

**THE SYNTHESIS AND SPECTROSCOPIC INVESTIGATIONS
OF SOME PENTACARBONYL(PYRIDINE)METAL(0) COMPLEXES
OF GROUP 6 B ELEMENTS**

by

ÇİĞDEM TUÇ

**THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
THE ABANT İZZET BAYSAL UNIVERSITY
IN PARTIAL FULLFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
MASTER OF SCIENCE
IN
THE DEPARTMENT OF CHEMISTRY**

January 2006

TABLE OF CONTENTS

ABSTRACT	iii
ÖZET	v
ACKNOWLEDGEMENT	vi
TABLE OF CONTENTS	vi
LIST OF FIGURES	x
CHAPTER I: INTRODUCTION	1
CHAPTER II:THEORETICAL BACKGROUND	6
II.1. Complexes of π - Acceptor (π -acid) Ligands.....	6
II.2. Metal-Carbonyl Bonding.....	7
CHAPTER III: EXPERIMENTAL	14
III.1. Basic Thecniques.....	14
III.1.1. FTIR-(Fourier Transform Infrared)-Spectra.....	19
III.1.2. ^1H -NMR.....	19
III.1.3. ^{13}C -NMR.....	19
III.2.The Synthesis Of The Complexes.....	20
III.2.1. Pentacarbonyl(4-methylpyridin)metal(0), $\text{M}(\text{CO})_5(4\text{-mp})$; M: Cr,Mo,W.....	20
III.2.2.Pentacarbonyl(4-tertbutylpyridin)metal(0), $\text{M}(\text{CO})_5(4\text{-tbp})$; M:Cr,Mo,W.....	21
III.2.3. Pentacarbonyl(4- dimethylaminopyridin)metal(0),	

M(CO) ₅ (4dmap);M:Cr,Mo,W.....	22
III.2.4. Cis-tetracarbonyl (4-tert-butylpyridin)tungsten(0), W(CO) ₄ (4dmap).....	23
CHAPTER IV: RESULTS AND DISCUSSION	24
IV.1. IR Spectra.....	24
IV.1.1. IR Spectra of M(CO) ₅ L Complexes.....	24
IV.1.2. Cis-tetracarbonyl (4-tert-butylpyridin)tungsten(0).....	29
IV.2. ¹ H-NMR Spectra.....	31
IV.2.1. Pentacarbonyl(4-methylpyridin)metal(0);M(CO) ₅ (4-mp); M: Cr,Mo,W.....	31
IV.2.2. Pentacarbonyl(4-tertbutylpyridin)metal(0); M(CO) ₅ (4-tbp); M: Cr,Mo,W.....	35
IV.2.3. Pentacarbonyl(4-dimethylaminolpyridin)metal(0), M(CO) ₅ (4-tbp); M: Cr,Mo,W.....	38
IV.2.4. Cis-tetracarbonyl (4-tert-butylpyridin)tungsten(0).....	40
IV.2. ¹³ C-NMR Spectra.....	44
IV.3.1. Pentakarbonyl(4-methylpyridin)metal(0), M(CO) ₅ (4-mp); M:Cr,Mo,W.....	44
IV.3.2. Pentacarbonyl(4-tertbutylpyridin)metal(0), M(CO) ₅ (4-tbp); M: Cr,Mo,W.....	47
IV.3.3. Pentakarbonyl(4-dimethylaminopyridin)metal(0), M(CO) ₅ (4-dmap); M: Cr,Mo,W.....	50

IV.3.4. Cis-tetracarbonyl(4-tert-butylpyridine) ₂ tungsten(0).....	54
CHAPTER V:CONCLUSION.....	59
REFERENCES.....	60

LIST OF FIGURES

Figure

II.1. Molecular orbital description of metal-carbonyl interaction.....	9
II.2. Competition of two ligands for the use of the same orbitals of the central atom.....	13
III.1. Schlenk type storage flask.....	15
III.2. The apparatus which was used for Photochemical reaction.....	17
III.3. A typical Schlenk system.....	23
IV.1.1. The IR spectrum of Mo(CO) ₅ (dmap) in hexane solution.....	26
VI.1.2. The IR spectrum of W(CO) ₅ (4-mp) in hexane solution.....	27
IV.1.3. The IR spectrum of W(CO) ₅ (tbp) in hexane solution.....	28
VI.1.4. The IR spectrum of cis-W(CO) ₄ (4-tert-butylpyridine) ₂ from dichloromethane solution.....	30
IV.2.1.a. The structure of pentacarbonyl(4-mp)metal(0).....	33
IV.2.1.b. The ¹ H-NMR spectrum of W(CO) ₅ (4-mp) complex measured from its d-chloroform solutions; TMS reference.....	34
IV.2.2.a. The structure of pentacarbonyl(4-tbp)metal(0).....	36
IV.2.2.b. The ¹ H-NMR spectrum of W(CO) ₅ (4-tbp) complex measured from its d-chloroform solutions; TMS reference.....	37

IV.2.3.a. The structure of pentacarbonyl(4-dmap)metal(0).....	39
IV.2.3.b. The ^1H -NMR spectrum of $\text{W}(\text{CO})_5(4\text{-dmap})$ complex measured from its d-chloroform solutions; TMS reference.....	40
IV.2.4.a. The proposed structure of $\text{W}(\text{CO})_4(4\text{-tbp})$	42
IV.2.4.b. The ^1H -NMR spectrum of $\text{W}(\text{CO})_4(4\text{-tbp})_2$ complex measured from its d-chloroform solutions; TMS reference.....	43
IV.3.1. The ^{13}C -NMR spectrum of $\text{W}(\text{CO})_5(4\text{-mp})$ complex measured from its d-chloroform solutions; TMS reference.....	46
IV.3.2. The ^{13}C -NMR spectrum of $\text{W}(\text{CO})_5(4\text{-tbp})$ complex measured from its d-chloroform solutions; TMS reference.....	49
IV.3.3. The ^{13}C -NMR spectrum of $\text{W}(\text{CO})_5(4\text{-dmap})$ complex measured from its d-chloroform solutions; TMS reference.....	53
IV.3.4. The ^{13}C -NMR spectrum of $\text{W}(\text{CO})_4(4\text{-tbp})_2$ complex measured from its d-chloroform solutions; TMS reference	56
IV.3.5. The possible isotopomeres of $\text{M}(^{12}\text{CO})_4(^{13}\text{CO})\text{L}$; M:Cr, Mo, W and L: 4-mp , 4-tbp, 4-damp.....	58

LIST OF TABLES

Table

IV.1.1. The CO-stretching frequencies ν_{CO} (cm^{-1}) of $\text{M}(\text{CO})_5\text{L}$; L: 4-mp, 4-tbp, 4-dmap and M: Cr, Mo, W, in n-hexane.....	25
IV.1.2. The CO stretching frequencies (cm^{-1}) for cis- $\text{W}(\text{CO})_4(4\text{-t-butylpyridine})_2$ from dichloromethane solution.....	29
IV.2.1. The ^1H -NMR chemical shifts (δ ppm) of $\text{M}(\text{CO})_5(4\text{-mp})$ complexes measured from their d-chloroform solutions; TMS reference.....	32
IV.2.2. The ^1H -NMR chemical shifts (δ ppm) of $\text{M}(\text{CO})_5(4\text{-tbp})$ complexes measured from their d-chloroform solutions; TMS reference.....	36
IV.2.3. The ^1H -NMR chemical shifts (δ ppm) of $\text{M}(\text{CO})_5(4\text{-dmap})$ complexes measured from their d-chloroform solutions; TMS reference.....	39
IV.2.4. ^1H -NMR chemical shifts (δ ppm) for cis- $\text{W}(\text{CO})_4(4\text{-tert-butylpyridine})_2$ complex measured from their d-chloroform solutions; TMS reference.....	42
IV.3.1. The ^{13}C -NMR chemical shifts (δ ppm) of $\text{M}(\text{CO})_5(4\text{-mp})$ complexes recorded from their d-chloroform solutions; TMS reference.....	45

IV.3.2. The ^{13}C -NMR chemical shifts (δ ppm) of M(CO) ₅ (4-tbp) complexes measured from their d-chloroform solutions; TMS reference.....	48
IV.3.3. The ^{13}C -NMR chemical shifts (δ ppm) of M(CO) ₅ (4-dmap) complexes measured from their d-chloroform solutions; TMS reference.....	52
IV.3.4. The ^{13}C -NMR chemical shifts (δ ppm) of cis-W(CO) ₄ (4-tbp) ₂ complexes measured from their d-chloroform solutions; TMS reference.....	55

CHAPTER I

INTRODUCTION

Organometallic chemistry, the chemistry of compounds containing metal carbon bonds, is one of the most interesting and certainly most rapidly growing area of chemical researches. Recently, coordination compounds including a lot of current inorganic researches have been reported in the last century. Although, the usual bonding theories can be extended to accommodate these compounds, they still provide stimulating problems to be resolved.

The modern study of coordination compounds began with two scientists, Alfred Werner and Mond Jorgensen [1], both are great chemists who made great contributions to the elucidation of the structure of complexes with coordination numbers higher than four.

Organotransition metal chemistry and the organometallic chemistry can be differentiated from each other by the greater versatility of organotransition metal chemistry. The first organometallic compound was reported in 1827 by Zeise, who obtained yellow needle-like crystals, $K[PtCl_3(C_2H_4)] \cdot H_2O$, after refluxing a mixture of $PtCl_4$ and $PtCl_2$ in ethanol, followed by the addition of KCl solution [2,3]. Nevertheless, the important development in this area could be occurred by the synthesis of ferrocene, $Fe(C_5H_5)_2$, in 1951 and the recognition of its sandwich-type structure [4,5].

The product was surprisingly stable; it could be sublimed in air without decomposition and was resistant to catalytic hydrogenation and Diels-Alder reactions. In 1956, X-ray diffraction analysis showed the structure to consist of an iron atom sandwiched between two parallel C_5H_5 rings [6].

One of the most important and common organometallic compounds type is the metal-carbonyl complexes. The first compound containing carbon monoxide as a ligand was reported in 1890 by Mond as tetracarbonylnickel (0), $[Ni(CO)_4]$ [6]. Followed the syntheses of $Ni(CO)_4$, in 1891, the discovery of pentacarbonyliron, $Fe(CO)_5$, was reported by Mond [7] and Berthelot [8]. During the next twenty years, iron, cobalt and molybdenum carbonyls were synthesized and the properties of these metal carbonyls were investigated. It was shown that most of organic chemicals have been produced by using transition metal complexes as homogenous catalysts [9]. The commonly known carbonyl complexes of group VB metals are synthesized and isolated as a volatile, white, air stable, and diamagnetic crystalline compounds with six coordinated octahedral complexes of the type $M(CO)_6$, M: Cr, Mo, W. Hexacarbonyl molybdenum(0) has been synthesized by Mond in 1910 [10], followed by the discovery of hexacarbonylchromium(0) and tungsten(0) which are isolated by Job and co-workers [11,12]. The applications of transition metals in catalytic organic reactions have a lot of industrial importance.

The development of organometallic compounds speed up with the application of photochemistry. The first recorded substance was the result

of conversion of the very newly discovered $\text{Fe}(\text{CO})_5$ into a new substance with sunlight in 1905 by Dewar and Jones [13]. The correct formula of which was later reported by Speyer and Wolf to be $\text{Fe}_2(\text{CO})_9$ [14]. The syntheses of $\text{Fe}_2(\text{CO})_9$ is described in Organometallic Synthesis to be the most influential syntheses reference in this area [15]. Photochemical studies began with a series of researches at Strohmeier laboratory in Würzburg at which the application of photochemistry to the substitution of carbonyl ligands in the group VI carbonyls [16], and $\text{CpMn}(\text{CO})_3$ [17] was reported.

The syntheses of new compounds by photochemical substitution of ligands, most commonly carbonyl groups, have been studied as a familiar application of photochemistry. Especially the photochemical reactions of group VI metal-carbonyls with terminal alkynes [18] and vinyl ferrocenes [19] to yield the $\text{M}(\text{CO})_5\text{L}$ derivatives. Consequently, numerous articles on the photochemistry have been dealt with the metal-carbonyl complexes and the particular interest has been shown in complexes of the type $\text{W}(\text{CO})_5\text{L}$ [20].

In the case of L is an electron donor ligand, the lowest absorption bands were assigned to ligand field (LF) transitions ($^1\text{A}_1 \rightarrow ^{1,3}\text{E}$) and the low temperature ($T = 77\text{K}$) emission starts from the ^3E [21]. For L is a substituted pyridine, there are also low lying $\text{M} \rightarrow \text{L}$ charge transfer (CT) absorptions into accessible π^* pyridine levels, varying in energy with variation of the pyridine substituents [22,23]. The description of syntheses

and the molecular structure of $\text{Cr}(\text{CO})_5(2,6\text{-diaminopyridine})$ is one of the most important example of these synthesis [24].

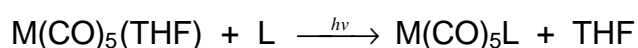
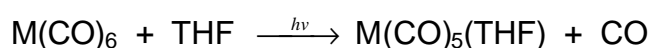
Pentacarbonylpyridinemetall(0) complexes of the group VI elements have been investigated since 1972 [25]. Since pyridine (py) is mainly a σ -donor with a little π -acceptor ability ligand [26], the M-N bond in these low valent metals is not very strong. As a result, $\text{M}(\text{CO})_5(\text{py})$ complexes are quite labile toward ligand substitution reactions [27]. The reactions of substituted pyridines with group VI metal carbonyls have been also known for a long time [28]. Pyridine derivatives having ligated atoms in 2-positions such as 2-phenylpyridine, 2-cyanopyridine as a ligand (L) in the complexes of $\text{M}(\text{CO})_5\text{L}$ [29,30], indicating that non-bulky groups in the position 2 does not hinder the coordination of pyridine to the transition metal. Therefore, pyridine derivatives with ligated atoms or groups in 2- or 6- positions are expected to show more than one binding possibilities. For example 2,6-diaminopyridine (dap) can bind the transition metal atom through the sp^3 -hybridized nitrogen atom of the ammine group and/or through the sp^2 -hybridized nitrogen atom of the aromatic pyridine ring.

Recently emission in fluid solution has been determined from a series of $\text{W}(\text{CO})_5\text{L}$ complexes, where L: pyridine derivatives such as 4-methylpyridine; 2-cyanopyridine; 3,5-dicyanopyridine; 4-phenylpyridine; 3-cyanopyridine; 4-cyanopyridine; 4-benzoylpyridine; 4-acetylpyridine; 4-formylpyridine [31].

Pyridine derivatives having ligating substituents in 4-position such as 4-methylpyridine and 4-phenylpyridine have already been reported to be isolable in the form of $M(\text{CO})_5\text{L}$ [32,33].

Therefore this work was aimed first at the photochemical syntheses and isolation of the pentacarbonyl(4-substituedpyridine)metal(0) complexes of group VIB elements. For this purpose 4-methylpyridine (4-mp) ; 4-tert-butylpyridine (4-tbp) and 4-dimethlyaminopyridine (4-dmap) ligands were used as the substituted pyridine ligands. For this reason the substituted pyridines were photochemically reacted with metal hexacarbonyls, M: Cr, Mo, W (Scheme 1) and resulting complexes were purified by recrystallization.

Scheme 1:



L: 4-methylpyridine (4-mp) ; 4-tert-butylpyridine (4-tbp) and 4-dimethlyaminopyridine (4-dmap)

M: Cr, Mo, W

The second part of this work was the structural identification of the synthesized complexes using IR, ^1H and ^{13}C -NMR spectroscopies.

CHAPTER II

THEORETICAL BACKGROUND

II. 1. Complexes of π -acceptor Ligands (π -acid)

A characteristic feature of the d group transition metals is their ability to form complexes with a variety of natural molecules such as carbon monoxide, isocyanide, nitric oxide, various molecules with delocalized π orbitals, such as pyridine, 2,2'-bipyridine, 1,10-phenanthroline, and with certain ligands containing 1,2-dithio-ketone. Very diverse type of complexes, ranging from binary compounds such as $\text{Cr}(\text{CO})_6$ or $\text{Ni}(\text{PF}_3)_4$ through mixed species such as $\text{Co}(\text{CO})_3\text{NO}$ and $[(\text{C}_6\text{H}_5)_3\text{P}]\text{Fe}(\text{CO})_4$ to complex ions such as $[\text{Fe}(\text{CN})_5\text{CO}]^{3-}$.

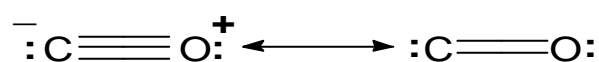
In many of these complexes, the metal atoms are in low-positive, zero or negative states. It is a characteristic of the ligands under discussion that they can stabilize low oxidation state metals; this property is associated with the fact that these ligands possess vacant π -orbitals in addition to lone pairs. These vacant π -orbitals accept electron density from the metal filled d-orbitals to form a π -bonding type that supplements the σ -bonding arising from the lone-pair donation. High electron density on the metal atom, in low oxidation states, can thus be delocalized onto the ligands.

The ability of ligands to accept electron density into low-lying empty π -orbitals can be called π -acidity, the word being used in the Lewis sense.

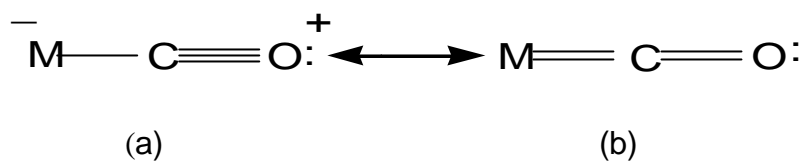
II .2. Metal-Carbonyl Bonding

Carbon monoxide is the most commonly used ligand in organometallic chemistry. It may serve as the only ligand in binary carbonyls such as $\text{Ni}(\text{CO})_4$, $\text{W}(\text{CO})_6$, and $\text{Fe}_2(\text{CO})_9$ or, more commonly in combination with other ligands, both organics and inorganics [34].

Carbon monoxide 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;



However, carbon monoxide is known to be a very poor electron donor to most Lewis acids. The metal-carbonyl bonding may be accounted for considering the following resonance forms;



While it is possible to formulate the bonding in terms of a resonance hybrid of (a) and (b), a molecular orbital formulation is more detailed, more graphic and probably more accurate.

Bonding of the metal and carbonyl ligand can be described with molecular orbital terms where it is believed that this type of bond is a combination of σ - and π - bonding [35], as shown in figure II.1.

becomes electropositive and susceptible to receiving electrons from the metal. At the same time, the flow of the metal electrons to the carbonyl orbitals makes the carbonyl ligand more negative and the donation from the carbonyl ligand to the metal orbitals easier.

Delocalization of electron density from metal d-orbitals to the carbonyl π^* orbitals (π -back bonding) also causes an increase in the metal effective nuclear charge. This increase in the effective nuclear charge of the metal (Z^*) increases the attraction ability of the metal towards electrons. As a result, a strong carbonyl-metal σ -bond might be possible. The result of this two way electron flow (σ - bond and π -back bond) is known to be stronger than the sum of the isolated ligand-to-metal σ -bonding and metal-to-ligand π -back bonding effects.

The carbon monoxide ligand has a filled σ -orbital and two empty π^* -orbitals located between carbon and oxygen atoms. It also has two lone pair of electrons localized on the carbon and oxygen atoms, but directed away from the molecule plane. Since the carbon and oxygen atoms have different electronegativities from each other, the spatial extent to the carbon lone pair is greater than the oxygen lone pair. On the other hand, carbon monoxide has two perpendicular empty π^* -antibonding orbitals, these empty orbitals are localized on the carbon atom rather than oxygen atom due to the electronegativity difference between carbon and oxygen atoms.

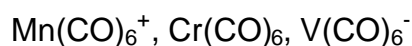
Metal used its ns, (n-1)d and (n-1)p orbitals in bonding to the ligand. Therefore, since the carbon monoxide has two orthogonal antibonding orbitals, it can form two orthogonal π -bonds with the metal atom.

As a result, the π -back bonding is expected to weaken the carbon-oxygen bond which will approach a double bond character, whereas, the metal-carbon bond will be strengthened, likewise approaching a double bond character. Since carbon monoxide ligand acts as an electron acceptor from the filled metal d-orbitals to the empty orbitals with π -symmetry, carbon monoxide is called σ -donor π -acceptor ligand or π -acid.

The extent of the π -back bonding and its effect on the metal-carbon and carbon-oxygen bonds depends mainly on the oxidation state of the metal ion. The lower oxidation state metals donate more electron density to the carbon monoxide through π -back bonding, so the metal-carbon bond becomes longer and weaker and the C-O bond shorter and stronger. This causes the stretching frequency of the carbonyl group to increase.

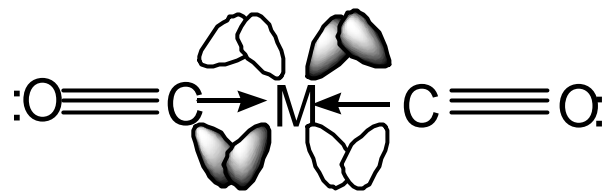
Although the elongation of the carbon oxygen bond upon coordination is small, the IR-absorption spectra of the metal carbonyl compounds are influenced by the back-bonding much more. Thus, the stretching frequency of the free carbonyl group at 2143 cm^{-1} shifts to lower frequency in the range of $2125\text{-}1850\text{ cm}^{-1}$ in metal carbonyls. The carbonyl stretching frequency further decreases when the metal carbonyl complexes contain a ligand of stronger electron donor ability or when the metal

complexes take an ionic character. On the other hand, if the carbonyl complex has a cationic character, the carbonyl stretching frequencies increase from those of the neutral complexes. As an example, in the following isoelectronic species,

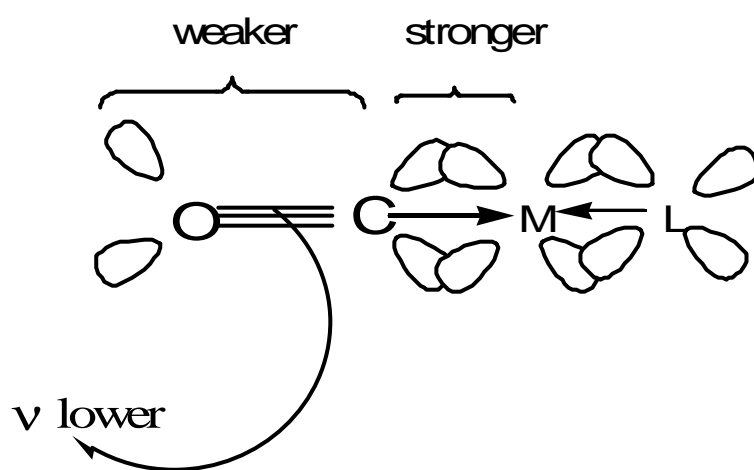


the carbonyl stretching frequencies are 2090cm^{-1} , 2000cm^{-1} , and 1869cm^{-1} , respectively [36]. Another factor which affects the metal-carbonyl bond is the nature of the ligand trans to the carbonyl group. This ligand competes with the carbonyl group for the same central atom π -orbitals electrons. When the trans ligand has a stronger σ -donor and a weaker π -acceptor ability than the carbonyl group, the carbonyl group will accept more electron density from the metal into its π^* -antibonding orbitals. On the other hand, the carbonyl ligand donates less electron density to the metal through σ -bond. As a result, the metal-carbon bond will be shorter and stronger, and the stretching frequency of the carbonyl group will be lower than the other groups. It is obvious that the trans ligand with greater π -acceptor ability and less σ -donor ability will have an opposite effect on the carbonyl stretching frequency.

The competition effect of the trans ligand on the carbonyl stretching frequency is shown in figure II.2.



(a)



(b)

Figure II.2. Competition of two ligands to the same central atom electrons.

(a) equivalent ligands

(b) ligands with different π -accepting abilities

CHAPTER III

EXPERIMENTAL STUDIES

III.1 Basic Techniques

Since most of the organometallic compounds are known to be thermodynamically unstable and air sensitive, all reactions and purification of organometallic compounds were carried out under dry and de-oxygenated nitrogen gas atmosphere. Solvents were purified by reflux (36) over metallic sodium.

Because of the air sensitivity of organometallic compounds, as mentioned before, all experiments of this work were carried out by using the vacuum line and schlenk glassware. Techniques using the vacuum line are sufficient and convenient. A modified type of schlenk tube is shown in figure III.1.a. The inlet is equipped with a stop cock (A) and main opening has a standard taper (B), which has a small glass ears (C) to hold the stopper or other component with a small metal spring. The schlenk tube can be evacuated or an inert gas can be passed to it through (D).

Transfer of a liquid sample under nitrogen gas atmosphere can be carried out by connecting two schlenk tubes by using an adaptor as shown in figure III.1.b.

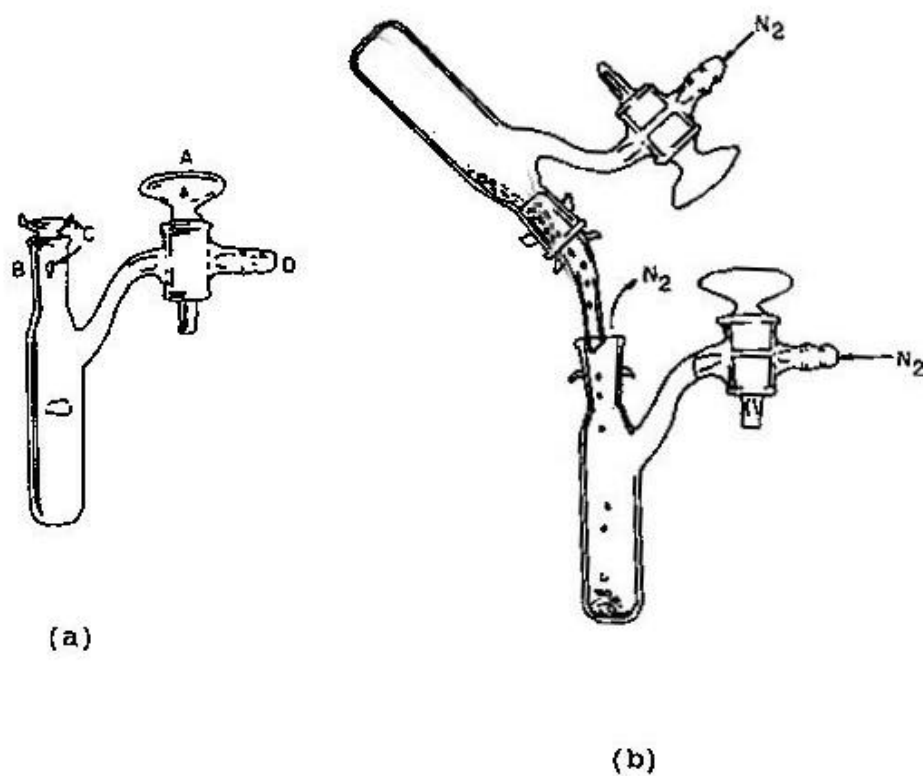


Figure III.1. Schlenk type storage flask

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

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

For the photochemical reactions, a special apparatus was used. As shown in figure III.2, the apparatus consists of three coaxial glass tubings. Into the inner part (a) a mercury lamp (b) (Hg-Tauchlampe TQ 150, Quarzlampen GmbH, Hanau, Germany) is immersed. To carry out photochemical reactions, the prepared solution mixtures (consist of metal hexacarbonyl (0); M: Cr, Mo, W, and the ligand dissolved in THF) is filled into the outer part (c) and cooled to room temperature by circuating tap water throught the space and third tubings.

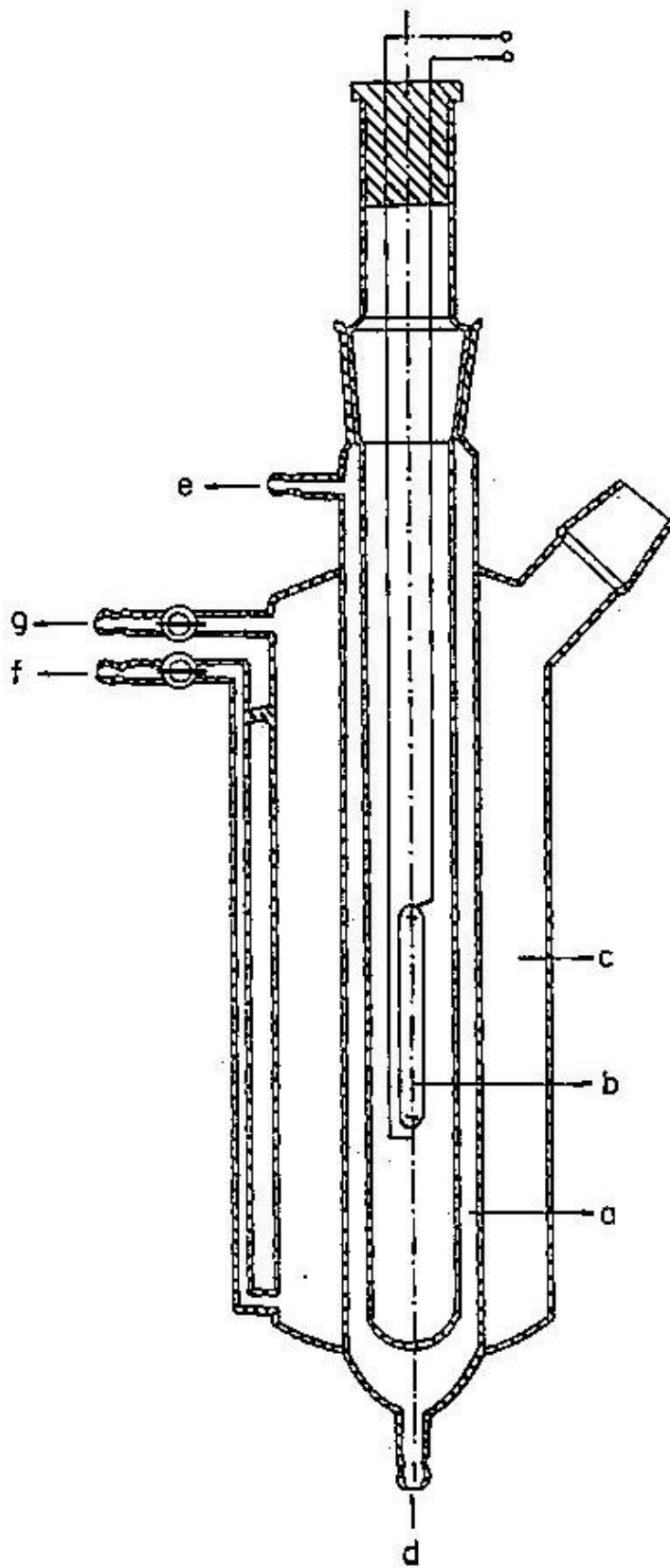


Figure III.2. The apparatus which was used for photochemical reaction ;

- (a) inner part,
- (b) mercury lamp,
- (c) outer part,
- (d) tap water inlet,
- (e) tap water outlet,
- (f) nitrogen gas inlet,
- (g) nitrogen gas outlet.

III.1.1. FT-IR (Fourier Transform Infrared) -Spectra:

The synthesis of complexes and substitution reactions were followed by taking infrared spectra at intervals during the reaction courses. The IR spectra were recorded using Jasco 430 spectrophotometer.

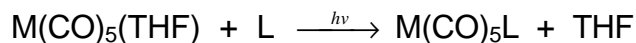
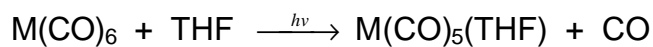
III.1.2.¹H-NMR Spectra:

The proton NMR spectra of these complexes were recorded from their d-chloroform solutions using Bruker-Spectroscopin DPX 400 MHz spectrometer.

III.1.3.¹³C-NMR Spectra:

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

III.2 The Synthesis of the Complexes



L: 4-methylpyridin, 4-tert-butylpyridine, 4-dimethylaminopyridine
ligands

M: Cr, Mo, W

III.2.1. Penta Carbonyl(4-methylpyridin)metal(0), $\text{M}(\text{CO})_5(4\text{-mp})$; M: Cr, Mo, W

0.5 g $\text{M}(\text{CO})_6$ [M: Cr(2.3 mmol), Mo(1.89mmol), W(1.42mmol)] was dissolved in THF and irradiated for 1hr at room temperature. At the end of the reaction time, a stoichiometric amounts of 4-methylpyridine (0.21g , 0.18 g and 0.13 g) was added to the reaction mixture and the irradiation continued (75 min for Cr; 60 min for Mo; 50 min for W). The reaction course was followed by IR spectra taken at 20 minutes intervals during the reaction. Nitrogen gas was passed through the reaction vessel during the reaction.

At the end of the reaction, the yellow solution mixture was filtered to an evacuated schlenk storage vessel under nitrogen gas atmosphere and the volatiles were removed by evaporating under high vacuum. The

residue was then purified by dissolving in minimum amount of dichloromethane followed by the addition of n-hexane until the appearance of the first crystals. Recrystallization from dichloromethane gave the pale yellow powder solids of the formula $M(\text{CO})_5(\text{C}_6\text{H}_7\text{N})$; M: Cr, Mo, W; which was stored in an evacuated schlenk vessel under nitrogen gas atmosphere for the routine spectroscopic analysis.

III.2.2. Pentacarbonyl(4-tert-butylpyridin)metal(0), $M(\text{CO})_5(4\text{-tbp})$; M: Cr, Mo, W

0.5 g $M(\text{CO})_6$ [M: Cr (2.3 mmol), Mo(1.89mmol), W(1.42mmol)] was dissolved in THF and irradiated for 1hr at room temperature. A stoichiometric amount of 4-tert-butyle pyridine (0.31g, 0.26g, 0.19g) was then added to the resulting $M(\text{CO})_5(\text{THF})$ solution and irradiation was continued for approximately one hour more until no more reacting compounds were exist in the solution mixture. The end of the reaction was followed by IR spectra taken at 20 minutes intervals during the reaction course. The resulting dark yellow solution was then filtered and evaporated under high vacuum (0.01 mmHg). The resulting solid was then dissolve in n-hexane and the n-hexane soluble part was purified by recrystallization from n-hexane at - 50°C. The light yellow crystals are best dried under vacuum for one day and stored under pure nitrogen atmosphere for the routine spectroscopic analysis. The insoluble part of the reaction is expected to be the disubstituted type of the complex which is discussed in part III.2.4 of this chapter.

III.2.3. Pentacarbonyl (4-dimethylaminopyridin)metal(0), $M(CO)_5(4\text{-dmap})$; M: Cr,Mo,W

A solution of 0.5 g $M(CO)_6$ [Cr (2.3 mmol), Mo (1.89mmol), W (1.42mmol)] in tetrahydrofuran, THF, was irradiated for 1hr using a high pressure mercury lamp which was housed in a water-cooled glass jacket (Figure III.2). At the end of irradiation time stoichiometric amounts of 4-dimethylaminopyridine (0.28g, 0.23g and 0.17g) was added to the reaction mixture and the irradiation continued for 1 more hour or until no more starting materials are exist in the reaction mixture (this can be achieved by taking IR spectra of the mixture at specific intervals during the reaction course). At the end of the reaction time, the green colored residue was filtered to an evacuated schlenk storage vessel under nitrogen gas atmosphere. Evaporating the solvents and excess starting materials under high vacuum leaving a dark yellow residue. This residue was then dissolved in n-hexane and separated to two parts, the n-hexane soluble and insoluble parts. The insoluble part was then dissolved in dichloromethane. The two parts of solutions were then purified and recrystallized in n-hexane-dichloromethane solutions leaving the pure complexes which were stored under nitrogen atmosphere for analysis.

III.2.4. Cis-tetracarbonylbis(4-tert-butylpyridin)tungsten(0), $W(CO)_4(4\text{-dmap})_2$

The n-hexane insoluble solution of the part III.2.2 was purified and recrystallized from dichloromethane solution to produce the dark yellow crystals of the disubstituted pyridine complex assigned as the tetracarbonyl type of complex.

Solvent evaporation, chemical reactions and all the purifications in this work were done under high vacuum using the modified schlenk system as shown in figure III.3.

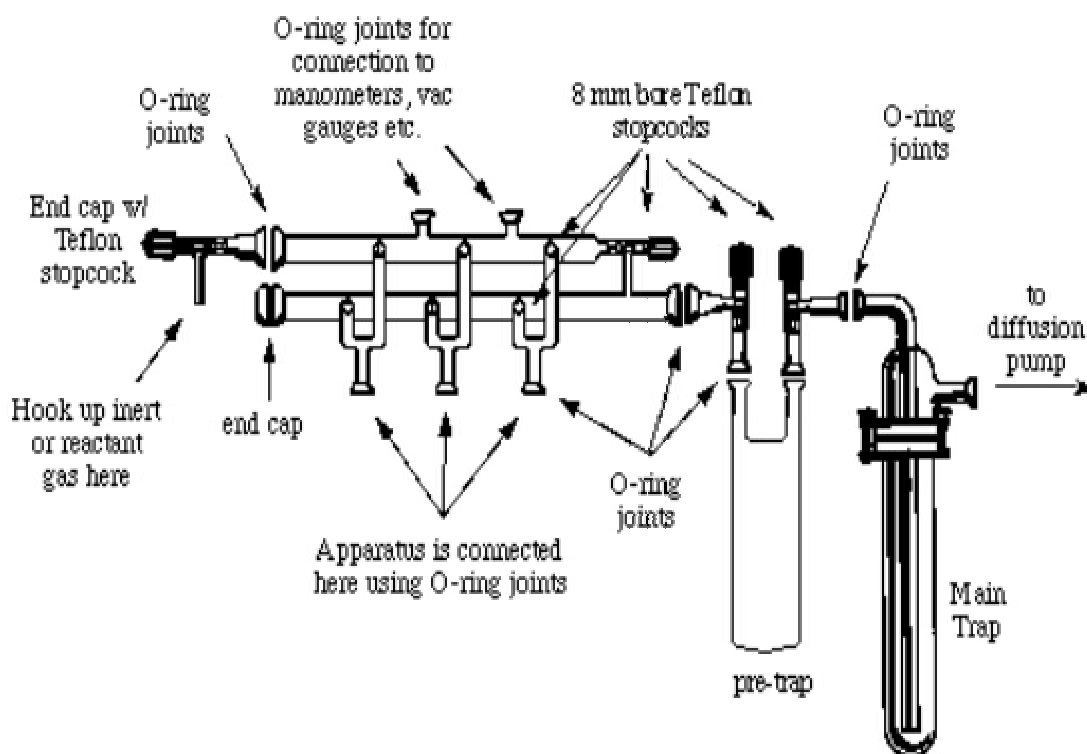


Figure III.3 : A typical Schlenk system

CHAPTER IV

RESULTS AND DISCUSSION

IV.1. IR Spectra

IV.1.1. IR Spectra of $M(CO)_5L$ Complexes:

The infrared spectra of the complexes were recorded from their n-hexane solutions. The IR spectra taken at intervals during the reactions showed development of bands, in accordance, the reactions course could be followed.

The infrared spectra of $M(CO)_5L$; L: 4-methylpyridine, 4-tert-butylpyridine and 4-dimethylaminopyridine; M: Cr, Mo, W, showed three absorption bands (one is strong, the others are medium intensities). As an example, the IR-spectra of these complexes are given in Fig. IV.1.1, IV.1.2 and IV.1.3 and all the IR-data are given in Table IV.1.1.

The appearance of three absorption bands in the carbonyl region of these complexes indicates that the $M(CO)_5$ -unit of the complexes has a local C_{4v} symmetry with a general pattern $2A_1 + E$. Both modes are IR-active and E-mode must be lower in frequency than one of the A_1 -modes [38]. These bands intensity distribution has already been explained by Orgel [39]. He showed that both A_1 -modes will be much weaker than the E-

mode intensity and usually the stretching frequency of the $A_1(1)$ -mode is lower in frequency than the $A_1(2)$ mode.

Table IV.1.1. The CO-stretching frequencies ν_{CO} (cm^{-1}) of $M(\text{CO})_5L$;
L: 4-mp, 4-tbp, 4-dmap and M: Cr, Mo, W, in n-hexan.

Complex	$\nu(\text{CO})$ (cm^{-1})		
	$A_1(2)$	E	$A_1(1)$
$\text{Cr}(\text{CO})_5(4\text{-mp})$	2073.6(m)	1942.2(vs)	1920.6(w)
$\text{Mo}(\text{CO})_5(4\text{-mp})$	2073.1(m)	1941.0(vs)	1919.8(w)
$\text{W}(\text{CO})_5(4\text{-mp})$	2071.2(m)	1932.3(vs)	1918.8(w)
$\text{Cr}(\text{CO})_5(4\text{-tbp})$	2070.3(m)	1936.0(vs)	1917.4(w)
$\text{Mo}(\text{CO})_5(4\text{-tbp})$	2072.0(m)	1941.0(vs)	1919.8(w)
$\text{W}(\text{CO})_5(4\text{-tbp})$	2071.2(m)	1932.3(vs)	1918.8(w)
$\text{Cr}(\text{CO})_5(4\text{-dmap})$	2065.4(m)	1934.3(vs)	1911.1(w)
$\text{Mo}(\text{CO})_5(4\text{-dmap})$	2070.2(m)	1936.2(vs)	1912.1(w)
$\text{W}(\text{CO})_5(4\text{-dmap})$	2069.3(m)	1922.7(vs)	1872.6(w)

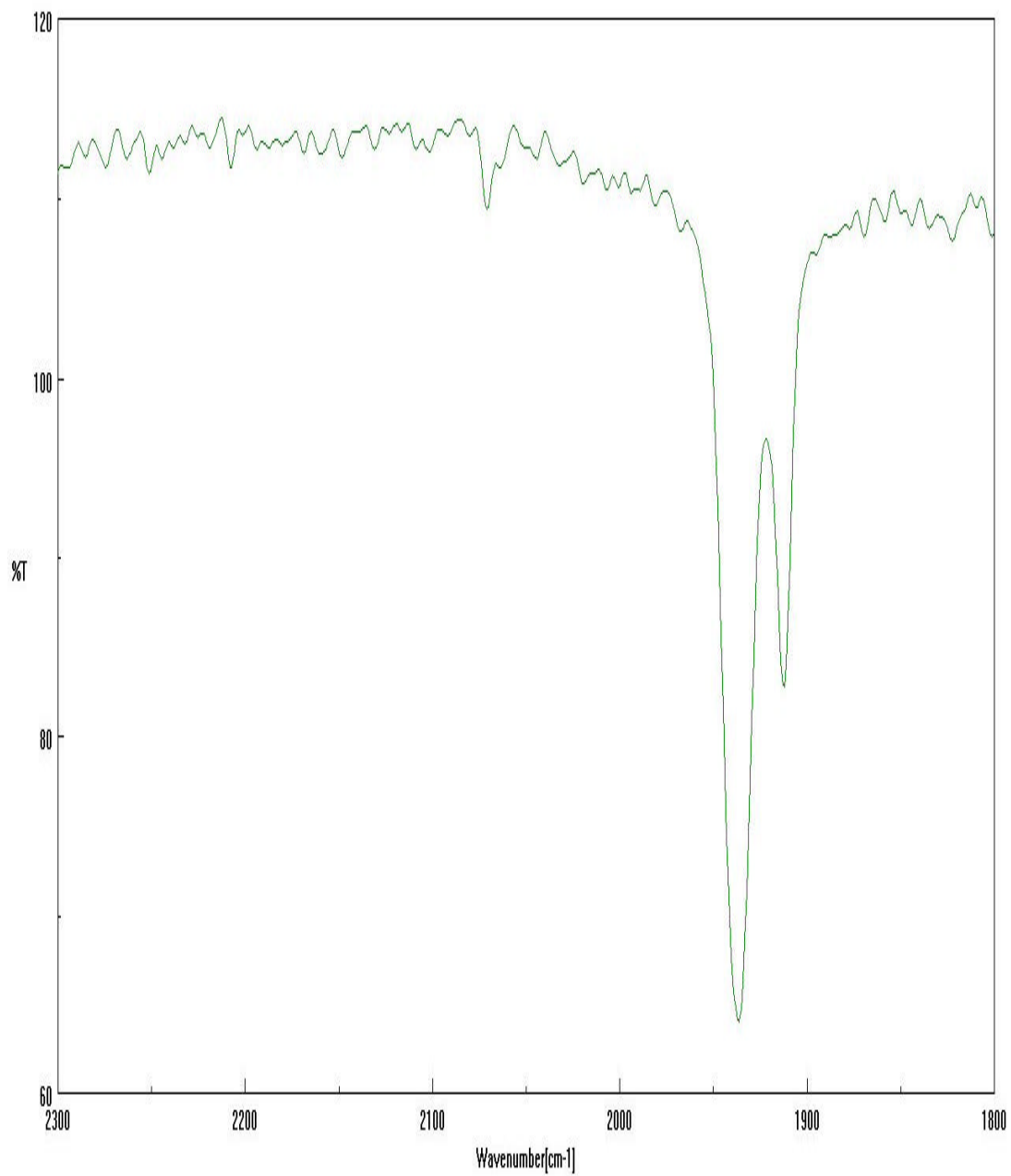


Figure IV.1.1. The IR spectrum of $\text{Mo}(\text{CO})_5(\text{dmap})$ in hexane solution.

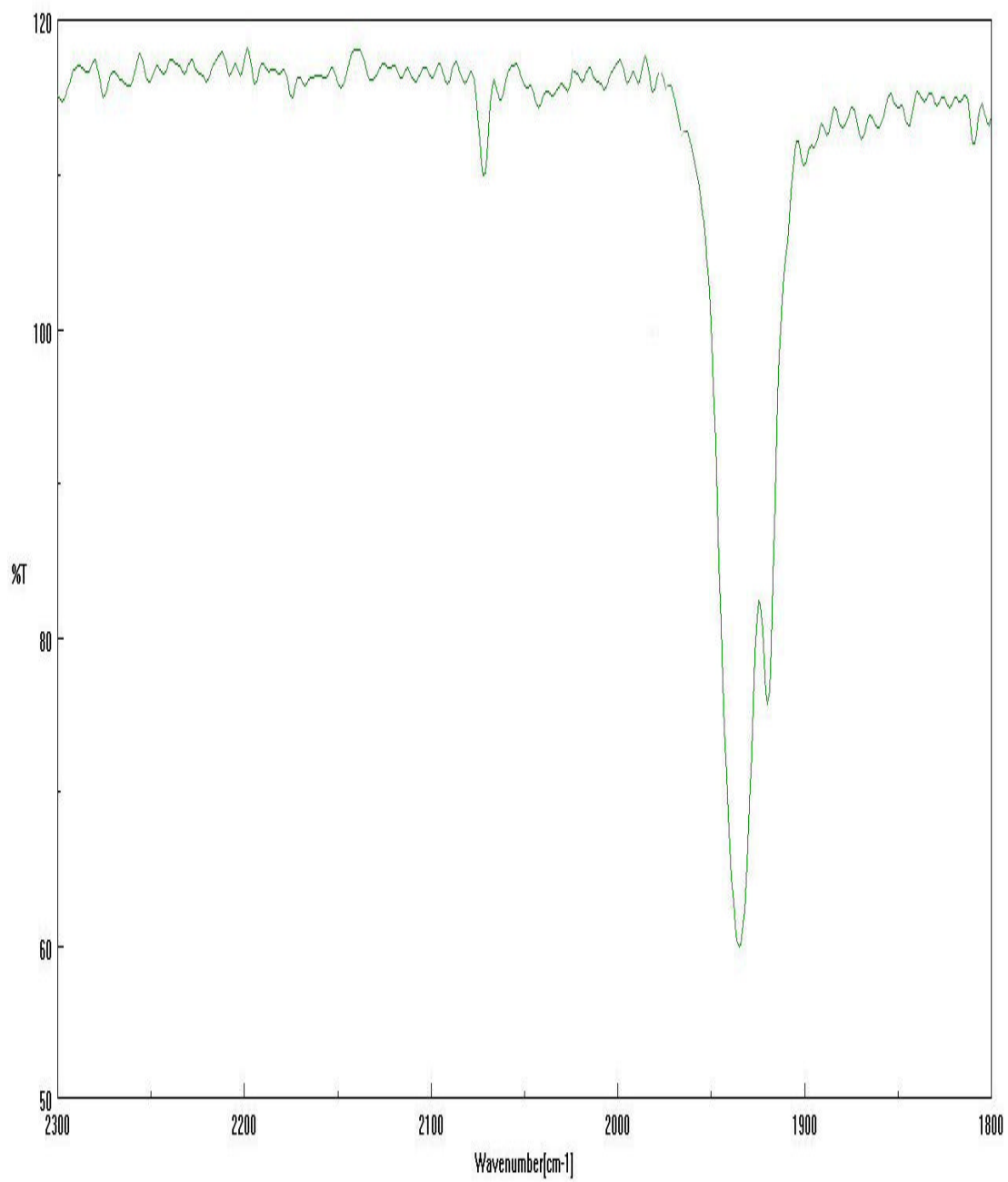


Figure IV.1.2. The IR spectrum of $W(CO)_5(4\text{-mp})$ in hexane solution.

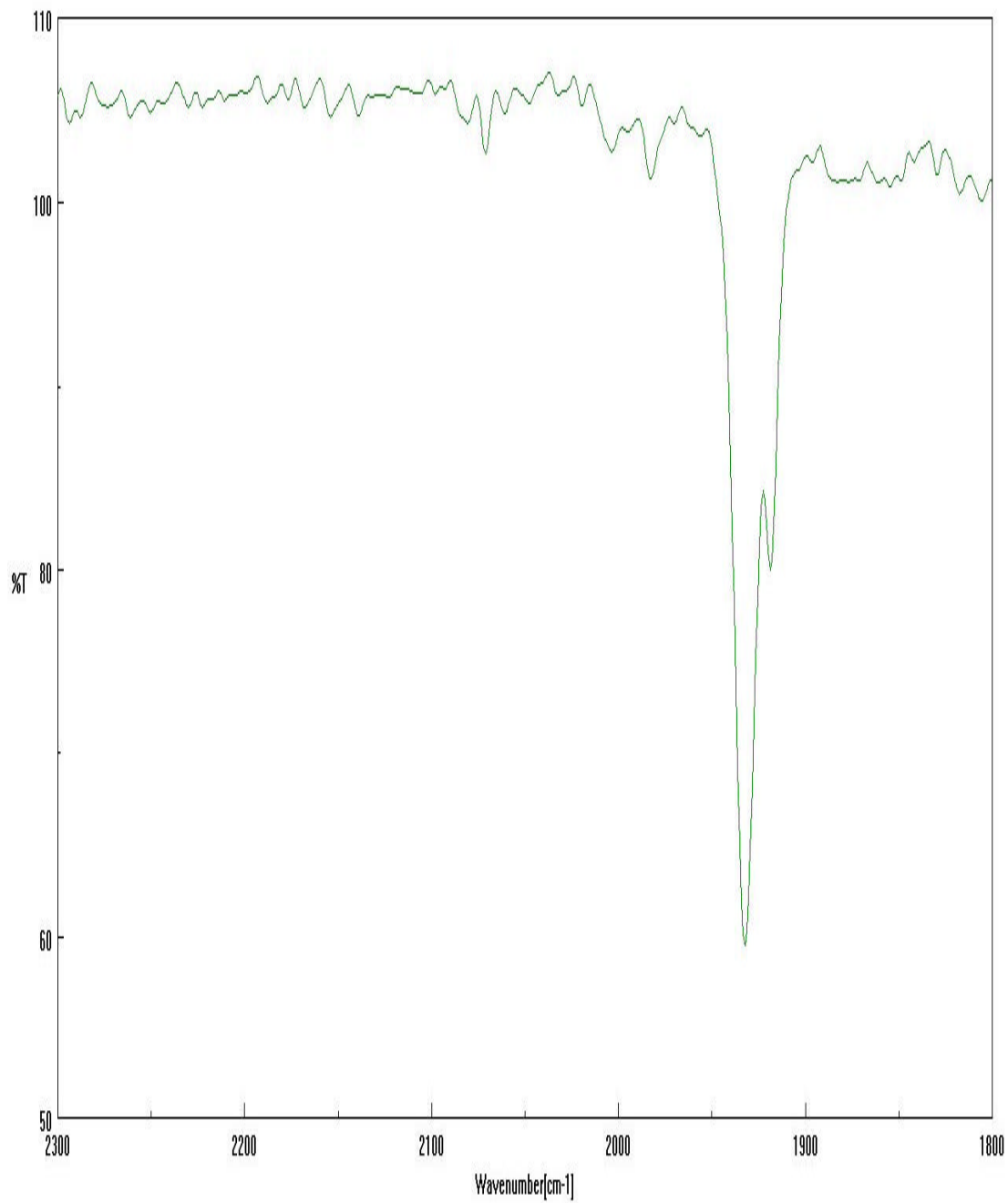


Figure IV.1.3. The IR spectrum of $W(CO)_5(tbp)$ in hexane solution.

IV.1.2. Cis-tetracarbonylbis(4-tert-butylpyridin)tungsten(0):

The infrared spectrum of the complex showed four strong absorption bands of approximately equal intensities in the region of carbonyl stretching ($1700 - 2300 \text{ cm}^{-1}$) as shown in Figure IV.1.4. This indicates that the $\text{M}(\text{CO})_4$ unit of the molecule has a C_{2v} symmetry with a general pattern $2A_1 + B_1 + B_2$ which are all IR-active (Table IV.1.2). Therefore two 4-tert-butylpyridine ligands are expected to occupy two cis coordination sites in the octahedral complex.

Table IV.1.2. The CO stretching frequencies (cm^{-1}) for cis- $\text{W}(\text{CO})_4(4\text{-tert-butylpyridine})_2$ from dichloromethane solution.

Complex	<u>$\nu(\text{CO}) \text{ (cm}^{-1}\text{)}$</u>			
	$A_1(1)$	$A_1(2)$	B_1	B_2
$\text{W}(\text{CO})_4(4\text{-tbp})_2$	2005.5	1876.4	1844.1	1822.4

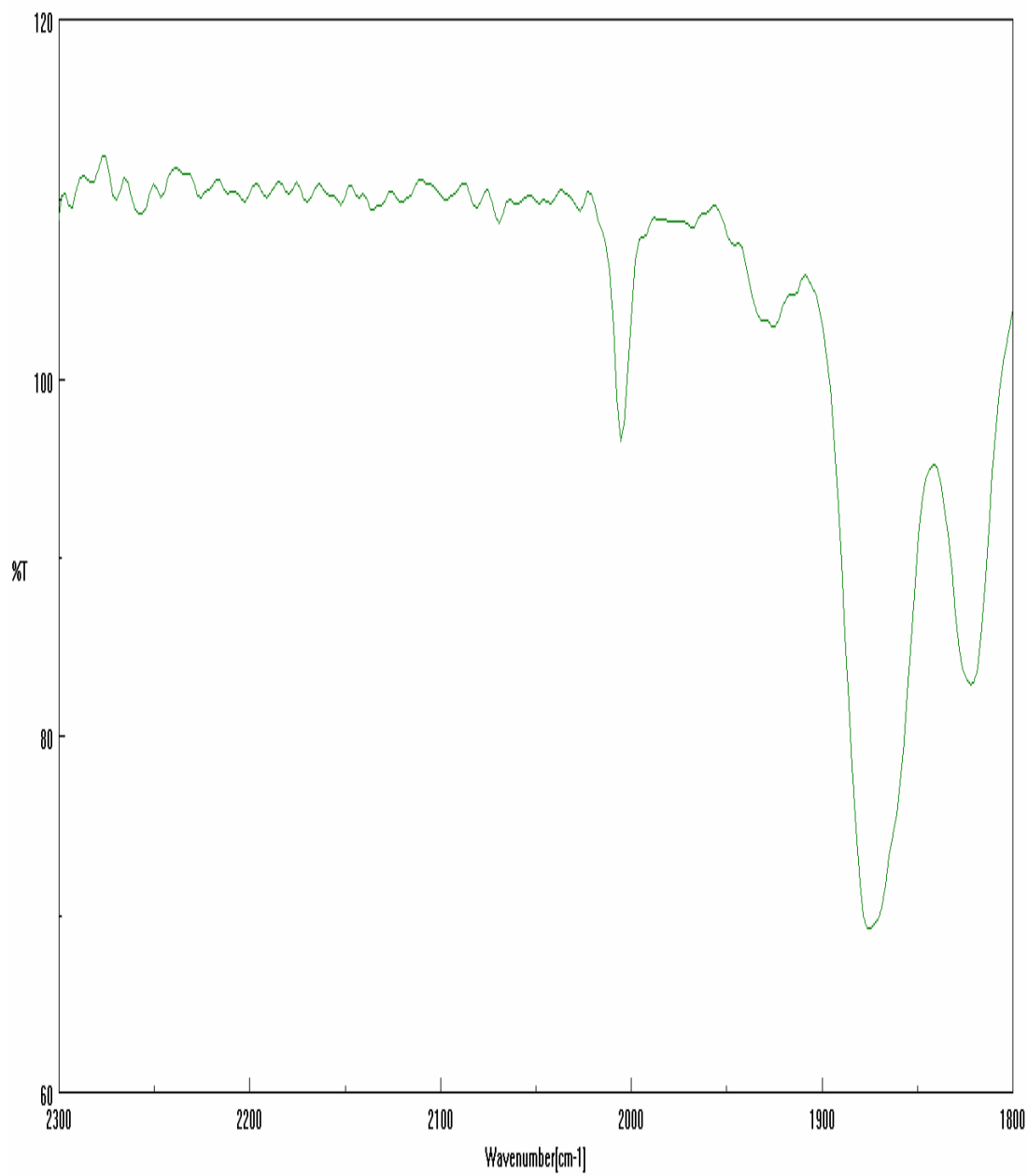


Figure VI.1.4. The IR spectrum of $\text{cis-W(CO)}_4(4\text{-tert-butylpyridine})_2$ from dichloromethane solution.

IV.2. $^1\text{H-NMR}$ Spectra

The $^1\text{H-NMR}$ spectra of the complexes $\text{M}(\text{CO})_5\text{L}$; (M: Cr, Mo, W ; L : 4-methylpyridine, 4-tertbutylpyridine, 4-dimethylaminopyridine) were recorded from their d -chloroform solutions and all chemical shift values are given relative to TMS signal which has been used as an internal reference.

IV.2.1. Pentacarbonyl(4-methylpyridin)metal(0); $\text{M}(\text{CO})_5(4\text{-mp})$; M: Cr,Mo,W

The $^1\text{H-NMR}$ spectra of these complexes show the appearance of a multiplet for each couple of protons $\text{H}_{2,6}$ and $\text{H}_{3,5}$ and a singlet for the methyl substituted group of the pyridine ligand as shown in Figure IV.2.1.b and Table IV.2.1. Two points are best to be discussed in the $^1\text{H-NMR}$ spectra of these complexes, first is the appearance of only one multiplet for each couple of protons $\text{H}_{2,6}$ and $\text{H}_{3,5}$ indicating a symmetric coordination between the central metal atom and the substituted pyridine ligand. Any unsymmetric coordination would cause a splitting for these protons signals to a doublet of multiplets. Therefore any unsymmetric coordination through one of the pyridin ring double bonds can be ruled out.

The second point of discussion for the $^1\text{H-NMR}$ spectra of these complexes is the chemical shifts of the pyridine ligands protons compared with those of the uncoordinated pyridine ligand. As it is shown in Figure

IV.2.1 and Table IV.2.1, the pyridine ring protons $H_{2,6}$ and $H_{3,5}$ and the substituted group CH_3 protons chemical shifts of free (uncoordinated) pyridine ligand [δ ppm =2.37(s, CH_3), 8.60 (d, $H_{2,6}$) and 7.28 (d, $H_{3,5}$)] show no significant shift to either higher or lower field upon metal coordination. This very small shift (not significant) is a provment for the presence of metal-pyridine σ -bonding instead of the stronger metal-pyridine π -bonding which is expected to cause a very large shifts upon coordination. Therefore the proposed structure of these complexes is given in Fig. IV.2.1.a.

Table IV.2.1. The 1H -NMR chemical shifts (δ ppm) of $M(CO)_5(4\text{-mp})$ complexes measured from their d-chloroform solutions; TMS reference.

Complex	$H_{2,6}$	$H_{3,5}$	CH_3
Free ligand	8.60 (m, 2H)	7.28 (m,2H)	2.37 (s,9H)
$Cr(CO)_5(4\text{-mp})$	8.30 (m, 2H)	6.92 (m,2H)	2.28 (s,9H)
$Mo(CO)_5(4\text{-mp})$	8.38 (m, 2H)	6.98 (m,2H)	2.30 (s,9H)
$W(CO)_5(4\text{-mp})$	8.57 (m, 2H)	7.13 (m,2H)	2.20 (s,9H)

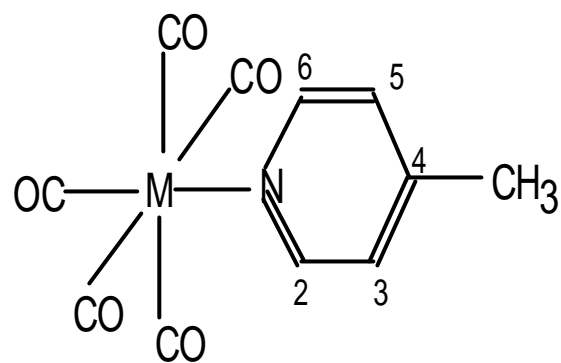


Figure IV.2.1.a. The structure of pentacarbonyl(4-mp)metal(0)

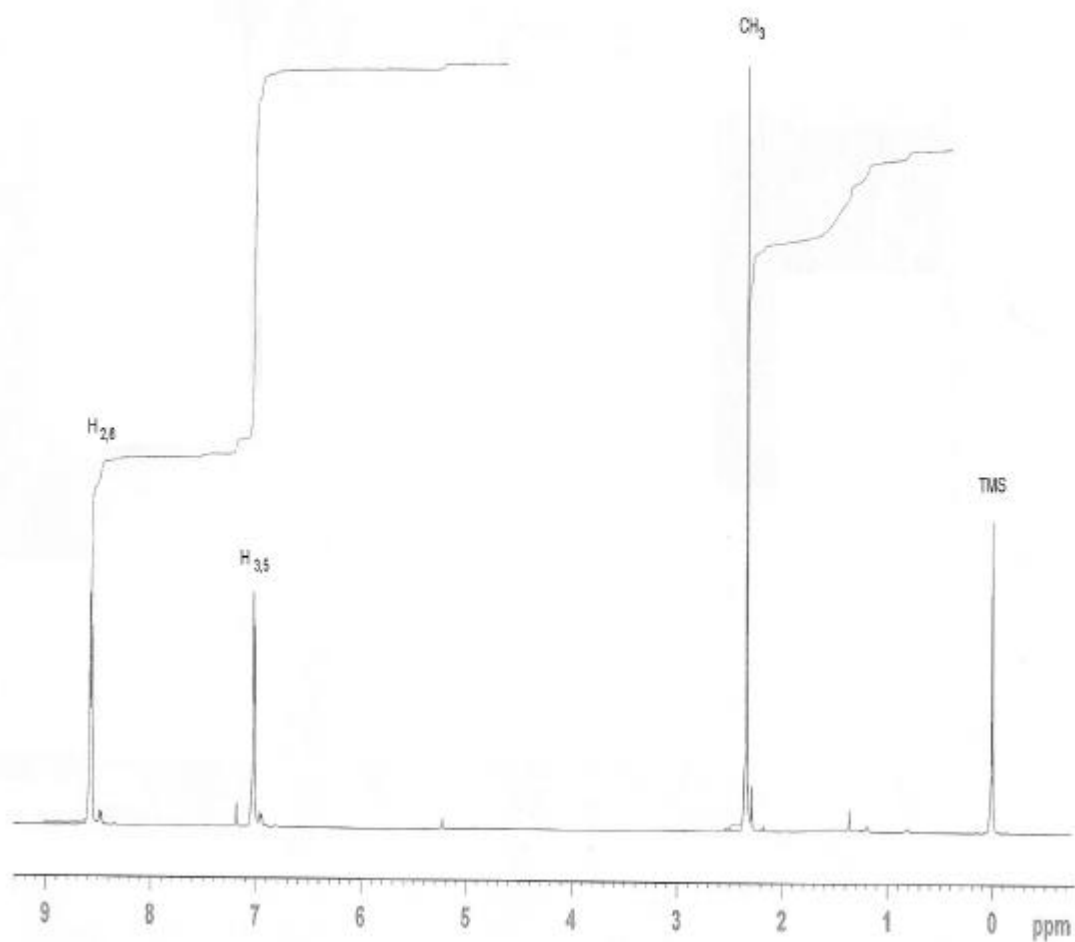


Figure IV.2.1.b. The $^1\text{H-NMR}$ spectrum of $\text{W}(\text{CO})_5(4\text{-mp})$ complex measured from its d-chloroform solutions; TMS reference

IV.2.2. Pentacarbonyl(4-tert-butylpyridin)metal(0); $M(CO)_5(4-tbp)$; M: Cr,Mo,W

The 1H -NMR spectra of these complexes show the appearance of a multiplet for each couple of protons $H_{2,6}$ and $H_{3,5}$ and a singlet for the tert-butyl groups protons of the pyridine ligand (Table IV.2.2). As an example for these complexes the 1H -NMR spectrum of the pentacarbonyl(4-tert-butylpyridine)tungsten(0) complex is given in Figure IV.2.2.b.

As discussed in the previous section, there are two important points to be discussed in order to prove the bonding type between the central atom and the pyridine ligand. The appearance of only one multiplet for each of the proton couples $H_{2,6}$ and $H_{3,5}$ is an indication of the symmetric metal-pyridine ligand coordination through the nitrogen lone pair. This can rule out any asymmetric metal coordination through one of the pyridine double bonds. The second important discussion point is the shift of the pyridine protons chemical shifts. As it is shown from Figure IV.2.2.b and the data in Table IV.2.2, the chemical shifts of the pyridine protons $H_{2,6}$ and $H_{3,5}$ show no significant shift upon metal coordination. This can easily indicate a weak metal-pyridine σ -bonding rather than the stronger metal-pyridine π -bonding. Therefore the expected octahedral structure shown in Figure IV.2.2.a is proposed for these complexes.

Table IV.2.2. The $^1\text{H-NMR}$ chemical shifts (δ ppm) of $\text{M}(\text{CO})_5(4\text{-tbp})$ complexes measured from their d-chloroform solutions; TMS reference.

Complex	$\text{H}_{2,6}$	$\text{H}_{3,5}$	CH_3
Free ligand	8.60 (m, 2H)	7.28 (m, 2H)	1.34 (s, 9H)
$\text{Cr}(\text{CO})_5(4\text{-tbp})$	8.40 (m, 2H)	7.26 (m, 2H)	1.34 (s, 9H)
$\text{Mo}(\text{CO})_5(4\text{-tbp})$	8.43 (m, 2H)	7.18 (m, 2H)	1.24 (s, 9H)
$\text{W}(\text{CO})_5(4\text{-tbp})$	8.52 (m, 2H)	7.13 (m, 2H)	1.36 (s, 9H)

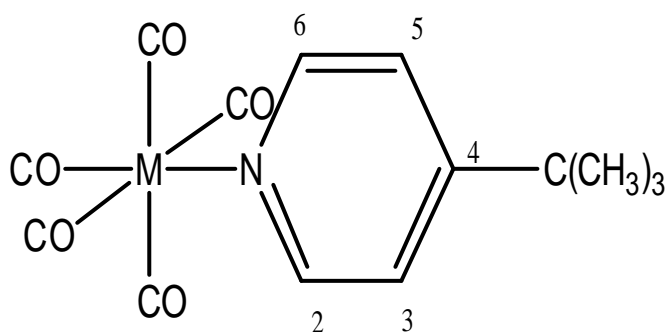


Figure IV.2.2.a. The structure of pentacarbonyl(4-tbp)metal(0)

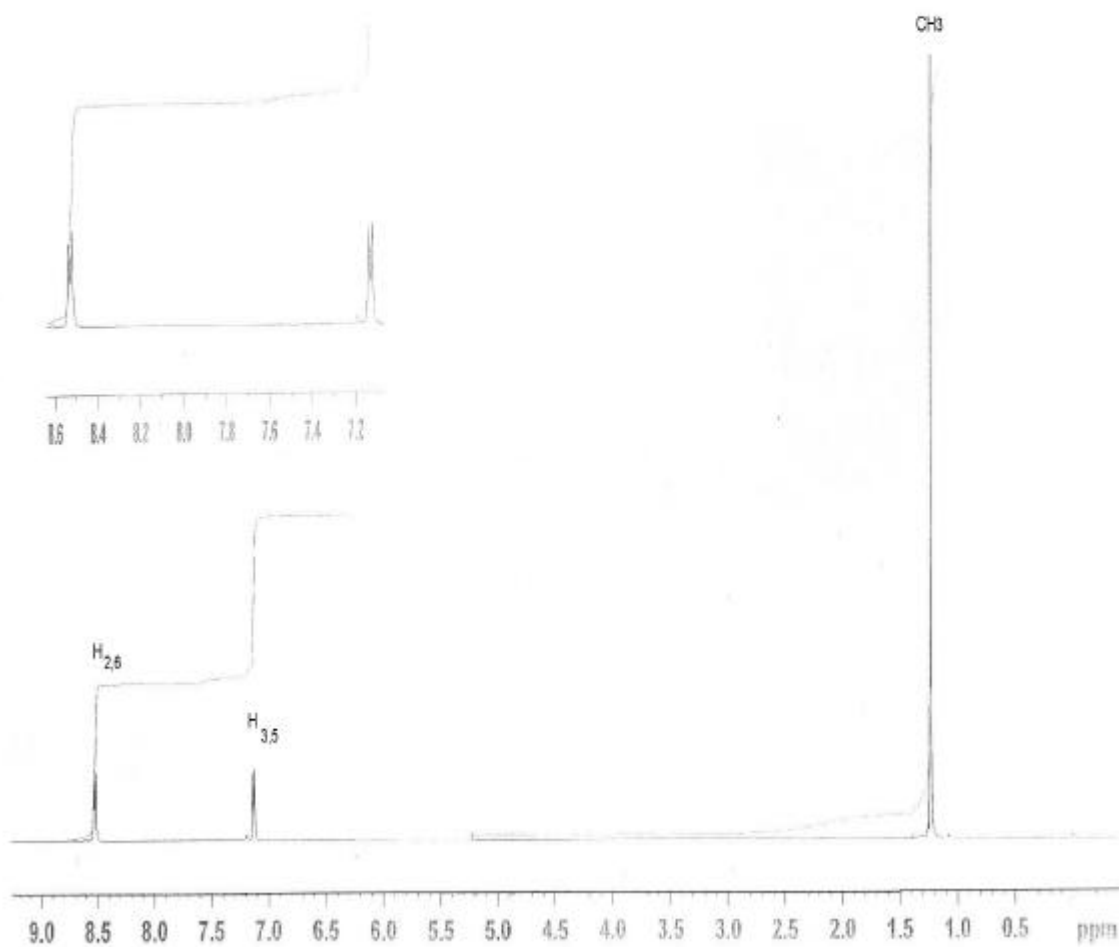


Figure IV.2.2.b. The $^1\text{H-NMR}$ spectrum of $\text{W(CO)}_5(4\text{-tbp})$ complex measured from its d-chloroform solutions; TMS reference

IV.2.3. Pentacarbonyl(4-dimethylaminopyridin)metal(0);

M(CO)₅(4-dmap); M: Cr,Mo,W

Similar to the ¹H-NMR spectra of those discussed in the previous two sections, three peaks are observed in the pyridine ligand region of the ¹H-NMR spectra of these complexes. Two of which are assigned for each pair of protons H_{2,6} and H_{3,5} and an additional singlet is observed at higher field which is assigned for the methyl groups protons of the N(CH₃)₂ substituted group of the ligand (Table IV.2.3). As an example for these spectra, the ¹H-NMR spectrum of Mo(CO)₅(4-dmap) is given in Figure IV.2.3.b. The appearance of only one peak for each H_{2,6}, H_{3,5} and N(CH₃)₂ groups is an indication for a symmetric metal ligand coordination through one of the nitrogen lone pairs. The most important point to be discussed for these complexes is the presence of two different nitrogen atoms at the pyridine ligands which are both available for the metal-ligand coordination. The insignificant shift of the singlet belongs to the methyl groups protons to either higher or lower field upon metal coordination indicates a metal ligand coordination through the pyridine ligand nitrogen atom lone pair rather than through the substituted group lone pair. Depending on these data one can propose a structure for these complexes which should be later supported by other spectroscopic data (Figure IV.2.3.a.)

Table IV.2.3. The $^1\text{H-NMR}$ chemical shifts (δ ppm) of $\text{M}(\text{CO})_5(4\text{-dmap})$ complexes measured from their d-chloroform solutions; TMS reference.

Complex	$\text{H}_{2,6}$	$\text{H}_{3,5}$	CH_3
Free ligand	8.44 (m, 2H)	6.64 (m, 2H)	2.47 (s, 6H)
$\text{Cr}(\text{CO})_5(4\text{-dmap})$	7.96 (m, 2H)	6.28 (m, 2H)	2.87 (s, 6H)
$\text{Mo}(\text{CO})_5(4\text{-dmap})$	8.12 (m, 2H)	6.38 (m, 2H)	2.92 (s, 6H)
$\text{W}(\text{CO})_5(4\text{-dmap})$	8.18 (m, 2H)	6.32 (m, 2H)	2.94 (s, 6H)

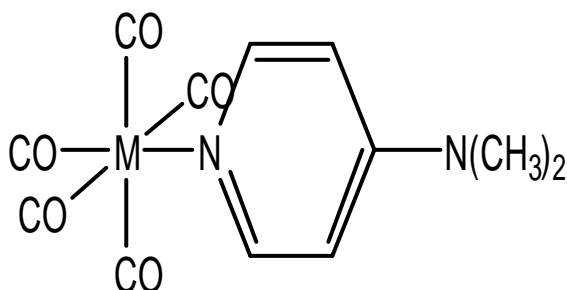


Figure IV.2.3.a. The structure of pentacarbonyl(4-dmap)metal(0)

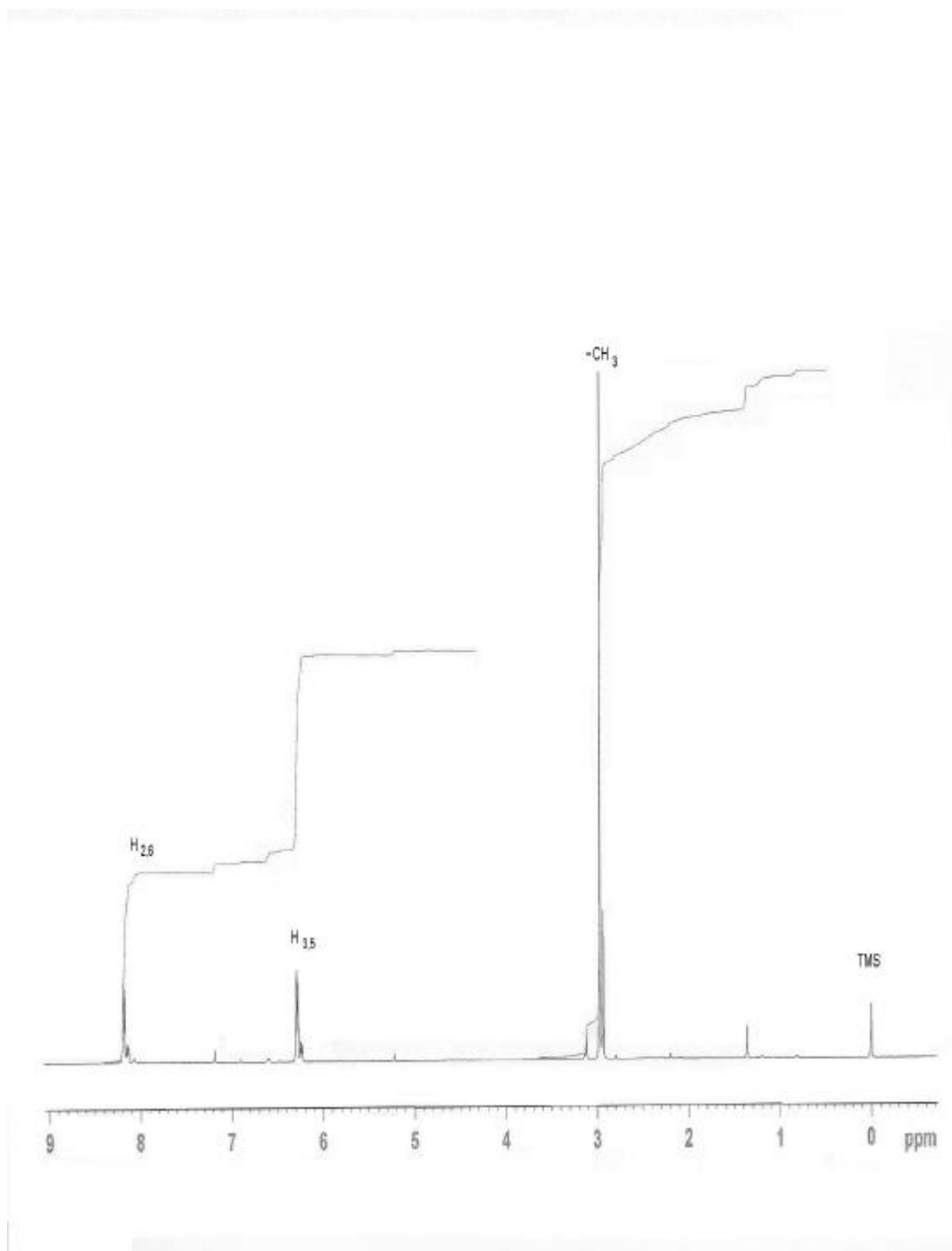


Figure IV.2.3.b. The $^1\text{H-NMR}$ spectrum of $\text{W(CO)}_5(4\text{-dmap})$ complex measured from its d-chloroform solutions; TMS reference.

IV.2.4. Cis-tetracarbonyl (4-tert-butylpyridin)tungsten(0);

The $^1\text{H-NMR}$ spectrum of this complex showed the appearance of a multiplet for each couple of protons $\text{H}_{2,6}$ and $\text{H}_{3,5}$ and a singlet for the tert-butyl groups protons of the pyridine ligand (Table IV.2.4.). As an example for these complexes the $^1\text{H-NMR}$ spectrum of the pentacarbonyl(4-tert-butylpyridine)tungsten(0) complex is given in Figure IV.2.4.b.

The $^1\text{H-NMR}$ spectrum showed no significant difference from those given for the pentacarbonyl(4-tbp)metal(0) complexes (section IV.2.2). Therefore it is not possible using $^1\text{H-NMR}$ data to assign whether the complex formed is pentacarbonyl or tetracarbonyl, since the molecule is expected to have a plane of symmetry bisecting the molecule passing the two cis-pyridine groups. In accordance it will be more effective to discuss the $^{13}\text{C-NMR}$ spectrum to support the cis-geometry that proposed from the IR spectral data of this molecule, in which a cis-isomer is proposed (Figure IV.2.4.a.)

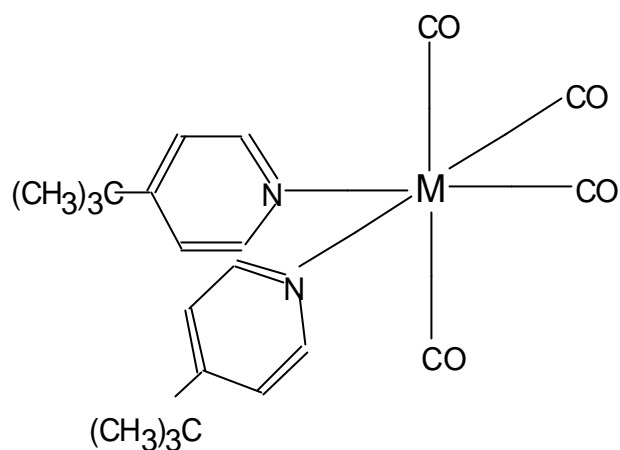


Figure IV.2.4.a. The proposed structure of $W(CO)_4(4\text{-tbp})_2$

Table IV.2.4. $^1\text{H-NMR}$ chemical shifts (δ ppm) for $\text{cis-}W(CO)_4(4\text{-tert-butylpyridine})_2$ complex measured from their $d\text{-chloroform}$ solutions; TMS reference.

Complex	$H_{2,6}$	$H_{3,5}$	CH_3
Free ligand	8.60 (m, 2H)	7.28 (m, 2H)	1.34 (s, 9H)
$W(CO)_4(4\text{-tbp})_2$	8.52 (m, 2H)	7.13 (m, 2H)	1.22 (s, 9H)

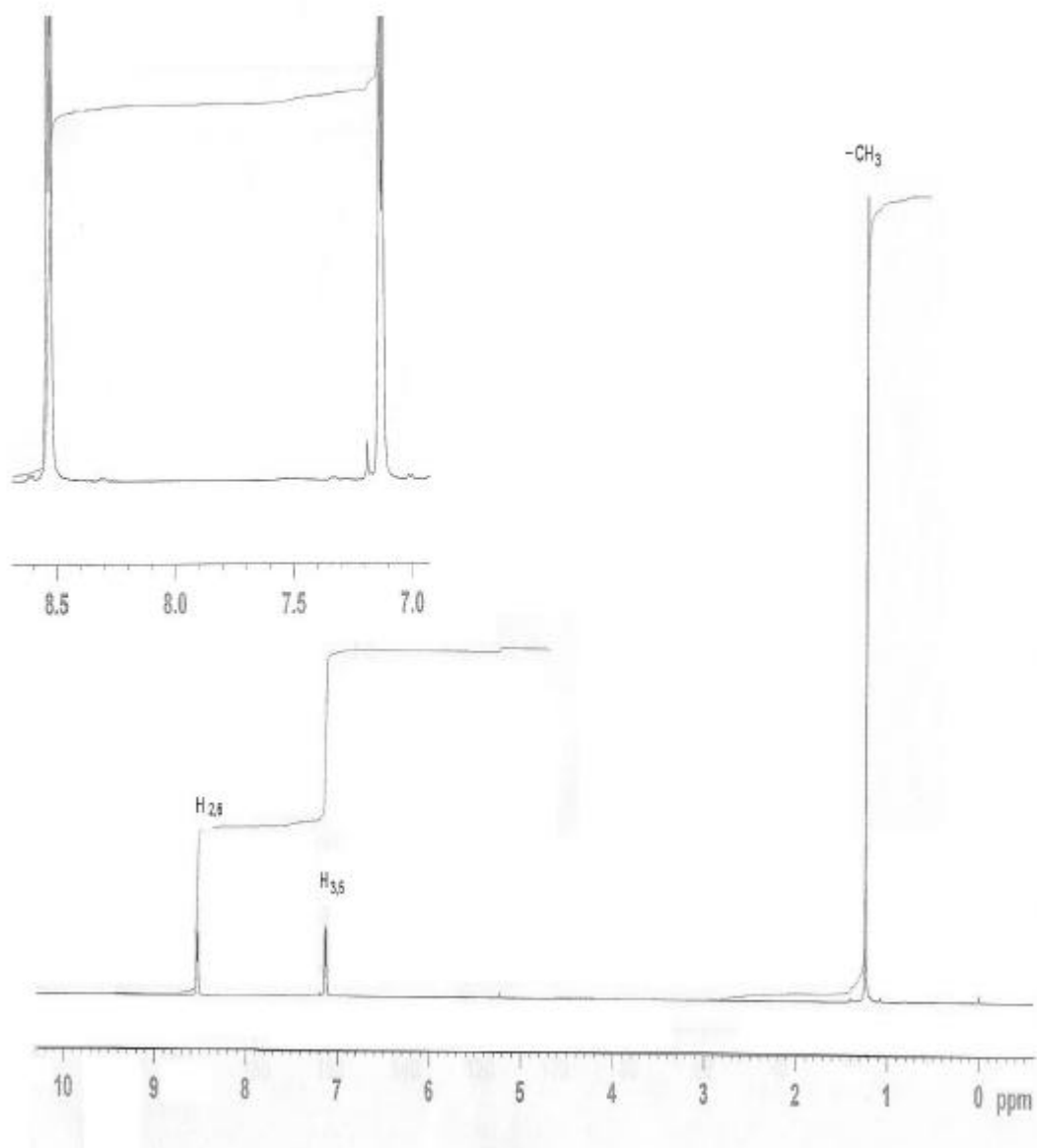


Figure IV.2.4.b. The $^1\text{H-NMR}$ spectrum of $\text{W}(\text{CO})_4(4\text{-tbp})_2$ complex measured from its d -chloroform solutions; TMS reference .

IV.3. ^{13}C -NMR Spectra

IV.3.1. Pentacarbonyl(4-methylpyridin)metal(0), $\text{M}(\text{CO})_5(4\text{-mp})$; M: Cr, Mo, W

The ^{13}C -NMR spectra of these complexes were recorded from their d-chloroform solutions. The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectra show the appearance of four signals of different intensities in the pyridine ligand region (20 – 160 ppm) and two singlets in the carbonyl region (190 – 230 ppm) (Table VI.3.1). Assignments of these signals to their carbon atoms is done based on the off-resonance technique [41]. As an example for these molecules is the $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of $\text{Cr}(\text{CO})_5(4\text{-mp})$ is given in Figure VI.3.1. One can notice the following points in discussing these data;

1. The appearance of only one singlet for each pair of carbon atoms $\text{C}_{2,6}$ and $\text{C}_{3,5}$ and a singlet for C_4 of the pyridine ligand is an indication for a symmetric coordination of the metal atom to the pyridine ligand. Any unsymmetric coordination will cause these signals to split for each couple of carbon atoms.
2. The chemical shifts of the pyridine ring carbon signals show no significant shift from those of the free 4-methylpyridine ligand upon metal coordination indicating the absence of a strong metal - ligand π -bonding between the central atom and the pyridine ligand.
3. In the carbonyl region of the spectra, two signals of relative intensities 1:4 are observed. The assignment of the carbonyl bands

is based on the relative intensities and the chemical shifts in the spectra. The chemical shifts of four carbonyl groups cis to the pyridine ligand are known to be different from those of the carbonyl group in trans position. Therefore the carbonyl group trans to the pyridine would expect to give a signal at lower magnetic field with relative intensity of one. Meanwhile the cis carbonyl groups will expect to have a signal at higher magnetic field with relative intensity of four.

Table IV.3.1. The ^{13}C -NMR chemical shifts (δ ppm) of $\text{M}(\text{CO})_5(4\text{-mp})$ complexes recorded from their d-chloroform solutions; TMS reference.

Complex	C_4	$\text{C}_{3,5}$	$\text{C}_{2,6}$	CH_3	CO
Free ligand	146.93	124.63	149.60	20.89	
$\text{Cr}(\text{CO})_5(4\text{-mp})$	148.13	124.65	152.65	22.60	198.24, 202.85
$\text{Mo}(\text{CO})_5(4\text{-mp})$	148.22	124.81	153.79	19.92	198.94, 202.36
$\text{W}(\text{CO})_5(4\text{-mp})$	149.62	126.50	155.49	21.10	198.94, 202.33

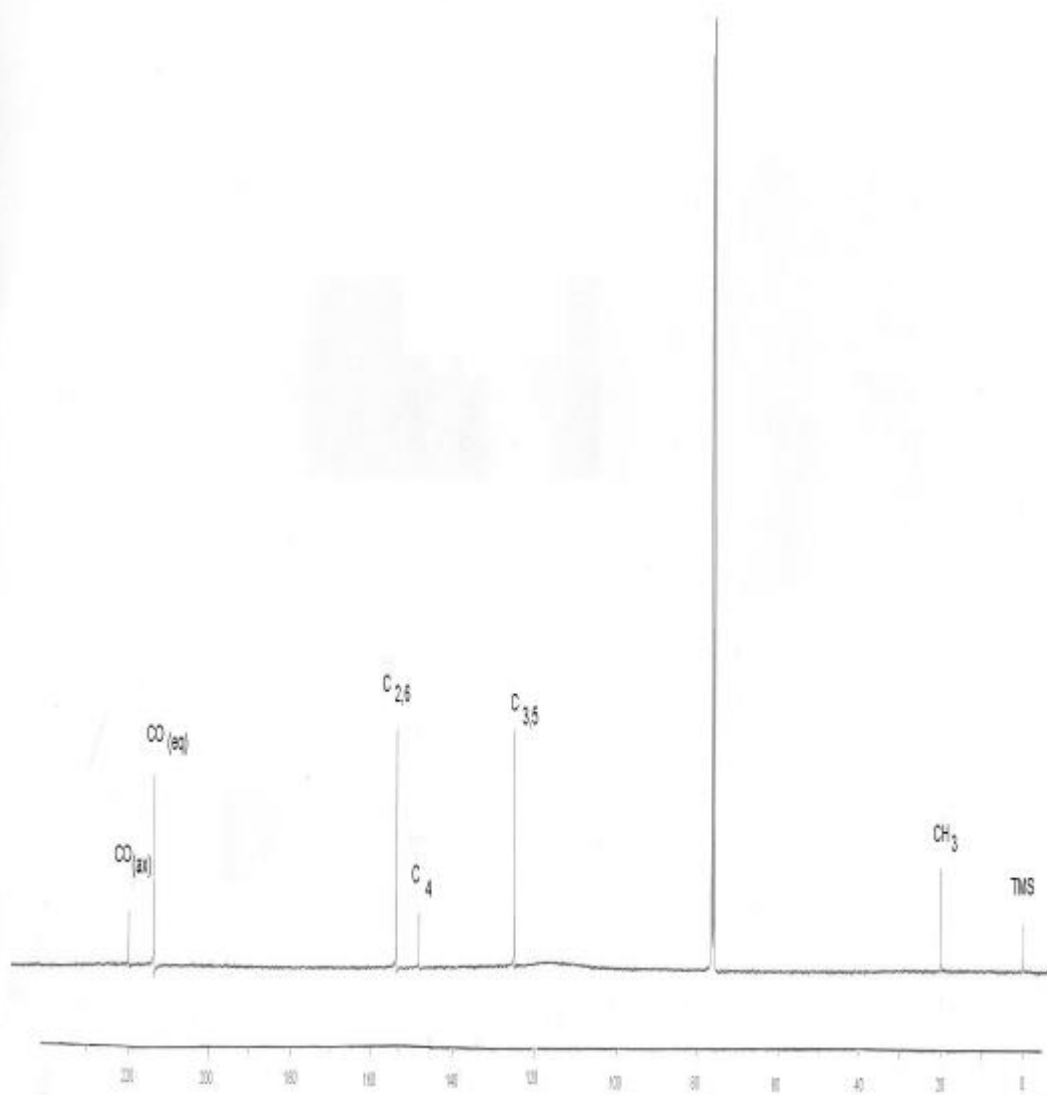


Figure IV.3.1. The ^{13}C -NMR spectrum of $\text{W}(\text{CO})_5(4\text{-mp})$ complex measured from its d-chloroform solutions; TMS reference

IV.3.2. Pentacarbonyl(4-tertbutylpyridin)metal(0),

M(CO)₅(4-tbp); M: Cr,Mo,W

The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectra of these complexes were recorded from their d-chloroform solutions. These spectra show the appearance of five signals of different intensities in the pyridine ligand region (20 – 160 ppm) and two singlets in the carbonyl region (190 – 230 ppm) (Table VI.3.2). Depending on the off resonance technique [40], these signals were assigned for their specific carbon atoms. These assignments show that each pair of the carbon atoms, C_{3,5} and C_{2,6} showed the appearance of only one signal for each pair of carbon atoms. Meanwhile one singlet is observed for the carbon C₄ of the pyridine ring. Carbon atoms of the substituted tert-butyl group showed also the appearance of only one singlet for the methyl groups and for C₇. It is important to notice that the signals of the pyridine ligand carbons showed no significant shift either to lower or to higher fields compared to those of free ligand upon metal coordination. In addition, two singlets of relative intensities 1:4 are observed in the carbonyl region of these spectra. It is important to notice that the appearance of only one singlet for each couple of carbon atoms C_{3,5}, C_{2,6}, C₄ and C₇ with no significant up field shift is an indication for a symmetric metal-tert-butylpyridine coordination through the nitrogen atom lone pair producing the corresponding σ -metal-pyridine complexes. Therefore any unsymmetric metal-pyridine coordination through carbon-carbon double bond could be ruled out since this will cause the splitting of these carbon atoms signals upon coordination. On the other hand, the appearance of two signals of

relative intensities 1:4 for the carbonyl groups (one axial : four equatorial CO groups) is an indication for the formation of $M(CO)_5$ pentacarbonyl complexes.

Table IV.3.2. The ^{13}C -NMR chemical shifts (δ ppm) of $M(CO)_5(4\text{-tbp})$ complexes measured from their d-chloroform solutions; TMS reference.

Complex	C _{2,6}	C _{3,5}	C ₄	C ₇	CH ₃	CO
Free ligand	149.67	120.64	159.76	34.54	30.46	
Cr(CO) ₅ (4-tbp)	152.68	120.73	160.84	35.51	29.93	203.12 212.83
Mo(CO) ₅ (4-tbp)	153.46	121.12	161.27	33.99	29.67	203.45, 213.05
W(CO) ₅ (4-tbp)	153.25	121.31	160.76	34.04	29.13	197.93, 218.99

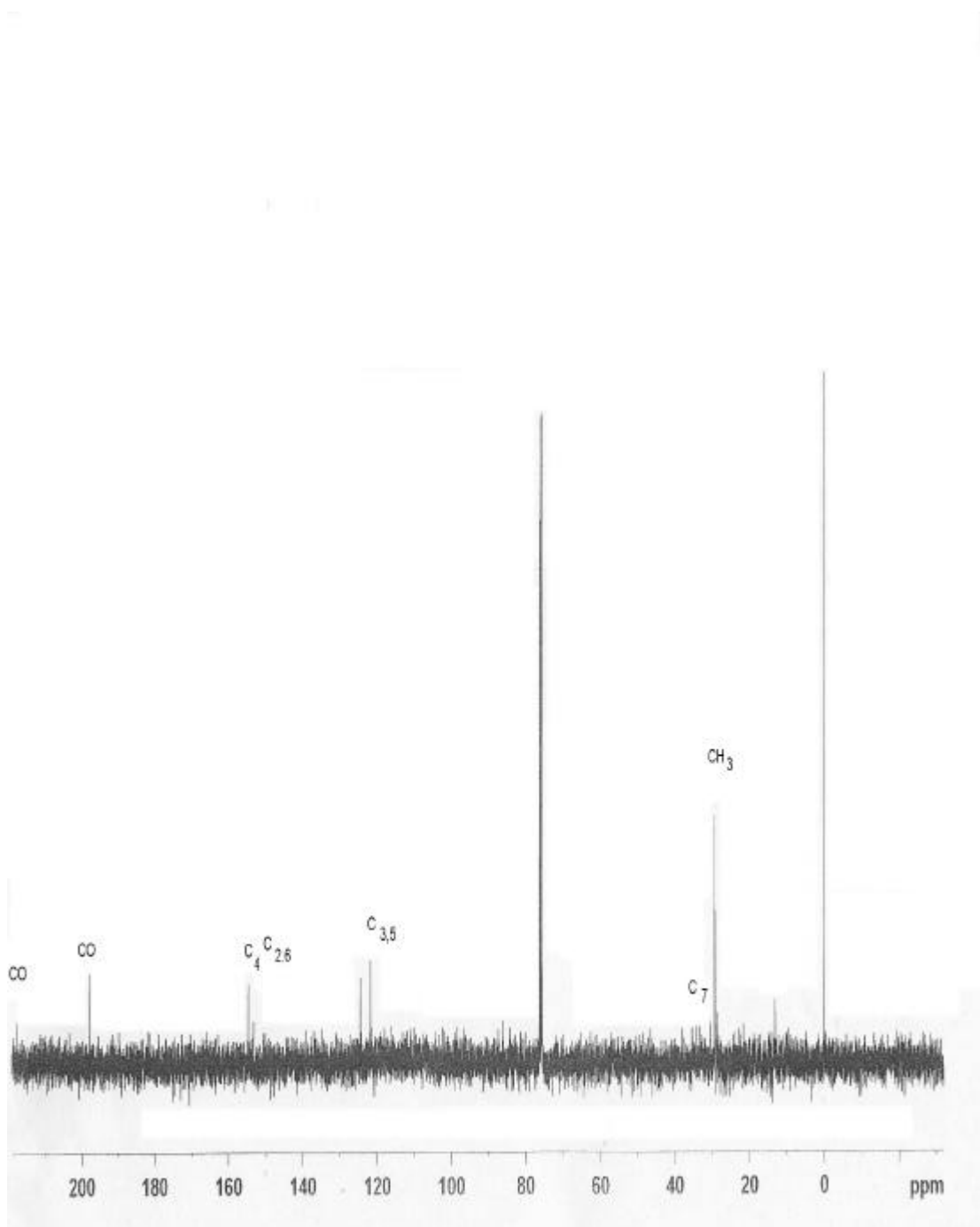


Figure IV.3.2. The ^{13}C -NMR spectrum of $\text{W}(\text{CO})_5(4\text{-tbp})$ complex measured from its d-chloroform solutions; TMS reference

IV.3.3. Pentacarbonyl(4-dimethylaminopyridin)metal(0),

M(CO)₅(4-dmap); M: Cr,Mo,W

The ¹³C-NMR spectra of these complexes were recorded from their d-chloroform solutions. The ¹³C-{¹H}-NMR spectra show the appearance of four signals of different intensities in the pyridine ligand region (20 – 160 ppm) and two singlets in the carbonyl region (190 – 230 ppm) (Table VI.3.3). Assignments of these signals to their carbon atoms is done based on the off-resonance technique [40]. As an example for these molecules is the ¹³C-{¹H}-NMR spectrum of Cr(CO)₅(4-mp) is given in Figure VI.3.3. In these complexes the multibonding possibilities between the central atoms and the 4-dimethylaminopyridine ligand make these complexes so important to study. As it is known, there are three different possibilities for the metal ligand coordination in these complexes, either through the pyridine carbon-carbon double bonds, or through the pyridine N-atom lone pair or through the N(CH₃)₂ groups nitrogen lone pair. Therefore one can notice the following points in discussing these complexes spectra;

1. In the region of the pyridine ligand part of the spectra, the appearance of only one singlet for each pair of carbon atoms, C_{2,6}, C_{3,5} pairs, C₄, and the insignificant shifts of these signals compared with those of the free 4-dmap ligand can rule out the formation of the metal carbon π-complexes, for which each carbon atom of these pairs will cause the appearance of one signal.

2. Another coordination possibility is that between the central atom and the substituted group $N(CH_3)_2$ lone pair. One singlet for the methyl group carbons is shown which is not shifted upon metal coordination is an indication that the metal-ligand coordination through this group is not possible, since this type of coordination will cause the methyl groups signal to shift to a higher field upon coordination.

Therefore the formation of the σ -complexes i.e: the coordination of the metal atoms through the pyridine Natom lone pair, can be proved after these discussions.

3. In the carbonyl region of the spectra, two signals of relative intensities 1:4 are observed. The assignment of the carbonyl bands is based on the relative intensities and the chemical shifts in the spectra. The chemical shifts of four carbonyl groups cis to the pyridine ligand are known to be different from those of the carbonyl group in trans position. Therefore the carbonyl group trans to the pyridine would expect to give a signal at lower magnetic field with relative intensity of one. Meanwhile the cis-carbonyl groups will expect to have a signal at higher magnetic field with relative intensity of four.

Table IV.3.3. The ^{13}C -NMR chemical shifts (δ ppm) of $\text{M}(\text{CO})_5(4\text{-dmap})$ complexes measured from their d-chloroform solutions; TMS reference.

Complex	$\text{C}_{2,6}$	$\text{C}_{3,5}$	C_4	$\text{N}(\text{CH}_3)_2$	CO
Free ligand	149.69	106.54	154.12	38.85	
$\text{Cr}(\text{CO})_5(4\text{-dmap})$	152.36	107.45	154.55	39.08	214.95, 221.08
$\text{Mo}(\text{CO})_5(4\text{-dmap})$	148.65	105.60	153.65	38.00	203.73, 213.92
$\text{W}(\text{CO})_5(4\text{-dmap})$	153.69	107.62	155.62	39.13	199.18, 212.70

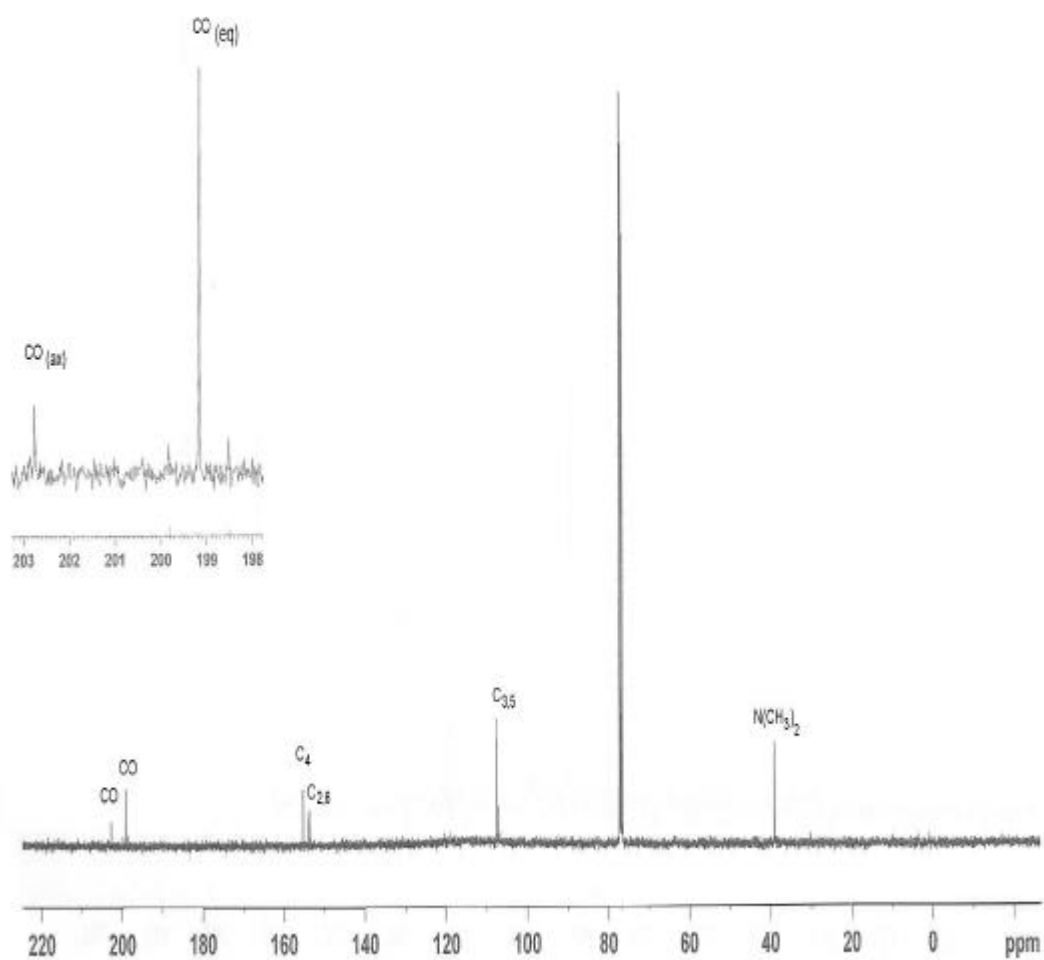


Figure IV.3.3. The ^{13}C -NMR spectrum of $\text{W}(\text{CO})_5(4\text{-dmap})$ complex measured from its d -chloroform solutions; TMS reference.

IV.3.4. Cis-tetracarbonylbis(4-tert-butylpyridine)tungsten(0)

The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of this complex recorded from its d -chloroform solution show the appearance of four signals (Table VI.3.4. and Figure IV.3.4.) which are assigned as discussed in section IV.3.2. of this chapter. The number and intensity ratios of these signals belong to the pyridine ligand in the region of 20 – 160 ppm show similarities with those discussed for the pentacarbonyl(4-tert-butylpyridine)metal(0) complexes. Therefore it is not possible to predict the formation of the disubstituted tetracarbonyl complexes from this region of the spectrum, meanwhile the IR spectrum data provided the tetracarbonyl complex formation. On the other hand, in the carbonyl region of the spectrum, two signals of relative intensity 1:1 are observed.

Since the IR data provided the formation of the disubstituted tetracarbonyl complex, this may be trans- or cis- type of complexes. For that cause, the relative intensities of the CO signals is important. The 1:1 ratio of these signals provides us the formation of the cis-isomer rather than the trans-isomer. For the later, only one signal would be expected for the four CO groups in which all the CO groups will have the same chemical environment.

Table IV.3.4. The ^{13}C -NMR chemical shifts (δ ppm) of $\text{cis-W}(\text{CO})_4(4\text{-tbp})_2$ complexes measured from their d-chloroform solutions; TMS reference.

Complex	$\text{C}_{2,6}$	$\text{C}_{3,5}$	C_4	C_7	CH_3	CO
$\text{W}(\text{CO})_4(4\text{-tbp})_2$	153.25	121.31	160.76	34.04	29.16	203.99 212.34

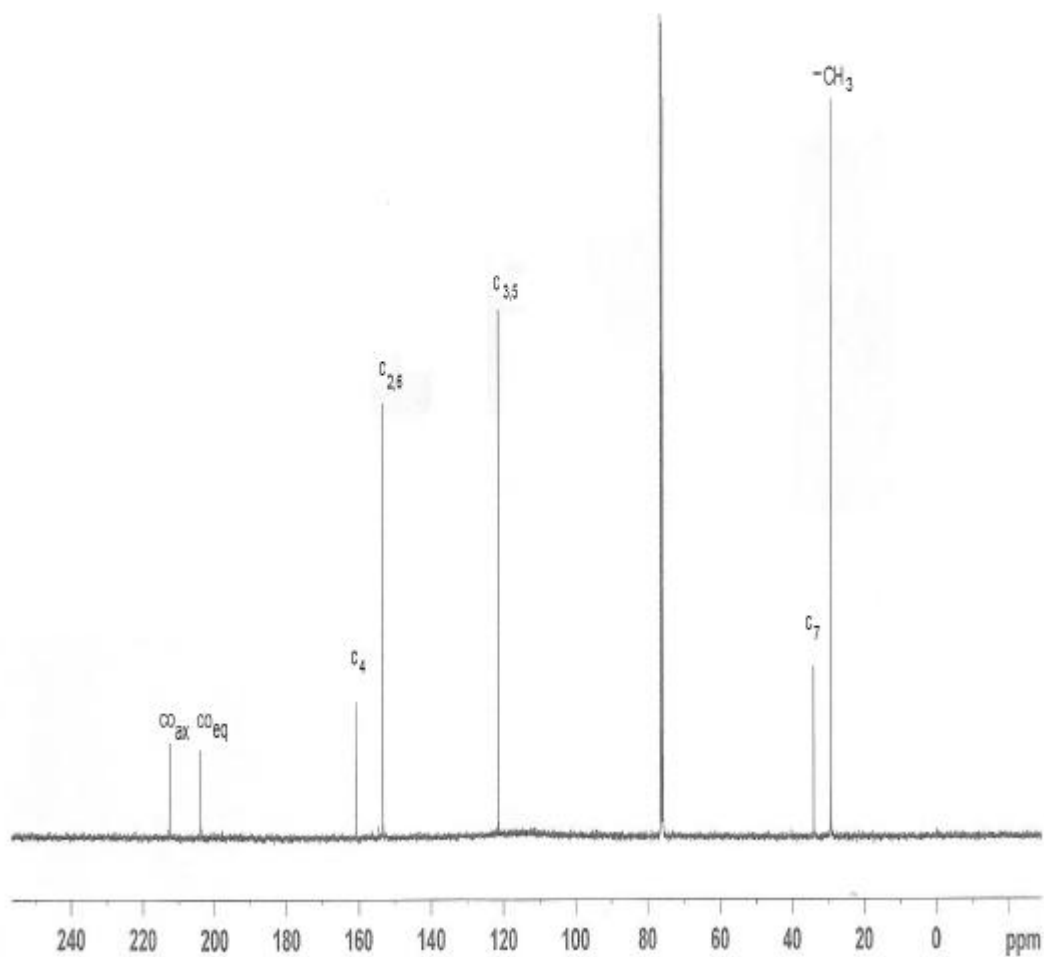


Figure IV.3.4. The ^{13}C -NMR spectrum of $\text{W}(\text{CO})_4(4\text{-tbp})_2$ complex measured from its d-chloroform solutions; TMS reference .

From all these ^{13}C -NMR data and the previous IR and ^1H -NMR data that have discussed in this chapter, one can conclude that either for pentacarbonyl or for tetracarbonyl complexes, the metal atoms bonded the substituted pyridine ligands through the sp^2 nitrogen atom lone pairs of the ligand rather than the available carbon-carbon double bonds to form what is called metal σ -complexes. Any coordination through on of the carbon-carbon double bond can be therefore ruled out, since this type of coordination (unsymmetric) will result in the appearance of more than one signal for the carbons $\text{C}_{2,6}$ and $\text{C}_{3,5}$ pairs.

The carbon atom is known to have two natural isotopes, ^{13}C and ^{12}C . Because of the low natural abundance of the ^{13}C - isotope (1.1 %), in the pentacarbonyl complexes, statistically, only one of the five carbonyl groups carbon atoms can be assumed to be ^{13}C -isotope (Figure IV.3.5). Depending on the position of this ^{13}C -carbonyl ligand in the complexes, only one isotopomeres of the complexes $(^{12}\text{CO})_4(^{13}\text{CO})\text{M L}$; M. Cr, Mo, W; L: 4-mp, 4-tbp, 4-dmap, are possible. Therefore, two carbonyl signals of relative intensity 1:4 shown up in the $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectra (the carbonyl groups region) of these complexes.

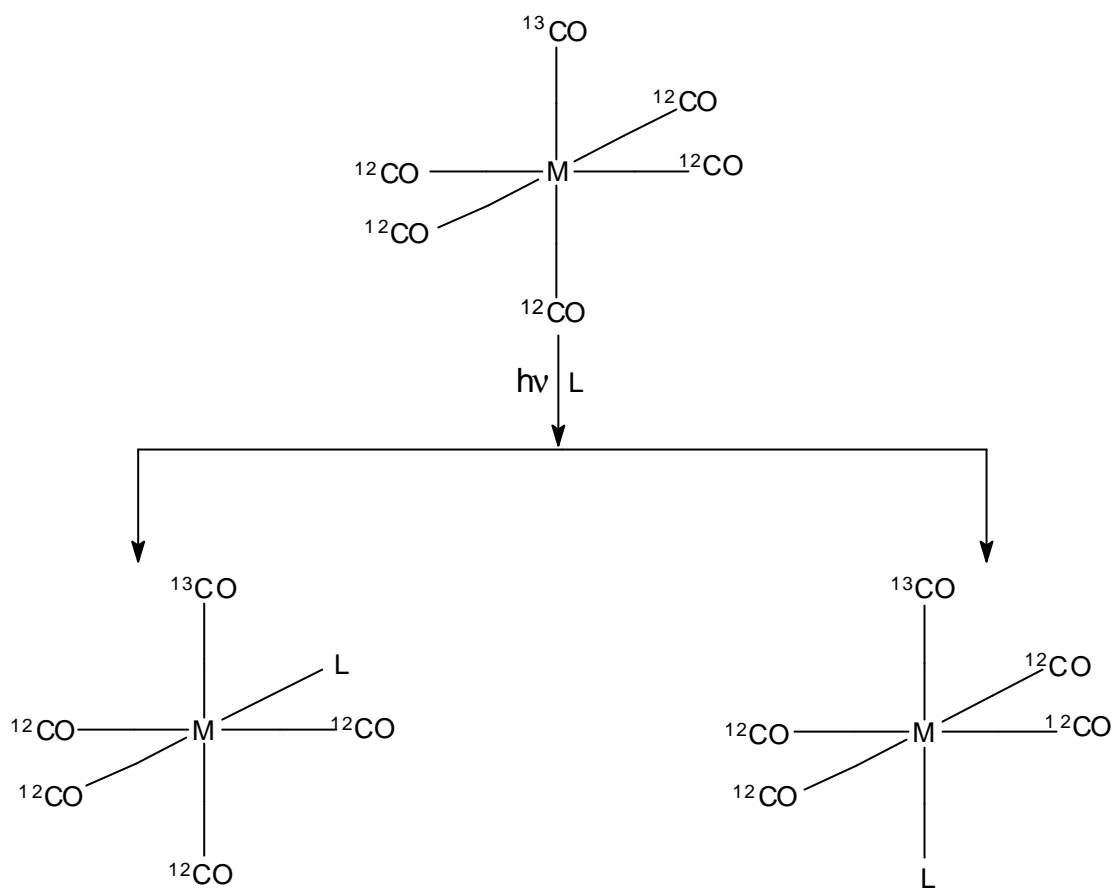


Figure IV.3.5 The possible isotopomers of $M(12CO)_4(13CO)L$;

M: Cr, Mo, W and L: 4-mp , 4-tbp, 4-damp.

CHAPTER V

CONCLUSION

In this study pentacarbonyl(pyridine)metal(0) M: Cr, Mo, W complexes and cis-tetracarbonyl(4-tert-butylpyridine)₂tungsten(0) complex were photochemically synthesized and their structures have been characterized by the mean of IR, ¹H-NMR and ¹³C-NMR spectroscopies.

The pyridine ligand can bond to central atoms by two ways, symmetrically (from N atom of pyridine) and unsymmetrically (from double bond). Since there is no certain change in chemical shifts of spectra of these complexes by comparing with the spectra of free ligand, we can conclude that symmetric binding occur between metal and pyridine. If it would have bonded to metal unsymmetrically, the high chemical shift would have been observed.

Although, only pentacarbonyl-pyridine-metal complexes were tried to synthesize at the beginning, the IR and NMR spectroscopies showed us that our products contained the mixture of tetracarbonyl and pentacarbonyl complexes surprisingly. Therefore, quite a long time was spent for isolation of these mixture and cis-tetracarbonyl(4-tert-butylpyridine)₂tungsten(0) complex could be separated successfully. From the ¹H- and ¹³C-NMR spectra results the two pyridine rings were placed the complex by cis position.

REFERENCES

- [1] Werner A. Z. Inorganic Chem., 3, 267 (1893)
- [2] Zeise W. C., Ann. Phys. Leipzig, 9, 632 (1827)
- [3] Zeise W. C., Pogg. Annalen, 21,497 (1831)
- [4] Kealy T. J., Pouson P. L., Nature, 168, 1039 (1951); Millar S. A.,
Tebboth J. A., Tremaine J. F., J. Chem. Soc., 73, 631(1952)
- [5] Wilkonson G., Rasenblum M., Whiting M. C., Woodward R. B., J.
Chem. Soc. 74, 2125 (1952)
- [6] Mord L., Hirtz H., Cowap M. D., J. Chem. Soc. 62, 789 (1910) Mord L.,
Hirtz H., Z. Anorg. Allgem. Chem., 68, 207 (1910)
- [7] Malatesta L., Angoletta M., J. Chem Soc., 1186 (1957)
- [8] Malatesta L., Cariello C., J. Chem Soc., 2323 (1958)
- [9] Stone F. G. A., West R., "Advances in Organometallic Chemistry ",V. 3
(1975)
- [10] Mord L., Hirtz H., Cowap M. D., J. Chem. Soc. 62, 789 (1910) Mord
L., Hirtz H., Z. Anorg. Allgem. Chem., 68, 207 (1910)
- [11] Job A., Cassel A., Bull. Chem . soc., France, 41, 1041, (1927)
- [12] Job A., Rauvilous J. Compt. Rend., 187, 564 (1928)
- [13] J. Dewar, H. O. Jones, Chem , News J. Indust. Sci. 95 (1907) 109
- [14] E. Speyer, M.Wolf, Chem. Ber. 60 (1927) 1424-1425
- [15] R. B. King, J. J Eisch, R. B. King (Eds.), Organometallic Synthesis,
vol. 1 Academic Press

- [16] a) $\text{Cr}(\text{CO})_6$: W. Strohmeier , K. Gerlach, Z. Natuforsch. 15b (1960) 413;
b) W. Strohmeier, K. Gerlach, Z. Natuforsch. 15b (1960) 622;
c) W. Strohmeier , K. Gerlach, Z. Natuforsch. 15b (1960) 1346-1349;
 $\text{Mo}(\text{CO})_6$: W. Strohmeier , K. Gerlach, G. Matthias , Z. Natuforsch 15b (1960) 621-622
- [17] W. Strohmeier , K. Gerlach, Z. Natuforsch. 15b (1960) 675-676
- [18] M. M. Abd-Elzaher, B. Weibert ,H. Fisher ,J. Organomet. chem 669 (2003) 6-13
- [19] S. Özkar, C. Kayran , N. Demir, J.Organomet. chem 688 (2003) 62-67
- [20] M. S. Wrigton, G. S. Hammond and H. B. Gray ,J. Am. Chem. Soc. 93 (1971) 4336; Inorg. Chem. 11 (1972) 3122; Mol. Photochem. 5 (1973) 179.
- [21] R. M. Dahlgren and J. I. Zink, Inorg. Chem. 16 (1977) 3154.
- [22] M. S. Wrigton, H. B. Abrahamson and D. L. Morse, J. Am. Chem. Soc. 98 (1976) 4105.
- [23] L. Tutt, D. Tannor, E. J. Heller and J. I. Zink, J. Phy. Chem. 87 (1983) 3017.
- [24] I. A. Morkan, K.Güven, S. Özkar, J. Organomet. Chem. 689 (2004) 2319-2323
- [25] R. J. Dennenberg, D. J. Darensbourg, Inorg. Chem. 11 (1972) 72
- [26] H. Van. Dam ,G. Boxhoorn, D. J. Stufkens , Ad.Oskam, Inorg. Chim. Acta 53(1981)235
- [27] M. J. Aroney , R. M. Clarkson, T. W. Hambley, R. K. Pierens, J. Organomet. Chem. 426 (1992) 331
- [28] M. A. Weiner, A. Gin, M. Lattman, Inorg. Chem. Acta 24 (1977) 235

- [29] R. M. Kolodziej, A. J. Lees, *Organometallics* 5 (1986) 450.
- [30] B. S. Creaven R. A. Howie, C. Long, *Acta Crystallogr. C* 56 (2000) 181.
- [31] Richard M. Kolodziej and Alistair J. Lees, *Organometallics* 5 (1986) 450
- [32] R. M. Kolodziej, A. J. Lees, *Organometallics* 5 (1986) 450.
- [33] B. S. Creaven, R. A. Howie, C. Long, *Acta Crystallogr. C* 57 (2001) 385.
- [34] *Organometallic chemistry*, Garry O. Spessard , Garry L. Miessler ,St Olaf College Northfield, Minnesota
- [35] Cotton F. A., and Wilkinson G., “*Advanced Inorganic Chemistry* ”, 3rd Edit., New York; 683-721
- [36] *Organikum*, Veb. Deutscher Verlag der Wissenschaften, Berlin, (1971).
- [37] P. S. Braterman, *Metal Carbonyl Spectra* , Academic Press, London, 1975
- [38] Dbson, G. R., Amrel S. M., Stolz I. W., Shiline R. K., *Inorg. Chem.* 21, 526 (1962)
- [39] Orgel L.E., *Inorg. Chem.* 1,29(1962)
- [40] Philipsborn W., *Angew. Chem.*, 83, 410 (1971)

