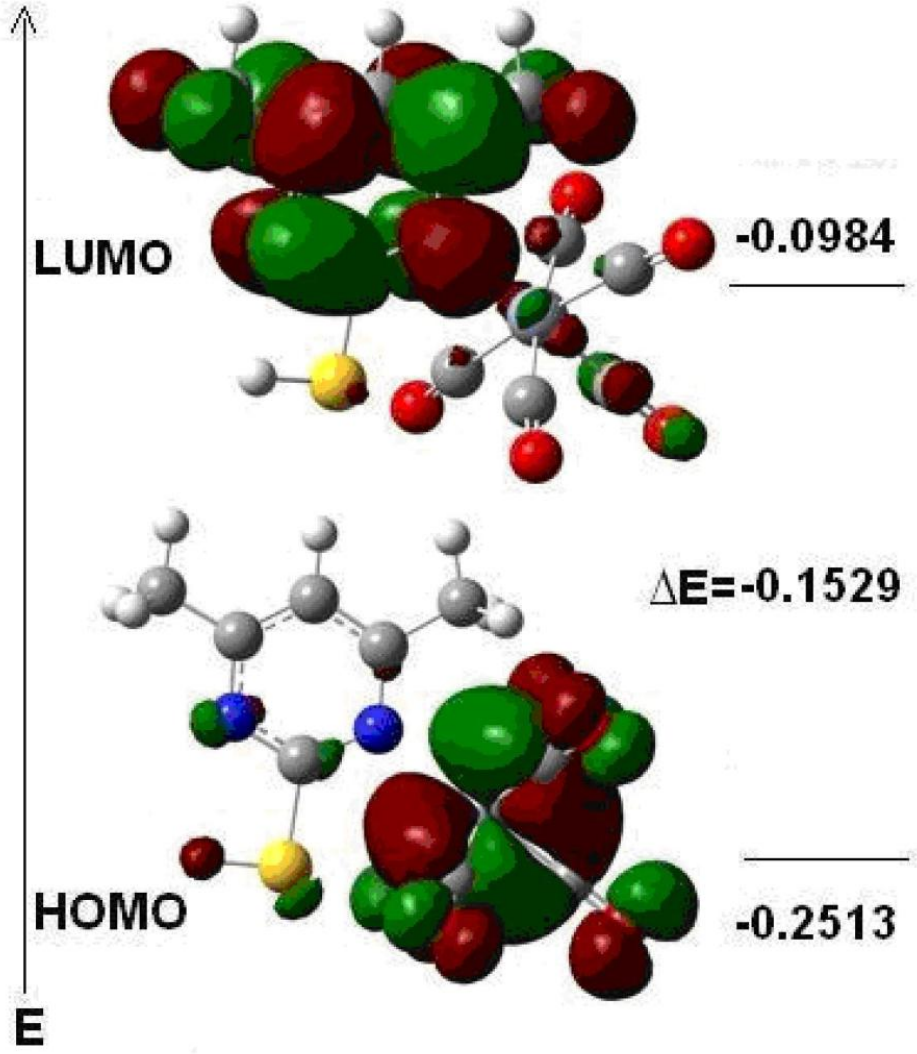


Figure.4.4.4. The electronic transition from HOMO to LUMO of the CrP(dmmp) complex

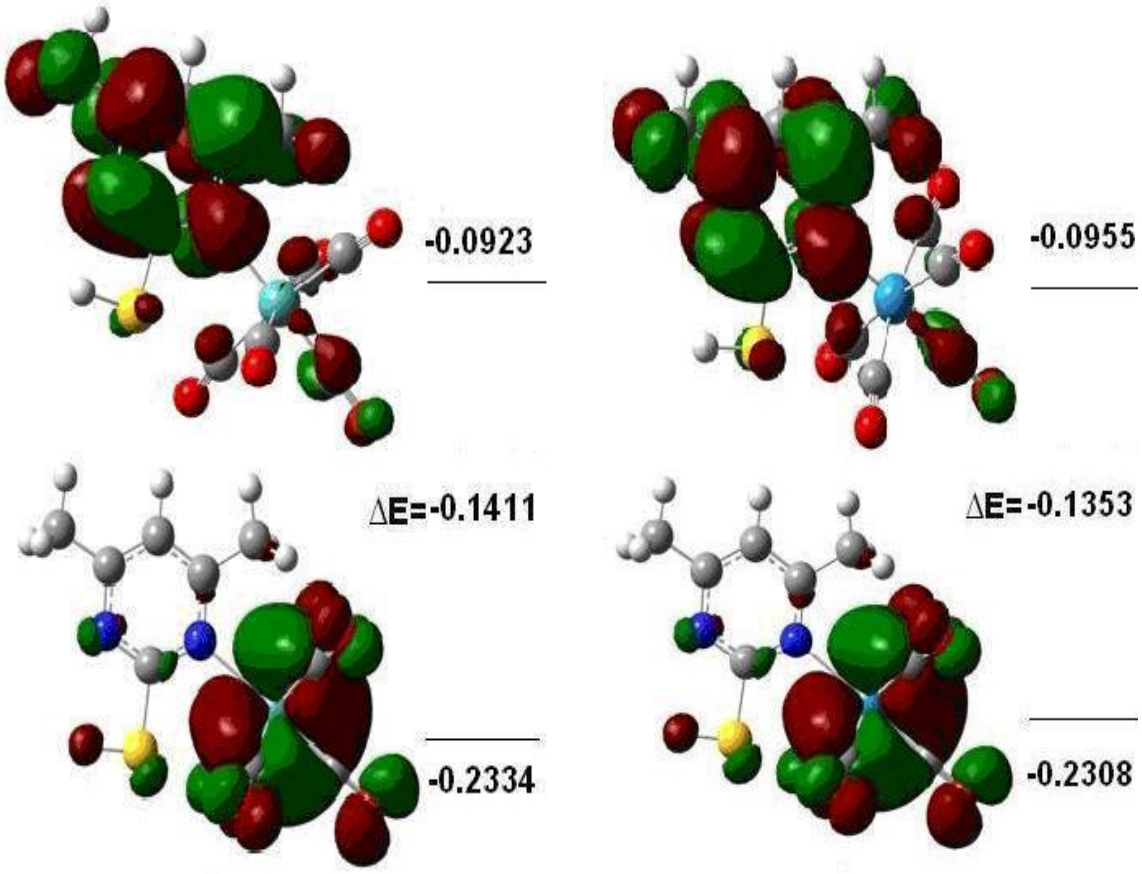


Figure. 4.4.4. The electronic transition from HOMO to LUMO of the MoP(dmmp) and WP(dmmp) complex

Table.4.4.1. DFT-Calculated (B3PW91/SDD) electronic transitions of the CrP(dmmp) complex

Exited States	λ (nm)	E (eV)	f
H - 2 → L + 4 H - 1 → L + 5	397.2	3.1214	0.0172
H - 2 → L + 3 H - 1 → L + 1	389.6	3.1822	0.0124
H → L	384.7	3.2226	0.0006
H - 2 → L + 1	372.6	3.3279	0.0030
H - 1 → L	364.6	3.4009	0.0762
H - 2 → L	344.9	3.5945	0.0000

Table.4.4.2. DFT-Calculated (B3PW91/SDD) electronic transitions of the MoP(dmmp) complex

Exited States	λ (nm)	E (eV)	f
H → L	399.6	3.1029	0.0011
H - 2 → L + 4	386.9	3.2048	0.0154
H → L + 1 H - 2 → L + 3	382.4	3.2424	0.0177
H → L + 5 H - 2 → L + 1	373.1	3.3233	0.0467

Table.4.4.3. DFT-Calculated (B3PW91/SDD) electronic transitions of the WP(dmmp) complex

Exited States	λ (nm)	E (eV)	f
H → L	421	2.9451	0.0004
H - 2 → L + 4	403.4	3.0738	0.0153
H - 2 → L + 3	397.9	3.1158	0.0160
H - 2 → L + 1	388.7	3.1894	0.0669

4.5 Thermal Analysis

The thermal analysis of the complexes $M(CO)_5L$; (M: Cr, W; L: 4,6-dimethyl-2-mercaptopyrimidine) was measured by using SII EXSTAR 6000 TG/DTA6300 (Fig.4.5.1). Thermal dissociations of the each complexes were calculated (Table.4.5.1) from the thermal analyse data.

The MoP(dmmp) complex dissociates at five different temperatures, in order of 59.7 ^oC, 119.8 ^oC, 169.7^oC, 370.2 ^oC and 900.9 ^oC and the main dissociation of the complex is occured at 160 ^oC. It can be postulated that in the first dissociation 2H, in the second one C=C, in the third 2 C=N, CH_2 and CH_3, and in the next dissociation 5 CO, S and C=N groups dissociates. It can be postulated from the last dissociation step of the complex MoP(dmmp) was dissociated to MoO_2.

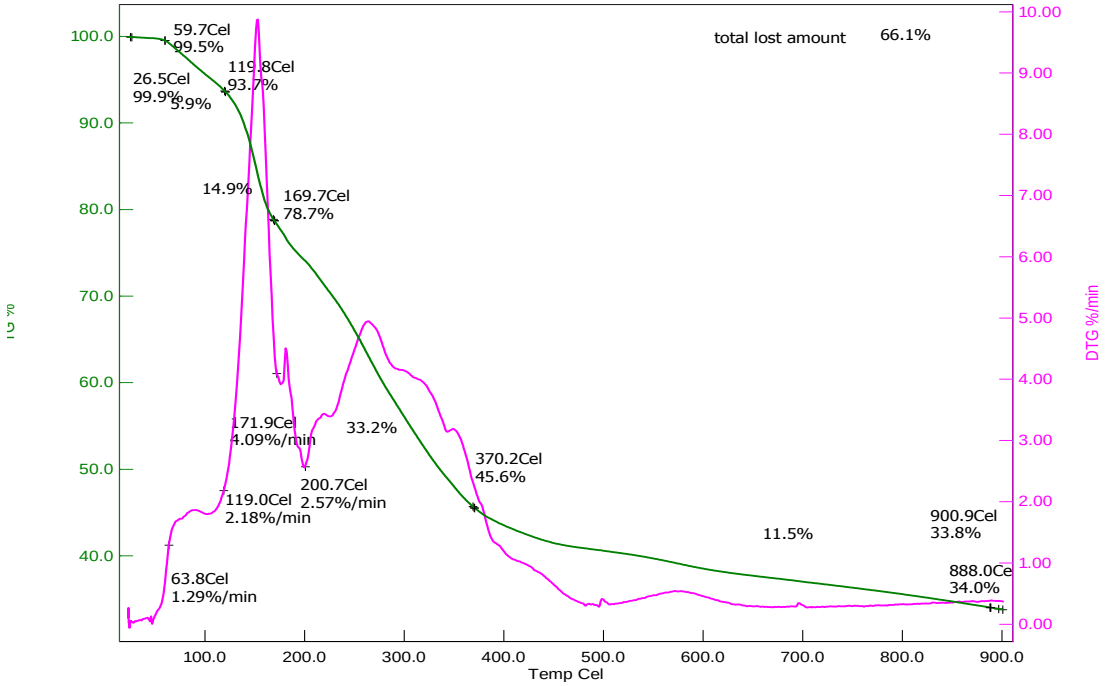


Figure.4.5.1. TG analysis of the MoP(dmmp) complex.

Table.4.5.1. Thermal dissociation of MoP(dmmp) complex

Decomposition Steps	Sample Amount (mg)	Lost Amount (%)	Lost Molecular Weight (g/mol)
1st	12.261	0.5	1.881
2nd	11.547	6.3%	23.70
3rd	9.698	21.3%	80.13
4th	5.6193	54.4%	204.65
5th	4.165	66.2%	249.04

4.6. Computional Details

The optimized molecular structure, energies, virational frequencies and the nuclear magnetic resonance chemical shift values of the pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0); M: Cr, Mo, W complexes have been performed using the Perdew and wang's 1991 gradient-corrected correlation functional (Perdew/Wang 91, B3PW91) [30].

One of the central tasks of computational chemistry is the reliable prediction of molecular structures. Assumed that density functional theory has adopted the role of a standard tool for the prediction of molecular structures[31], by using the B3PW91 method, the molecular structure of the pentacarbonyl(4,6-dimethyl-2-mercaptopyrimidine)metal(0); M: Cr, Mo, W complexes were simulated in Figure.4.2.1. Moreover the bond lenghts, bond angles and dihedral angles of the complexes were calculated and given in Table 4.6.1-3.

Vibrational spectroscopy is of almost important in many areas of chemical researchs and the applications of electronic structure methods for the calculation of harmonic frequencies has been of great value for the interpretation of complex experimental spectra. The pioneering comprehensive study of monometal carbonyls by Jonas and Thiel, 1995, was probably the first devoted to the computation of vibrational spectra for such compounds using density functional theory. These authors systematically compared experimental spectra and calculated vibrational data for several neutral tetra-, penta-, and hexacarbonyl complexes, $M(CO)_n$, n = 4-6) [29]. The computational prediction of vibrational spectra is among the important areas of application for modern quantum chemical methods because it allows the interpretation of experimental spectra and can be very instrumental for the identification of unknown species. A vibrational spectrum could be consist of two characteristics, the frequency of the incident light at which the absorption occurs and how much of the radiation is absorbed. The first quantity can be obtained computationally by calculating the harmonic

vibrational frequencies of a molecule. By this way, most of the DFT results reported were in good agreement with the experimental data as mentioned in Table.4.2.1. where the DFT calculted vibrational frequencies compared with the experimental data.

The most important magnetic property by far is the chemical shift of NMR spectroscopy. While ^{1}H- and ^{13}C- shifts hold a prominent place in organometallic chemistry. Computational studies in ^{1}H chemical shifts are less frequent than for other nuclei because proton shifts span only some ten ppm and rovibrational and solvent effects might be comparable to the range of chemical shifts itself [31]. It have been reported in Table.4.2.1. where DFT calculated proton shifts compared with both free ligand and experimental data , there is an successful application of density functional theory to proton chemical shifts. However for ^{13}C shieldings the compututional results were not give a successful result.

Table.4.6.1. DFT-Calculated (B3PW91/SDD) Bond distances between atoms of the MP(dmmp); M: Cr, Mo, W, complexes.

Atoms	CrP(dmmp)	MoP(dmmp)	WP(dmmp)
$Cr_{(1)}$ - $C_{(2)}$	1.8264	1.9691	1.9852
$Cr_{(1)}$ - $C_{(4)}$	1.8892	2.0450	2.0541
$Cr_{(1)}$ - $C_{(6)}$	1.8649	2.0232	2.0340
$Cr_{(1)}$ - $C_{(8)}$	1.8893	2.0448	2.0539
$Cr_{(1)}$ - $C_{(10)}$	1.8647	2.0240	2.0351
$Cr_{(1)}$ - $N_{(12)}$	2.2434	2.3667	2.3509
$C_{(2)}$ - $O_{(3)}$	1.1832	1.1845	1.1857
$C_{(4)}$ - $O_{(5)}$	1.1766	1.1775	1.1789
$C_{(6)}$ - $O_{(7)}$	1.1811	1.1818	1.1834
$C_{(8)}$ - $O_{(9)}$	1.1765	1.1772	1.1786
$C_{(10)}$ - $O_{(11)}$	1.1810	1.1817	1.1832
$N_{(12)}$ - $C_{(13)}$	1.3746	1.3739	1.3770
$N_{(12)}$ - $C_{(14)}$	1.3842	1.3827	1.3847
$C_{(13)}$ - $N_{(15)}$	1.3447	1.3437	1.3425
$C_{(13)}$ - $S_{(19)}$	1.8034	1.8017	1.8010
$C_{(14)}$ - $C_{(16)}$	1.4054	1.4044	1.4038
$C_{(14)}$ - $C_{(21)}$	1.5013	1.4993	1.4990
$N_{(15)}$ - $C_{(17)}$	1.3527	1.3538	1.3537
$C_{(16)}$ - $C_{(17)}$	1.4008	1.4017	1.4015
$C_{(16)}$ - $H_{(18)}$	1.0828	1.0829	1.0828
$C_{(17)}$ - $C_{(25)}$	1.4994	1.4994	1.4991
$S_{(19)}$ - $H_{(20)}$	1.3741	1.3747	1.3752
$C_{(21)}$ - $H_{(22)}$	1.0922	1.0949	1.0949
$C_{(21)}$ - $H_{(23)}$	1.0932	1.0932	1.0932
$C_{(21)}$ - $H_{(24)}$	1.0920	1.0911	1.0913
$C_{(25)}$ - $H_{(26)}$	1.0960	1.0961	1.0962
$C_{(25)}$ - $H_{(27)}$	1.0930	1.0931	1.0930
$C_{(25)}$ - $H_{(28)}$	1.0959	1.0959	1.0959

Table.4.6.2. DFT-Calculated (B3PW91/SDD) Bond angles between atoms of the MP(dmmp); M: Cr, Mo, W, complexes.

Atoms	CrP(dmmp)	MoP(dmmp)	WP(dmmp)
$C_{(2)}$-$Cr_{(1)}$-$C_{(4)}$	85.99	85.82	85.84
$C_{(2)}$ - $Cr_{(1)}$ - $C_{(6)}$	86.60	86.21	86.20
$C_{(2)}$ - $Cr_{(1)}$ - $C_{(8)}$	86.17	86.63	86.59
$C_{(2)}$ - $Cr_{(1)}$ -$C_{(10)}$	86.80	87.05	86.99
$C_{(4)}$ - $Cr_{(1)}$ - $C_{(8)}$	95.01	94.36	94.41
$C_{(4)}$ - $Cr_{(1)}$ -$C_{(10)}$	86.29	86.19	86.23
$C_{(4)}$ - $Cr_{(1)}$ -$C_{(12)}$	93.01	93.19	93.13
$C_{(6)}$ - $Cr_{(1)}$ - $C_{(8)}$	86.33	86.92	86.96
$C_{(6)}$ - $Cr_{(1)}$ -$C_{(10)}$	91.46	91.65	91.51
$C_{(6)}$ - $Cr_{(1)}$ -$C_{(12)}$	94.42	94.80	94.86
$C_{(8)}$ - $Cr_{(1)}$ -$C_{(12)}$	93.09	92.60	92.53
$C_{(10)}$ -$Cr_{(1)}$-$C_{(12)}$	93.98	93.73	93.91
$Cr_{(1)}$- $N_{(12)}$-$C_{(13)}$	121.07	121.19	121.31
$Cr_{(1)}$- $N_{(12)}$-$C_{(14)}$	124.28	123.80	123.77
$C_{(13)}$-$N_{(12)}$- $C_{(14)}$	114.65	114.97	114.90
$N_{(12)}$-$C_{(13)}$ -$N_{(15)}$	126.52	126.35	126.26
$N_{(12)}$ - $C_{(13)}$-$S_{(19)}$	119.86	119.30	119.39
$N_{(15)}$ - $C_{(13)}$-$S_{(19)}$	113.62	114.36	114.36
$N_{(12)}$- $C_{(14)}$-$C_{(16)}$	120.95	120.85	120.83
$N_{(12)}$ -$C_{(14)}$-$C_{(21)}$	121.78	121.06	121.19
$C_{(16)}$ -$C_{(14)}$-$C_{(21)}$	117.27	118.09	117.98
$C_{(13)}$ -$N_{(15)}$-$C_{(17)}$	118.95	118.85	119.02
$C_{(14)}$ -$C_{(16)}$-$C_{(17)}$	120.05	119.90	120.01
$C_{(14)}$ -$C_{(16)}$-$H_{(18)}$	119.42	119.52	119.42
$C_{(17)}$-$C_{(16)}$ -$H_{(18)}$	120.53	120.58	120.57
$N_{(15)}$ -$C_{(17)}$-$C_{(16)}$	118.87	119.06	118.97
$N_{(15)}$ -$C_{(17)}$-$C_{(25)}$	117.35	117.28	117.30
$C_{(16)}$ -$C_{(17)}$-$C_{(25)}$	123.77	123.67	123.73
$C_{(13)}$ -$S_{(19)}$-$H_{(20)}$	92.97	93.03	92.91
$C_{(14)}$-$C_{(21)}$- $H_{(22)}$	111.78	110.75	110.86
$C_{(14)}$-$C_{(21)}$- $H_{(23)}$	109.61	110.02	109.93
$C_{(14)}$-$C_{(21)}$- $H_{(24)}$	112.02	112.13	112.17
$H_{(22)}$-$C_{(21)}$- $H_{(23)}$	107.72	107.91	107.90
$H_{(22)}$ -$C_{(21)}$-$H_{(24)}$	107.79	107.43	107.42
$H_{(23)}$-$C_{(21)}$- $H_{(24)}$	107.73	108.45	108.41
$C_{(17)}$-$C_{(25)}$- $H_{(26)}$	109.98	109.96	109.96
$C_{(17)}$-$C_{(25)}$- $H_{(27)}$	111.85	111.85	111.86
$C_{(17)}$-$C_{(25)}$- $H_{(28)}$	110.01	110.03	110.03
$H_{(26)}$-$C_{(25)}$- $H_{(27)}$	108.94	108.92	108.92
$H_{(26)}$-$C_{(25)}$- $H_{(28)}$	106.94	106.94	106.92
$H_{(27)}$-$C_{(25)}$- $H_{(28)}$	108.99	109.01	109.02

Table.4.6.3. DFT-Calculated (B3PW91/SDD) dihedral angles between atoms of the MP(dmmp); M: Cr, Mo, W, complexes.

Atoms	CrP(dmmp)	MoP(dmmp)	WP(dmmp)
$C_{(4)}$-$Cr_{(1)}$-$N_{(12)}$-$C_{(13)}$	-46.9099	-43.6786	-44.1016
$C_{(4)}$-$Cr_{(1)}$-$N_{(12)}$-$C_{(14)}$	132.4499	134.1222	134.1032
$C_{(6)}$-$Cr_{(1)}$-$N_{(12)}$-$C_{(13)}$	134.8309	137.9635	137.6205
$C_{(6)}$-$Cr_{(1)}$-$N_{(12)}$-$C_{(14)}$	-45.8093	-44.2358	-44.1746
$C_{(8)}$-$Cr_{(1)}$-$N_{(12)}$-$C_{(13)}$	48.2771	50.8378	50.4579
$C_{(8)}$-$Cr_{(1)}$-$N_{(12)}$-$C_{(14)}$	-132.3630	-131.3615	-131.3373
$C_{(10)}$-$Cr_{(1)}$-$N_{(12)}$-$C_{(13)}$	-133.3964	-130.0648	-130.5282
$C_{(10)}$-$Cr_{(1)}$-$N_{(12)}$-$C_{(14)}$	45.9634	47.7360	47.6766
$Cr_{(1)}$-$N_{(12)}$-$C_{(13)}$-$N_{(15)}$	178.9545	176.1639	176.6465
$Cr_{(1)}$-$N_{(12)}$-$C_{(13)}$-$S_{(19)}$	-1.1828	-4.3706	-3.8146
$Cr_{(1)}$-$N_{(12)}$-$C_{(14)}$-$C_{(16)}$	-178.9950	-176.2058	-176.6962
$Cr_{(1)}$-$N_{(12)}$-$C_{(14)}$-$C_{(21)}$	1.1975	4.9175	4.3320
$N_{(15)}$-$C_{(17)}$-$C_{(25)}$-$H_{(26)}$	59.2844	59.7539	59.8950
$N_{(15)}$-$C_{(17)}$-$C_{(25)}$-$H_{(27)}$	-179.5172	-179.0913	-178.9484
$N_{(15)}$-$C_{(17)}$-$C_{(25)}$-$H_{(28)}$	-58.2481	-57.7784	-57.6162
$C_{(16)}$-$C_{(17)}$-$C_{(25)}$-$H_{(26)}$	-120.7519	-120.4143	-120.2350
$C_{(16)}$-$C_{(17)}$-$C_{(25)}$-$H_{(27)}$	0.4465	0.7406	0.9216
$C_{(16)}$-$C_{(17)}$-$C_{(25)}$-$H_{(28)}$	121.7156	122.0534	122.2538
$S_{(19)}$-$C_{(13)}$-$N_{(15)}$-$C_{(17)}$	-179.7153	-178.9541	-179.0556
$N_{(12)}$-$C_{(14)}$-$C_{(21)}$-$H_{(22)}$	60.7241	67.9368	67.6937
$N_{(12)}$-$C_{(14)}$-$C_{(21)}$-$H_{(23)}$	-179.9080	-172.8426	-173.0915
$N_{(12)}$-$C_{(14)}$-$C_{(21)}$-$H_{(24)}$	-60.3780	-52.0571	-52.3879
$C_{(16)}$-$C_{(14)}$-$C_{(21)}$-$H_{(22)}$	-119.0900	-110.9701	-111.3064
$C_{(16)}$-$C_{(14)}$-$C_{(21)}$-$H_{(23)}$	0.2778	8.2506	7.9084
$C_{(16)}$-$C_{(14)}$-$C_{(21)}$-$H_{(24)}$	119.8078	129.0360	128.6120

The knowledge of accurate thermochemical data for individual metal-ligand bond strengths is of major importance for the rational design of catalytic processes [31]. It can said that computational thermochemistry is an important tool however it cannot be covered by experimental means alone. In this study thermochemcal behaviour of the prepared complexes is investigated experimentaly by using DTA/TGA method and computitionaly by using B3PW91 method of DFT (Table.4.6.4).

Table.4.6.4. DFT calculated Thermodynamic properties of $M(CO)_5$(4,6-dimethyl-2-mercaptopyrimidine) ; M: Cr, Mo, W complexes

DFT-B3PW91/SDD	$M(CO)_5$(4,6-dimethyl-2-mercaptopyrimidine)		
Thermodynamic Properties	Cr	Mo	W
Total Energy (a.u.)	-1394.2030	-1375.5869	-1374.4947
Zero-Point Energy (KCal/Mol)	110.1081	109.0723	109.0984
	0.4306	0.3995	0.3970
Rotational Constants (GHZ)	0.2339	0.2130	0.2063
	0.2017	0.1861	0.1807
	0.0207	0.0192	0.0191
Rotational Temperatures (K)	0.0112	0.0102	0.0099
	0.0097	0.0089	0.0087
Dipole Moment (Debye)	9.0125	9.3578	9.7212
RMS Gradient Norm (a.u.)	0.00000186	0.00001508	0.00000674
Virial Ratio (a.u.)	2.0361	2.0381	2.0375
Entropy (Cal/Mol-Kelvin)			
Total	161.660	162.360	162.524
Electronic	0.000	0.000	0.000
Translational	43.295	43.681	44.293
Rotational	34.025	34.273	34.340
Vibrational	84.341	84.406	83.892
Thermal Energy (KCal/Mol)			
Total	123.809	123.102	123.087
Electronic	0.000	0.000	0.000
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	122.031	121.325	121.309

CHAPTER 5

CONCLUSION

In this study, pentacarbonyl(4,6-dimethyl-2-pyrimidinethiol)metal(0); M: Cr, Mo, W complexes were photochemically synthesized, their structures have been characterized by the mean of IR-, UV-, ^{1}H-NMR and ^{13}C-NMR spectroscopies and their thermal behaviour investigate by TG/DTA methods.

The ligand 4,6-dimethyl-2-pyrimidinethiol is chosen because of its multifunctional groups and multibonding probability. There are three basic centers in the ligand which are available to bond lewis acid (metal center). The most basic center is that N atom due to the spectroscopic investigations so the central atom is bonded to ligand from N atom of pyrimidinethiol. Although the change in the bond distances is that the CO group is the most strongest π- acceptor ligand which results M-C bond becomes less strong and of course occuring a synergistic energy in M-CO bond.

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