

SYNTHESIS AND CHARACTERIZATION
OF
TETRACARBONYLPYRAZINETRIMETHYLPHOSPHITETUNGSTEN(0)
COMPLEXES

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FATMA ALPER

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Prof.Dr. Canan Özgen
Director

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

Prof. Dr. Hüseyin İşçi
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.

Prof. Dr. H. Ceyhan Kayran
Co-Supervisor

Prof. Dr. Saim Özkâr
Supervisor

Examining Committee Members

Pof. Dr.Hüseyin İşçi	(METU,CHEM)	_____
Prof. Dr.Saim Özkâr	(METU,CHEM)	_____
Prof. Dr.H. Ceyhan Kayran	(METU,CHEM)	_____
Prof. Dr.Yavuz İmamoğlu	(HÜ,CHEM)	_____
Doç.Dr.Gülsün Gökağaç	(METU,CHEM)	_____

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF TETRACARBONYLPYRAZINETRIMETHYLPHOSPHITETUNGSTEN(0) COMPLEXES

Alper, Fatma

M.S., Department of Chemistry

Supervisor: Prof. Dr. Saim Özkâr

Co-Supervisor: Prof. Dr. H.Ceyhan Kayran

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In this study, the effect of a donor ligand on the stabilization of a carbonyl pyrazine tungsten complex was studied. The pentacarbonylpyrazinetungsten(0) complex could be formed from the photolysis of hexacarbonyltungsten(0) in the presence of pyrazine and could be isolated as crystalline solid. However, the complex was found to be unstable in solution, being converted to a bimetallic complex, $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ and free pyrazine molecule. Two complexes exist in solution at equilibrium. The equilibrium constant could be determined by ^1H -NMR spectroscopy and found to be 0.0396 at 25°C . To test whether the introduction of a second pyrazine ligand might provide stability for the carbonyl-pyrazine-tungsten complex, $\text{W}(\text{CO})_4(\text{pyz})_2$ was attempted to be synthesized. The *cis*- $\text{W}(\text{CO})_4(\text{pyz})_2$ complex could be generated from the thermal substitution reaction of *cis*-

$\text{W(CO)}_4(\text{piperidine})_2$ with excess pyrazine in dichloromethane. However, this complex could not be isolated because of the lack of stability. The complex could only be identified by IR spectroscopy in solution.

To stabilize the pentacarbonylpyrazinetungsten(0) complex, trimethylphosphite was introduced to the complex as a donor ligand. For this purpose, $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{thf})$, photogenerated from $\text{W(CO)}_5[\text{P(OCH}_3)_3]$ in tetrahydrofuran (thf), was reacted with pyrazine. The replacement of tetrahydrofuran with pyrazine (pyz) yielded $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$. The complex could be isolated from the reaction solution and characterized by means of IR, ^1H -, ^{13}C -, ^{31}P -NMR, and Mass spectroscopies. The introduction of $\text{P(OCH}_3)_3$ has proved that a donor ligand will strengthen the metal-pyrazine bond and thus stabilizes the complex. As a result of this stabilization, the complex could be isolated as the first example of tungsten pyrazine complexes that contain a donor ligand.

Keywords: Pyrazine, Trimethylphosphite, Carbonyl, Tungsten, Photolysis.

ÖZ

TETRAKARBONYLPİRAZİNTRİMETİLFOSFİTTUNGSTEN(0) KOMPLEKSİNİN SENTEZİ VE KARAKTERİZASYONU

Fatma, Alper

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. Saim Özkâr

Tez Yönetici Yardımcısı: Prof. Dr. H. Ceyhan Kayran

Kasım 2004, 61 sayfa

Bu çalışmada, donör bir ligandın, karbonil pirazin tungsten kompleksinin kararlı hale getirilmesi üzerindeki etkisi incelendi.

Pentakarbonilpirazintungsten(0) kompleksi heksakarboniltungsten(0) kompleksi ile fazla miktarda pirazin ligandının fotokimyasal tepkimesiyle oluşturularak elde edildi. Fakat kompleksin çözelti içinde kararsız olduğu, iki metalli kompleks, $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$, ve serbest pirazin ile denge halinde olduğu gözlemlendi. Denge sabiti, $^1\text{H-NMR}$ spektroskopisi kullanılarak 25°C 'de 0.0396 olarak hesaplandı. İkinci bir pirazin ligandının karbonil-pirazin-tungsten kompleksini kararlı hale getirip getirmeyeceğini test etmek için, $\text{W}(\text{CO})_4(\text{pyz})_2$ kompleksi sentezlenmeye çalışıldı. $\text{cis-W}(\text{CO})_4(\text{pyz})_2$ kompleksi, $\text{cis-W}(\text{CO})_4(\text{piperidin})_2$ kompleksi ile fazla miktarda pirazin ligandının diklorometanda termal tepkimesi ile

oluşmasına rağmen kompleksin kararsız olmasından dolayı izole edilemedi. Kompleks IR spektroskopisi ile çözeltide tanımlandı.

Pentakarbonilpirazintungsten(0) kompleksini kararlı hale getirmek için donör ligand olarak trimetilfosfit $[P(OCH_3)_3]$ kompleks ile tepkimeye sokuldu. Bu amaçla, $W(CO)_5[P(OCH_3)_3]$ kompleksi öncelikle tetrahidrofuranda (thf) ısınladı ve oluşan cis- $W(CO)_5[P(OCH_3)_3](thf)$ kompleksi pirazinle tepkimeye sokuldu. Tetrahidrofuranın pirazinle yerdeğiřtirmesi sonucu cis- $W(CO)_4[P(OCH_3)_3](pyz)$ kompleksi elde edildi. Kompleks izole edilerek yapısı IR, 1H -, ^{13}C -, ^{31}P -NMR, ve Kütle spektroskopileri kullanılarak tanımlandı. $P(OCH_3)_3$ gibi bir donör ligandın komplekste bulunmasının, metal-pirazin bağıını güçlendirdiğı ve böylece kompleksi kararlı hale getirdiğı gözlemlendi. Böylelikle cis- $W(CO)_4[P(OCH_3)_3](pyz)$ kompleksi donör ligand içeren pirazin komplekslerinin ilk örneğı olarak izole edilebildi.

Anahtar kelimeler: Pirazin, Trimetilfosfit, Karbonil, Tungsten, Fotoliz.

To my family, Rıfat, Zekiye and Rabia

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CHAPTER 1

INTRODUCTION

Organometallic chemistry is the chemistry of compounds containing metal-carbon bonds¹. It encompasses a wide variety of chemical compounds and their reactions, including compounds both σ and π bonds between metal atoms and carbon. The development of transition-metal organometallic chemistry dated back to 1827 when Zeise has reported the first organometallic compounds, $K[PtCl_3(C_2H_4)]$, which was synthesized by the reaction of ethylene with potassium tetrachloroplatinate(II).^{2,3}

Transition-metal carbonyls, the compounds of various transition metals with carbon monoxide, are among the oldest known classes of organometallic compounds. Transition metals mostly form complexes in which carbonyl group acts as a two electron donor ligand. The first carbonyl complex, $Ni(CO)_4$ was synthesized in 1890 by Mond, Langer, and Quincke.⁴ It was followed almost immediately by the discovery of pentacarbonyl-iron, $Fe(CO)_5$ in 1891 independently by Mond^{5,6} and Berthelot.⁷ After this discovery, there was no significant development in this area until the synthesis of ferrocene, $Fe(C_5H_5)_2$, in 1951.⁸ It was subsequently realized that transition metals have the capability of forming a wide variety of organometallic compounds.

Transition metal carbonyls are commonly used as starting materials for the synthesis of many organometallic compounds which serve as a catalyst for the reaction of unsaturated hydrocarbons⁹ and are of structural and stereochemical

importance.¹⁰ The chemistry of the transition metals involves processes in which ligands are coordinated to metals, ligands are exchanged, the coordination sphere is rearranged, oxidation and reduction occurs and the reactivity of the ligands is changed by coordination.

Chemical reactions in which the composition of the first coordination sphere around metal changes is called ligand substitution reactions. One or more CO-groups in the hexacarbonylmetal(0) of the Group 6 elements can be substituted thermally or photochemically by a variety of ligands producing complexes of the type $M(CO)_{6-n}L_n$ where L indicates the incoming ligand:

- a) Direct CO-substitution in $M(CO)_6$ with any potential ligand L.



- b) Substitution of labile ligand into metal hexacarbonyl to form metastable metal carbonyl derivatives, which then react with any potential ligand.

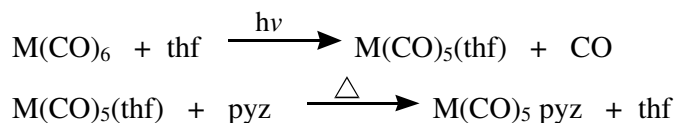
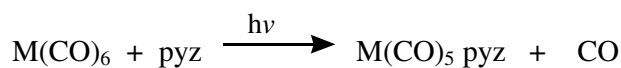


L: a weakly coordinated ligand such as cis-cyclooctene, tetrahydrofuran, piperidine, acetonitrile,...

L': trialkylphosphine, dialkyl phosphinoalkane, pyrazine, diolefin and dimine.^{11,12,13}

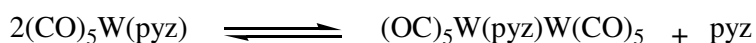
Among these potential ligands, pyrazine is one of the most interesting ligand which is an aromatic heterocycle containing two nitrogen atoms in trans positions to each other. It is π acceptor ligand because of its relatively low energy π^* orbitals, which facilitate electron transfer between metal and pyrazine.^{14,15} Pyrazine and substituted pyrazines have long been known to form linear bridges between the metal

ions generating oligomeric species^{16,17,18,19} or polymeric arrays^{20,21} in the presence of metal ions containing more than one stable oxidation states (Cu, Ag). Besides this, Creutz-Taube type of complexes have been prepared²² in which pyrazine acts as a bridging ligand between two pentaammine ruthenium units. Pyrazine containing group 6 metal carbonyl complexes have also been known and can be prepared either by direct photolysis of $M(CO)_6$ ($M = Cr, Mo, W$) with pyrazine, or $M(CO)_5(THF)$ ($M = Cr, Mo, W$) complexes can react thermally with pyrazine ligand according to the equations:

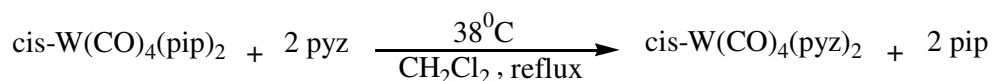


Pyrazine bridged homobimetallic $(OC)_5M(py)M(CO)_5$ and heterobimetallic $(OC)_5M(py)M'(CO)_5$ complexes have been prepared from $M(CO)_5(py)$ or $M(CO)_5(THF)$ ($M = Cr, Mo, W$), Zulu et al¹⁶ have reported on the photophysical, photochemical and redox behaviour of such complexes. Excited-state properties of binuclear Group 6 metal carbonyl complexes have also been studied.²³ The $(OC)_5M(py)M(CO)_5$ complexes have been found to be moderately stable in the solid form when kept in the dark at 273 K; storing under argon greatly increased their long-term stability. The chromium complexes have been found to be particularly susceptible to oxidation on exposure to air and, therefore, had to be handled under argon environment. In solution at 298 K, the complexes exhibited varying degrees of stability, with chromium and molybdenum complexes showing the fastest decomposition. Only the $(OC)_5W(py)W(CO)_5$ complex has been found to be sufficiently stable thermally to obtain accurate photochemical data.

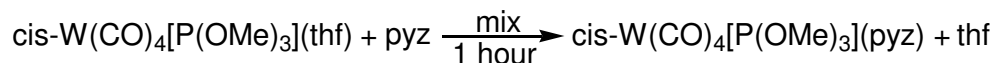
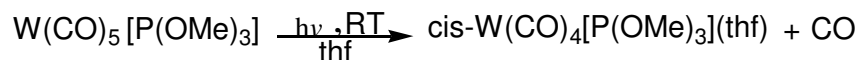
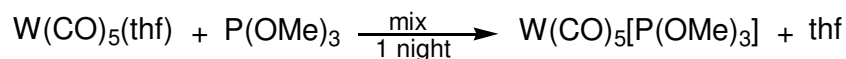
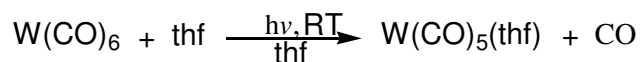
All these previous studies show that pyrazine complexes of Group 6 metal(0) are not stable enough for isolation due to the fact that the metal-pyrazine bond is not strong. The reason is that back-bonding from metal to pyrazine is not so effective as one would expect. In fact, during the preparation of $\text{W(CO)}_5(\text{pyz})$, the monometallic complex is unavoidably contaminated with the bimetallic $(\text{OC})_5\text{W}(\text{pyz})\text{W(CO)}_5$ complex which can not be differentiated by means of IR spectroscopy. This indicates that the pyrazine complex could be stabilized by the formation of bimetallic complex, because, the energies of the π^* -acceptor orbitals on pyrazine are effectively lowered as the ligand binucleates. Indeed, a possible equilibrium exists between monometallic and bimetallic complexes as observed in the previous work.²⁴ The ^{13}C - $\{^1\text{H}\}$ -NMR and ^1H -NMR spectra show that the equilibrium is shifted towards monometallic complex when the excess pyrazine is added into the solution during the measurement.



In this study, the equilibrium constant (K_{eq}) that exist between monometallic, $(\text{CO})_5\text{W}(\text{pyz})$ and bimetallic complex, $(\text{CO})_5\text{W}(\text{pyz})\text{W(CO)}_5$ was determined by means of ^1H -NMR spectroscopy in the presence of variable concentration of pyrazine. Additionally, we attempted to prepare the $\text{cis-W(CO)}_4(\text{pyz})_2$ complex in order to test whether the introduction of a second pyrazine ligand might provide stability for the carbonyl-pyrazine-tungsten complex. It was seen that the complex is fairly stable as solid but like monometallic $\text{W(CO)}_5(\text{pyz})$ complex, exhibits a low degree of thermal stability in solution, and even it undergoes rapid decomposition at room temperature. Therefore, this $\text{cis-W(CO)}_4(\text{pyz})_2$ complex was identified by taking the IR spectra in solution. Although many methods were tried, the best way to prepare the $\text{cis-W(CO)}_4(\text{pyz})_2$ complex was found to be the ligand substitution reaction of the $\text{cis-W(CO)}_4(\text{pip})_2$ complex with excess pyrazine in dichloromethane.



On the other hand, it is known that the presence of a donor ligand can effect the metal ligand bonding in the complex sterically as well as electronically.²⁵. Therefore, we thought that the introduction of a donor ligand would increase the stability of metal-pyrazine bond by making the metal center electron rich hence increase the back-donation from metal to pyrazine ligand. P(OCH₃)₃ was considered as a promising candidate for such a ligand. Therefore, in this study we developed a method for the synthesis of cis- W(CO)₄[P(OCH₃)₃](pyz) which was isolated as the first example of tungsten-pyrazine complexes that contain a donor ligand and characterized by means of IR, ¹H-, ¹³C-, ³¹P-NMR, and Mass spectroscopies. In essence, the method is based on a sequence of simple substitution reactions starting with the uv irradiation of W(CO)₆ in tetrahydrofuran. The method consists of the following substitution reactions:



CHAPTER 2

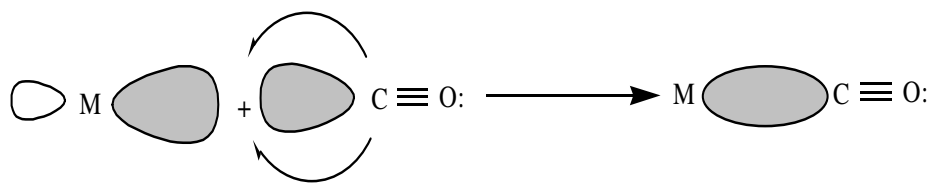
BONDING

2.1 Metal Carbonyl Bonding

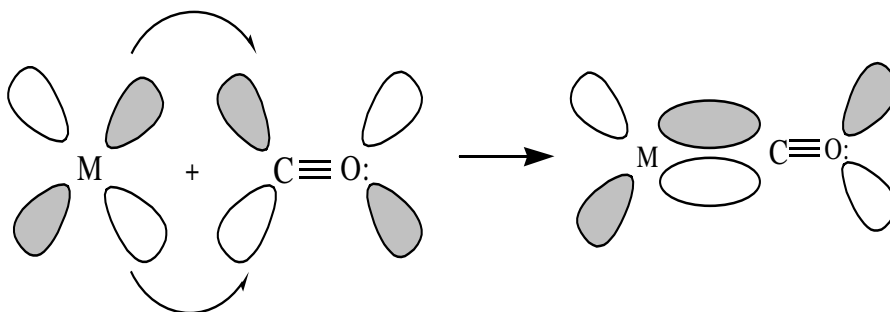
In organotransition metal chemistry, carbon monoxide is considered to be most commonly encountered ligand which forms complexes with metals known as metal carbonyls.²⁶

Overlapping of σ -orbital with a lower lying orbital on the metal atom allows flowing of electron density from carbon to metal atom (Figure 2.1.a). According to Pauling's Electroneutrality Principle, metal atom tends to reduce its charge therefore, the electrons from d-orbital on the metal delocalize into the low lying empty π^* orbitals of carbon monoxide, thus acting as a π -acceptor (Figure 2.1.b)

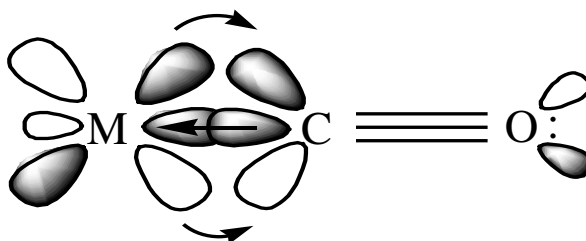
These two types of bonding mechanisms (π -backbonding and σ -dative bonding) are said to be *synergic*, (Figure 2.1.c) since the drift of metal electrons into CO-orbital through π -back bonding will tend to make the CO-group as a whole negative and hence increases its basicity. This leads to drift of electrons to metal through the σ bond, and tends to make the CO positive and increases the acidity and π -acceptor ability. As a result of this, π back bonding increases the M-C bond strength, while CO bond strength decreases.



(a)



(b)



(c)

Figure 2.1. Molecular orbital description of metal-carbonyl interaction.

- (a) Metal $\leftarrow$ carbon σ -bond: σ -bonding
- (b) Metal $\rightarrow$ carbon $d_{\pi}-\pi^*$ bond: π -backbonding
- (c) Synergic effect

There are two important factors that affect the strength of metal-carbon bonding and extent of the π -backbonding. The first one is the charge on the metal carbonyl or the oxidation state of the metal. The metals of lower oxidation states donate more electron density to the CO through π -bonding. When the metal donates more electron density to CO, the M-C bond becomes shorter and stronger. As a result of this effect the C-O bond becomes longer and weaker. This causes a reduction of the CO stretching frequency.

The replacement of carbonyl group with other ligands has also an effect on the M-C and C-O bondings of the remaining carbonyl groups in the complex, and thus on their CO stretching frequencies. The trans ligand competes with the carbonyl group for the same d_{π} -orbitals of the metal in bonding. If the ligand has a strong σ -donor but weak π -acceptor ability than carbonyl group the stretching frequency of the carbonyl becomes lower, since the carbonyl group accepts more electron density from the metal ion into its antibonding orbitals. Consequently, M-C bond becomes stronger whereas C-O bond weakened. It is obvious that trans ligands with greater π -acceptor and less σ -donor ability compared to the carbonyl group will have an opposite effect on the C-O stretching frequency. The competitive effect of trans ligand on the carbonyl stretching frequency is shown in figure 2.2.

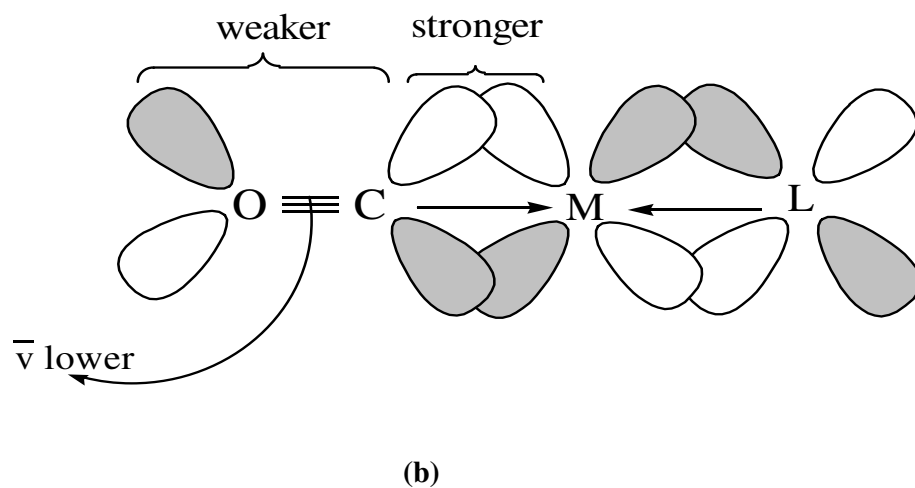
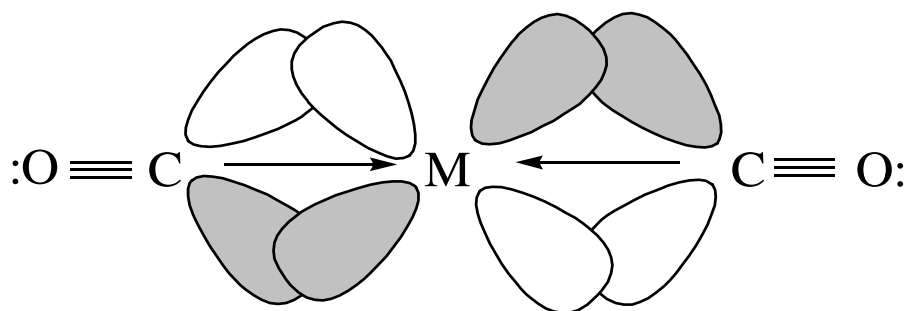


Figure 2.2. Competition for π -bonding in metal carbonyl derivatives.

a) The π -bonding of C-O molecules cis to L but trans to C-O

b). The π -bonding of C-O trans to weak π -bonding ligand L

2.2 Metal Phosphorous Bonding

A variety of trivalent phosphorous compounds can give stable complexes with transition metals. Because this donor atom (phosphorous) has empty $3d_{\pi}$ -orbitals of the appropriate symmetry and energy so back-bonding into these orbitals is also possible.

The bonding of these ligands with a metal is very similar to the CO; in addition to the σ -interaction between HOMO of the phosphine and empty σ -orbital of the metal, there is a donation of electron density from the filled d-orbitals of metal atom to the vacant orbitals of phosphorous atom through back bonding as shown in figure 2.3.

An important difference, in comparison with the M-CO bonding is that: phosphorous atom uses its d-orbital in bonding to the metal, whereas CO uses its π^* -orbitals. Therefore, metal-phosphorous bonding is called d_{π} - d_{π} bonding and the other is d_{π} - $p\pi$ bonding²⁷. Other difference of phosphorous ligands from carbonyl group is that, they are weaker π -acceptor than CO. But their π -accepting ability depend on the nature of the substituents present on the phosphorous atom.

Phosphorous ligand with electronegative substituents becomes electron deficient and demands electron density from the metal atom. This causes the phosphorous ligand to be a strong π -accepting ligand. For example trifluorophosphine (PF_3) has a π -acceptor ability comparable with that of carbonyl.

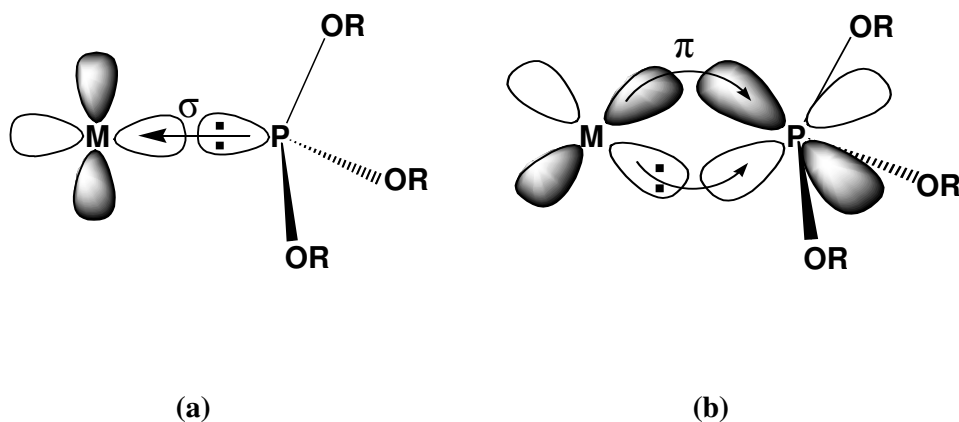


Figure 2.3. MO description of Metal-Phosphorous bonding

- a) $(\text{OCH}_3)_3\text{P} \rightarrow \text{Metal } \sigma\text{-bonding}$
- b) $\text{Metal} \rightarrow \text{P(OR)}_3 d_\pi\text{-}d_\pi \text{ bonding}$

The presence of a donor ligand in metal-carbonyls affects the M-CO bonding, especially when it is trans to the carbonyl group as mentioned before. Since both phosphorous ligand and CO tend to use the d-orbital of the metal atom, there will be a competition between CO and phosphine ligands for the use of the same d-orbital of the metal in the back bonding.

2.3. Metal Pyrazine Bonding

The nitrogen atoms in pyrazine are sp^2 hybridized. In the pyrazine ring the two nitrogen sp^2 orbitals that contain only one electron overlap with sp^2 orbitals of the 2- and 6-carbon atoms to form σ bonds. The remaining sp^2 orbital (with two electrons) does not form a bond and is in the same plane as the ring but directed away from it (Figure 2.4). The remaining p orbital of nitrogen (containing one electron) is perpendicular to the plane of the ring and overlaps with the p orbitals of 2- and 6-carbon atoms to form a π system of the six electrons. The π system of pyrazine is isoelectronic with the π -system of benzene and shows aromatic

properties. While bonding to a metal center, lone pair of nitrogen is transferred to the d-orbital of the metal through σ -bond. In addition to the σ -interaction, pyrazine ligand acts as a π -acceptor ligand as well. As a conclusion, one can assume that the pyrazine ligand is a σ -donor and π -acceptor ligand.²⁸

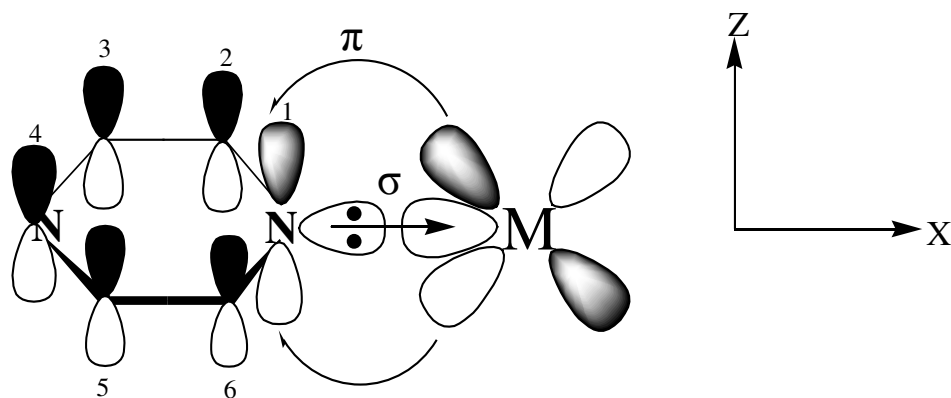


Figure 2.4. Metal-Pyrazine Bonding Model

CHAPTER 3

EXPERIMENTAL

3.1 Basic Techniques

Most of the organometallic compounds are air sensitive and tend to decompose if not handled properly. In many cases, oxidation occurs at a significant rate at room temperature. Their sensitivity to oxygen and water is usually greater in solution than in solid state. Therefore, handling of organometallic compounds and all reactions should be carried out under dry, deoxygenated nitrogen atmosphere or under vacuum.

Organometallic compounds may be handled as easily as ordinary compounds if the reaction is carried out in the absence of oxygen, for example dry and deoxygenated nitrogen gas atmosphere. For this reason, nitrogen or argon gas is allowed to pass through different purification steps (Figure 3.1). The bubbler in which glycerin is used to see the gas passage. The gas is then allowed to pass through dried molecular sieves to dry it up from its moisture and finally through a catalyst (BASF R3, Ludwigshafen, West Germany) for removal of oxygen. The catalyst is heated to 120⁰C using an electrical resistance, and hydrogen gas is allowed to pass through the system from time to time to regenerate the catalyst.

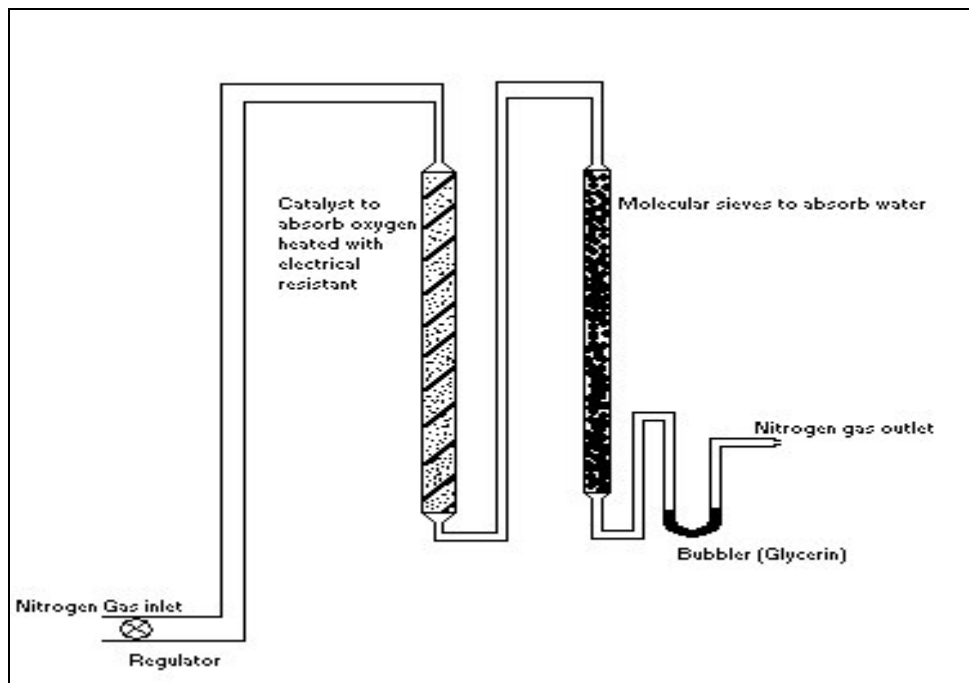


Figure 3.1. Nitrogen and Argon gas purification system.

For carrying out experiments with exclusion of air, the following techniques are generally employed;

- (1) vacuum line technique is used to get rid of the solvent by evaporation in vacuum. Solvent is trapped in a tube which is immersed into liquid nitrogen.
- (2) schlenk technique (Figure 3.2) in which a simple two-necked vessel designed to permit passage of a nitrogen stream through the narrow neck with the stopcock while using the wider neck without a stopcock for operations such as inserting a spatula for scraping or removal of material can be used. Depending on the objectives and the air sensitivity of the compounds, one technique or a combination of techniques are used. The thermal reactions were performed in a reaction flask with nitrogen connection.

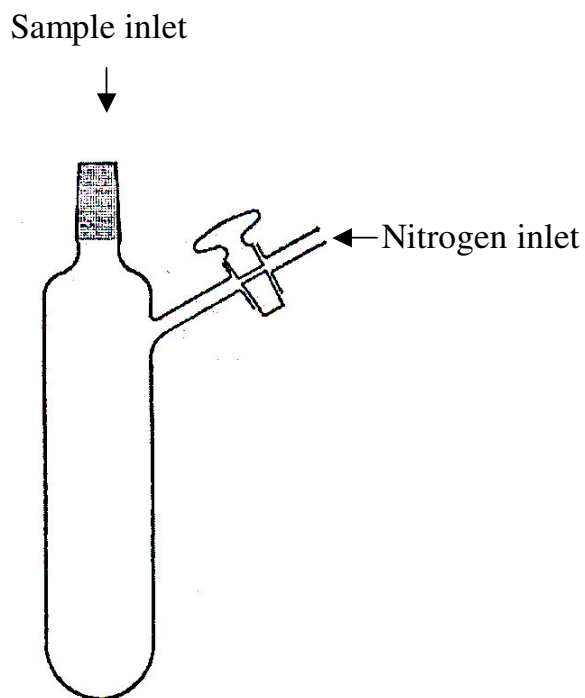


Figure 3.2 Standard schlenk tube

The photochemical reactions were performed in a special apparatus described in Figure 3.3. An ultraviolet lamp (b) (Hg-Tauchhlampe TQ 150, Quarzlampen GmbH, Hanau, West Germany) is immersed in the inner part (a). In order to carry out photochemical reactions, the solution is filled into the outer part (c) and cooled to the desired temperature by circulating precooled methanol through (d) to (e) then irradiated by the UV lamp.

Since the complexes are also sensitive towards temperature elevation, it is necessary to bear in mind the possible thermal instability of reactants and products and use mild temperatures. In order to do this, methanol precooled in a cryostat is circulated through cooling jackets of the reaction vessels.

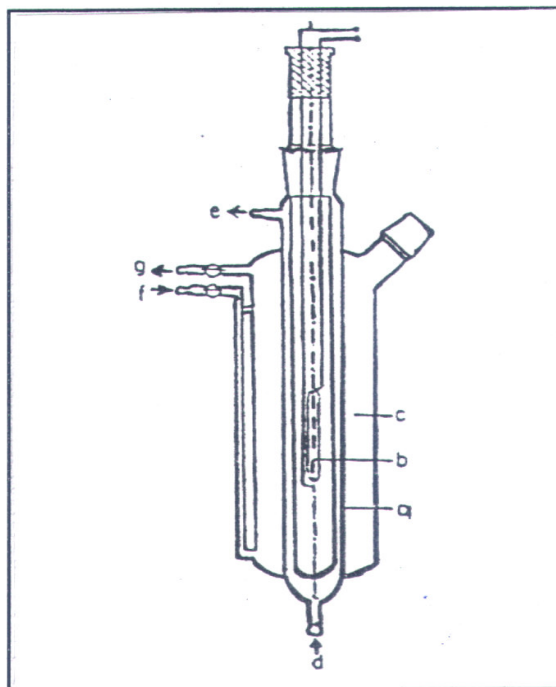


Figure.3.3 The Apparatus used for the photochemical reactions.

- a) inner part for the methanol circulation,
- b) Mercury lamp,
- c) Outer part for the solution,
- d) Precooled water inlet,
- e) Precooled water outlet,
- f) Nitrogen gas inlet,
- g) Nitrogen gas outlet.

Prepared complex is purified by recrystallization in a solvent at low temperature or by use of the column chromatography. The column is prepared with silicagel and it is eluted by a solvent. (Figure 3.4).

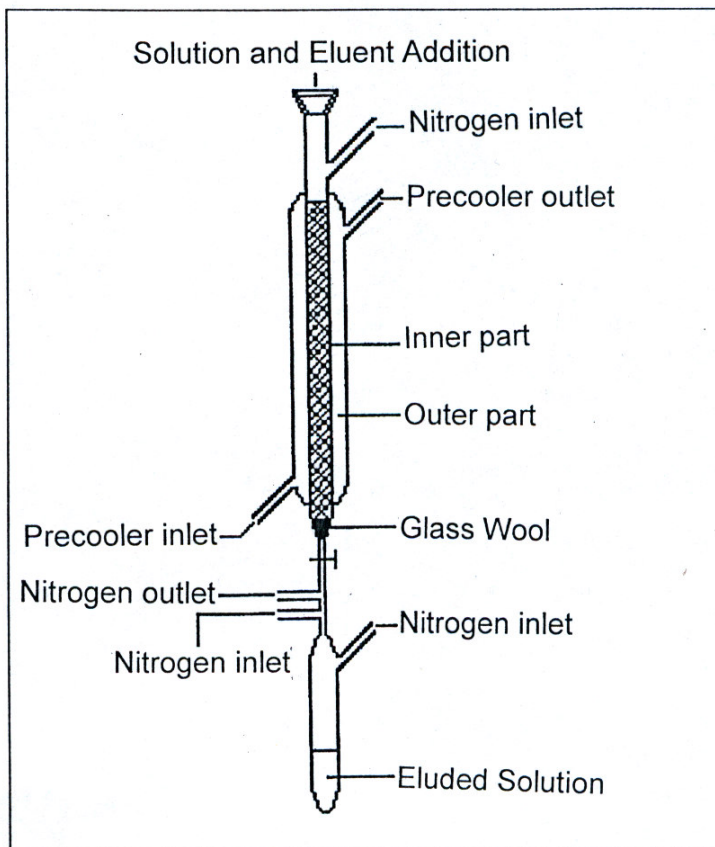


Figure 3.4. Standard Column for further purification.

Organometallic compounds also need a special filtration apparatus called inverse filtration (Figure 3.5) which is performed by using 100% pure polyethylene capillaries and cotton. The principle of it is the refreshment of a closed system that contains the solution with argon passed continuously. This causes the solution to be transferred from the capillary leaving insoluble impurities on the cotton, which had been inpinged into one end of the pure polyethylene capillary.

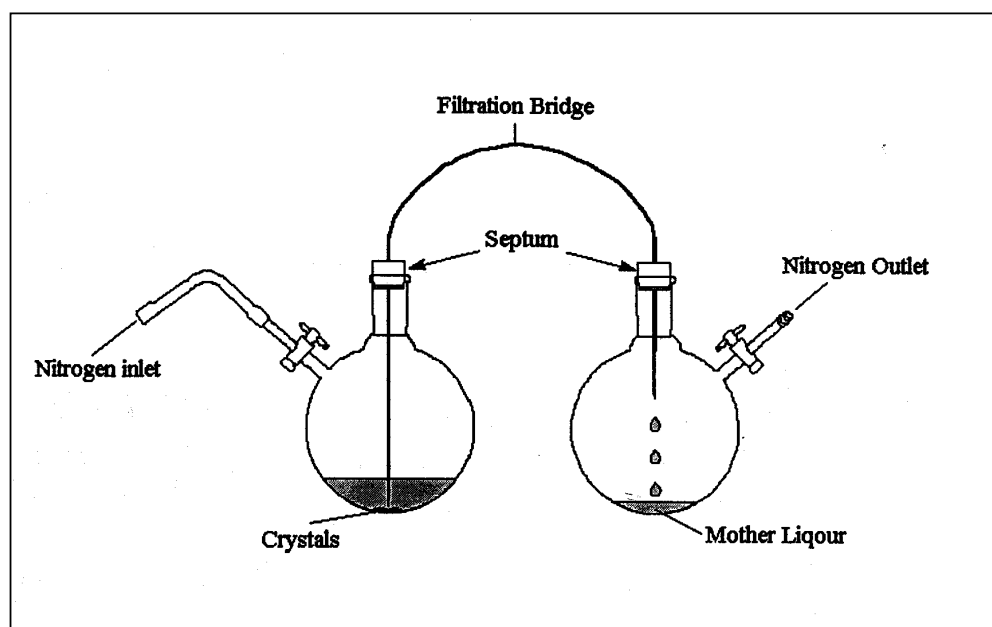


Figure 3.5. Inverse Filtration Apparatus.

Before using, solvents were purified by refluxing over metallic sodium or diphosphorous pentoxide (P_2O_5) under nitrogen for three to four days.

Hexacarbonyltungsten(0), $W(CO)_6$; trimethylphosphite, $P(OCH_3)_3$; pyrazine, (pyz) were purchased from Merk GMBH, Darmstadt, Germany, and used without further purification.

The photochemical and thermal reactions and other treatment of organometallic compounds such as purification and recrystallization were followed by IR spectra taken at various intervals.

3.2 Infrared Spectra

The synthesis of complexes and substitution reactions were followed by infrared spectroscopy. Several spectra were collected from tetrahydrofuran, n-hexane or dichloromethane solutions using Nicolet 510 FTIR Spectrometer with OMNIC software.

3.3. ^{13}C -NMR Spectra

^{13}C -NMR Spectrum of $\text{cis-W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz})$, was recorded from d-chloroform solution on a Bruker-Spectrospin, Avance, DPX400 Ultra Shield. NMR frequency 100 MHz at a field of 9.4 T

3.4. ^1H -NMR Spectra

^1H -NMR spectrum of product $\text{cis-W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz})$, was taken from its d-chloroform solution on a Bruker-Spectrospin, Avance, DPX400 Ultra Shield. NMR frequency is 400 MHz at a field of 9.4 T and the computer software is Xwin-NMR.

3.5. $^{31}\text{P}\{-^1\text{H}\}$ -NMR Spectra

The ^{31}P -NMR spectrum of the complex was recorded from its d-chloroform solution by using the same instrument and software as in ^1H -NMR spectra. NMR frequency is 161 MHz at a field of 9.4 T ^{31}P -NMR spectra. Proton broad-band decoupling technique was used to simplify the spectra complicated due to ^{31}P - ^1H couplings. The chemical shift values were given relative to phosphoric acid which has been used as an internal reference in capillary.

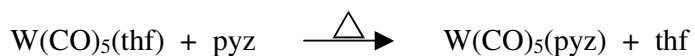
3.6. Mass Spectra

Mass spectrum of cis-W(CO)₄[P(OCH₃)₃](pyz) was taken on a Fisons VG Autospec with m-nitrobenzylalcohol as matrix for FAB+MS. Since many transition-metal organometallic compounds are appreciably volatile, mass spectrometry technique is a very powerful analytical technique that is used to identify unknown compounds, to quantify known compounds, and to elucidate the structure from the fragmentation pattern.

3.7. Synthesis of Complexes

3.7.1. Synthesis of Pentacarbonylpyrazinetungsten(0), W(CO)₅(pyz)

Pentacarbonylpyrazinetungsten(0), W(CO)₅(pyz),²⁴ was prepared from thermal substitution reaction of pentacarbonyltetrahydrofuran tungsten(0), W(CO)₅(thf),²⁹ photogenerated by UV irradiation of hexacarbonyltungsten(0), W(CO)₆, in tetrahydrofuran (thf) at 10°C. 1.0 g (2.84 mmol) W(CO)₆ was irradiated in 250 mL thf for one hour until the peaks of W(CO)₆ disappeared. The orange-yellow solution of pentacarbonyltetrahydrofuran tungsten(0), W(CO)₅(thf), which was stable only in solution, was mixed with two fold excess pyrazine (pyz) 0.454 g (5.68 mmol) for two hours at room temperature under an argon atmosphere. The color of the solution was turned from dark-orange to red which was a clear indication for exchange reaction of thf with pyrazine according to the following equation.



After the thf was removed under vacuum (-10⁻³ Bar), the product washed several times with n-hexane to remove unreacted W(CO)₆ and dried under vacuum (-10⁻³ Bar) (Yield = 93 % for W(CO)₅(pyz). Since the complex was unavoidably contaminated with bimetallic complex, (CO)₅W(pyz)W(CO)₅, which could not be differentiated in solution by means of IR spectroscopy, there exist two complex as at

equilibrium. Both of them would be characterized by IR, NMR and MS. $\text{W(CO)}_5(\text{pyz})$, IR (CH_2Cl_2): $\nu(\text{CO})$; 2069 cm^{-1} , 1941 cm^{-1} , and 1912 cm^{-1} . (Figure 3.6); Molecular peak (m/z) = 404; ^{13}C -NMR (d-acetone) δ = 202.99 ppm (CO (trans), s), 199.17 ppm (CO (cis), s, $J(^{183}\text{W}-^{13}\text{C}) = 131.1\text{ Hz}$), 151.40 ppm (C (2,6), s), 148.30 ppm (C (3,5), s); ^1H -NMR (d-acetone) δ = 9.07 ppm (H (2,6), s), 8.74 ppm (H (3,5), s). $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$, ^{13}C -NMR (d-acetone) δ = 203.08 ppm (CO(trans), s), 198.86 ppm (CO(cis), s, $J(^{183}\text{W}-^{13}\text{C}) = 130.8\text{ Hz}$), 153.27 ppm (C (coordinated side of pyrazine), s); ^1H -NMR (d-acetone) δ = 9.10 ppm. (Figure 3.7).

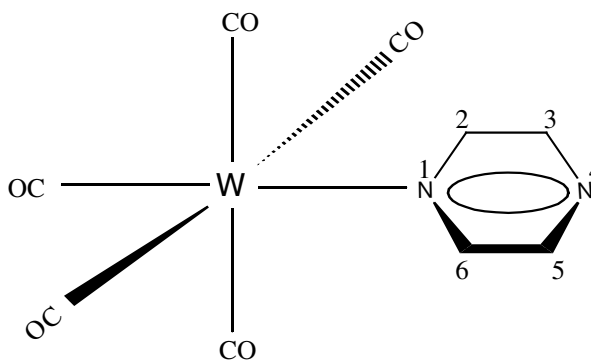


Figure 3.6. The structure of $\text{W(CO)}_5(\text{pyz})$

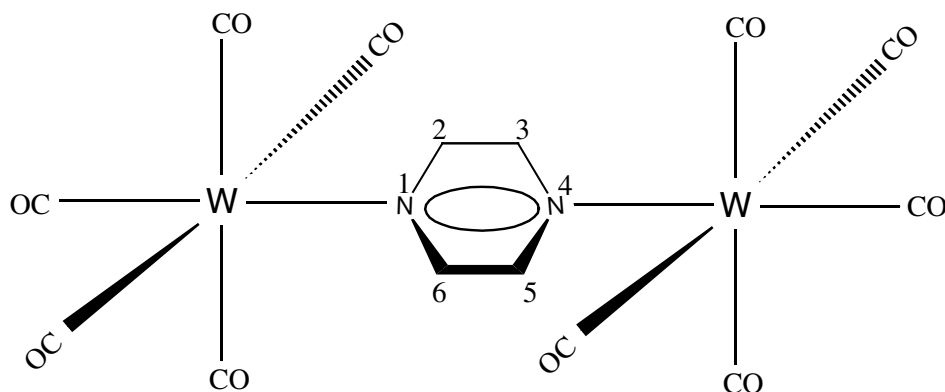


Figure 3.7. The structure of $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$

3.7.2. Synthesis of cis-tetracarbonylbis(pyrazine)tungsten(0), cis-W(CO)₄(pyz)₂

The cis-tetracarbonylbis(pyrazine)tungsten(0), cis-W(CO)₄(pyz)₂ was prepared from the thermal substitution reaction of cis-tetracarbonylbis(piperidine)tungsten(0), cis-W(CO)₄(pip)₂ in dichloromethane at 38°C. The cis-tetracarbonylbis(piperidine)tungsten(0) complex was prepared from hexacarbonyltungsten(0), W(CO)₆, and piperidine (pip) as described in the literature.³⁰ 2 g of W(CO)₆ (5.68 mmol) and 5 mL of piperidine (50.6 mmol) was refluxed at 160°C in 60 mL of decahydronaphthalene (decaline) for 24 hours. After decaline was decanted, the yellow precipitate was washed with n-hexane and dried under vacuum to yield desired product cis-W(CO)₄(pip)₂. (Yield = 76%, 1.525 g (4.33 mmol)). A suspension of cis-W(CO)₄(pip)₂ 0.3 g (0.80 mmol) in methylene chloride, CH₂Cl₂ (25 mL) refluxed with three fold pyrazine (0.190 g, 2.4 mmol) at 38°C for six hours. As the exchange reaction proceeded, the solution turned from yellow to red. The course of the reaction was followed by taking the IR spectrum of the solution in every 15 minutes. After reflux period was over, the red solution containing cis-W(CO)₄(pyz)₂ complex was transferred into another schlenk tube by using inverse filtration method. The solvent was evaporated under vacuum till 2 mL solution was left. In order to start the crystallization, 2mL n-hexane was added. Cooling the solution in the deep freeze for one day yields red crystals of cis-W(CO)₄(pyz)₂ (Figure 3.8) which was separated from the supernatant liquid by decantation and dried under vacuum in ice-bath. Due to the instability of the complex in solution at room temperature, the complex was identified only by taking the IR spectrum in solution. IR (CH₂Cl₂); $\nu(\text{CO})$; 2007 cm⁻¹, 1922 cm⁻¹, 1875 cm⁻¹, and 1835 cm⁻¹.

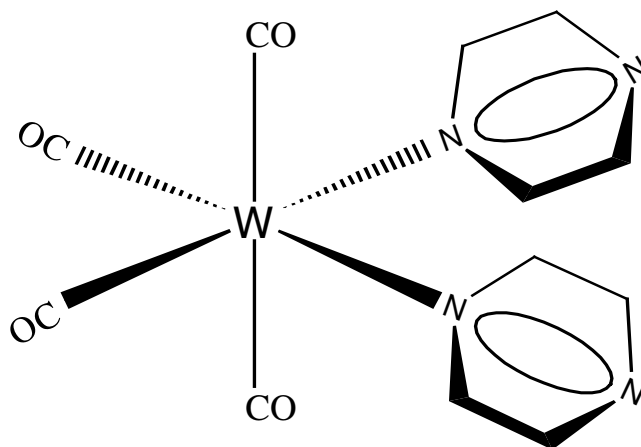


Figure 3.8. The structure of $\text{cis-W(CO)}_4(\text{pyz})_2$

3.7.3. Synthesis of tetracarbonyltrimethylphosphitepyrazinetungsten(0), $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$

2.0 g (5.68 mmol) W(CO)_6 was irradiated in 250 mL tetrahydrofuran (thf) in a special apparatus described in experimental part (Figure 3.3) for one hour until the peaks of W(CO)_6 disappeared. The orange-yellow solution of $\text{W(CO)}_5(\text{thf})$ was mixed with 1.34 mL (11.4 mmol) trimethylphosphite, $\text{P(OCH}_3)_3$ overnight and isolated as colorless solid. (Yield = 71%, 1.42 g). The resulting pentacarbonyltrimethylphosphitetungsten(0), $\text{W(CO)}_5[\text{P(OCH}_3)_3]$, (0.60 g, 1.34 mmol) was further irradiated in 250 mL thf which gave $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{thf})$, an intermediate complex, stable in solution. Upon addition of 1.5 fold excess (0.161 g, 2.01 mmol) pyrazine (pyz), the color of the solution was turned from dark-orange to red which was a clear indication for the exchange reaction of thf with pyrazine. After removal of the solvent completely, the remaining solid was dissolved in n-hexane and the column chromatography was done on a column (20 cm length, 3 cm diameter) packed with silica gel in toluene. The red complex was eluted with toluene. Then, the solution was brought to dryness in vacuum. The red oil-like residue was

dissolved in n-hexane and solution was cooled down to -78°C overnight. The red precipitate was separated from the supernatant solution by decantation, then dried under vacuum. (Figure 3.9). (Yield = 10%, 0.06 g) IR (n-hexane); $\nu(\text{CO})$; 2024 cm^{-1} , 1929 cm^{-1} , 1901 cm^{-1} and 1887 cm^{-1} ; Molecular peak (m/e) : 499; ^{13}C -NMR (d-chloroform); $\delta = 202.52\text{ ppm}$ (CO (1,2), d, $J(^{31}\text{P}-^{13}\text{C}) = 10.9\text{ Hz}$), 206.48 ppm (CO (3), d, $J(^{31}\text{P}-^{13}\text{C}) = 51.2\text{ Hz}$), 207.59 ppm (CO (4), d, $J(^{31}\text{P}-^{13}\text{C}) = 7.3\text{ Hz}$), 52.25 ppm ($-\text{OCH}_3$, d, $J(^{31}\text{P}-^{13}\text{C}) = 3.1\text{ Hz}$), 150.73 ppm (C (2,6), s, $J(^{31}\text{P}-^{13}\text{C}) = 2.2\text{ Hz}$), 146.38 ppm (C (3,5), s); ^1H -NMR (d-chloroform) $\delta = 8.78\text{ ppm}$ (H (2,6), s), 8.41 ppm (H (3,5), s), 3.55 , and 3.52 ppm ($-\text{OCH}_3$, d, $J(^{31}\text{P}-^1\text{H}) = 11.2\text{ Hz}$); ^{31}P -NMR (d-chloroform) $\delta = 148.09\text{ ppm}$ ($\text{P}(\text{OCH}_3)_3$, s, $J(^{183}\text{W}-^{31}\text{P}) = 392\text{ Hz}$).

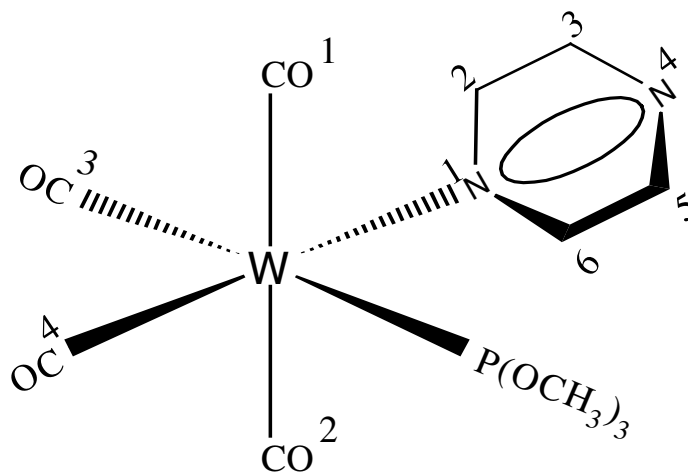


Figure 3.9. The structure of $\text{cis-W(CO)}_4[\text{P}(\text{OCH}_3)_3](\text{pyz})$

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Pentacarbonylpyrazinetungsten(0), $\text{W(CO)}_5(\text{pyz})$:

The pentacarbonylpyrazinetungsten(0), $\text{W(CO)}_5(\text{pyz})$, complex was prepared starting with hexacarbonyltungsten(0) and pyrazine by using the literature procedure.²⁴ The product was purified by recrystallization and characterized by means of IR, ^1H and ^{13}C -NMR spectroscopies.

The infrared spectrum of the $\text{W(CO)}_5(\text{pyz})$ complex shows three prominent bands for CO stretching at 2069, 1941 and 1912 cm^{-1} (Figure 4.1). The observation of a three-band pattern for the CO stretching indicates that the W(CO)_5 moiety of the complex has a C_{4v} symmetry with vibrational modes of $2\text{A}_1 + \text{B}_1 + \text{E}$. The B_1 mode is IR inactive while the A_1 and E modes are IR active.³¹ The low intensity band at 2069 cm^{-1} is assigned to the $\text{A}_1^{(1)}$ mode of the in-phase symmetric stretching of the five CO ligands (Figure 4.2). The shoulder band at 1912 cm^{-1} can be ascribed to the other $\text{A}_1^{(2)}$ mode of the out-of-phase symmetric stretching of the five CO ligands. The intense band at 1941 cm^{-1} is the E mode of the pairwise out-of-phase asymmetric stretching of the equatorial CO ligands. The CO stretching vibrations are shown all together in Figure 4.2.

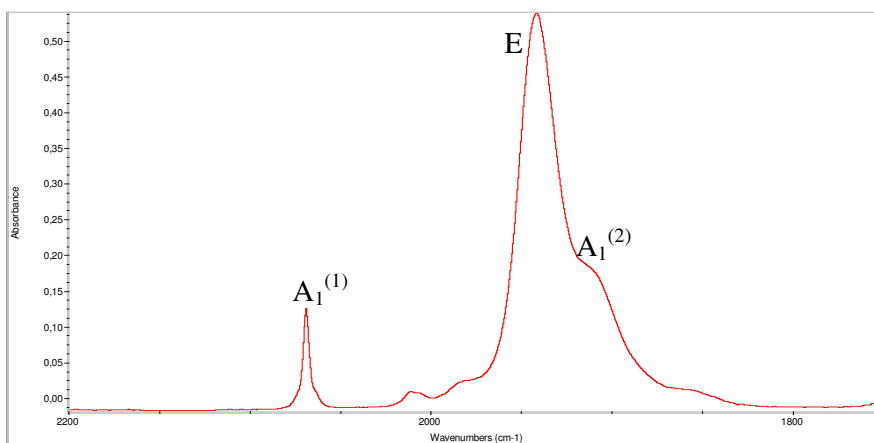


Figure 4.1. The CO-stretching region ($2200\text{--}1700\text{ cm}^{-1}$) of the IR spectrum of $\text{W(CO)}_5(\text{pyz})$ taken in CH_2Cl_2 solution

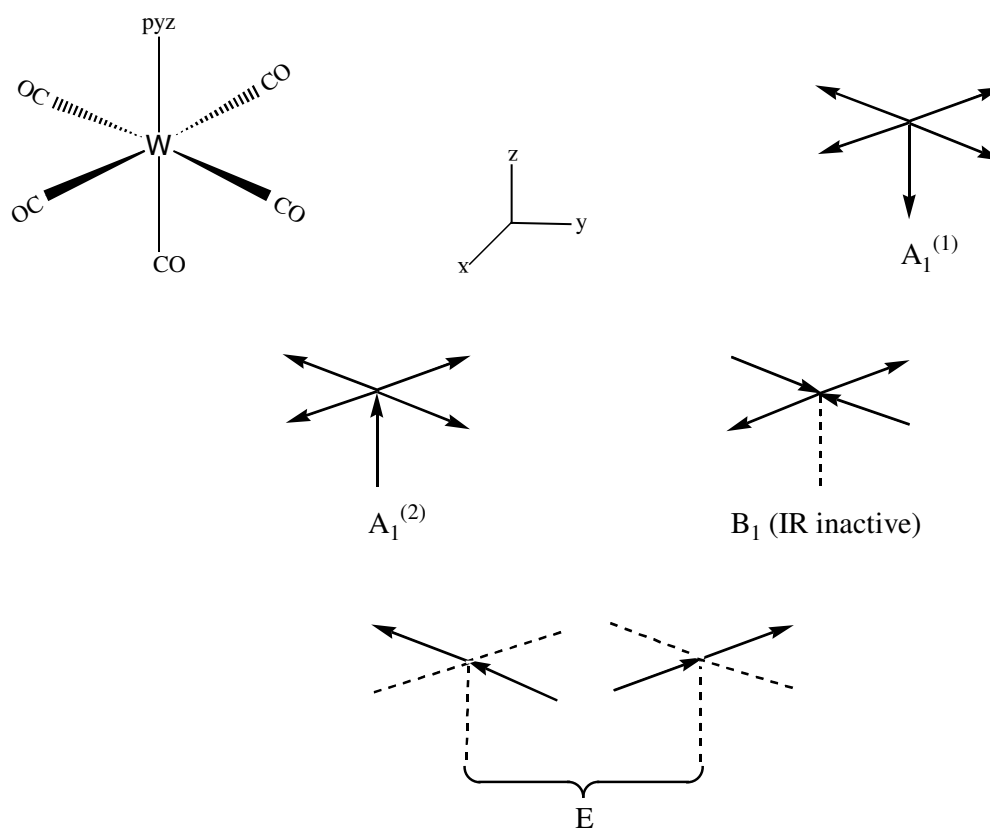


Figure 4.2. CO stretching vibrations of $\text{W(CO)}_5(\text{pyz})$ having the C_{4v} symmetry

A compelling evidence for the C_{4v} symmetry of the $W(CO)_5$ unit comes from the ^{13}C -NMR spectrum which gives two carbonyl signals at 202.99 and 199.17 ppm with an intensity ratio of 1:4. The ^{13}C -NMR signals of the carbonyl ligands are also expected to be affected from the $M \rightarrow N$ backbonding. The CO ligand trans to the pyrazine gives ^{13}C -NMR signal at lower magnetic field (higher chemical shift) than the cis ones do. This is a consequence of the known fact that the π -competition for the use of the metal d-orbitals between the two trans ligands is stronger than that of the two cis.³² The tungsten satellites could be observed only for the intense signal at 199.17 ppm. The $J(^{183}W-^{13}C)$ coupling constant is 131.1 Hz for the four equatorial carbonyl carbon atoms. The tungsten satellite for the signal at 202.99 is not observable, probably due to the low intensity.

The $^{13}C\{-^1H\}$ -NMR spectrum of the $W(CO)_5(pyz)$ complex also shows two signals for the carbon atoms of the pyrazine ligand (Figure 4.3). The signal at 151.40 ppm is readily assigned to the carbon atoms next to the nitrogen coordinated to the metal atom (The C2 and C6 carbon atoms). The signal at 148.30 ppm is assigned to the C3 and C5 carbon atoms of the pyrazine ligand coordinated to the metal atom through N1 nitrogen atom. Since the ^{13}C -NMR chemical shift of the free pyrazine molecule is 146.09 ppm, the signals of pyrazine ligand in the complex $W(CO)_5(pyz)$ are slightly shifted to lower magnetic field. The coordination shift is more pronounced for the C2, C6 carbon atoms ($\Delta\delta = 5.3$ ppm) than that for the C3, C5 carbon atoms. ($\Delta\delta = 2.2$ ppm). The coordination shift to the lower magnetic field indicates a reduction of electron density in the pyrazine molecule upon coordination to the transition metal. This implies on a stronger σ -donor ability of pyrazine rather than π -acceptor character.

The 1H -NMR spectrum of complex $W(CO)_5(pyz)$ shows two doublets at 9.07 and 8.74 ppm for the H2, H6 and H3, H5 hydrogen atoms, respectively (Figure 4.4). Since the pyrazine molecule has a chemical shift of 8.60 ppm, the both signals of the pyrazine ligand in the complex $W(CO)_5(pyz)$ are shifted to lower magnetic field upon coordination to the tungsten atom. The 1H -NMR coordination shift in the signal of the pyrazine ligand is also slightly more pronounced for the H2, H6 hydrogen

atoms than that for the H3, H5 hydrogen atoms ($\Delta\delta = 0.14$ ppm). Since the hydrogen atoms of the pyrazine ligand are pairwise different after coordination, their ^1H -NMR signals show splitting due to the spin-spin interaction. The coupling constants are $J(\text{H2-H3}) = J(\text{H5-H6}) = 3.0$ Hz, $J(\text{H2-H6}) = J(\text{H3-H5}) = 1.3$ Hz. The coupling constants are not large but observable if the spectrum is taken with high resolution.

The pentacarbonylpyrazinetungsten(0), $\text{W}(\text{CO})_5(\text{pyz})$ complex unavoidably contaminated with bimetallic complex, $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$, which could not be distinguished by means of IR spectroscopy. This latter complex gives the same CO stretching bands at 2069, 1941, and 1912 cm^{-1} as the $\text{W}(\text{CO})_5(\text{pyz})$ complex. The observation of three-band pattern for the CO stretching shows that the $\text{W}(\text{CO})_5$ moiety in the bimetallic complex has also C_{4v} symmetry with vibrational modes of $2\text{A}_1 + \text{B}_1 + \text{E}$. The B_1 mode is IR inactive while the two A_1 and E modes are IR active.

The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of the bimetallic complex, $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ also shows two signals with an intensity ratio of 1:4 like the monometallic complex at 203.08 and 198.86 ppm. The higher frequency signal is assigned to the carbonyl trans to the pyrazine ligand and the lower frequency signal to the CO groups cis to the pyrazine ligand.

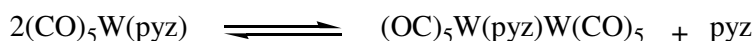
The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of the bimetallic complex, $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ gives only a signal for the carbon atoms of the pyrazine ligand at 153.27 ppm which appears to be slightly larger than the signal of the carbon atom at the coordinated side of the pyrazine ligand in the $\text{W}(\text{CO})_5(\text{pyz})$ complex. The ^{13}C -NMR signals of pyrazine ligand in the bimetallic complex are shifted to lower magnetic field when the complex binucleates. The coordination shift of the ^{13}C -NMR signals of pyrazine in the $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ complex is 7.2 ppm.

The ^1H -NMR spectrum of bimetallic complex $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ shows a singlet at 9.10 ppm close to the protons of coordinated side of pyrazine ligand in $\text{W}(\text{CO})_5(\text{pyz})$. Since the pyrazine molecule has a chemical shift of 8.60 ppm, the signal of the pyrazine ligand in the bimetallic complex $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ is

shifted to lower magnetic field upon coordination to the tungsten atoms. Table 4.1-4.2. lists the ^{13}C - and ^1H -NMR chemical shifts of the both complexes, $\text{W}(\text{CO})_5(\text{pyz})$ and $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$, for comparison.

One point that deserves attention is that the monometallic complex, $\text{W}(\text{CO})_5(\text{pyz})$, is unavoidably contaminated with the bimetallic $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ complex in solution which can not be differentiated by means of IR spectroscopy. However, both the ^{13}C - and ^1H -NMR spectra can easily be used to distinguish two complexes, as it can be realized in table 4.1-4.2.

Both the ^1H - and ^{13}C -NMR spectra of the complex freshly dissolved in d-acetone shows signals for the mononuclear complex $\text{W}(\text{CO})_5(\text{pyz})$, the dinuclear complex $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ and the free pyrazine molecule at the respective resonance frequencies given in table 4.1-4.2. The observation of all the three species in solution implies on the existence of an equilibrium. To test the hypothesis that these three species are at equilibrium, the free pyrazine molecule was added to the solution and the behaviour of the solution was followed by taking ^1H - and ^{13}C -NMR spectra (Figure 4.5). Both NMR spectra show that the concentration of the complex $\text{W}(\text{CO})_5(\text{pyz})$ increases while the concentration of the bimetallic complex $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ decreases upon addition of the free pyrazine into the solution. This observation indicates clearly the existence of the following equilibrium:



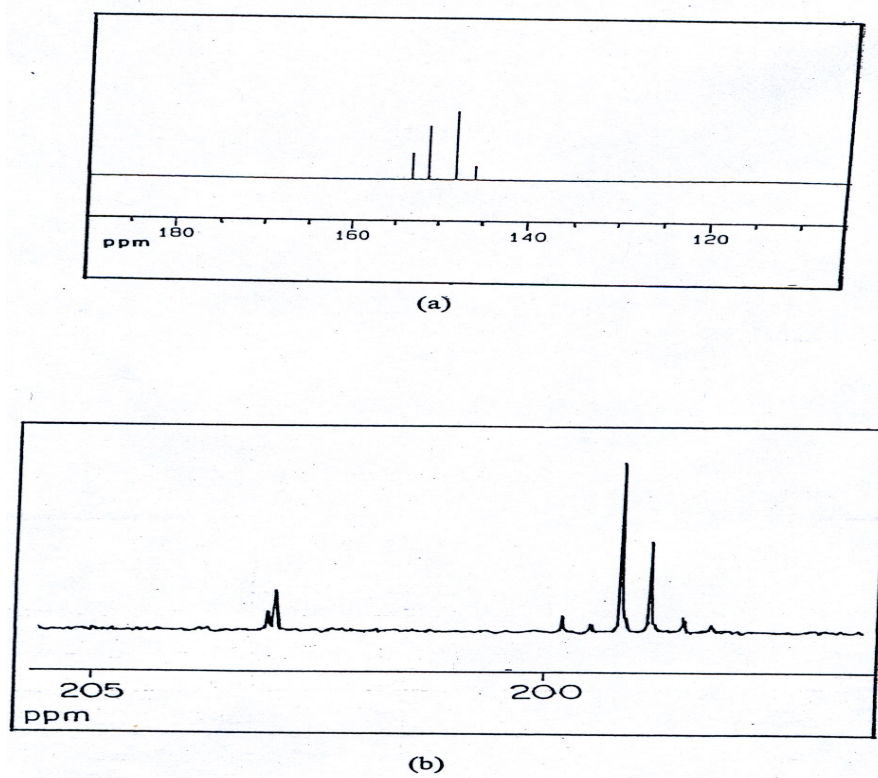


Figure 4.3. ^{13}C -NMR Spectrum of $\text{W}(\text{CO})_5(\text{pyz})$

(a) Carbon atoms of pyrazine

(b) $\text{W}(\text{CO})_5$ moiety

Table 4.1. ^{13}C -NMR Chemical Shifts (ppm) of $\text{W}(\text{CO})_5(\text{pyz})$ and $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ taken in d-acetone.

	$\text{W}(\text{CO})_5(\text{pyz})$	$(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$
CO (trans)	202.29	203.08
CO (cis)	199.17	198.86
Coordinated side of pyrazine	151.40	153.27
Non-coordinated side of pyrazine	148.30	-
Free pyrazine	146.09	146.09

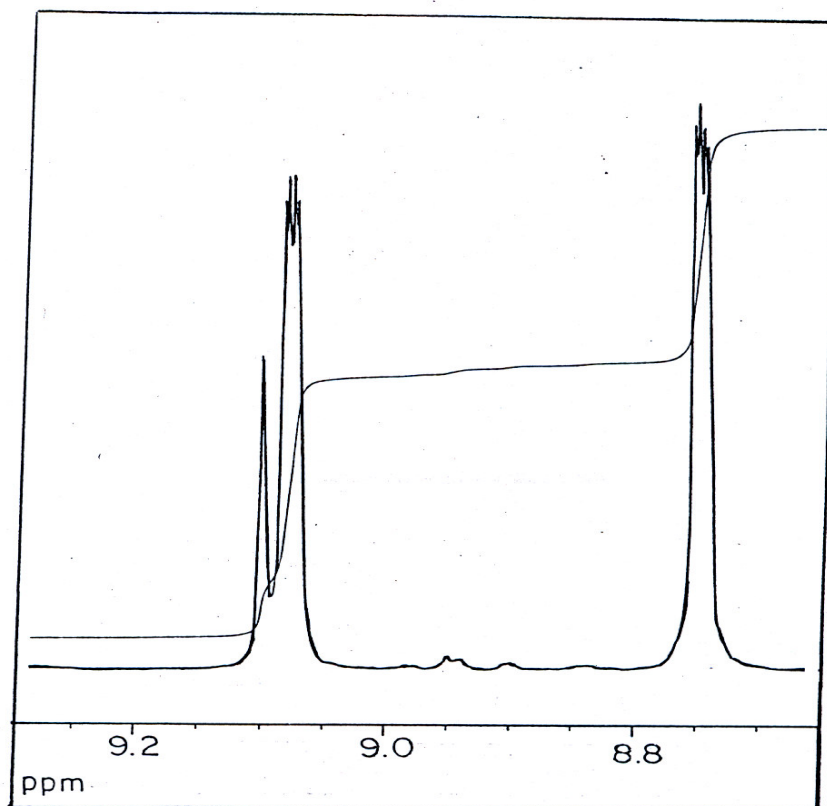


Figure 4.4. ^1H -NMR spectrum of $\text{W(CO)}_5(\text{pyz})$.

Table 4.2. ^1H -NMR Chemical Shifts (ppm) of $\text{W(CO)}_5(\text{pyz})$ and $(\text{CO})_5\text{W}(\text{pyz})\text{W(CO)}_5$ taken in d-acetone.

	$\text{W(CO)}_5(\text{pyz})$	$(\text{CO})_5\text{W}(\text{pyz})\text{W(CO)}_5$
Coordinated side of pyrazine	9.07	9.10
Non-coordinated side of pyrazine	8.74	-
Free pyrazine	8.60	8.60

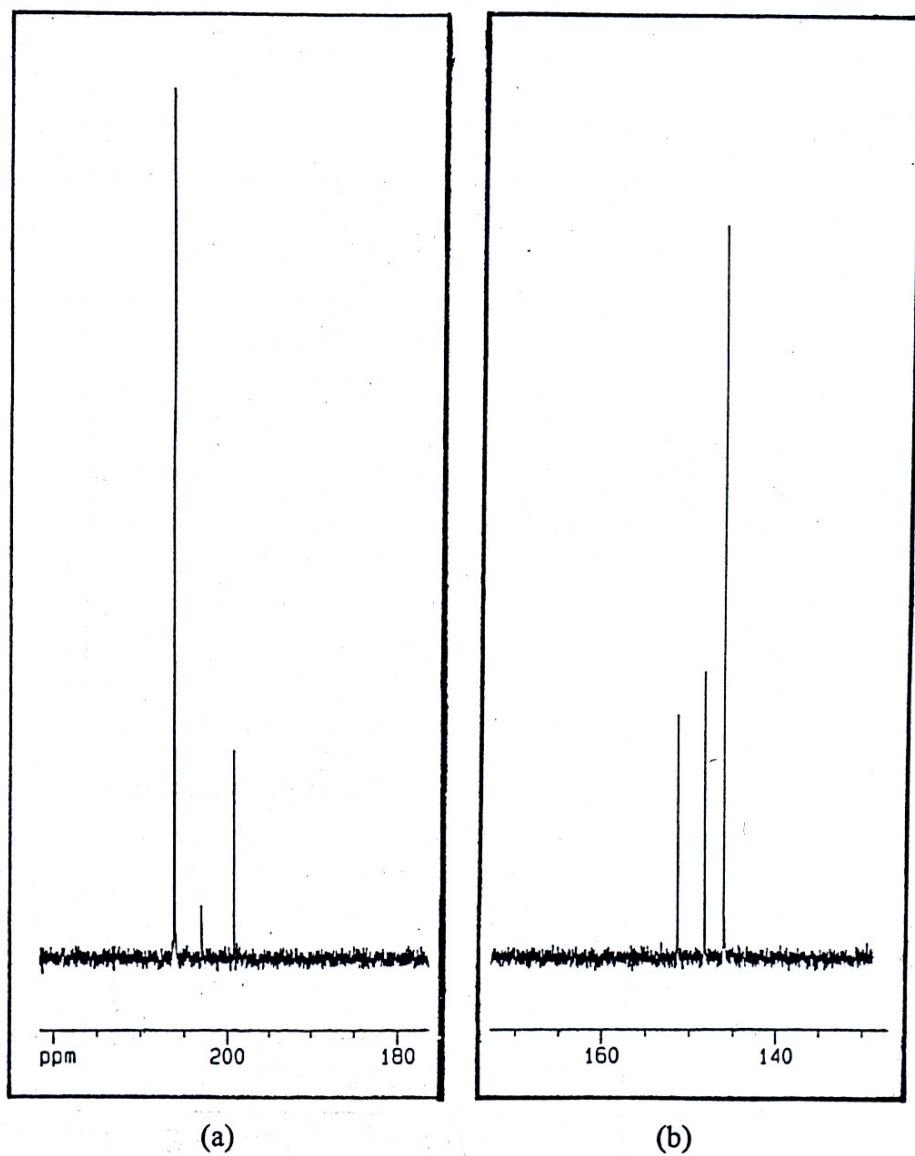


Figure 4.5. ^{13}C -NMR spectrum of $\text{W(CO)}_5(\text{pyz})$ in the presence of excess pyrazine
(a) W(CO)_5 moiety
(b) Carbon atoms of pyrazine

The comparison of Figure 4.3 and 4.5 illustrates the effect of adding the free pyrazine molecule into the solution on the equilibrium composition. Figure 4.3 shows the ^{13}C -NMR spectrum taken from the solution freshly prepared by dissolving the complex. This spectrum has the signals of all the three species at equilibrium. The ^{13}C -NMR spectrum taken from the same solution after addition of the free pyrazine shows essentially the signals of the monometallic complex $\text{W}(\text{CO})_5(\text{pyz})$ and the free pyrazine molecule, but no signals of the bimetallic complex $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$. (Figure 4.5). A similar effect is also observed in ^1H -NMR spectrum. The ^1H -NMR spectra can be used for the quantification of the relative concentrations of the species at equilibrium and, thus, for the determination of the equilibrium constant. The equilibrium constant was determined from the ^1H -NMR spectra taken from the solution of the complex after addition of various amount of the free pyrazine molecule. The calculation given below:

Table 4.3. The equilibrium concentrations of the three species from which the equilibrium constant was calculated. The mean value of the equilibrium constant is 0.040 (4.0×10^{-2}).

Spectrum	[Pyz] (μM)	$[(\text{CO})_5\text{W}(\text{pyz})]$ (μM)	$[(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5]$ (μM)	(K_{eq})
1	0.0139	0.0770	0.0139	0.0326
2	0.0572	0.0958	0.0075	0.0466

Spectrum 1 (in the absence of added pyrazine)

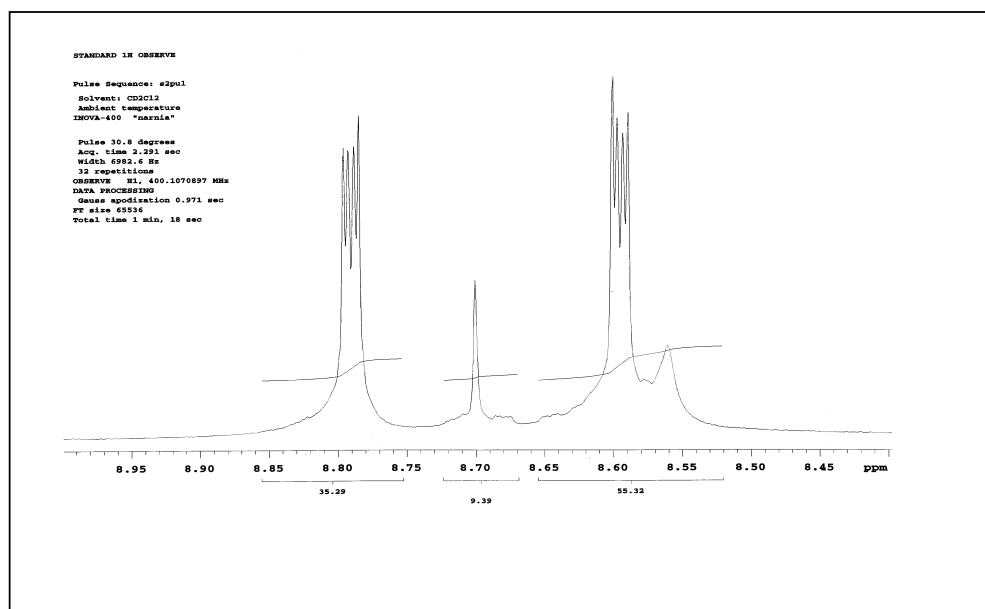


Figure 4.6. ^1H -NMR spectrum of the complex without adding the free pyrazine molecule into the solution

The solution was prepared by dissolving 21.2 mg of the complex in 0.5 mL dichloromethane- d_2 . No free pyrazine was added into the solution. The areas under the peaks were measured by taking the integral as follows:

	Integral
$(\text{CO})_5\text{W}(\text{pyz})$	35.3 for 2 H
$(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$	9.39 for 4 H

Dissociated fraction of $(\text{CO})_5\text{W}(\text{pyz})$ $= \left(\frac{9.39}{2 \times 35.3} \right) \times 2 = 0.266$

The number of μ moles of

$(\text{CO})_5\text{W}(\text{pyz})$ $= \left(\frac{21.2 \text{ mg}}{404 \text{ mg/mmol}} \right) \times \left(1000 \frac{\mu\text{mol}}{\text{mmol}} \right) = 52.5 \mu\text{mol}$

The concentration of the monometallic complex $\text{W}(\text{CO})_5(\text{pyz})$:

$[(\text{CO})_5\text{W}(\text{pyz})]$ $= \left(\frac{52.5 \mu\text{mol} \times (1 - 0.266)}{0.5 \text{ mL} \times 1000} \right) = 0.077 \mu\text{M}$

The concentration of the free pyrazine molecule:

$[\text{pyz}]$ $= \left[\frac{52.5 \mu\text{mol} \times \left(\frac{0.266}{2} \right)}{0.5 \text{ mL} \times 1000} \right] = 0.0139 \mu\text{M}$

The concentration of the bimetallic complex $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$:

$[(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5]$ $= \left[\frac{52.5 \mu\text{mol} \times \left(\frac{0.266}{2} \right)}{0.5 \text{ mL} \times 1000} \right] = 0.0139 \mu\text{M}$

The equilibrium constant:

K_{eq} $= \frac{[(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5] \times [\text{pyz}]}{[(\text{CO})_5\text{W}(\text{pyz})]^2} = \left[\frac{0.0139 \times 0.0139}{(0.0777)^2} \right] = 0.0326$

Spectrum 2 (in the presence of 0.52 fold excess pyrazine)

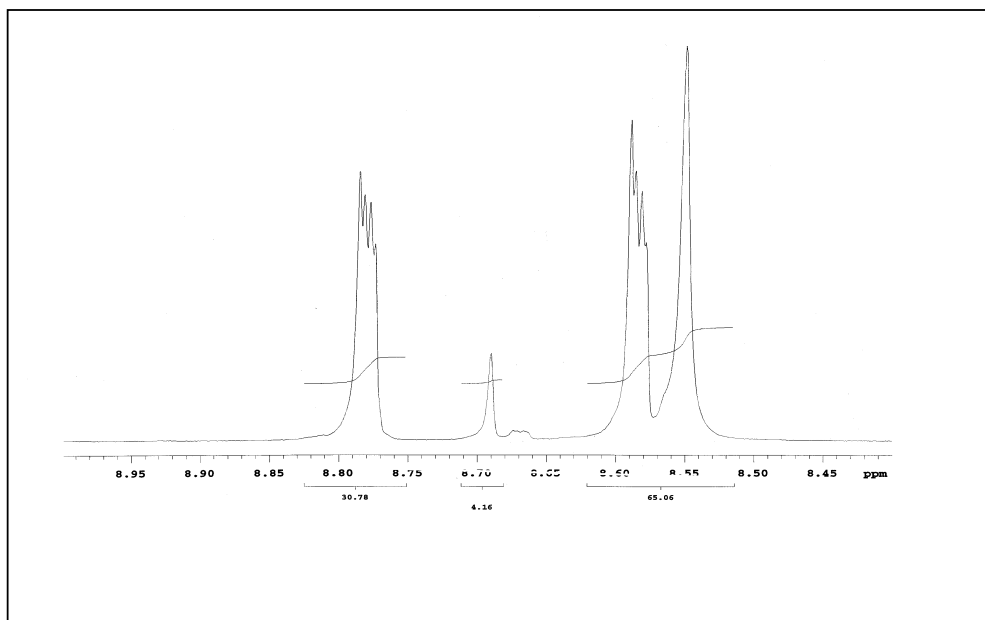


Figure 4.7. ^1H -NMR spectrum of the complex by addition of 2.0 mg of the free pyrazine molecule into the solution.

The solution was prepared by dissolving 22.4 mg of the complex in 0.5 mL dichloromethane- d_2 . The 2.0 mg free pyrazine was added into the solution. The areas under the peaks were measured by taking the integral as follows:

	Integral
$(\text{CO})_5\text{W}(\text{pyz})$	30.78 for 2 H
$(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$	4.16 for 4 H

Dissociated fraction of $(\text{CO})_5\text{W}(\text{pyz})$ $= \left(\frac{4.6}{2 \times 30.8} \right) \times 2 = 0.135$

The number of μ moles of $(\text{CO})_5\text{W}(\text{pyz})$ $= \left(\frac{22.4 \text{ mg}}{404 \text{ mg/mmol}} \right) \times \left(1000 \frac{\mu\text{mol}}{\text{mmol}} \right) = 55.4 \mu\text{mol}$

The concentration of the monometallic complex $\text{W}(\text{CO})_5(\text{pyz})$:

$$[(\text{CO})_5\text{W}(\text{pyz})] = \left(\frac{55.4 \mu\text{mol} \times (1 - 0.135)}{0.5 \text{ mL} \times 1000} \right) = 0.0958 \mu\text{M}$$

The concentration of the free pyrazine molecule:

$$[\text{pyz}] = \left[\frac{\left[55.4 \mu\text{mol} \times \left(\frac{0.135}{2} \right) \right] + \left[\left(\frac{2.0 \text{ mg}}{80.09 \text{ mg/mmol}} \right) \times 1000 \frac{\mu\text{mol}}{\text{mmol}} \right]}{0.5 \text{ mL} \times 1000} \right]$$

$$= 0.0572 \mu\text{M}$$

The concentration of the bimetallic complex $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$:

$$[(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5] = \left[\frac{55.4 \mu\text{mol} \times \left(\frac{0.135}{2} \right)}{0.5 \text{ mL} \times 1000} \right] = 0.0075 \mu\text{M}$$

The equilibrium constant:

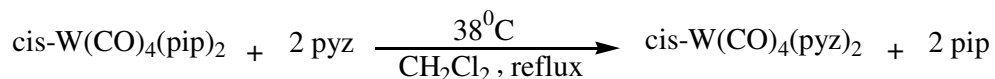
$$\mathbf{K_{eq}} = \frac{[(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5] \times [\text{pyz}]}{[(\text{CO})_5\text{W}(\text{pyz})]^2} = \left[\frac{0.00748 \times 0.0572}{(0.0958)^2} \right] = 0.0466$$

$$\mathbf{K_{eq(av)}} = \left(\frac{\mathbf{K_{eq}(1)} + \mathbf{K_{eq}(2)}}{2} \right) = \left(\frac{0.0326 + 0.0466}{2} \right) = 0.0396$$

4.2. Attempts to prepare cis-tetracarbonylbis(pyrazine)tungsten(0), cis-W(CO)₄(pyz)₂

Complexes containing two pyrazine ligands are of interest for testing whether the introduction of a second pyrazine molecule may affect the stability of carbonyl-pyrazine-tungsten(0) complexes. Therefore, many attempts were made for preparation of the tetracarbonylbis(pyrazine)tungsten(0) complex. For this purpose, the known W(CO)₄-transfer reagents were employed. Neither tetracarbonyl($\eta^{2:2}$ -norbornadiene)tungsten(0) nor tetracarbonyl($\eta^{2:2}$ -1,5-cyclooctadiene)tungsten(0) gives any substitution in toluene or dichloromethane. At temperatures above 60°C, both complexes give hexacarbonyltungsten(0) as the sole product, probably of decomposition.

Tetracarbonylbis(piperidine)tungsten(0), which has been known to be a good W(CO)₄-transfer reagent,³³ appears to be a suitable starting material for the preparation of tetracarbonylbis(pyrazine)tungsten(0). A suspension of tetracarbonylbis(piperidine)tungsten(0) in dichloromethane reacts with pyrazine, whereby the piperidine ligands are replaced by pyrazine forming the tetracarbonylbis(pyrazine)tungsten(0) according to the equation:



pip: piperidine

Tetracarbonylbis(pyrazine)tungsten(0) is soluble in dichloromethane. Therefore, the yellow suspension turns to the red colour solution when the reaction is completed. The reaction could be followed by taking the IR spectra (Figure 4.8), since the tetracarbonylbis(piperidine)tungsten(0) is not soluble in dichloromethane, no absorption bands is observed for the CO-stretching in the IR spectrum at the beginning of the reaction (Figure 4.8.a). As the reaction proceeds four absorption bands grow in. These absorption bands at 2008 cm⁻¹, 1924 cm⁻¹, 1876 cm⁻¹ and 1837

cm^{-1} are assigned to the tetracarbonylbis(pyrazine)tungsten(0) (Figure 4.8.b). The observation of four absorption bands for the CO-stretching indicates that the tetracarbonylbis(pyrazine)tungsten(0) complex has a cis arrangement for the $\text{W}(\text{CO})_4$ moiety, thus, the complex has the $\text{cis-W}(\text{CO})_4(\text{pyz})_2$ formula. The molecule has a C_{2v} symmetry with the $2\text{A}_1+\text{B}_1+\text{B}_2$ CO-stretching modes (Figure 4.9). One of the A_1 bands is designated as $\text{A}_1^{(1)}$ and the other $\text{A}_1^{(2)}$. The strongest intensity band can be ascribed to the B_1 , the out of phase asymmetric stretching of the axial CO's. $\text{A}_1^{(2)}$ mode at 1924 cm^{-1} is most probably the out-of-phase symmetric stretching of the four CO ligands (two carbonyl group stretching and two carbonyl groups are contracting).³⁴ The highest frequency CO band is the $\text{A}_1^{(1)}$ mode of in-phase stretching vibration of all the CO's make the band much more intense relative to $\text{A}_1^{(2)}$. The shoulder with lower frequency is recognized as B_2 , belonging to the out-of-phase asymmetric stretching vibration of the equatorial CO ligands.

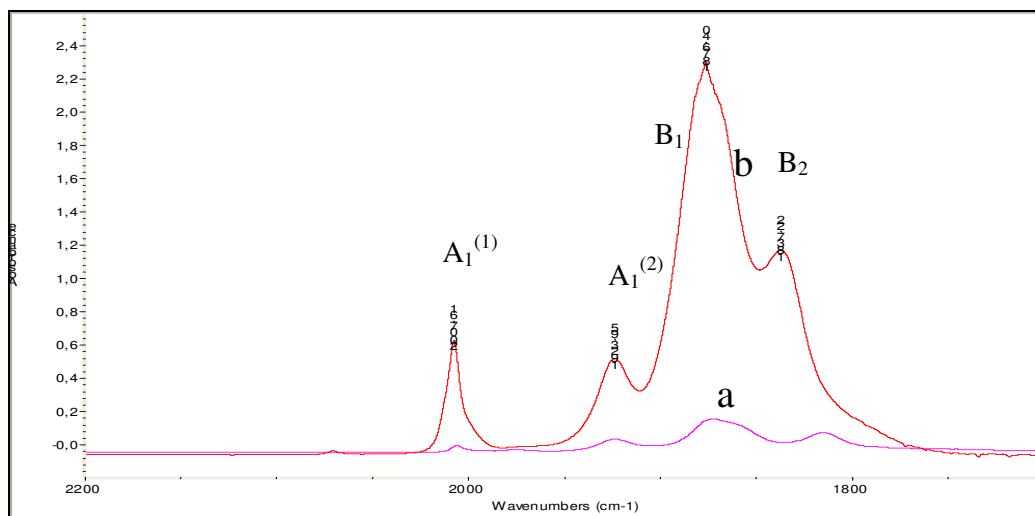


Figure 4.8. The CO stretching region ($2200\text{-}1700 \text{ cm}^{-1}$) of the IR spectra of $\text{cis-W}(\text{CO})_4(\text{pyz})_2$ taken in CH_2Cl_2 :

- a) after 15 minutes stirring (The starting complex, $\text{cis-W}(\text{CO})_4(\text{pip})_2$ is not soluble enough in CH_2Cl_2 , so the peaks can not be observed).
- b) after 6 hours stirring

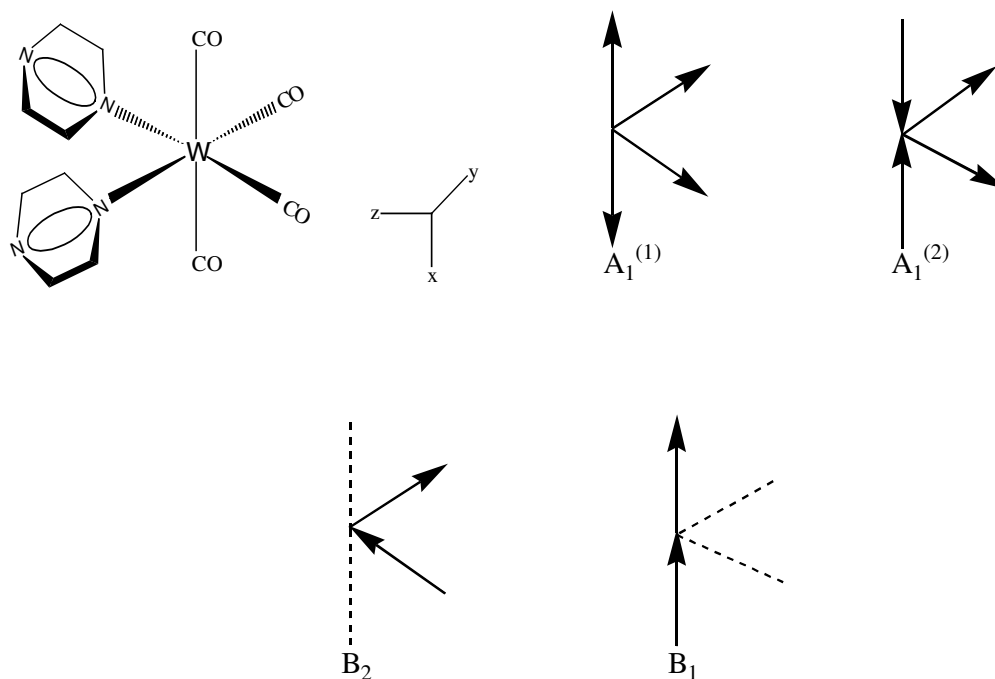
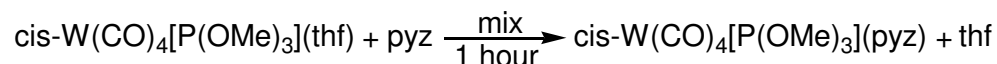
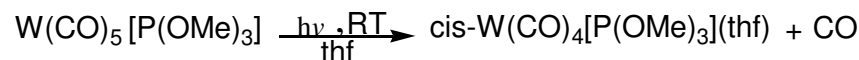
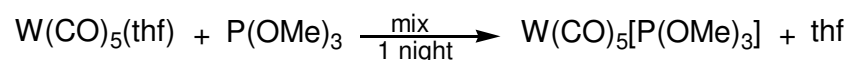
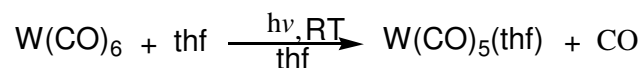


Figure 4.9. CO stretching vibrations of $\text{cis-W(CO)}_4(\text{pyz})_2$ ³⁵

$\text{Cis-W(CO)}_4(\text{pyz})_2$ complex could be generated from the thermal substitution reaction of $\text{cis-W(CO)}_4(\text{pip})_2$ with pyrazine, as determined by the IR spectra taken from the solution. However, this complex could not be isolated from the reaction solution. Both the chromatographic separation and the crystallization failed in obtaining the complex in solid form. The IR spectra taken at various stages of the manipulation show that the complex is not stable and decomposes. The instability of $\text{cis-W(CO)}_4(\text{pyz})_2$ complex is found to be much higher compared to $\text{W(CO)}_5(\text{pyz})$. This obviously shows the weak π accepting ability of pyrazine ligand compared to carbonyl ligand.

4.3. Tetracarbonyltrimethylphosphitepyrazinetungsten(0), cis-W(CO)₄[P(OCH₃)₃](pyz)

It is known that the presence of a donor ligand can affect the metal ligand bonding in the complex sterically as well as electronically. Therefore, we thought that the introduction a donor ligand may increase the stability of the metal-pyrazine bond. A donor ligand makes the metal center electron rich and, hence, increase the back-donation from metal to pyrazine ligand. For this purpose, cis-W(CO)₄[P(OCH₃)₃](pyz), was synthesized, isolated and fully characterized. The complex was prepared starting with hexacarbonyltungsten(0) according to the following reaction scheme:



First, W(CO)₅[P(OCH₃)₃] was prepared from the thermal substitution of W(CO)₅(thf), photogenerated in tetrahydrofuran, with trimethylphosphite.³⁶ then, this W(CO)₅[P(OCH₃)₃] complex was irradiated in tetrahydrofuran to form the metastable W(CO)₅[P(OCH₃)₃](thf), which was then reacted with pyrazine to form the product complex, cis-W(CO)₄[P(OCH₃)₃](pyz). The complex could be isolated from reaction solution and characterized by means of IR, ¹H-, ¹³C-, ³¹P-NMR, and Mass spectroscopies

The IR spectrum of the complex taken in n-hexane features four strong absorption bands at 2024, 1929, 1901, and 1887 cm^{-1} for CO stretching. The observation of four bands indicates that the $\text{M}(\text{CO})_4$ moiety has a cis arrangement rather than trans which would give only one strong absorption.³⁷ The $\text{W}(\text{CO})_4$ moiety has C_s local symmetry with a general pattern of $3\text{A}' + \text{A}''$ for CO stretching modes³¹ (Figure 4.10). The highest frequency band is attributed to A' when all the four carbonyls have in-phase symmetric stretching vibration mode. Modes in which CO groups stretch in phase have higher frequencies than those in which they stretch out of phase.³⁸ The next band at 1929 cm^{-1} is ascribed to the out-of-phase symmetric stretching mode of A' . The absorption with the strongest intensity is assigned to A'' caused by the asymmetric stretching mode of the axial carbonyls (carbonyl ligand trans to each other) and the band at 1887 cm^{-1} is recognized as the third A' resulting from the asymmetric stretching mode of the equatorial CO ligands (carbonyl ligand trans to a ligand different than CO). The CO stretching vibrations are shown in Figure 4.11.

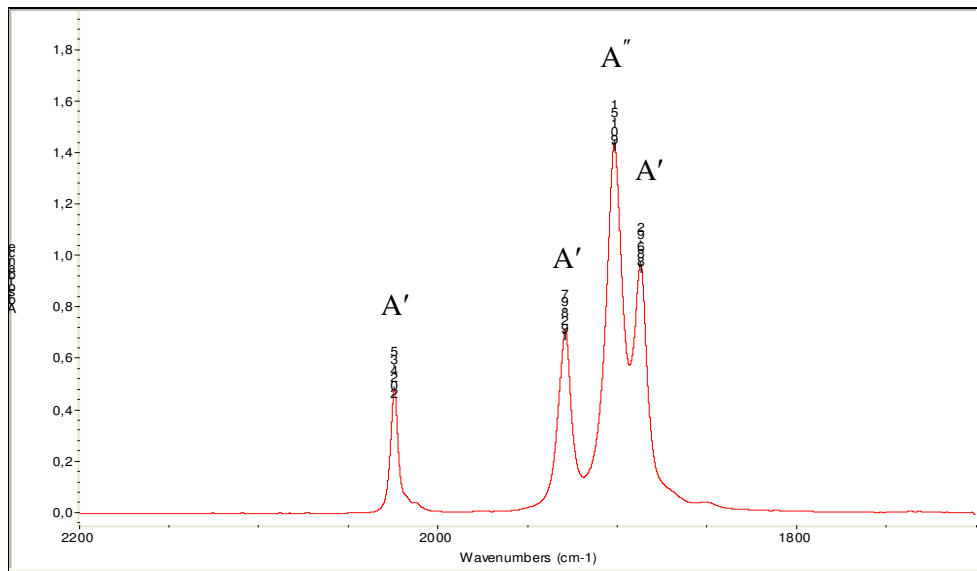


Figure 4.10. The CO-stretching region ($2200\text{--}1700\text{ cm}^{-1}$) of the IR spectrum of $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$ taken in n-hexane.

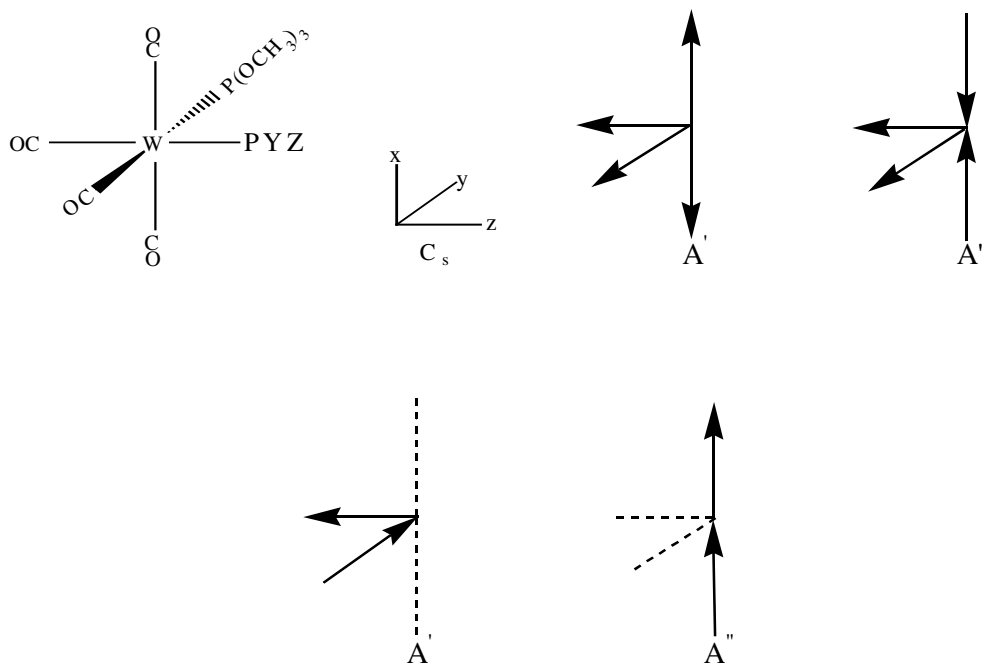


Figure 4.11. CO stretching vibrations of $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$

As known pyrazine is one of the aromatic nitrogen heterocycles which represent an important class of ligands in coordination chemistry; having two donor atoms (N) and π^* acceptor orbital which can accept electron density from metal d-orbitals via metal-ligand backbonding. The CO-stretching frequencies for two complexes, cis-W(CO)₄(pyz)₂ and cis- W(CO)₄[P(OCH₃)₃](pyz) are listed in Table 4.4 for comparison. The complex cis- W(CO)₄[P(OCH₃)₃](pyz) has, in general, higher frequencies than the cis-W(CO)₄(pyz)₂. In the latter complex, the W→CO backbonding is stronger than that in the former complex. This indicates that the pyrazine is a good σ -donor, but a poor π -acceptor ligand. The presence of trimethylphosphite which also has some π -accepting ability reduces the electron density on the metal atom and, thus, the W→CO backbonding compared to that in the cis-W(CO)₄(pyz)₂ complex.

Table 4.4. The CO Stretching Frequencies (cm⁻¹) of cis-W(CO)₄(pyz)₂ and cis-W(CO)₄[P(OCH₃)₃](pyz) taken in CH₂Cl₂ and n-hexane respectively.

	v (CO) (cm ⁻¹)			
Cis-W(CO) ₄ (pyz) ₂	2008	1924	1876	1837
Cis- W(CO) ₄ [P(OCH ₃) ₃](pyz)	2024	1929	1901	1887

The ³¹P-NMR spectrum of cis-W(CO)₄[P(OCH₃)₃](pyz) was recorded from its d-chloroform solution. H₃PO₄ was used as an external reference in capillary tube.

The ³¹P-{¹H}-NMR spectrum of the complex shows only one signal at 148.09 ppm for P(OCH₃)₃ which is accompanied by two small peaks which are symmetrically positioned on both sides of the main peaks (Figure 4.12). Those small peaks are called tungsten satellites which are arising from the spin-spin coupling of ³¹P with ¹⁸³W having a natural abundance of 14.4 % and nuclear spin of ½. The distance between the two satellite peaks gives a value of 392 Hz for the ¹⁸³W-³¹P coupling constant.

The coordination shift, ($\Delta\delta = \delta$ (coordinated ligand) – δ (uncoordinated ligand)³⁹ is included in table 4.5. The coordination shift to lower magnetic field may be explained by the fact that phosphite ligand is known to be a good σ -donor but weak π -acceptor compared with carbonyl groups. Therefore it transfers electron to the empty orbitals of the metal through σ -bonding when it is coordinated to the metal. By this way, electron density around phosphorous atom will be less so the resonance frequency of the phosphorous atom is shifted towards lower magnetic field (higher chemical shift value). This can be seen from the comparison of chemical shifts of coordinated $\text{P}(\text{OCH}_3)_3$ ligand with those of free $\text{P}(\text{OCH}_3)_3$ (Table 4.5).

Table 4.5. ^{31}P -NMR chemical shifts (ppm relative to H_3PO_4), coordination shifts ($\Delta\delta$, relative to free phosphite) in CDCl_3 . ^{183}W - ^{31}P coupling constant is given in Hz

complex	δ (ppm)	$\Delta\delta$ (ppm)	$J(^{183}\text{W}-^{31}\text{P})(\text{Hz})$
$\text{P}(\text{OCH}_3)_3$	141.00	–	–
$\text{Cis-W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz})$	148.09	7.09	393

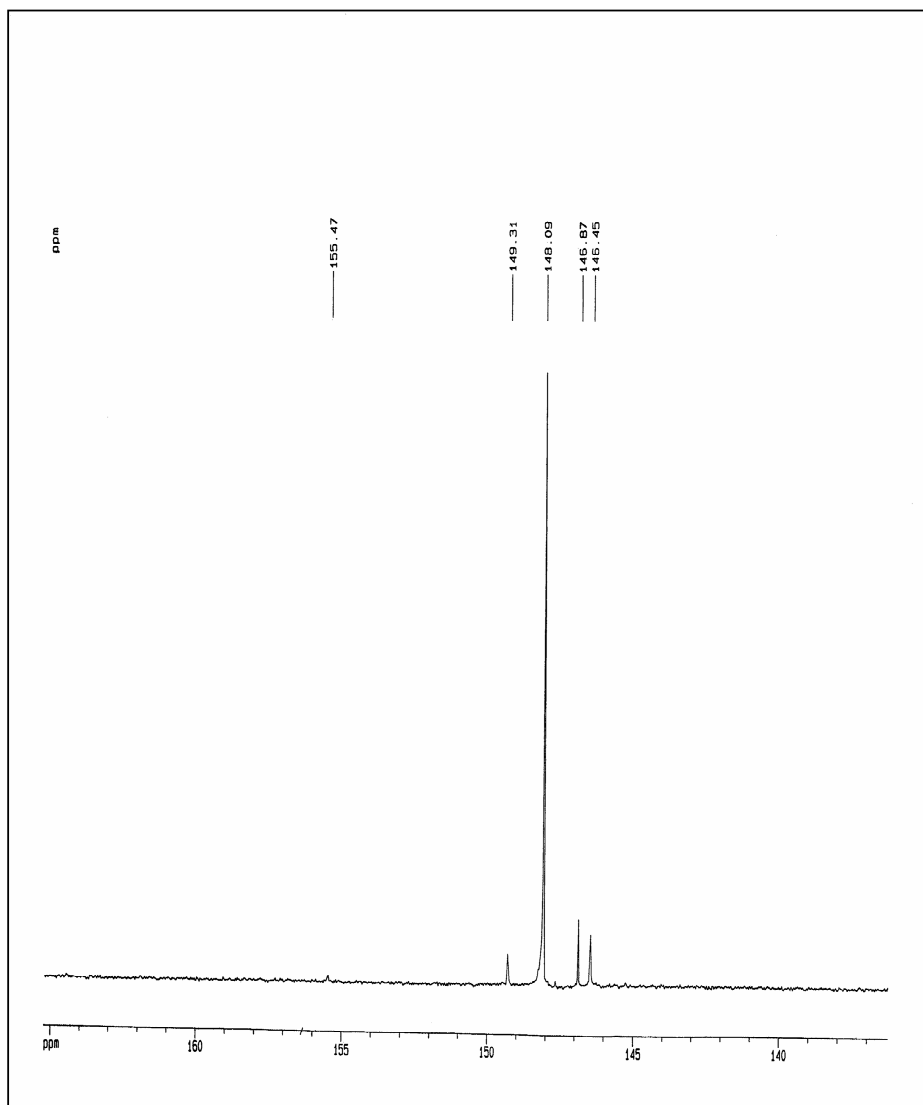


Figure 4.12. $^{31}\text{P}\{-^1\text{H}\}$ -NMR spectrum of $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$
in CDCl_3

The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of the complex was recorded from its d-chloroform solution by using broad band proton decoupling technique.

The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of the complex is given in Figure 4.13 - 4.15. and the ^{13}C -NMR spectral data of the complex is given in Table 4.6. The complex $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$ gives three doublet for the carbonyl groups with the relative intensities 2:1:1 (Figure 4.13). This indicates a cis arrangement of the four CO groups, consistent with the IR result. The doublet structure of the signals is due to $^{31}\text{P}\text{-}^{13}\text{C}$ coupling. The signal of the relative intensity 2 at 202.52 ppm is readily assigned to the CO groups trans to each other but cis to both of nitrogen- and phosphorous-containing ligands (CO1 and CO2 in Table 4.5). Since these two carbonyls are cis to the trimethylphosphite ligands, the $^{31}\text{P}\text{-}^{13}\text{C}$ coupling constant is small as expected ⁴⁰. One of the other two doublets of relative intensities 1:1 at 206.48 ppm has a large $^{31}\text{P}\text{-}^{13}\text{C}$ coupling constant (51.2 Hz) and therefore can be assigned to the CO group trans to the trimethylphosphite (CO3 in Table 4.6). The difference between the coupling constant of cis- and trans carbonyl groups with ^{31}P can be explained by the competition for bonding with d_π orbitals of metal between CO groups and phosphite ligand. Axial carbonyl group (trans carbonyl group to phosphite ligand) shares two d-orbitals of the metal with phosphite for backbonding (strong communication), while equatorial carbonyl group (cis to phosphite ligand i.e. trans to each other) uses only one d-orbital of metal in common with phosphite ligand. Therefore, the coupling constant $J(^{31}\text{P}\text{-}^{13}\text{C})$, for axial carbonyl (trans to phosphite ligand) is larger than that of cis carbonyl. Moreover, trimethylphosphite is strong σ -donor ligand which will increase the $\text{M}\rightarrow\text{CO}$ π -back bonding. This provides more electron density into the π^* -orbital of carbonyl group trans to donor ligand. As a result, carbonyl ligand CO3 is deshielded and shifted to downfield with respect to CO carbonyl groups trans to each other (cis to donor ligand) (Table 4.6). The other one with small $^{31}\text{P}\text{-}^{13}\text{C}$ coupling constant is assigned to the CO group trans to pyrazine ligand which is more deshielded than the carbonyl group trans to trimethylphosphite, hence shifted to downfield with respect to carbonyl group trans to phosphite ligand. This can be attributed to the π -accepting property of pyrazine ligand.

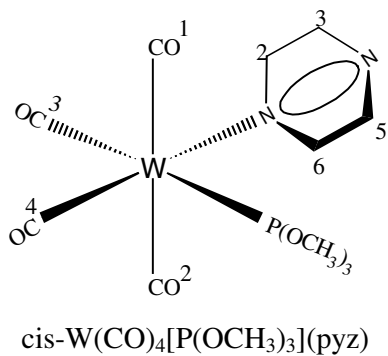
The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of the complex $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$ also shows two signals for the pyrazine ligand, one doublet at 150.73 ppm, and one singlet 146.38 ppm. The doublet is due to the $^{31}\text{P}\text{-}^{13}\text{C}$ coupling (2.2 Hz) and assigned to the C2 and C6 carbon atoms of the pyrazine ligand, while the singlet is assigned to the C3 and C5 carbon atoms. The signal of the C2 and C6 carbon atoms is shifted toward the lower magnetic field compared to that of the free pyrazine molecule. (145.6 ppm). The small coordination shift of $\Delta\delta = 5.1$ ppm toward the lower magnetic field indicates that the pyrazine molecule acts as a σ -donor rather than a π -acceptor ligand.

In the $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of the complex $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$ one observes also a doublet at 52.25 ppm, which is readily assigned to the methyl carbons of the trimethylphosphite ligand. The $^{31}\text{P}\text{-}^{13}\text{C}$ coupling constant is 3.1 Hz.

The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of pyrazine ligand gives two signals for two different carbon atoms at the coordinated and uncoordinated side of the pyrazine ligand. (Figure 4.14, Table 4.6). This shows that pyrazine ligand coordinates to the metal through one of its nitrogen atom.

The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of $\text{P(OCH}_3)_3$ gives one signal which is splitted into three due to $^{31}\text{P}\text{-}^{13}\text{C}$ coupling but one of the splitting overlaps with the other. (Figure 4.15). This is also proved that there is only one isomeric form. The $^{31}\text{P}\text{-}^{13}\text{C}$ coupling constant is given in table 4.6.

Table 4.6. The ^{13}C - $\{^1\text{H}\}$ -NMR chemical shifts values (δ , relative to SiMe_4) taken in CDCl_3 . ^{13}C - ^{31}P coupling constants are given in Hz.



Carbon	δ (ppm)	$J(^{31}\text{P}-^{13}\text{C})$ (Hz)
CO (1,2)	202.52	10.9
CO (3)	206.48	51.2
CO (4)	207.59	7.3
OCH_3	52.25	3.1
C (2,6)	150.73	2.2
C (3,5)	146.38	-
Free pyrazine	145.6	-

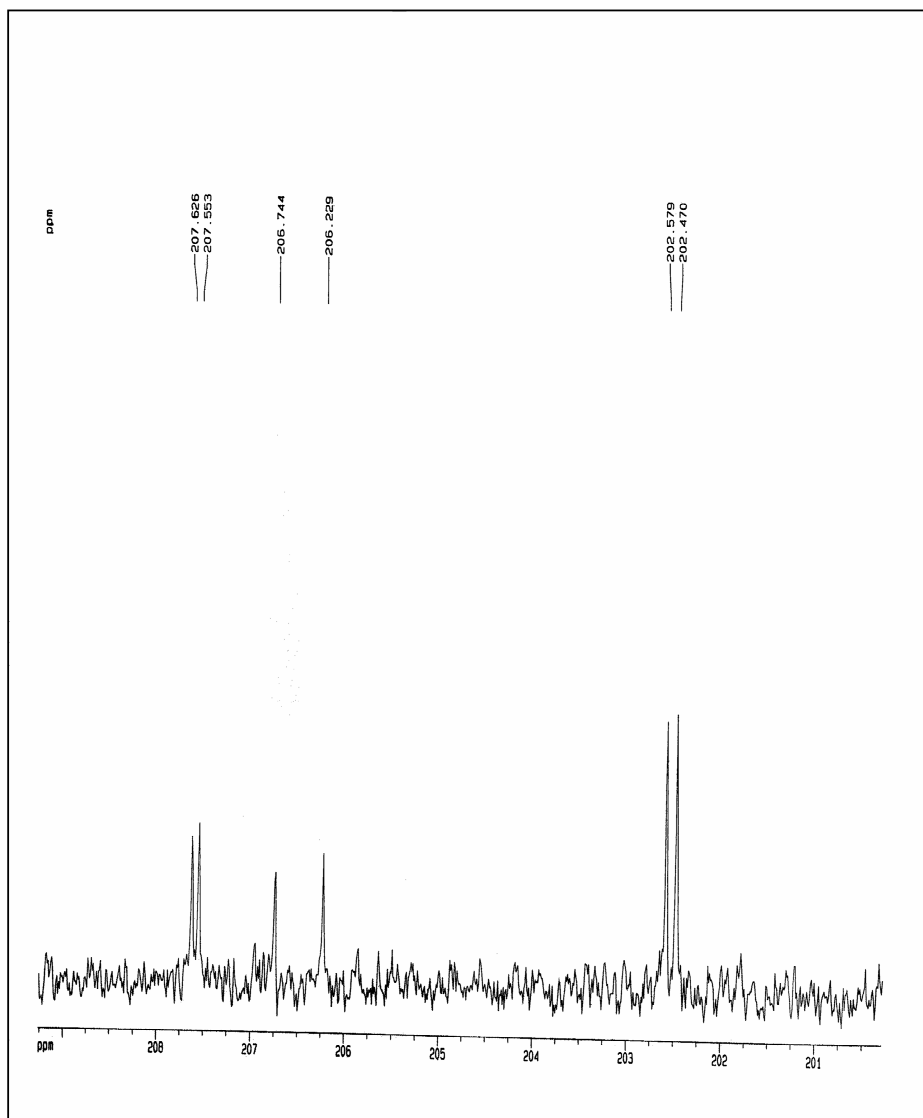


Figure 4.13. The carbonyl region of the ^{13}C - $\{^1\text{H}\}$ -NMR spectrum of *cis*- $\text{W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz})$ in CDCl_3 , showing three doublets for the CO groups.

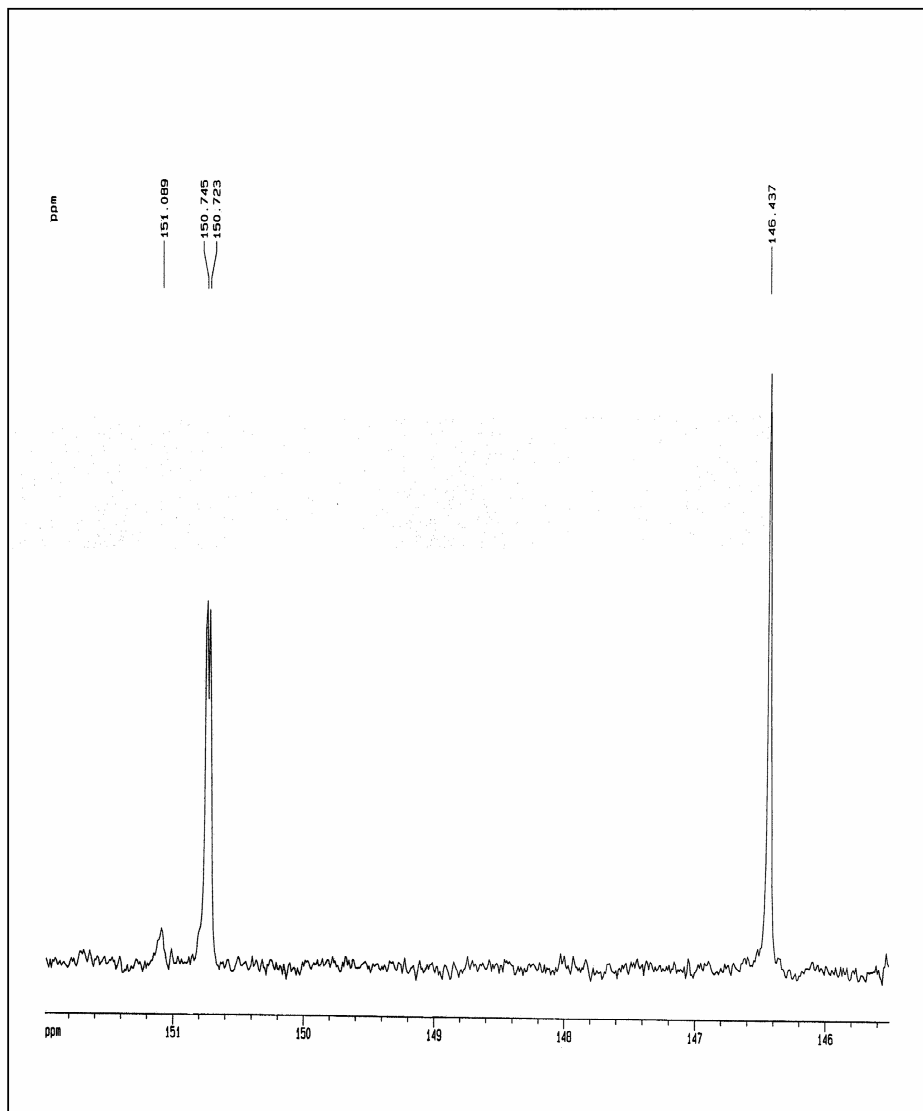


Figure 4.14. The ^{13}C - $\{^1\text{H}\}$ -NMR spectrum of $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$ in CDCl_3 , showing two signals for the pyrazine ligand.

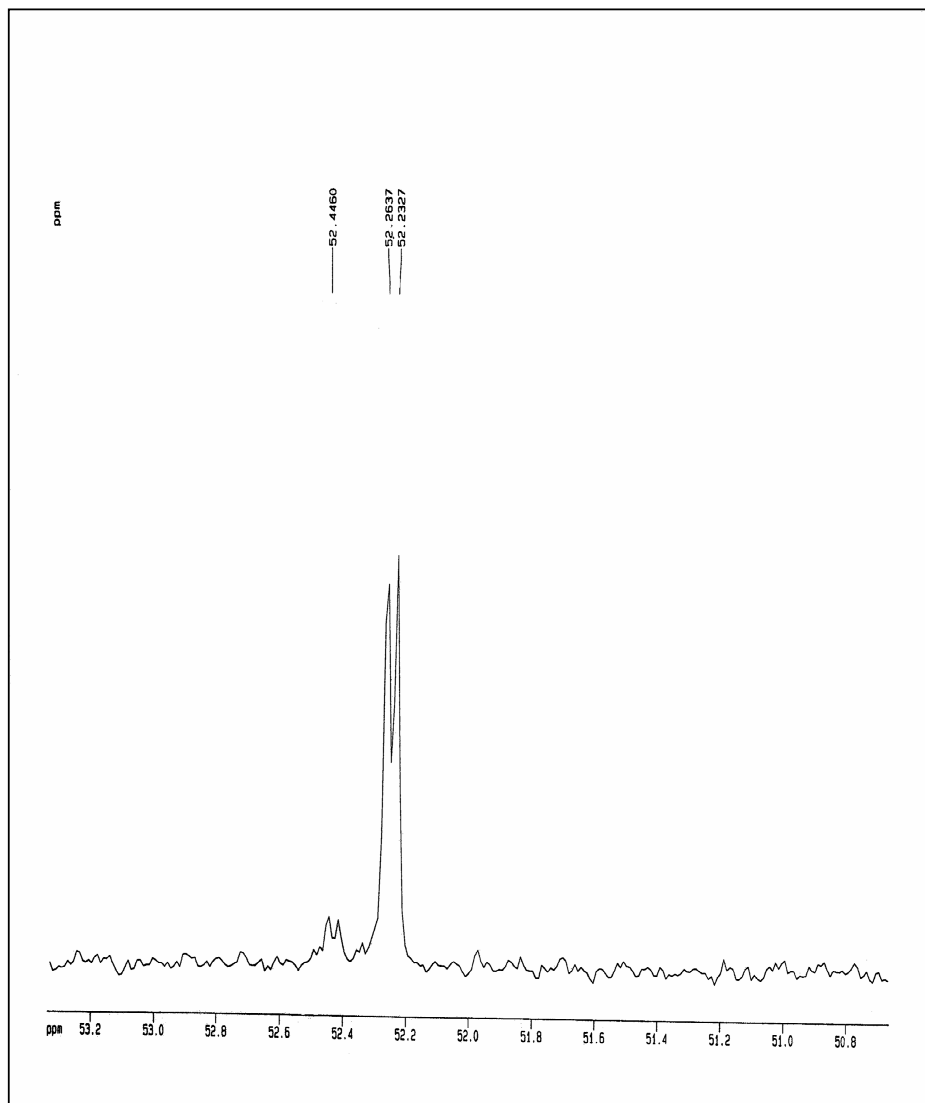
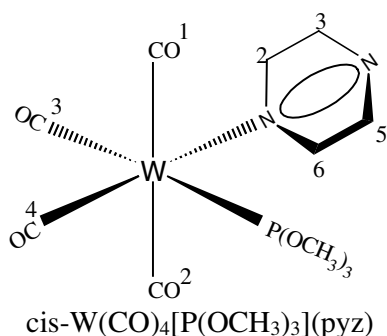


Figure 4.15. The ^{13}C - $\{^1\text{H}\}$ -NMR spectrum of $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$ in CDCl_3 , a doublet for the trimethylphosphite ligand

The ^1H -NMR spectrum of the complex $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$ was recorded from its d-chloroform solution (Figure 4.16 - 4.17), and gives two signals for the pyrazine ligand and one signal for the trimethylphosphite ligand (Figure 4.16). The observation of two signals for the pyrazine ligand can be considered as a further evidence for the fact that the pyrazine ligand coordinates to the metal through one of its nitrogen atom. The coordinated side of the pyrazine ligand gives a signal at lower magnetic field (higher chemical shift) stating that the hydrogen atoms on the coordinated side of pyrazine ligand are deshielded compared with uncoordinated side of the pyrazine.⁴¹ This is also a strong support for the results obtained from the interpretation of ^{13}C -NMR data which indicates that pyrazine ligand coordinates to tungsten atom through only one of its nitrogen atom.

The signal of the methyl protons of $\text{P(OCH}_3)_3$ in the complex appears to be doublet due to the ^{31}P - ^1H coupling. The coupling constant is 11.2 Hz. (Figure 4.17, Table 4.7).

Table 4.7. ^1H -NMR chemical shift values of $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$ in d- chloroform.



Hydrogen	δ (ppm)
pyrazine	8.53
H(2,6)	8.78
H(3,5)	8.41
OCH_3	3.55, 3.52

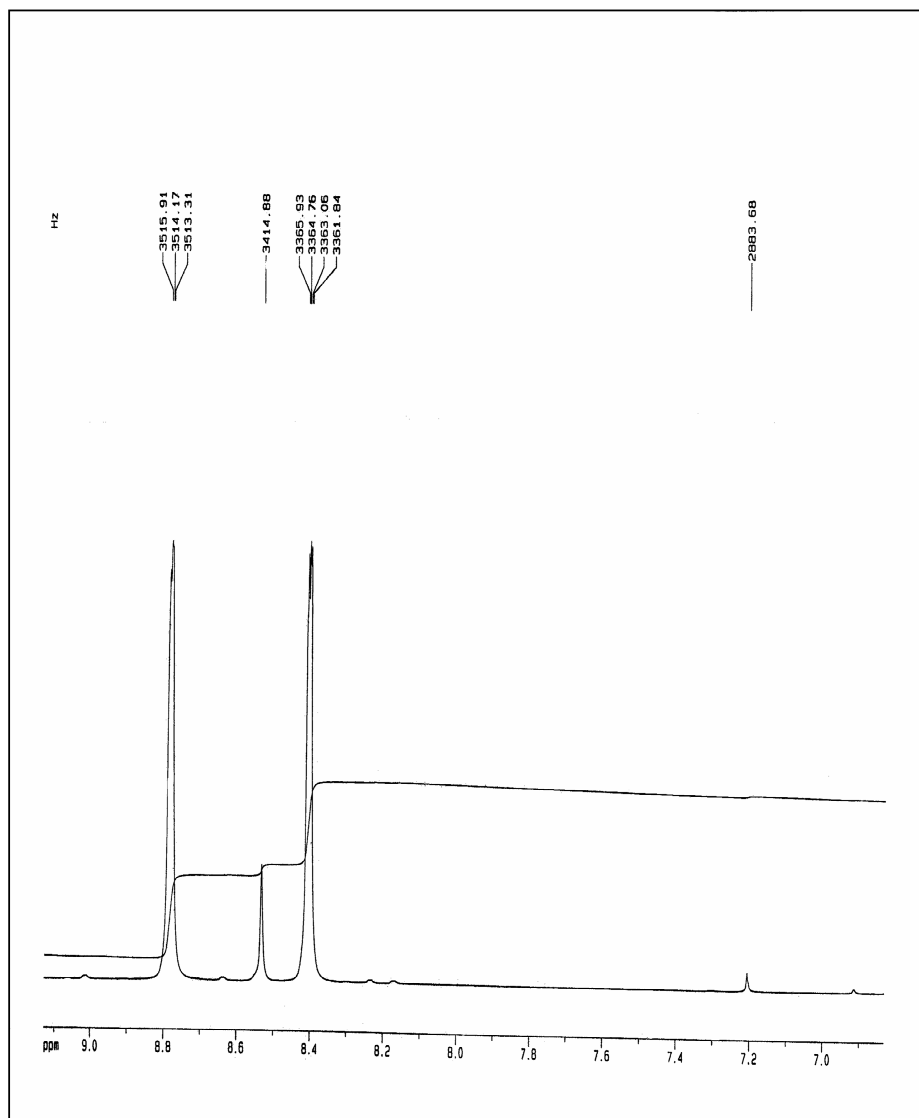


Figure 4.16. The ^1H -NMR spectrum of pyrazine in $\text{cis-W(CO)}_4[\text{P(OCH}_3)_3](\text{pyz})$ in CDCl_3

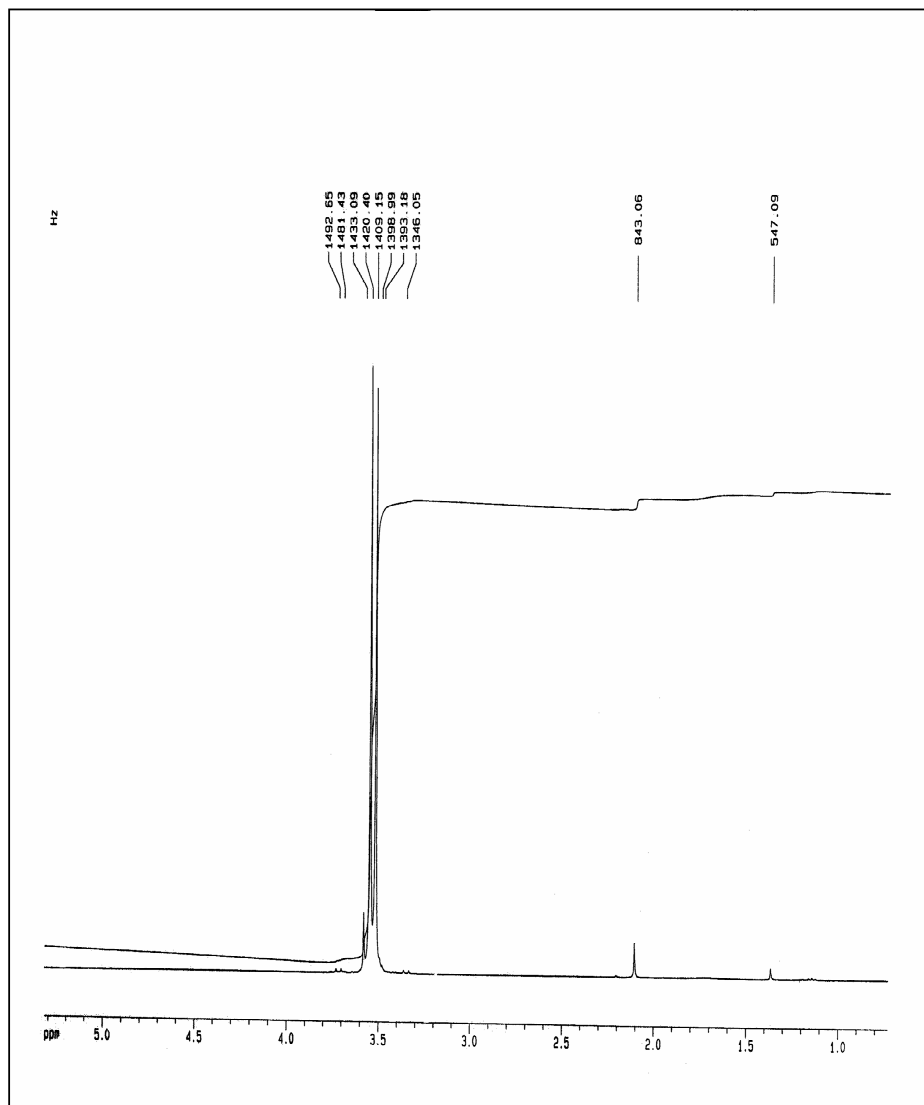


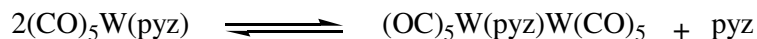
Figure 4.17. The ^1H -NMR spectrum of $\text{P}(\text{OCH}_3)_3$ in $\text{cis-W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz})$ in CDCl_3

CHAPTER 5

CONCLUSIONS

Our study on the stabilization of the pyrazine-carbonyl-tungsten(0) complexes reveals the following conclusions:

- Pentacarbonylpyrazinetungsten(0) can be formed and isolated as solid. However, it is not stable in solution and undergoes conversion to a bimetallic complex, $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$. The stability of the complex is attributed to the poor π -accepting ability of the pyrazine ligand.
- The mononuclear⁴² complex, $\text{W}(\text{CO})_5(\text{pyz})$, the dinuclear complex, $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$, and the free pyrazine molecule exist at equilibrium according to the equation:



The equilibrium constant was determined to be 0.0396 at room temperature by using quantitative ^1H -NMR spectroscopy.

- cis-tetracarbonylbis(pyrazine)tungsten(0) could be generated from the thermal substitution reaction of piperidine in tetracarbonylbis(piperidine)tungsten(0). However, the complex can not be isolated because of instability. Therefore, it could be identified only by IR spectrum in solution. The instability of tetracarbonylbis(pyrazine)tungsten(0) complex is found to be much higher compared to

pentacarbonylpyrazinetungsten(0). This clearly emphasizes the weak π accepting ability of pyrazine ligand compared to carbonyl ligand.

- The cis-tetracarbonyltrimethylphosphitepyrazinetungsten(0) complex could be synthesized by a series of reactions starting with hexacarbonyltungsten(0). The complex could be isolated from the reaction solution and fully characterized by IR, ^1H -, ^{13}C -, ^{31}P -NMR, and Mass spectroscopies. The pseudo-octahedral complex has a cis arrangement of the $\text{W}(\text{CO})_4$ -moiety. The presence of the trimethylphosphite ligand stabilizes the complex. The stabilization is due to the electronic effect. Trimethylphosphite acts as good σ -donor and has some π -accepting ability, better than the pyrazine ligand.

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