SYNTHESIS AND CHARACTERIZATION OF PENTACARBONYLACRYLOYLFERROCENETUNGSTEN(0) COMPLEX

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Approval of the Graduate School of Natural and Applied Sciences

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF PENTACARBONYLACRYLOYLFERROCENETUNGSTEN(0)

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Pentacarbonylacryloylferrocenetungsten(0) complex was synthesized photochemically from hexacarbonyltungsten(0) and acryloyferrocene (acfc). UV irradiation of $W(CO)_6$ in the presence of acryloylferrocene at 10 ^{o}C for 4 hours in n-hexane solution generates the $W(CO)_5(\eta^2\text{-acfc})$ complex as the sole monosubstitution product of the photolysis, as monitored by FT-IR spectroscopy. The product complex could be isolated from the reaction solution and characterized by IR, Raman, ^{1}H-NMR, ^{13}C-NMR spectroscopies, mass spectrometry and elemental analysis. The complex was found to be unstable in solution and to decompose to the parent $W(CO)_6$ complex and free acryloylferrocene molecule. The instability of the complex makes its isolation as analytically pure substance difficult.

In order to stabilize the tungsten-olefin bond, trimethylphosphite was introduced as a donor ligand into the molecule. Thus, a complex containing a donor ligand in addition to the olefinic ligand was prepared starting with $W(CO)_6$, trimethylphosphite, and acryloylferrocene. UV irradiation of $W(CO)_5[P(OMe)_3]$ with acryloylferrocene in n-hexane solution at room temperature generates $W(CO)_4[P(OMe)_3](\eta^2\text{-acfc})$, which was isolated from the reaction solution and characterized by IR, ^{1}H-NMR, ^{13}C-NMR spectroscopies and mass spectrometry. The complex was found to have a cis arrangement of four CO groups in the pseudo-octahedral geometry. However, the cis-$W(CO)_4[P(OMe)_3](\eta^2\text{-acfc})$ complex was found to be less stable than $W(CO)_5(\eta^2\text{-acfc})$.

Keywords: acryloylferrocene, tungsten, carbonyl, trimethylphosphite, photolysis.

ÖZ

PENTAKARBONİLAKRİLOİLFERROSENTUNGSTEN(0)'İN SENTEZİ VE TANIMLANMASI

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Pentakarbonilakriloilferrosentungsten(0) kompleksi, fotokimyasal olarak hegzakarboniltungsten(0) ve akriloilferrosen (acfc) bileşiklerinden sentezlendi. Akriloilferrosen eşliğinde $W(CO)_6$ kompleksinin n-hegzan çözeltisinde 10 ^oC de 4 saat süre UV ışınlanması tek fotosübstitüsyon ürünü olarak $W(CO)_5(\eta^2$-acfc) kompleksini oluşturdu. Fotokimyasal tepkime, FT-IR spektroskopisi ile izlendi. Oluşan ürün $W(CO)_5(\eta^2$-acfc) kompleks tepkime ortamından izole edildi ve FT-IR, Raman, ^{1}H-NMR, ^{13}C-NMR spektroskopisi, elemental analiz ve kütle spektrometrisi yöntemleri kullanılarak tanımlandı. Kompleksin özellikle çözeltide pek kararlı olmadığı ve $W(CO)_6$ başlangıç kompleksi ile serbest akriloilferrosene dönüştüğü gözlendi. Kompleksin bu kararsızlığı onun saf bir madde olarak çözeltiden izolasyonunu güçleştirmektedir.

Tungsten-olefin bağını kararlı hale getirmek amacıyla trimetilfosfit donör ligand olarak molekülle tepkimeye sokuldu. Böylece, olefinik liganda ek olarak donör ligand içeren bir kompleks, $W(CO)_6$, trimetilfosfit ve akriolilferrosenden yola çıkılarak hazırlandı. $W(CO)_5[P(OMe)_3]$ kompleksinin n-hegzan çözeltisi içerisinde 10 ^{o}C de UV-ışınlanması, $W(CO)_4[P(OMe)_3](\eta^2$-acfc) kompleksini oluşturdu. Oluşan kompleks, tepkime çözeltisinden izole edilerek, IR, ^1H-NMR, ^{13}C-NMR spektroskopileri ve kütle spektrometrisi yöntemleri kullanılarak tanımlandı. Kompleksin dört CO grubuyla pseudo-oktahedral geometride, cis yapıda olduğu gözlendi. Bununla birlikte, $W(CO)_4[P(OMe)_3](\eta^2$-acfc) kompleksinin $W(CO)_5(\eta^2$-acfc) kompleksinden daha az kararlı olduğu gözlendi.

Anahtar kelimeler: akriloilferrosen, tunsgten, karbonil, trimetilfosfit, fotoliz.

To my family

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CHAPTER 1

INTRODUCTION

Organometallic compounds are defined as substances containing direct metal carbon interaction. The variety of the organic moiety in such compounds is practically infinite, ranging from alkyl substituents to alkenes, alkynes, carbonyls, and aromatic and heterocyclic compounds.[1]

Organotransition metal chemistry is distinguished from the organometallic chemistry of the main group metals by its greater versatility. Although reactive main group organometallics generally add to carbonyl compunds and some activated carbon-carbon double bonds, transition metal compounds frequently react with unactivated, unsaturated organic compounds, often in a catalytic manner. The subject of organotransition metal chemistry as a distinct area of chemistry was of relatively little interest before about 1960. Even though the first recognized organometallic complex, Zeise's salt, $K[PtCl_3(C_2H_4)]\cdot 2H_2O$,[2] was prepared in 1827, significant interest in such compounds did not develop until after the structure of ferrocene was determined in 1952,[3] and it was subsequently realised that the transition metals possessed the capability of forming a wide variety of isolable organometallic compounds.[4]

The development of organometallic chemistry has occured unusually in the last five decades. This development could be attributed to the relation between general theory of structural chemistry and organometallic chemistry, which contributed to generalization and broadening of certain concepts such as multicenter bonding and cluster compounds. The continuing development of structural chemistry (including structural organometallic chemistry) in turn stimulates the synthesis and structural investigations of new organometallic compounds. Another important factor influencing the intensification of research in this field is application of organometallic compounds in organic synthesis, catalysis, and technology, for example, preparation of metals and their new compounds.[5]

Metal π-complexes possess a relatively new type of direct carbon-to-metal bonding that cannot be designated as one of the classic ionic, σ-, or π-bonds. It is known that a large number of both molecules and ions such as mono- and diolefins, polyenes, arenes, cyclopentadienyl ions, tropylium ions, and π-allylic ions can form metal π–complexes with transition metal atoms or ions. In 1827 Zeise reported that ethylene reacted with platinum(II) chloride to form a salt $K(C_2H_4)PtCl_3.2H_2O$ which was proven to be the first reported metal π-complex.[6]

A common feature of the extensive class of π-complexes is the fact that the L→M donor as well as the L←M acceptor interaction utilizes ligand orbitals which –with regard to the intra-ligand bond – have π-symmetry. The ligand-metal bond in π-complexes always contains an L←M π-acceptor component; the L→M donor contribution can have σ-symmetry (monoolefins) or σ- or π-symmetry (oligoolefins, enyl ligands, arenes and heteroarenes). Olefin complexes are widespread among transition metals. These complexes play an important role in reactions that are catalyzed by organotransition-metal compounds, such as hydrogenation, oligomerization, polymerization, cyclization, hydroformylation, isomerization, and oxidation.[7]

Transition metal carbonyls are among the longest known classes of organometallic compounds. They are common starting material for the synthesis of other low-valent metal complexes, especially clusters. The carbonyl ligand can not only be substituted for a large number of other ligands (Lewis bases, olefins, arenes), but the remaining CO groups stabilize the molecule against oxidation or thermal decomposition. Metal carbonyl derivatives play an important role as intermediates in homogeneous catalysis. Carbonyl groups are also useful probes for determining the electronic and molecular structure of organometallic species by spectroscopic methods.[7] The vibrational spectra of metal carbonyls have proved particularly informative. The CO stretching bands observed in the infrared and Raman spectra are to a good approximation specific group frequencies. They are also sharp, sensitive to environment, and commonly intense.[8] The vibrations of individual MCO groups interact strongly,[9] so that the observed spectra are rich in well-resolved bands. The number and pattern of these give information about molecular symmetry and geometry, while the positions of the bands are related to bonding.[10]

Metal carbonyls are the compounds of transition metals with carbon monoxide ligand. They find applications in many catalytic processes and in organic synthesis. Thus, research on preparations, structures, and applications of metal carbonyls and their derivatives has been intensive for several decades. The first metal carbonyl, $Ni(CO)_4$, was prepared by A. Mond, G. Langer, and F. Quinke,[11] in 1890 by the reaction of metallic nickel with carbon monoxide. It has found application immediately; it has been used for industrial preparation of pure nickel. Many other carbonyls were synthesized shortly thereafter.[12]

Almost all of the transition metals form compounds in which carbon monoxide acts as a ligand. There are three points of interests with respect to these compounds: (1) Carbon monoxide is not ordinarily considered a very strong Lewis base and yet it forms strong bonds to the metals in these complexes; (2) the metals are always in a low oxidation state, most often formally in an oxidation state of zero, but sometimes also in a low positive or negative oxidation state; and (3) the 18-electron rule is obeyed by these complexes with remarkable frequency, perhaps 99% of the time.[13]

There are two methods for the synthesis of the Group 6 metalcarbonyl derivatives starting with $M(CO)_6$. The first method is the direct photolysis of hexacarbonylmetal(0), $M(CO)_6$, in the presence of an appropriate ligand L,

$$M(CO)_6 + nL \xrightarrow{h\nu} M(CO)_{6-n}L_n + nCO \qquad \textbf{Eqn 1.1}$$

Photosubstitution of group 6 metal hexacarbonyls has been established to occur with high quantum yield,[14] which is the ratio of the number of molecules undergoing photochemical process to the number of photons absorbed by the reactant, and has found a wide range of applications[15] including the preparation of carbonyl-olefin-metal complexes.[16]

The second method is the thermal substitution of a labile ligand, such as tetrahydrofuran (THF), in an intermediate compex which has already been generated by photolysis of $M(CO)_6$ with a respective ligand, L

$$M(CO)_6 + THF \xrightarrow{h\nu\ /\ -CO} M(CO)_5(THF) \xrightarrow{+\ L\ /\ -\ THF} M(CO)_5L \qquad \textbf{Eqn 1.2}$$

In the case of olefins, photosubstitution appears to be the most convenient route for the synthesis of carbonyl-olefin-metal complexes. The sequential photosubstitution of CO in $M(CO)_6$ by olefins has already been established by using (E)-cyclooctene as the olefinic ligand.[16] The photolysis of $M(CO)_6$ in the presence of an olefin is expected to yield the stable final product trans-$M(CO)_4(\eta^2\text{-olefin})_2$ through the intermediate $M(CO)_5(\eta^2\text{-olefin})$ and cis- $M(CO)_4(\eta^2\text{-olefin})_2$ as shown in Figure 1.1.

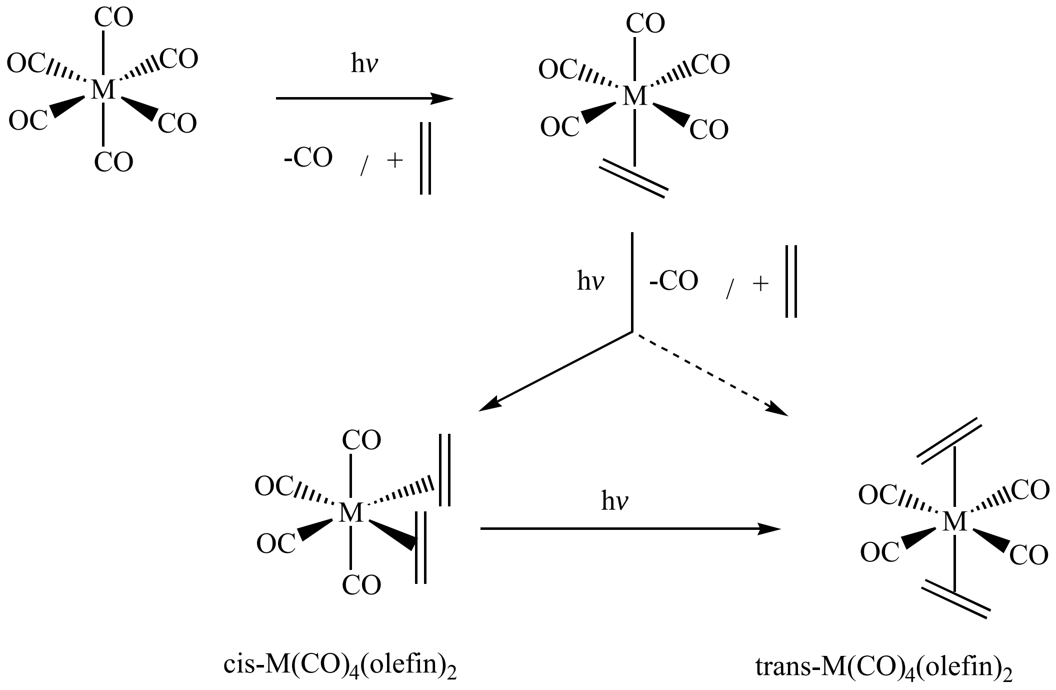


Figure 1.1. Sequential photolytic substitution of CO ligands in $M(CO)_6$ (M = Cr, Mo and W) by olefin.

Ferrocene has been used in the synthesis of many new materials having interesting properties.[17,18] For instance, molecules containing ferrocene moiety have been used as homogeneous catalysts,[18] molecular sensors,[19] molecular magnets,[20] non-linear optic materials,[21] and liquid crystals.[22] The presence of ferrocene in a molecule is expected to influence its electron transfer ability.[23]

Introducing the ferrocenyl moiety into an olefin ligand is expected to influence the stability and catalytic properties of its complexes with the transition metal. Vinylferrocene has already been employed as an olefin ligand containing ferrocenyl unit.[24] However, its Group 6 metal carbonyl complexes of the type $M(CO)_5(\eta^2$-vinylferrocene) have been reported to be unstable, which can be considered as an indication that they might be active catalyst.[24] Another potential olefinic ligand containing ferrocenyl moiety is acryloylferrocene (Figure 1.2.) which has been recently isolated.[25] Acryloyferrocene is an olefin bearing a carbonyl group in addition to the ferrocenyl moiety. This carbonyl group may additionally interact with the transition metal atom to which the olefin ligand is already coordinated through its C=C bond. Therefore, this potential feature of acryloylferrocene prompted us to investigate its carbonyl-metal complexes with the Group 6 elements.

In this study, it was aimed to synthesize $W(CO)_5(\eta^2$-acryloylferrocene), an olefin-substituted metal carbonyl complex, by using acryloylferrocene (acfc) as the olefinic ligand with an appropriate method. $W(CO)_5(\eta^2$-acryloylferrocene) complex contains two different metal atoms, iron and tungsten which can enhance the catalytical properties of the complex.

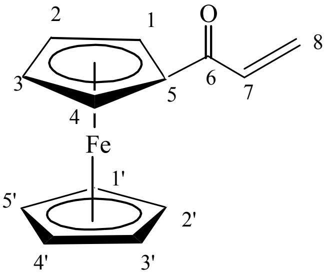


Fig. 1.2. Acryloylferrocene (acfc)

Attempts to synthesize $W(CO)_5(\eta^2$-acryloylferrocene) by using thermal substitution of a labile ligand failed. Neither $W(CO)_5$(btmse) (btmse: bis(trimethlsilyl)ethyne)[26] nor $W(CO)_5$(THF) (THF: tetrahydrofuran), gives the olefin substituted product, rather $W(CO)_6$ as the decomposition product.

The direct photochemical substitution method was found to be a convenient route to synthesize the complex, $W(CO)_5(\eta^2$-acryloylferrocene). A solution of the parent complex $W(CO)_6$ in n-hexane was irradiated at 10 °C in the presence of acryloylferrocene (acfc) to form $W(CO)_5(\eta^2$-acfc) which could be isolated from reaction solution by crystallization. The complex $W(CO)_5(\eta^2$-acfc) was characterized by IR, Raman, ^{1}H-NMR, ^{13}C-NMR spectroscopies, mass spectrometry and elemental analysis.

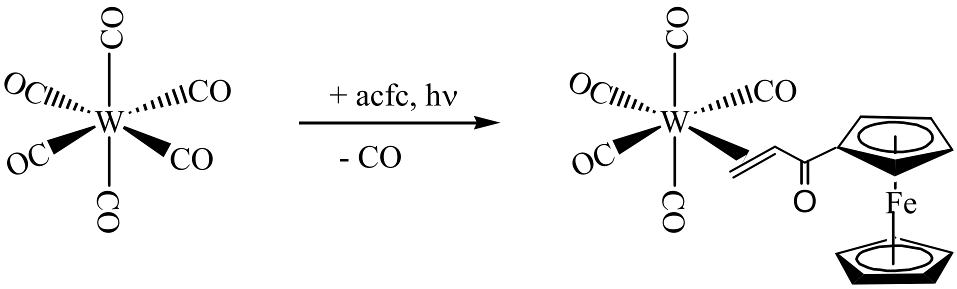


Figure 1.3. Photolytic CO substitution in $W(CO)_6$ with acryloylferrocene forming the product $W(CO)_5(\eta^2$-acfc)

Since $W(CO)_5(\eta^2$-acfc) appears to be unstable, particularly in solution, we attempted to stabilize the tungsten-acryloylferrocene complex by introducing trimethylphosphite as a donor ligand into the molecule. For this purpose cis-$W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) was synthesized from the irradiation of $W(CO)_5[P(OCH_3)_3]$ and acryloylferocene in n-hexane at 10 °C. The complex cis-$W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) was characterized by IR, ^{1}H-NMR, ^{13}C-NMR spectroscopies and mass spectrometry. However this complex was found to be even less stable than $W(CO)_5(\eta^2$-acfc) complex.

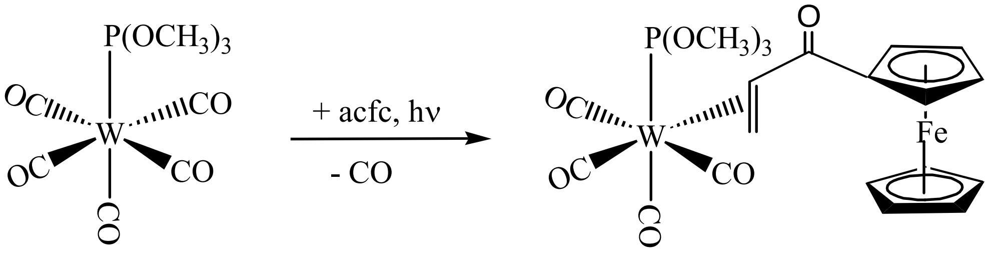


Figure 1.4. Formation of cis-$W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) from the irradiation of $W(CO)_5[P(OCH_3)_3]$ in the presence of acryloylferrocene (acfc) in n-hexane at 10 °C.

CHAPTER 2

BONDING

2.1. Metal –Carbonyl Bonding

One of the most commonly encountered ligand in organotransition metal chemistry is carbon monoxide which forms complexes with these metals known as metal-carbonyls. Its primary mode of attachment to the metal is through the carbon atom.

The bonding of CO to a transition metal can be described in terms of two synergic components; σ-dative bonding and π-back-bonding. The more σ-donation by the carbonyl, the stronger π-back-bonding by the metal.[27]

i) σ-dative bonding: Two electron donation of the lone pair on carbon into a vacant metal d-orbital; This electron donation makes the metal more electron rich and in order to compensate for this increased electron density, a filled metal d-orbital may interact with empty π^*-orbital on the carbonyl ligand to relieve itself of the added electron density.

ii) π-back-bonding: Effective overlap of the metal d-orbital and carbon monoxide π^*-orbital results in an extensive back-bonding. These interactions are shown diagramatically in Figure 2.1.

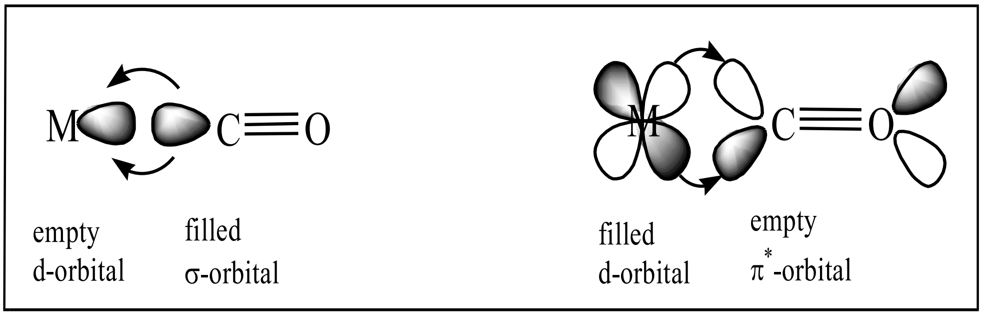


Figure 2.1. Molecular orbital description of metal-carbonyl interaction a) σ-dative bonding, b) π-back-bonding

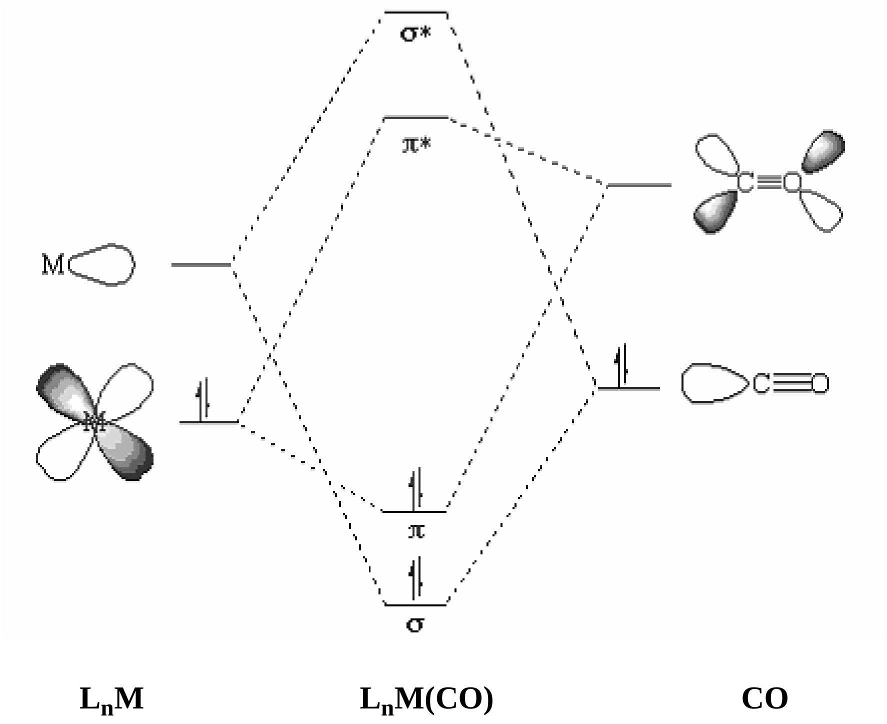


Figure 2.2. Molecular orbital diagram of M-CO bond

Since π-back-bonding depends crucially on the electron density of the metal, it not only strengthens the M-CO bond, but also provides a very sensitive probe for the electronic characteristics of the metal center. Extensive back bonding in electron rich complexes lowers the CO stretching frequency. This is consistent with the bonding model, an increase in the electron density on the metal atom is delocalized over the CO ligands, by populating the carbonyl π^*-orbital thus weakening the CO bond. Nevertheless, the converse is true if the complex is positively charged. Also the presence of a strong σ-donor and weak π-acceptor ligand attached trans to CO ligand in a mixed metal ligand carbonyl strengthens M-CO bond and weakens the C≡O bond further, concomitantly. This weakening or strenthening is due to the sharing of the same d-orbital by the carbonyl and the L ligand, trans to that carbonyl (π-competition).[13] (Figure 2.3)

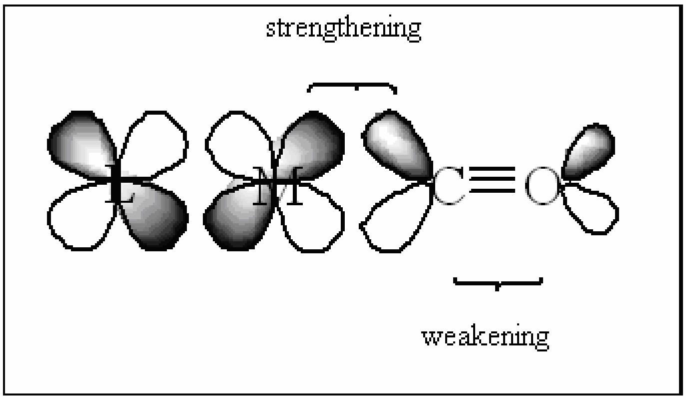


Figure 2.3. Competition for π-bonding in metal-carbonyl derivatives. L denotes the ligand which is stronger σ donor, but weaker π-acceptor than carbon monoxide.

2.2. Metal – Olefin Bonding

The bond between ethylene molecule and the metal ion may be considered as a dative σ bond to an available orbital on the metal. The bonding scheme is analogous to that in carbon monoxide complexes in which there is a ligand to metal σ donation and a reciprocal metal to ligand π donation. The extent of backbonding varies depending on the metal, the substituents on ethylene, and the other ligands on the metal.[13]

π-bonding molecular orbital of olefin is of σ-symmetry with respect to metal-olefin interaction axis and, therefore, interacts with a σ-symmetry orbital on the metal atom. Since the olefin donates electron to the metal atom through this interaction, it causes an increase of the electron density on the metal. As a result of interaction between a d_π metal orbital and antibonding π^* alkene orbital, electron density will be donated back to the olefin and this leads to an increase of electron density on the π^* orbital of the olefin and a decrease of electron density on the central atom.[28]

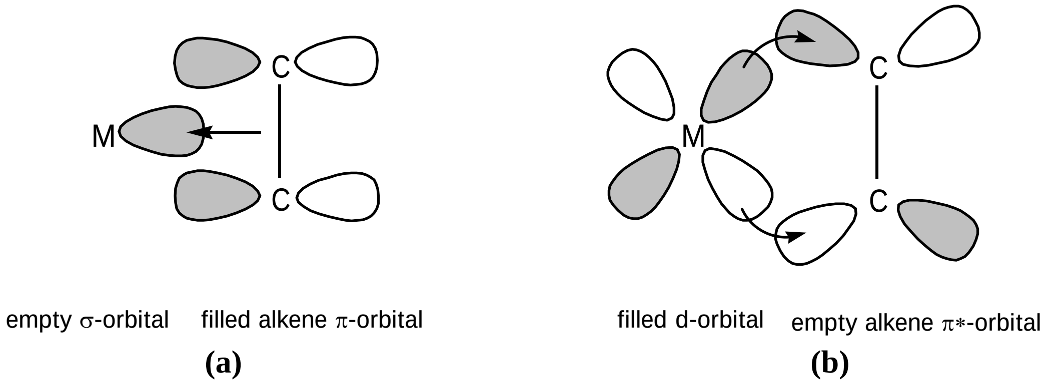


Figure 2.4. Metal-alkene bonding: a) alkene to metal σ-donation,
b) metal to alkene π-back donation.

2.3. Metal-Phosphorus Bonding

The bonding in phosphite ligands is similar to that of carbonyls, so it can be thought of having two important components. The first one is σ-donation of the phosphine lone pair to an empty orbital on the metal. The second component is back donation from a filled metal d_π orbital to an empty d orbital on the phosphine ligand (Figure 2.4.)

These ligands are somewhat different from carbonyl ligand regarding the type of orbitals used for bonding to a metal, as phosphorus uses its d-orbitals for π-interaction with metal while carbon monoxide uses its π* orbitals. The former is called dπ-dπ and the latter is dπ-pπ bonding.[29]

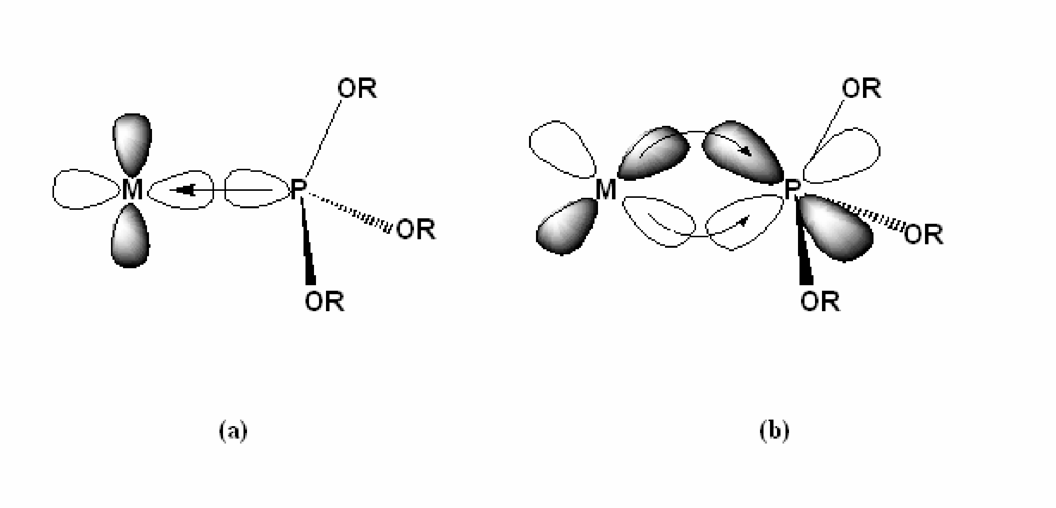


Figure 2.4. MO description of Metal-Phosphorous bonding (R: CH_3)

a) $(OCH_3)_3P \rightarrow$ Metal σ-bonding

b) Metal$\rightarrow P(OCH_3)_3$ d_π-d_π bonding

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. This sensitivity to oxygen and water is usually more in solution than in solid state. Therefore handling and all reactions of organometallic compounds should be carried out under dry and deoxygenated nitrogen or argon atmosphere.

Organometallics may be handled almost as easily as ordinary compounds if the reactions are carried out in the absence of oxygen. For this reason dry and deoxygenated nitrogen or argon atmosphere is obtained by passing through nitrogen or argon gas when the organometallic substances are open to air. Circulated nitrogen or argon gas passes through some purification steps as shown in Figure 3.1. Firstly, nitrogen or argon gas is allowed to pass through a catalyst (BASF R3.11, Ludwigshafen, Germany) heated up to 120°C to remove oxygen and then dried molecular sieves to remove its moisture. Last step is the bubbler which contains glycerine to see the gas passage.

The basic techniques used during the experiments are;

(1) Vacuum line technique, which 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 nitroen 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.

(3) Crystallization technique,[30] is commonly used for isolation and purification of products.

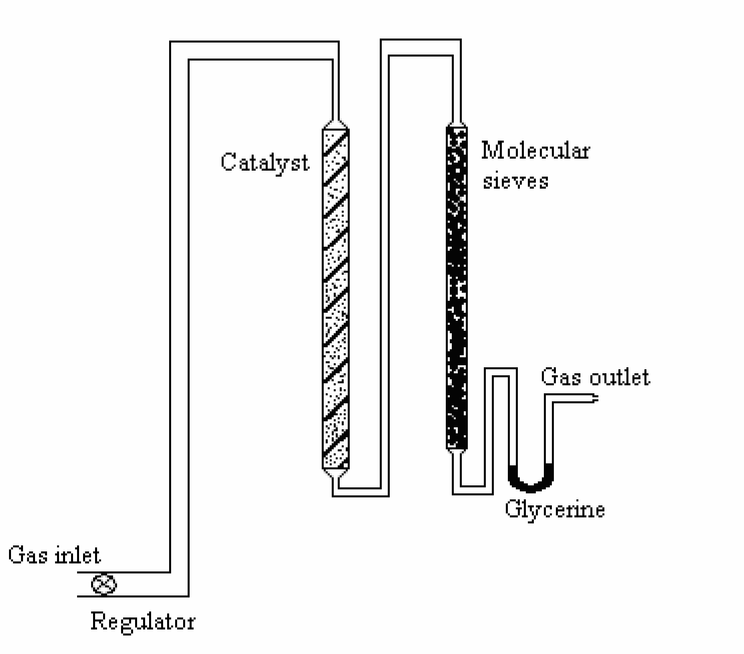


Figure 3.1. Nitrogen gas purification steps

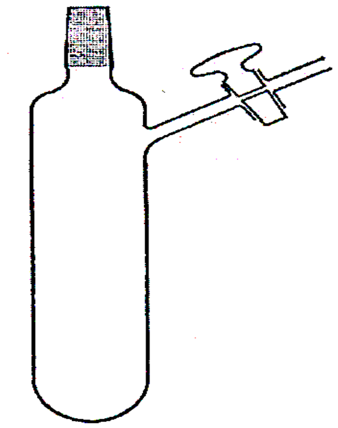


Figure 3.2. Standard schlenk tube

Photochemical reactions were performed with a special glass apparatus having two parts; an inner part in which a Mercury-Arc Lamp (Hg-Tauchlampe TQ-150) was immersed and an outer part where water was circulated (Figure 3.3).

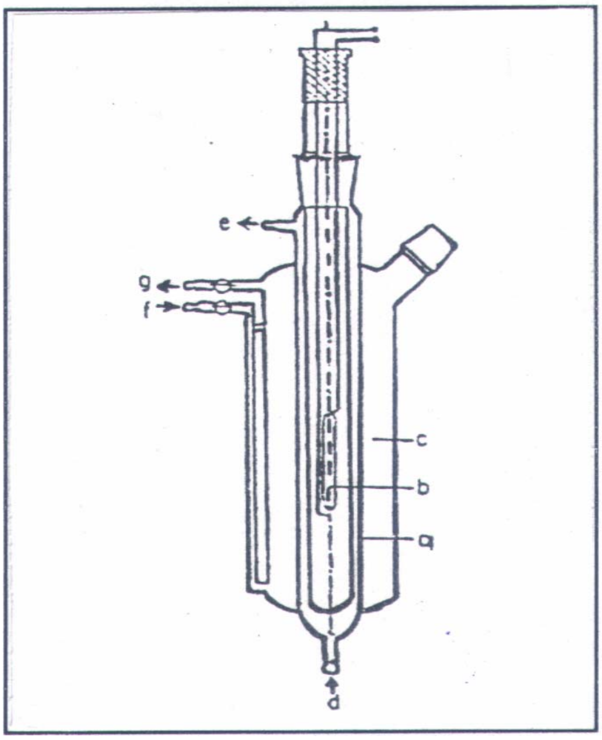


Figure 3.3. The apparatus used for the photochemical reactions

a) inner part
b) Mercury lamp,
c) Outer part
d) Water inlet,
e) Water outlet,
f) Nitrogen gas inlet,
g) Nitrogen gas outlet.

All solvents used were purified and dissolved oxygen was removed by refluxing over metallic sodium except CH_2Cl_2 under nitrogen atmosphere for 2 to 3 days before use. CH_2Cl_2 was refluxed over phosphorus pentoxide for purification.

All solvents, ferrocene, acryloyl chloride, trimethylaluminum, ethylaluminumdichloride, hexacarbonyltungsten were purchased from Aldrich, trimethylphosphite was purchased from Ventron.

3.2. Physical Measurements

3.2.1. Infrared Spectra

Infrared spectra of the complexes were recorded from their dichloromethane or hexane solutions using a Specac IR-Liquid cell with CaF_2 windows on a Nicolet 510 FTIR Spectrometer instrument with Omnic software.

3.2.2. Raman Spectra

The Raman spectrum of the $W(CO)_5(\eta^2$-acfc) complex in solid form was recorded by using a Bruker FRA 106/S Spectrometer with Opus software.

3.2.3. NMR Spectra

The ^1H-NMR and ^{13}C-NMR spectra of the acryloylferrocene molecule and the complexes were recorded from their $CDCl_3$ or CD_2Cl_2 solutions, on a Bruker-Spectrospin DPX 400 Ultrashield NMR Spectrometer with Avance software. Samples of the complexes were particularly prepared under nitrogen atmosphere. All the chemical shift values were given relative to the signal of TMS used as an internal reference.

3.2.4. Mass spectra

FAB-MS was taken on a Fisons VG Autospec with m-nitrobenzylalcohol as matrix at Colorado State University, Fort Collins, USA.

3.2.5. Elemental Analysis

Elemental analysis of $W(CO)_5(\eta^2\text{-acfc})$ was carried out by using LECO CHNS-932 instrument at METU Central Laboratory.

3.3. Synthesis of complexes

3.3.1. Synthesis of acryloylferrocene

Acryloylferrocene was prepared according to the literature procedure.[25] To a stirred solution of ferrocene (1,216 g, 6,98 mmol) and acryloylchloride (0.624 mL, 8.37 mmol) in CH_2Cl_2 (21.36 mL) at 0 °C was added Me_3Al (1.602 mL, 3.47 mmol) and $EtAlCl_2$ (6.42 mL, 6.98mmol) drop by drop over 10 min consecutively. The resulting mixture was stirred for another 20 min at this temperature. At the end of this time, deep blue colored reaction mixture was hydrolized with water , and more CH_2Cl_2 was added to the reaction flask. Two layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel. (1.34 g, 80% yield). IR (n-hexane) ν(CO)= 1665.1 cm^{-1}. ^1H NMR ($CDCl_3$) δ= 6.74 (dd, H7, J= 17.0 and 10.3 Hz), δ= 6.38(dd, H8 (trans to H7), J= 17.0 and 1.7 Hz), δ= 5.64 (dd, H8' (cis to H7), J= 10.3 and 1.7 Hz), δ= 4.76 (t, H1, H4, J= 1.7 Hz), δ= 4.50 (t, H2, H3, J= 1.7 Hz), δ= 4.12 (s, H1'-H5'). ^{13}C-NMR ($CDCl_3$) δ= 193.5 (C6), δ= 133.4 (C7), δ= 126.7 (C8), δ= 80.1 (C5), δ= 73.1 (C1,C4), δ= 70.4 (C2,C3), δ= 70.1 (C1'-C5')

3.3.2. Synthesis of pentacarbonylacryloylferrocenetungsten(0), $W(CO)_5(\eta^2$-acfc)

$W(CO)_5$(acfc) was synthesized photochemically by the direct photolysis of $W(CO)_6$ with acryloylferrocene in n-hexane solution. For this purpose 478.5 mg (1.36 mmol) $W(CO)_6$ was dissolved in n-hexane (150 mL) and 327.6 mg (1.36 mmol) acfc was added into the solution (every hour 25% of the ligand was added to the medium in order to prevent precipitation of unreacted ligand during the reaction). The solution was irradiated for 4 hours at room temperature. The reaction was followed by IR spectroscopy. When the reaction was completed volatiles were evaporated under vacuum and the dark red residue dissolved in n-hexane and the solution was left overnight at –35 °C. The red precipitate was seperated from the supernatant solution and was dried under vacuum. (0.2 g, 26% yield). Anal. Calcd. for $C_{18}H_{12}O_6WFe$ (M = 563.9): C, 38.30; H, 2.13; Found: C, 38.85; H, 2.26%. MS: m/z 563.9 (M^+). IR (n-hexane) ν(CO)= 2091.0, 2013.2, 1974,6 and 1955.9 cm^{-1} . IR (KBr pellet) ν(CO)= 2083.8, 1960.2, 1943.2, 1920.5 cm^{-1}. Raman ν(CO)= 2084.4, 2007.9, 1964.2, 1944.5 and 1917.5 cm^{-1}. ^1H NMR (CD_2Cl_2) δ= 4.99 (m, H1), δ= 4.95 (m, H7), δ= 4.94 (m, H4), δ= 4.71 (m, H2), δ= 4.66 (m, H3), δ= 4.14 (d, H8, J=17.9 Hz), δ= 4.30 (s, H1'-H5') and δ= 3.80 (d, H8', J=12.6 Hz). ^{13}C-NMR (CD_2Cl_2), δ= 202.4 (CO trans to acfc), δ= 195.2 (CO cis to acfc), δ= 194.4 (C6, CO of acfc ligand), δ= 78.94 (C5), δ= 73.50 (C2), δ= 73.13 (C3), δ= 70.56 (C1'-C5'), δ= 70.28 (C7), δ= 69.86 (C1), δ= 69.33 (C8), δ= 68.63 (C4)

3.3.3. Synthesis of tetracarbonylacryloylferrocenetrimethylphosphitetungsten(0), $W(CO)_4[(P(OCH_3)_3](\eta^2$-acfc)

$W(CO)_4[(P(OCH_3)_3](\eta^2$-acfc) was prepared from irradiation of $W(CO)_5(POCH_3)_3$ with acryloylferrocene at 10 °C. $W(CO)_5(POCH_3)_3$ was prepared according to the literature procedure.[31] 1.0 g (2.8 mmol) $W(CO)_6$ was dissolved in 150 mL tetrahydrofuran (THF) and the solution was irradiated in a special glass apparatus used for photochemical reactions for about 4 hours at 10 °C. During the irradiation, nitrogen gas was allowed to pass through the solution in order to remove the free CO from the reaction medium. The reaction was followed by IR spectroscopy. After all $W(CO)_6$ was converted to $W(CO)_5(THF)$, 0.33 mL (2.8 mmol) trimethylphosphite, $P(OCH_3)_3$ was added to the reaction vessel and the solution was stirred overnight at room temperature. After the completion of the ligand substitution reaction, the solvent was evaporated under vacuum and solid residue was obtained. The $W(CO)_5(POCH_3)_3$ complex was crystallized from n-hexane solution over dry ice. Yellow-white $W(CO)_5(POCH_3)_3$ crystals were obtained and identified by IR spectroscopy. ν(CO)= 2080.5, 1989.8, 1962.9, 1950.6 and 1919.3 cm^{-1}.

To prepare $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) complex; 637 mg (1.44 mmol) $W(CO)_5P(OCH_3)_3$ was dissolved in n-hexane and 343 mg (1.44 mmol) acryloylferrocene was added to the medium and the reaction mixture was irradiated about 4 hours at 10 ^{o}C. The reaction was followed by IR spectroscopy. After the reaction was completed the solvent was evaporated in vacuum. Solid residue was dissolved in n-hexane and the solution was left overnight at –35 ^{o}C. $W(CO)_4[(P(OCH_3)_3](\eta^2$-acfc) complex was seperated from the solution and dried under vacuum. (0.14 g, 15% yield). MS: m/z 660.0 (M^+). IR(n-hexane) ν(CO) = 2050.7, 1966.3, 1943.8, 1925.6 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ= 4.92 (H1), δ= 4.78 (H7), δ= 4.59 (H2), δ= 4.55 (H3), δ= 4.51 (H8), δ= 4.24 (H1'-H5'), δ= 4.18 (H4), δ= 3.68 (d, $P(OCH_3)_3$, $J(^{31}P-^{13}C)$= 14 Hz), 3.56 (H8'). ^{13}C-NMR (CD_2Cl_2) δ= 198.06 (s, C6), δ= 207.26 (d, CO trans to acfc, $J(^{31}P-^{13}C)$= 16.4 Hz), δ= 204.50 (d, CO trans to trimethylphosphite, $J(^{31}P-^{13}C)$= 27.3 Hz), δ= 197.37 (d, CO cis to acfc and $P(OCH_3)_3$, $J(^{31}P-^{13}C)$= 11), δ= 196.97 (d, CO cis to acfc and $P(OCH_3)_3$, $J(^{31}P-^{13}C)$= 10.9 Hz), δ= 79.99 (C5), δ= 72.64 (C1), δ= 72.42 (C4), δ= 70.31 (C1'-C5'), δ= 69.87 (C2), 69.34 (C3), 69.03 (C7), δ= 62.49 (C8), δ= 52.85 (d, $P(OCH_3)_3$, $J(^{31}P-^{13}C)$= 5.4 Hz).

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Synthesis and the characterization of the ligand, acryloyferrocene

Acryloylferrocene was synthesized by the procedure given in the literature.[25] First, ferrocene was dissolved in CH_2Cl_2 solution and acryloylchloride was added to the solution at room temperature. Then the solution was cooled down to 0 ^oC and Me_3Al and $EtAlCl_2$ was added to the medium dropwise, subsequently. The resulting mixture was stirred for 20 minutes at this temperature. Then, the reaction mixture was hydrolyzed with water and more CH_2Cl_2 was added to the reaction flask. Two layers were seperated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Mg_2SO_4 and purified by column chromatograpy on silica gel.

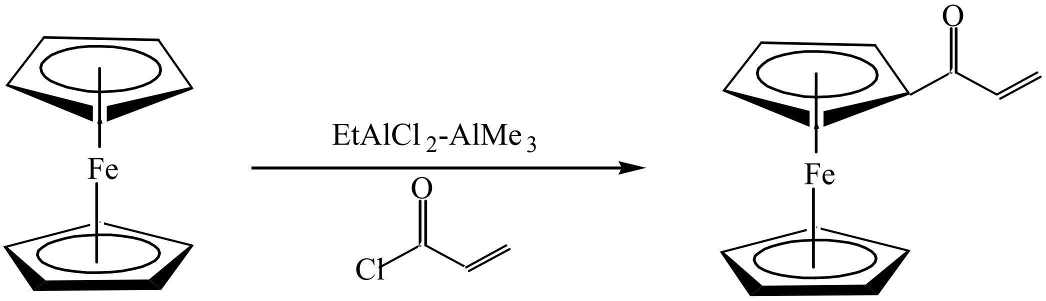


Figure 4.1. Synthesis of acryloylferrocene (acfc) by Friedel-Crafts acylation

The resulting solid acryloylferrocene was identified by IR, ^1H NMR and ^{13}C NMR spectroscopies. The IR spectrum (Figure 4.2.) exhibits a characteristic absorption band at 1665.05 cm^{-1} for CO stretching.

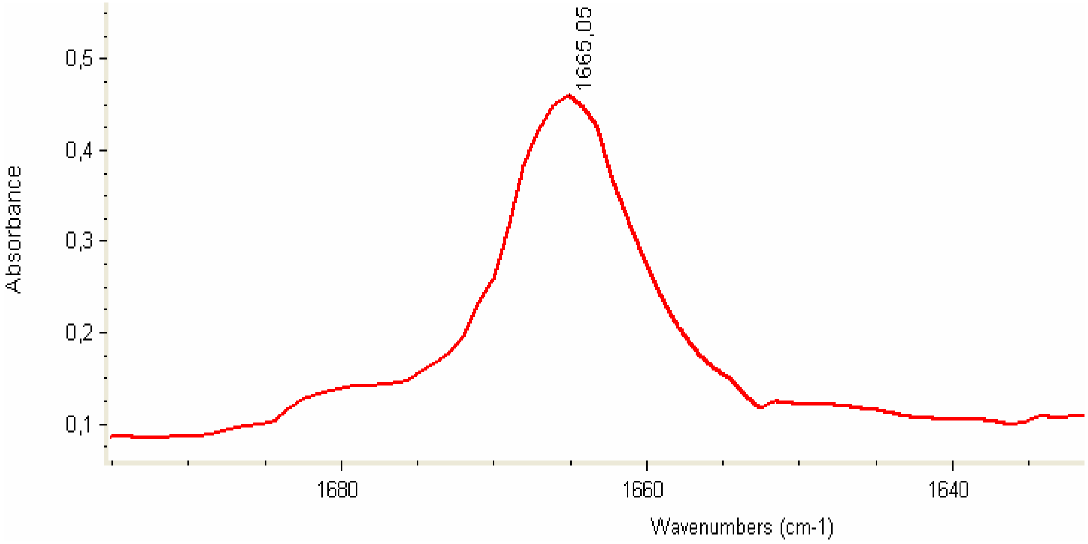


Figure 4.2. Infrared spectrum of acryloylferrocene taken in n-hexane at room temperature

^{1}H NMR and ^{13}C NMR spectra were also taken to identify the synthesized acryloylferrocene molecule. In the ^{1}H NMR spectrum (Figure 4.3.) six different signals were observed for the six different protons of the molecule. The signal at 6.74 ppm belongs to the CH-α (H7) proton. The signal at 6.38 ppm belongs to the olefinic proton trans to CH-α (H8) and the signal at 5.64 ppm belongs to the olefinic proton cis to CH-α (H8') . In the ferrocenyl region three different signals were observed. The signals at 4.76 ppm and at 4.50 ppm belong to the monosubstituted cyclopentadienyl ring (H1,H4 and H2,H3, respectively) and the signal at 4.12 ppm belongs to the 5H of the unsubstituted ferrocenyl ring (H1'-H5'). The protons on the monosubstituted cyclopentadienyl ring resonates at lower field than the five equal protons on the unsubstituted cyclopentadienyl ring, because of the electron withdrawing effects of the substituents. The protons of the monosubstituted ring closer to the electron withdrawing group should be less shielded, so they give a peak at lower magnetic field.

In the ^{13}C-NMR spectrum (Figure 4.4.), the signal at 193.5 ppm belongs to the carbonyl carbon (C6) of the molecule. The signals at 133.4 ppm and ppm 126.7 can be assigned to the olefinic carbons of the molecule (C7 and C8, respectively). The signals at 80.1 ppm, 70.4 ppm and 73.1 ppm belong to the monosubstituted cyclopentadienyl ring of the ferrocenyl moiety (C5; C1,C4 and C2,C3, respectively). Because of the electron withdrawing effect of the substitution the ipso carbon resonates at lower field than the other carbon atoms in the substituted ferrocenyl part of the molecule. The signal at 70.1 ppm belongs to the five equal carbon atoms of the unsubstituted cyclopentadienyl ring of the ferrocenyl moiety (C1'-C5').

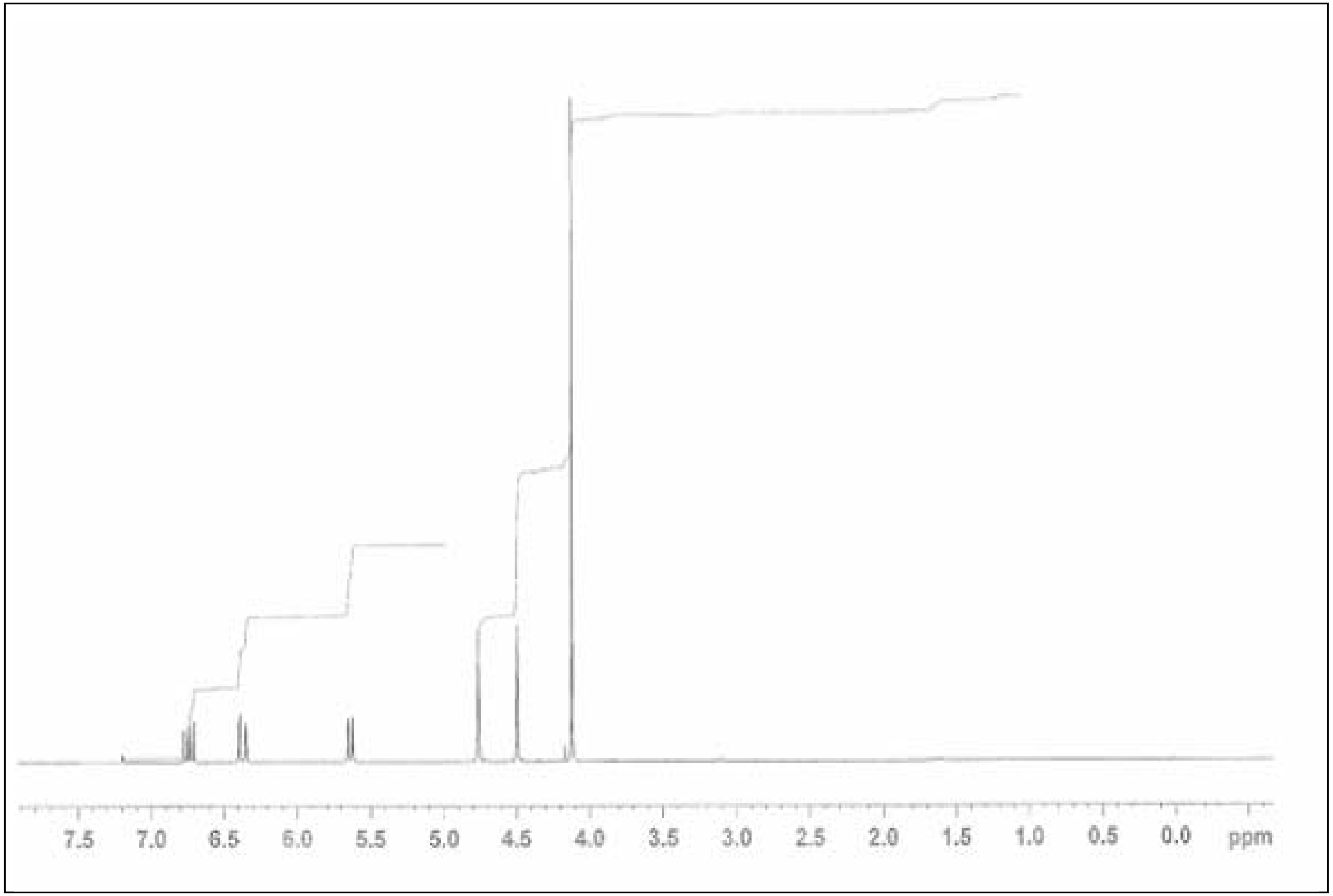


Figure 4.3. ^{1}H-NMR spectrum of acryloylferrocene in $CDCl_3$

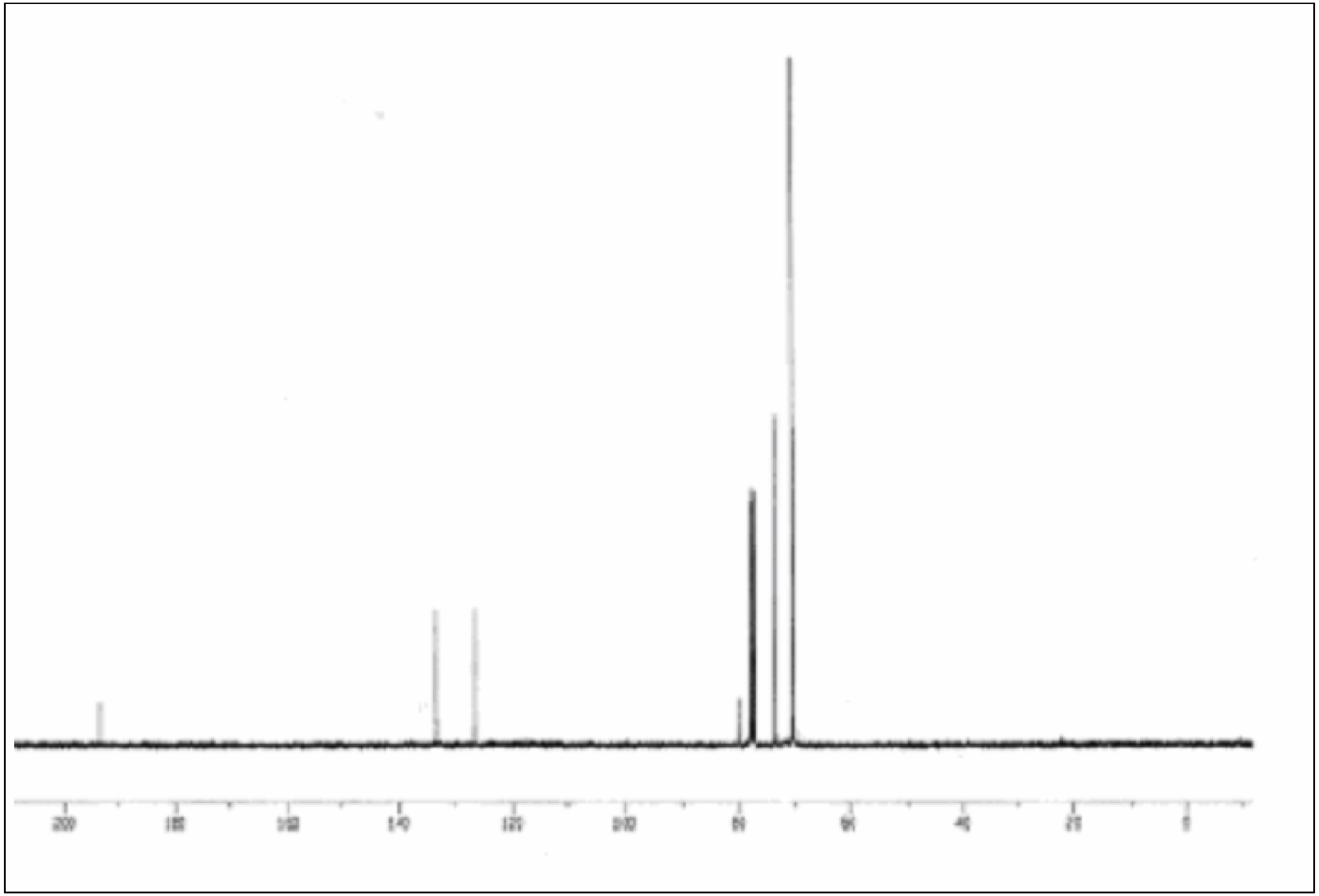


Figure 4.4. ^{13}C-NMR spectrum of acryloylferrocene in $CDCl_3$

4.2. Synthesis and Characterization of the complexes

4.2.1. Synthesis of the pentacarbonylacryloylferrocenetungsten(0), $W(CO)_5(\eta^2\text{-acfc})$

Synthesis of the $W(CO)_5(\eta^2\text{-acfc})$ complex was carried out by the photochemical reaction of $W(CO)_6$ and acryloylferrocene at room temperature. The photosubstitution of one of the CO groups in $W(CO)_6$ with acryloylferrocene resulted in the formation of $W(CO)_5(acfc)$.

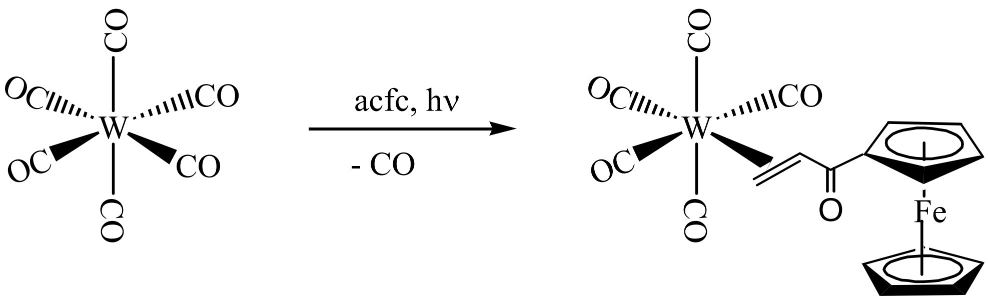


Fig. 4.5. Synthesis of $W(CO)_5(\eta^2\text{-acfc})$

$W(CO)_6$ was dissolved in distilled n-hexane and acryloylferrocene was added into the solution. The solution was irradiated for about 4 hours at room temperature. The decrease in the concentration of the reactant, $W(CO)_6$, and the increase in the concentration of the product, $W(CO)_5(\eta^2\text{-acfc})$, was monitored by means of IR spectra (Figure 4.6. and Figure 4.7.) When the gradual decrease in the signal of hexacarbonyltungsten(0) ceased, the irradiation process was stopped. After evaporation of volatiles in vacuum, the residue was dissolved in n-hexane and the solution was left overnight at –35 °C. Dark red precipitates were seperated from the supernatant solution, dried in vacuum and characterized by IR, Raman, ^1H-NMR and ^{13}C-NMR spectroscopies, mass spectrometry and elemental analysis.

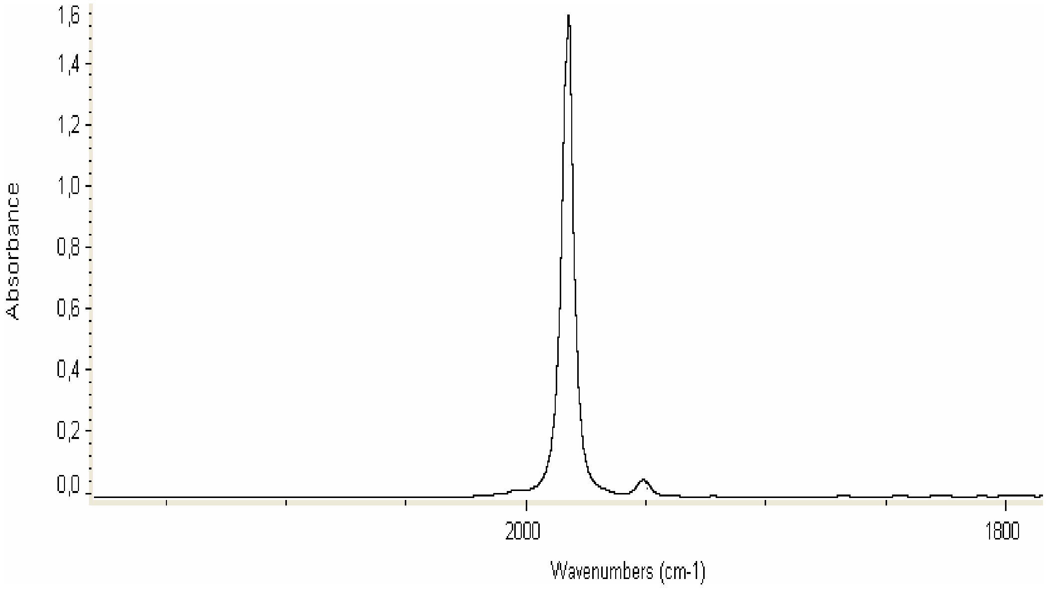


Figure 4.6. IR spectrum of $W(CO)_6$ in n-hexane before irradiation

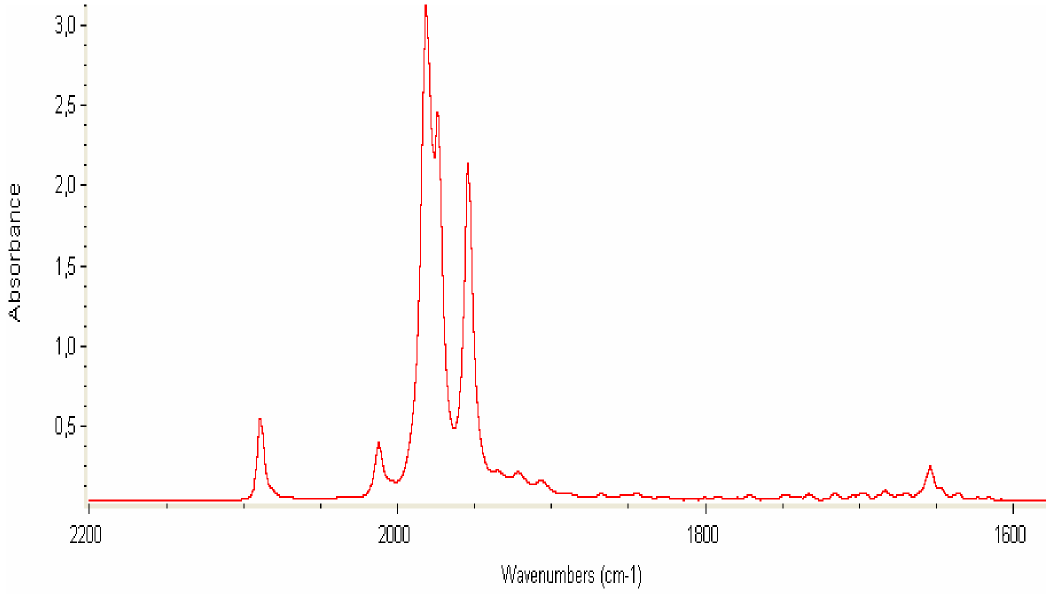


Figure 4.7. IR spectrum of $W(CO)_5(\eta^2\text{-acfc})$ formed after 4 hours irradiation of $W(CO)_6$ in n-hexane solution

The IR spectrum of the product, $W(CO)_5(\eta^2\text{-acfc})$ complex, which was taken in n-hexane, shows four prominent peaks at 2091.0, 2013.2, 1974.6 and 1955.9 cm^{-1}. Five IR active CO stretching vibrations $[3A_1+B_1+B_2]$ are predicted under C_{2v} symmetry. However, one of the A_1 mode should be intrinsically weak in intensity and may remain unobserved or barely observable. According to the spectrum a local C_{2v} symmetry can be assigned to the $W(CO)_5$ moiety of the complex. Besides these four absorption bands, a peak at 1983.0 cm^{-1} was observed in the IR spectrum taken from solution. This peak was attributed to the hexacarbonyltungsten(0) complex. The IR spectrum of the complex taken in KBr pellet (Figure 4.8.), doesn't show the absorption band at 1983.0 cm^{-1}. According to this result, it can be concluded that the complex is not stable in solution and decomposes into hexacarbonyl complex. The CO stretching frequency of the carbonyl group for the acfc molecule shifts from 1665.05 cm^{-1} to 1654.7 cm^{-1} in the $W(CO)_5(\eta^2\text{-acfc})$ complex. This result also shows that acryloylferrocene is coordinated to the complex. Since the shift in the CO stretching frequency is relatively small (about 10 cm^{-1}), acryloylferrocene must be coordinated to the tungsten through C=C bond, not through carbonyl oxygen. The latter coordination would cause a remarkably large shift in the CO stretching frequency of the acryloylferrocene ligand.

In Raman spectrum which was also taken from the solid sample (Figure 4.9.) characteristic hexacarbonyl peak at 1999 cm^{-1} was not observed. All of the five CO stretching bands of the $W(CO)_5$ unit are observable, however, one band at 1964.2 cm^{-1} is intrinsically weak in the Raman spectrum: $\nu(CO)$ = 2083.9, 2007.7, 1964.2, 1943.7 and 1917.5 cm^{-1}. Additionally, a band at 1647.3 cm^{-1} is observed for the CO stretching of the carbonyl group of the acryloylferrocene ligand. The CO stretching frequencies recorded in the IR and Raman spectra differ from each other slightly as they have been taken in different media.

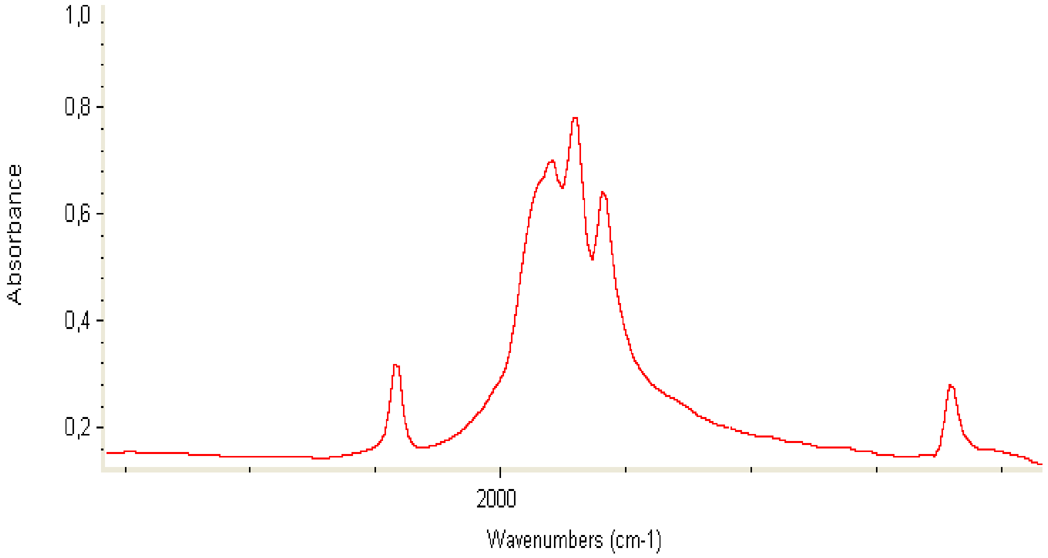
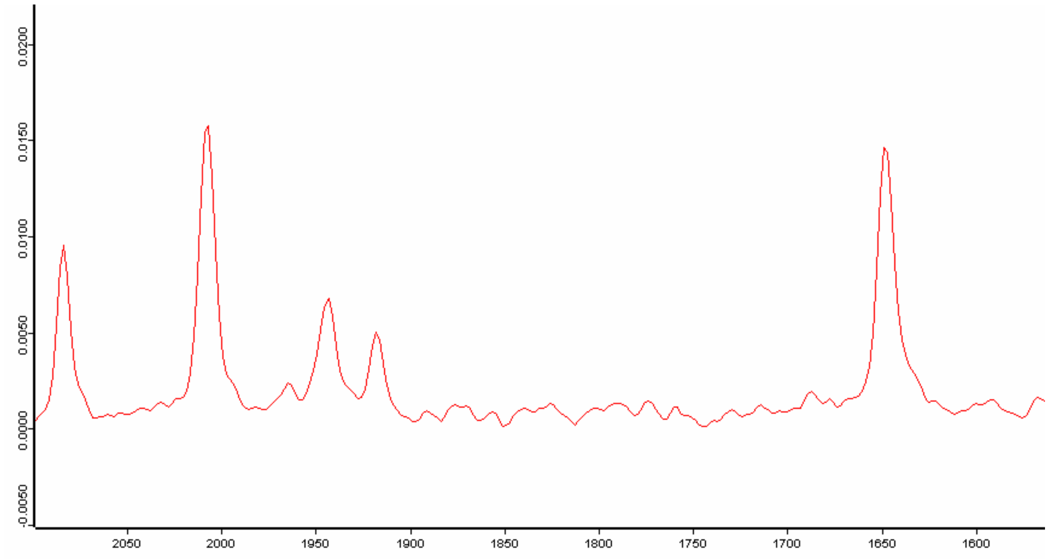
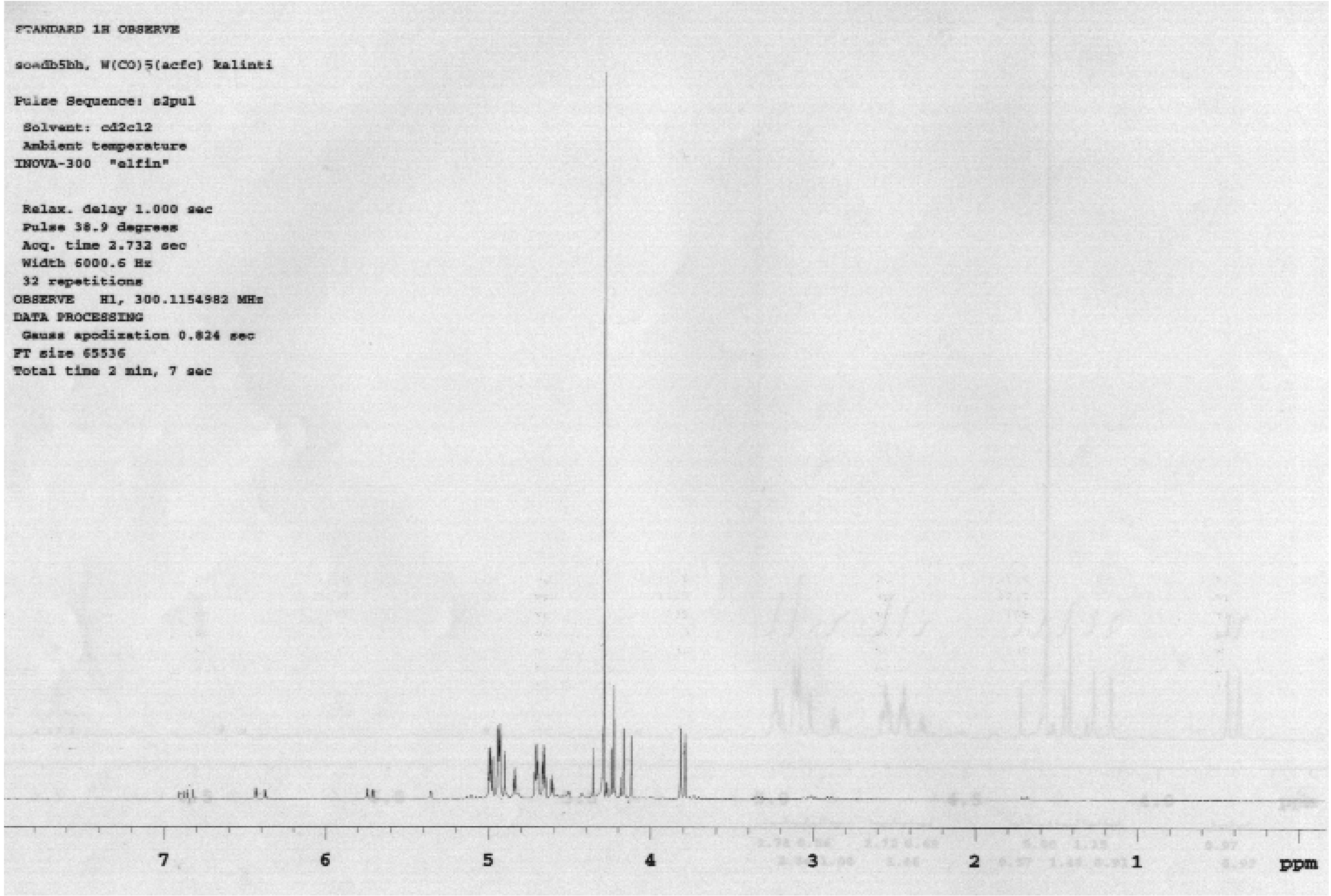


Figure 4.8. Infrared spectrum of W(CO)$_5$(η^2-acfc) in KBr pellet



4.9. Raman spectrum of W(CO)$_5$(η^2-acfc) in solid form

The ^{1}H-NMR spectrum of $W(CO)_5(\eta^2$-acfc) in CD_2Cl_2 (Figure 4.10.), shows two doublets and a multiplet for the three olefinic protons of the acryloylferrocene ligand at 4.95, 4.14 and 3.80 ppm, respectively. Compared to the free acryloylferrocene molecule, the shift of the olefinic proton signals toward higher magnetic field verifies the coordination of acryloylferrocene to the metal. Very weak signals observed at 6.85, 6.40, 5.73 ppm show the existence of free acryloylferrocene as impurity. Consequently, the coordination shifts of the olefinic protons are $\Delta\delta$= 1.90 ppm, $\Delta\delta$= 2.26 ppm, $\Delta\delta$= 1.93 ppm, respectively. The relatively large coordination shift of the olefinic protons shows that acryloylferrocene coordinates to the metal through its C=C double bond.



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STANDARD 1H OBSERVE

soadb5bh, W(CO)5(acfc) kalinti

Pulse Sequence: s2pul

 Solvent: cd2cl2
 Ambient temperature
INOVA-300  "elfin"


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 Pulse 38.9 degrees
 Acq. time 2.732 sec
 Width 6000.6 Hz
 32 repetitions
OBSERVE   H1, 300.1154982 MHz
DATA PROCESSING
 Gauss apodization 0.824 sec
FT size 65536
Total time 2 min, 7 sec
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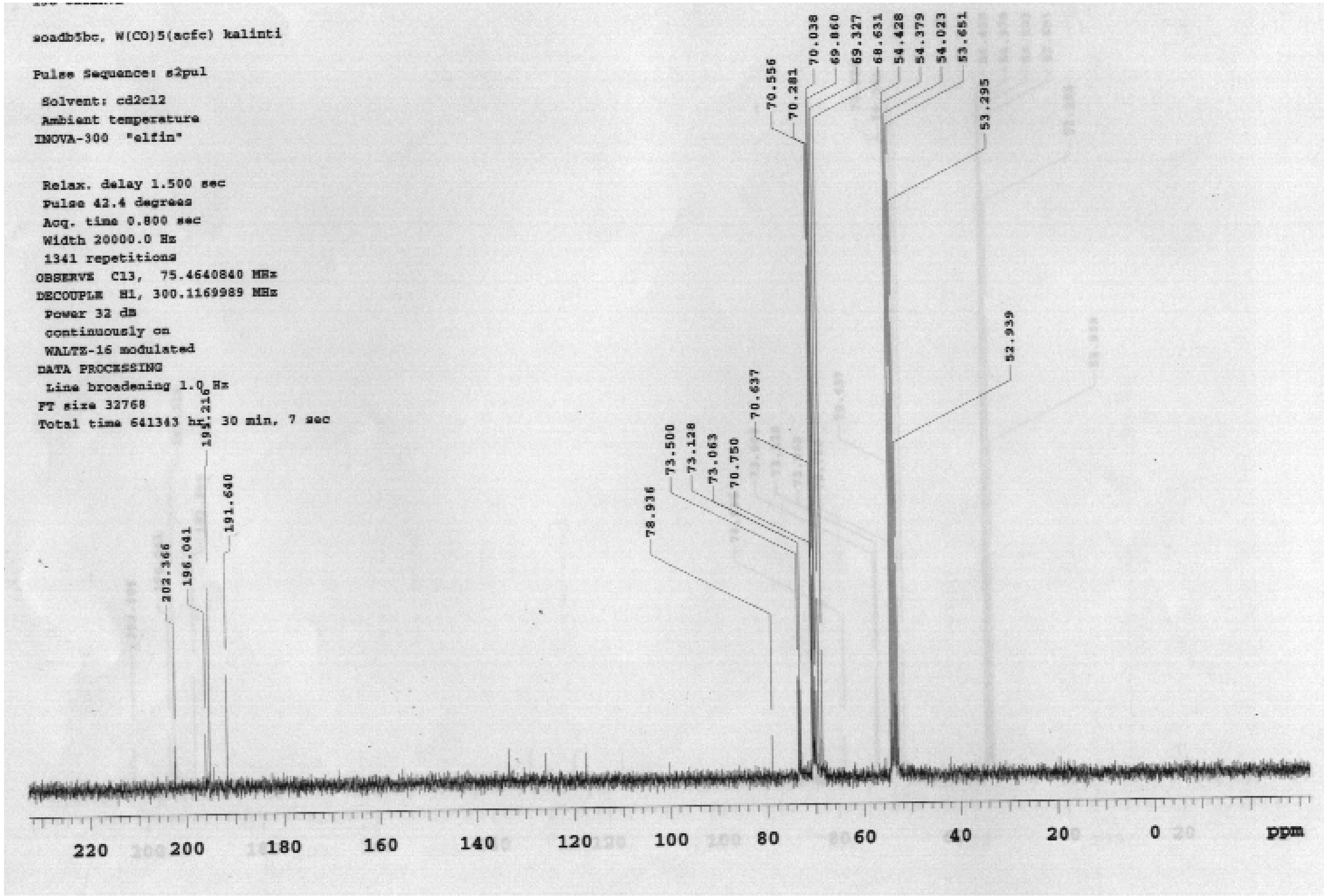
Figure 4.10. ^{1}H-NMR spectrum of $W(CO)_5(\eta^2\text{-acfc})$ in CD_2Cl_2

The ^{13}C-NMR spectrum of $W(CO)_5(\eta^2$-acfc) taken in CD_2Cl_2 (Figure 4.11.), gives five signals in the carbonyl region. The comparison with literature data shows that the signal at 191.6 ppm[32] is due to the $W(CO)_6$ while the signal at 196.0 ppm is attributed to the carbonyl carbon of the free acryloylferrocene molecule. The most intense signal at 195.2 ppm is assigned to the four CO groups cis to the acryloylferrocene ligand, while the signal at 202.4 ppm is assigned to the CO group trans to the acryloylferrocene ligand. The remaining signal at 194.4 ppm is due to the carbonyl carbon of the acryloylferrocene ligand in the complex. The signals at δ 78.94, 73.50, 73.13, 70.56, 69.86 and 68.63 can be attributed to the ferrocenyl carbons of the ligand. The signals observed at δ 70.28 and δ 69.33 belong to the olefinic carbons of the acryloylferrocene ligand. When it is compared with the ^{13}C-NMR spectrum of the free acryloylferrocene molecule, the coordination shifts of olefinic carbons are $\Delta\delta = 63.1$ and 57.4 ppm, respectively, while the shift of the carbonyl carbon of the ligand in the complex is $\Delta\delta = 2.6$ ppm. The large coordination shift of the olefinic carbon signals shows that acryloyferrocene molecule coordinates to the metal through its C=C double bond.



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soadb5bc, W(CO)5(acfc) kalinti

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 Ambient temperature
INOVA-300  "elfin"

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 1341 repetitions
OBSERVE  C13,  75.4640840 MHz
DECOUPLE  H1, 300.1169989 MHz
 Power 32 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 32768
Total time 641343 hr, 30 min, 7 sec
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Figure 4.11. ^{13}C-NMR spectrum of $W(CO)_5(\eta^2\text{-acfc})$ in CD_2Cl_2

In order to understand the stability of the complex, ^{13}C-NMR spectrum was taken again two days later. In the characteristic CO region of the spectrum (Figure 4.12.) it is clear that the signal of $W(CO)_6$ at 191.60 ppm and the signal for the carbonyl group of the free acryloylferrocene molecule at 195.17 ppm increase. This increase explicitly shows that the complex is unstable in the solution and decompose into hexacarbonyltungsten(0) and acryloylferrocene.

Another characterization technique, mass spectroscopy, was used to identify the $W(CO)_5(\eta^2\text{-acfc})$ complex. Figure 4.13. shows the mass spectrum of the complex. The calculated molecular weight of the complex fits to the experimentally observed value of 563.9 g/mol. Furthermore, the characteristic isotop distribution pattern observed for the complex fits to the simulated one for the $C_{18}H_{12}O_6WFe$ formula. So, it can be concluded that the $W(CO)_5(\eta^2\text{-acfc})$ complex was formed and determined by mass spectroscopy.

Table 4.1. gives the results of the elemental analysis for the $W(CO)_5(\eta^2\text{-acfc})$ complex. The experimentally found values are slightly different from the calculated ones. This difference may arise from the fact that the complex is not stable particularly in air.

Table 4.1. Elemental analysis values and theoretical mass percentages of carbon and hydrogen atoms in $W(CO)_5(\eta^2\text{-acfc})$

ATOM	EXPERIMENTAL %	THEORETICAL %
CARBON	38.85	38.30
HYDROGEN	2.26	2.13

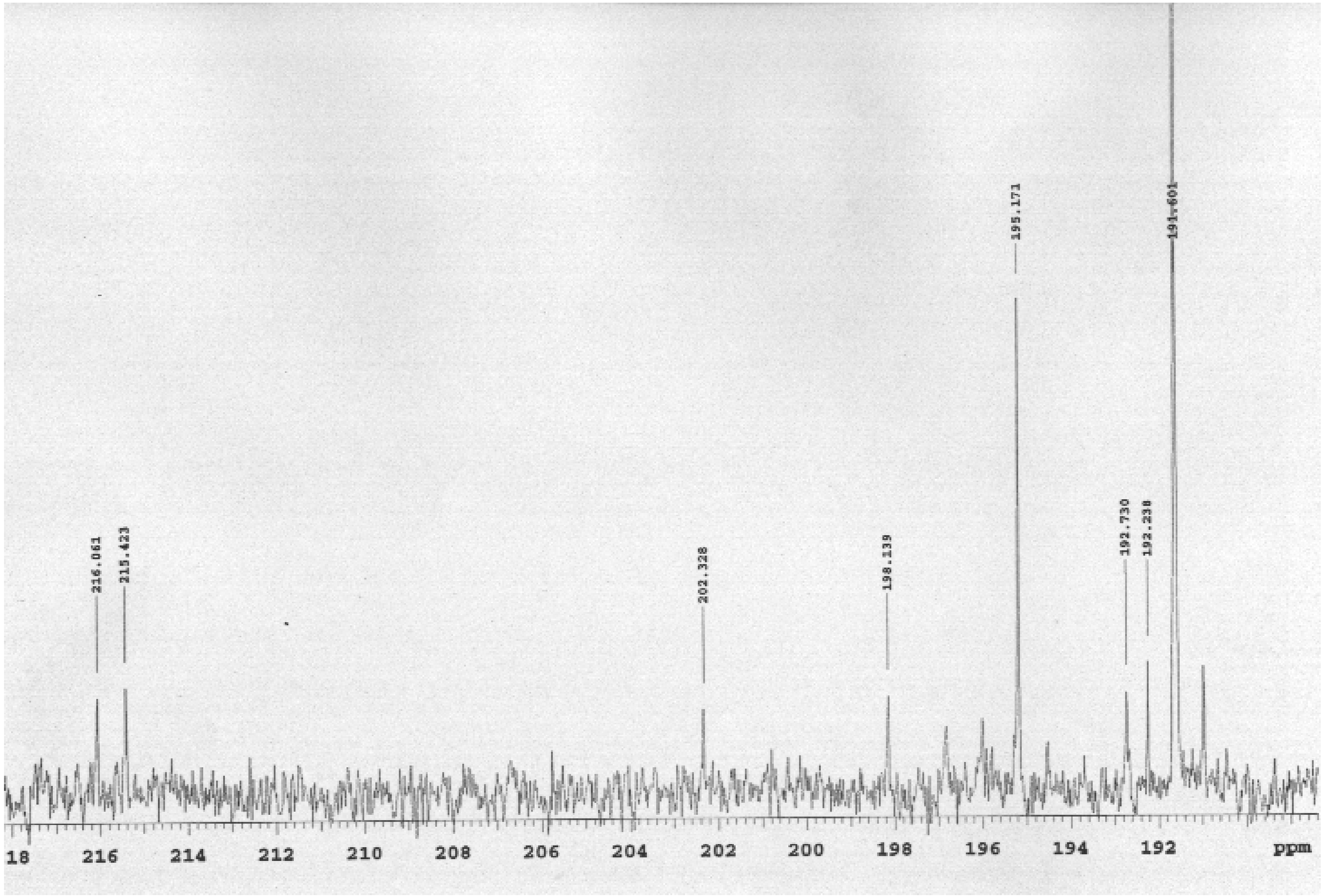

Figure 4.12. ^{13}C-NMR spectrum of W(CO)$_5$(η^2-acfc) taken in CD_2Cl_2 solution two days after synthesis

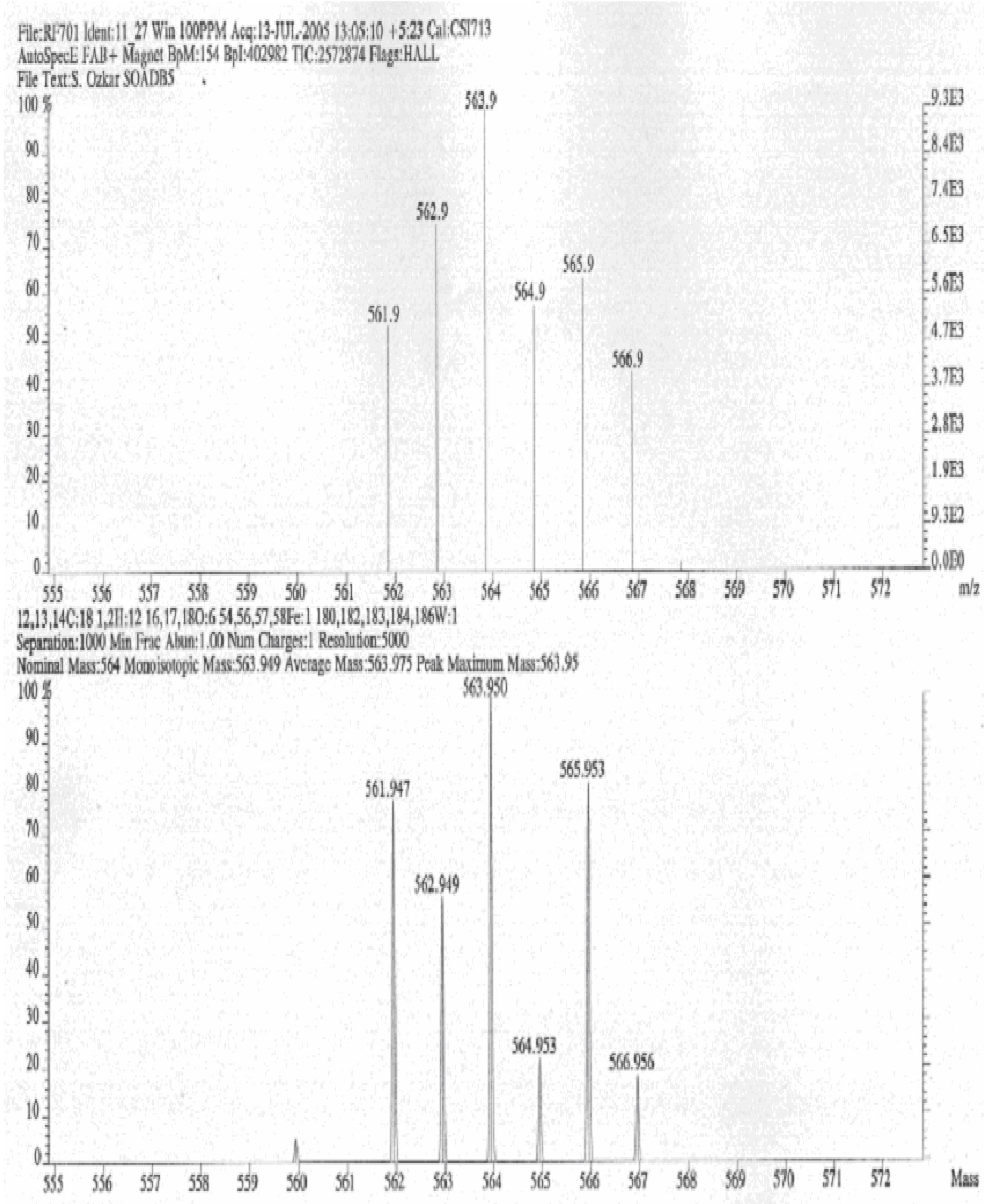

Figure 4.13. Mass spectrum of $W(CO)_5(\eta^2$-acfc): Molecular peak of $W(CO)_5(\eta^2$-acfc) complex, observed (top) and calculated (bottom).

4.2.2. Synthesis and characterization of $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) complex

The presence of a donor ligand can affect the bond between metal and ligand in the complex sterically and electronically. $W(CO)_5(\eta^2$-acfc) could not be isolated as analytically pure substance from the solution because it is unstable with respect to decomposition to $W(CO)_6$ and free acryloylferrocene. Therefore, introducing a donor ligand to the complex may increase the stability of the metal-olefin. A donor ligand makes the metal center electron rich and, hence, increase the back-donation from metal to olefinic ligand. Trimethylphosphite was used as donor ligand. Thus, $W(CO)_4[P(OCH_3)_3]$ (η^2-acfc), a complex containing a donor ligand in addition to the olefinic ligand, could be synthesized photochemically starting with $W(CO)_5[P(OCH_3)_3]$.

$W(CO)_5[P(OCH_3)_3]$ was prepared by the thermal substitution reaction of $W(CO)_5(THF)$ with trimethylphosphite. $W(CO)_5(THF)$ was photogenerated by UV-irradiation of $W(CO)_6$ in THF solution. The reaction was followed by IR spectroscopy. During the irradiation process THF substituted for one carbonyl group. After the monosubstitution reaction was completed, the irradiation was stopped, trimethylphosphite was added to the solution and was stirred overnight at room temperature. The thermal substitution of tetrahydrofuran with trimethylphosphite was also monitored by taking the IR spectrum. Following the formation of the $W(CO)_5[P(OCH_3)_3]$ complex, the solvent was evaporated to isolate the complex. The isolated solid was crystallized in n-hexane solution over dry ice. Yellow-white $W(CO)_5[P(OCH_3)_3]$ crystals were obtained and identified by IR spectrum: $\nu(CO)$= 2080.5, 1989.8, 1962.9, 1950.6 and 1919.3 cm^{-1}.

Then, $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) complex was prepared photochemically by the reaction of $W(CO)_5[P(OCH_3)_3]$ with acryloyferrocene in n-hexane solution. The $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) complex was characterized by means of IR, NMR spectroscopies and mass spectrometry. The IR spectrum of the complex was taken in n-hexane (Figure 4.14.) and shows four prominent absorption bands at 2050.7, 1966.7, 1943.8 and 1925.6 cm^{-1} for the CO stretching .The observation of four bands indicates a cis arrangement of the $W(CO)_4$ moiety, which has then a C_s local symmetry with 3 A' + A" stretching modes.[8] The IR spectrum shows some weak features in addition to the four intense absorption bands due to the cis-$W(CO)_4[P(OCH_3)_3](\eta^2$-acfc). These weak absorption bands can be attributed to the unreacted $W(CO)_5[P(OCH_3)_3]$ (only the band at 2079 cm^{-1} is observable, the others are hidden under the strong absorptions), and $W(CO)_3[P(OCH_3)_3]_2(\eta^2$-acfc) (2001 and 1891 cm^{-1}, the third one is hidden under the strong absorptions). $W(CO)_3[P(OCH_3)_3]_2(\eta^2$-acfc) complex was also monitored by mass spectrometry. Molecular weight: 756.1 g/mol

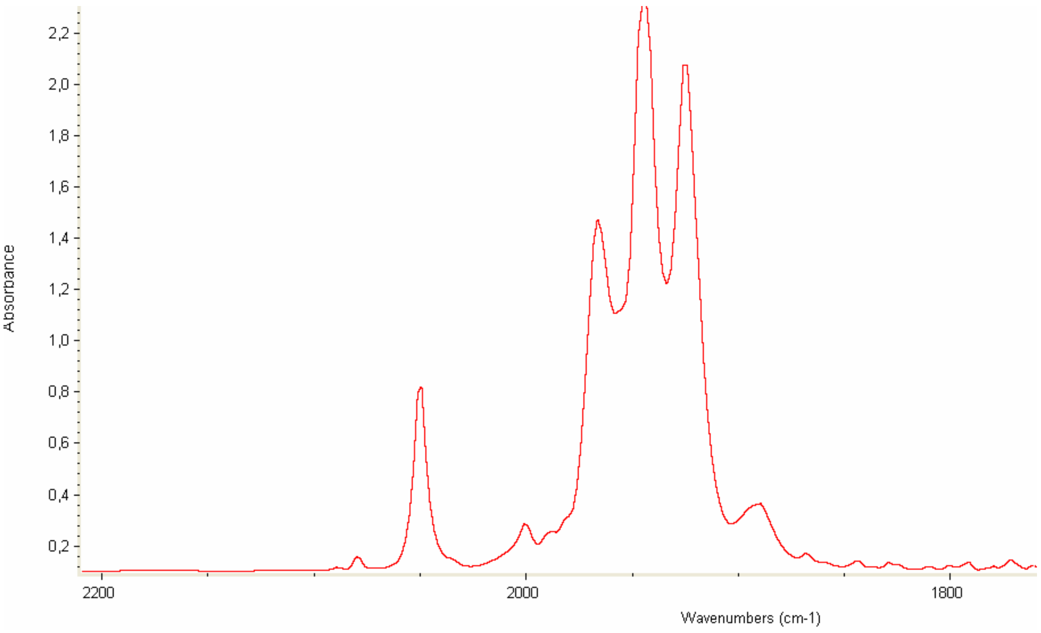

Figure 4.14. IR spectrum of $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) in n- hexane

The ^{1}H-NMR spectrum of cis-$W(CO)_4[P(OCH_3)_3]$(η^2-acfc) taken in CD_2Cl_2 solution (Figure 4.15) shows one doublet at 3.68 ppm with a ^{31}P-^{1}H coupling constant of 14 Hz for the $P(OCH_3)_3$ ligand, four signals at 4.92, 4.59, 4.55 and 4.18 ppm for the ferrocenyl moiety and three multiplets centered at about 4.78, 4.51, and 3.56 ppm for the olefinic protons of acryloylferrocene ligand. The multiplets of the olefinic protons are further complicated by the ^{31}P-^{1}H coupling and therefore difficult to analyze. Compared to the free acryloylferrocene molecule, the signal of olefinic protons show a remarkable coordination shift $\Delta\delta$=1.91 ppm, 1.88 ppm and 2.1 ppm, respectively, indicating the coordination of acryloylferrocene through the C=C bond.

^{13}C-NMR spectrum of the $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) complex was taken (Figure 4.16.) in CD_2Cl_2 solution. The spectrum exhibits four doublets and one singlet for the cis-$W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) in carbonyl region. The singlet at 198.06 ppm can readily be assigned to the carbonyl carbon of the acryloylferrocene ligand. The four doublets are due to the four different CO ligands in cis-$W(CO)_4[(P(OCH_3)_3](\eta^2$-acfc) (Figure 4.17). Because of ^{31}P-^{13}C coupling, all of the four carbonyl signals are of doublet structure. The doublet at the highest chemical shift of 207.26 ppm with J(^{31}P-^{13}C)= 16.4 Hz is assigned to the CO ligand trans to the acryloylferrocene ligand. The doublet at 204.5 ppm with the largest ^{31}P-^{13}C coupling constant of 27.3 Hz is assigned to the CO ligand trans to the trimethylphosphite. The other two doublets at 197.37 and 196.97 ppm with ^{31}P-^{13}C coupling constant of 11 and 10.9 Hz, respectively, are assigned to the CO ligands trans to each other (cis to both acfc and $P(OCH_3)_3$ ligands). There exists two additional doublets at 199.9 and 195.54 ppm with ^{31}P-^{13}C coupling of 12.9 Hz and 9.1 Hz, respectively. By comparison with the literature values,[33] these can readily be attributed to the $W(CO)_5[(POCH_3)_3]$ complex, which remains unreacted as seen also in IR and mass spectra. The doublet at 52.85 ppm with the ^{31}P-^{13}C coupling constant of 6 Hz is due to the methyl carbons of the trimethylphosphite ligand. The weak doublet at 52.40 ppm with J(^{31}P-^{13}C)= 10.9 Hz can be attributed to the methyl carbons of the trimethylphosphite ligand of the $W(CO)_5[(POCH_3)_3]$ complex which remains unreacted in small amount. The olefinic carbon atoms give two signals at

69.03 and 62.49 ppm which have been shifted by $\Delta\delta = 64.4$ and 64.2 ppm, respectively, compared to the free acryloylferrocene molecule.

In the mass spectrum of the complex (Figure 4.18.), the observed and the calculated values of the molecular peak are in accordance. The formation of the $W(CO)_4[P(OCH_3)_3](\eta^2\text{-acfc})$ complex can be concluded from mass spectrum as well as ^{13}C-NMR and ^{1}H-NMR spectra. Mass spectrum also shows the existence of the $W(CO)_3[P(OCH_3)_3]_2(\eta^2\text{-acfc})$ complex with the molecular weight of 756.1 g/mol and $W(CO)_4[P(OCH_3)_3]_2$ with the molecular weight of 543.8 g/mol (Figure 4.19).

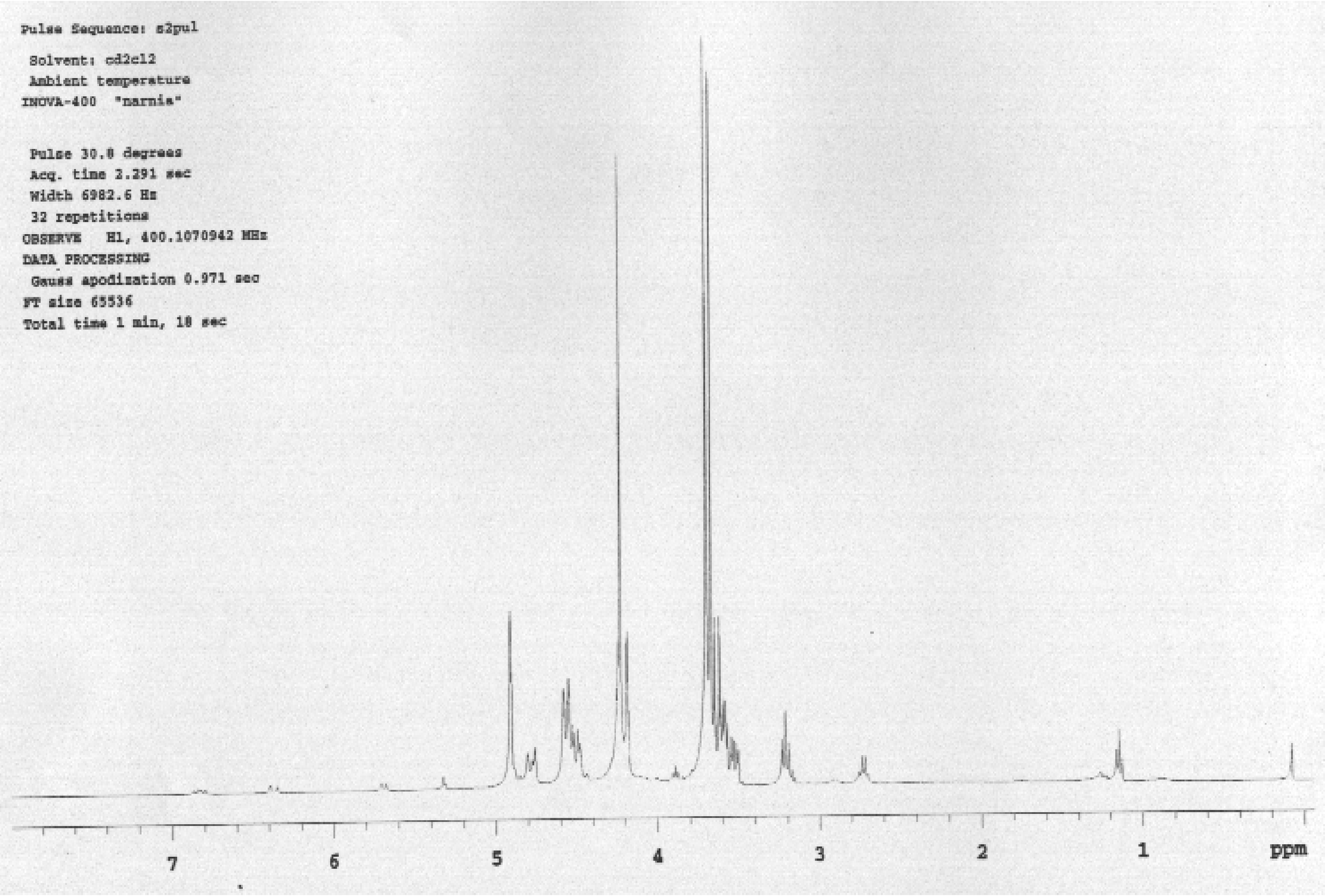

Figure 4.15. ^{1}H-NMR spectrum of cis-W(CO)$_4$[P(OCH$_3$)$_3$](η^2-acfc) taken in CD$_2$Cl$_2$ solution

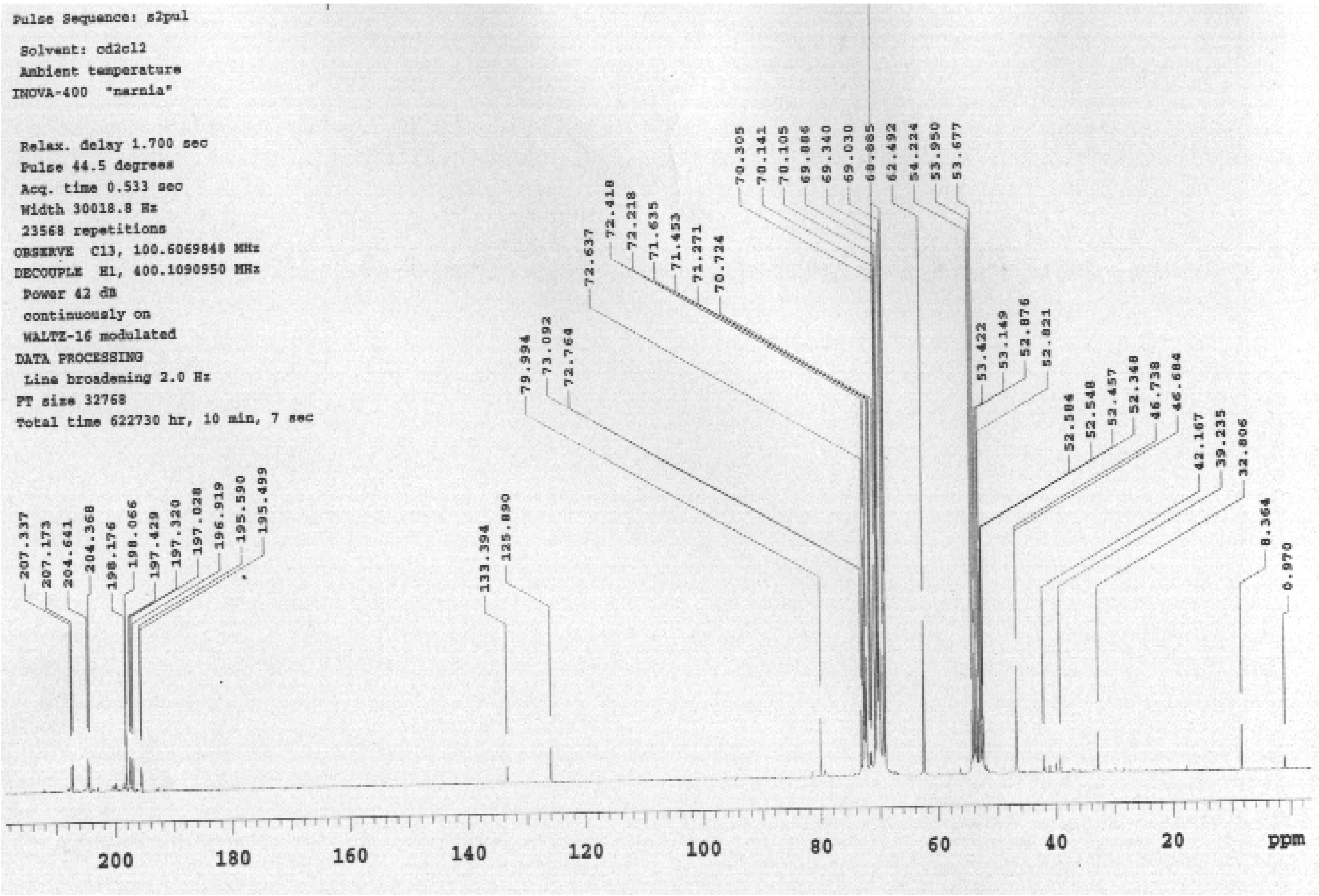

Figure 4.16. ^{13}C-NMR spectrum of cis-W(CO)$_4$[P(OCH$_3$)$_3$](η^2-acfc) taken in CD$_2$Cl$_2$ solution

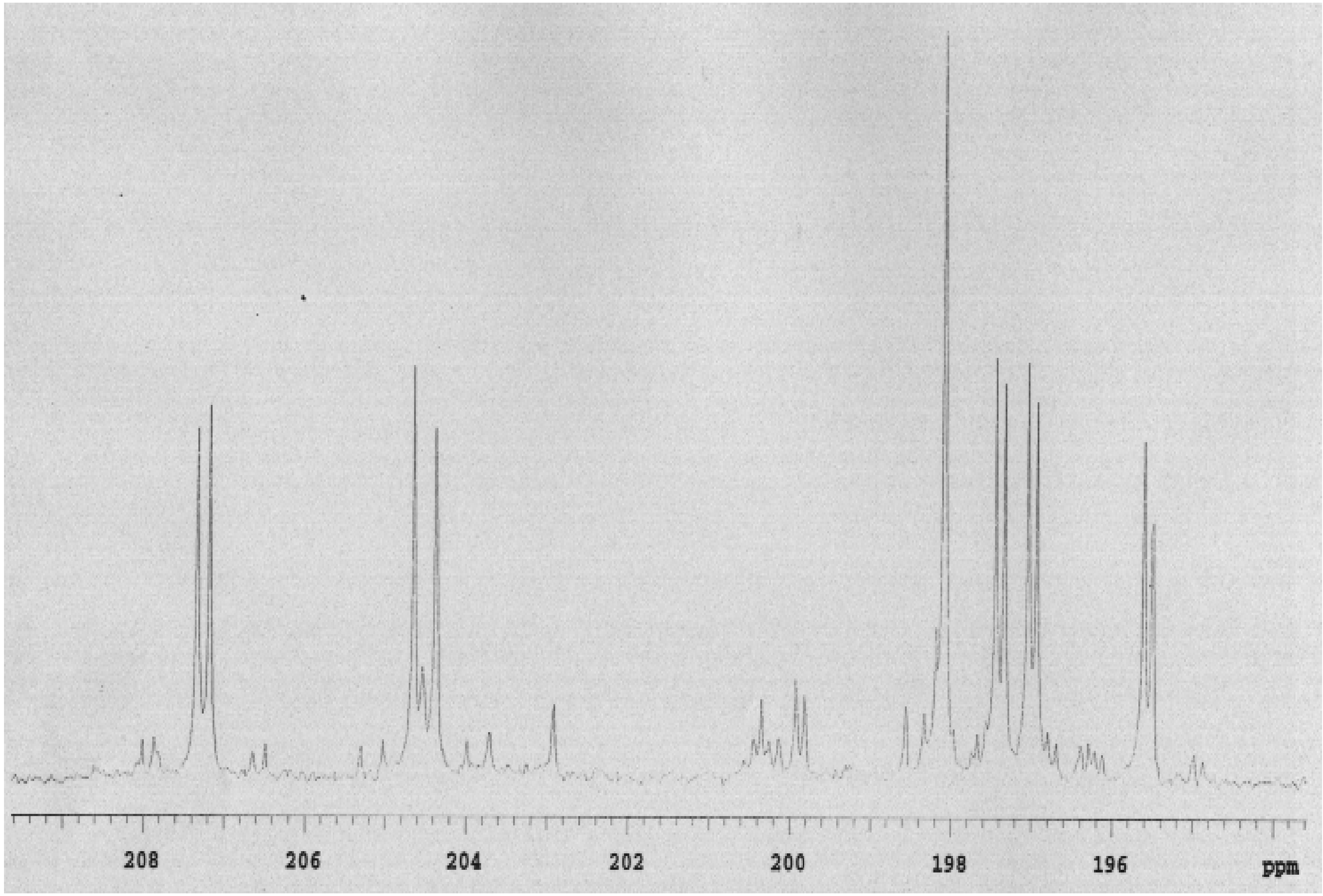

Figure 4.17. CO region of ^{13}C-NMR spectrum of cis-W(CO)$_4$[P(OCH$_3$)$_3$](η^2-acfc) taken in CD$_2$Cl$_2$ solution

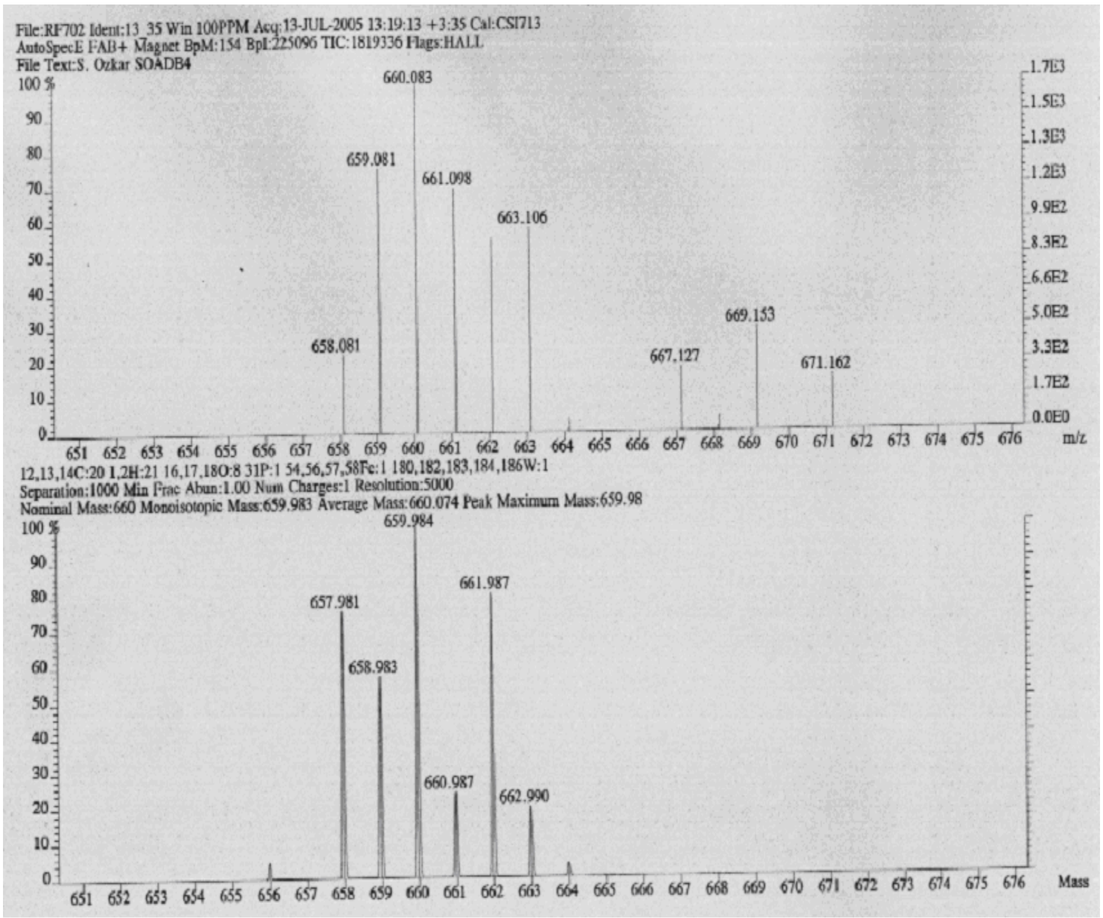

Figure 4.18. Mass spectrum of cis-W(CO)$_4$[P(OCH$_3$)$_3$](η^2-acfc): Molecular peak of cis-W(CO)$_4$[P(OCH$_3$)$_3$](η^2-acfc) complex, observed (top) and calculated (bottom).

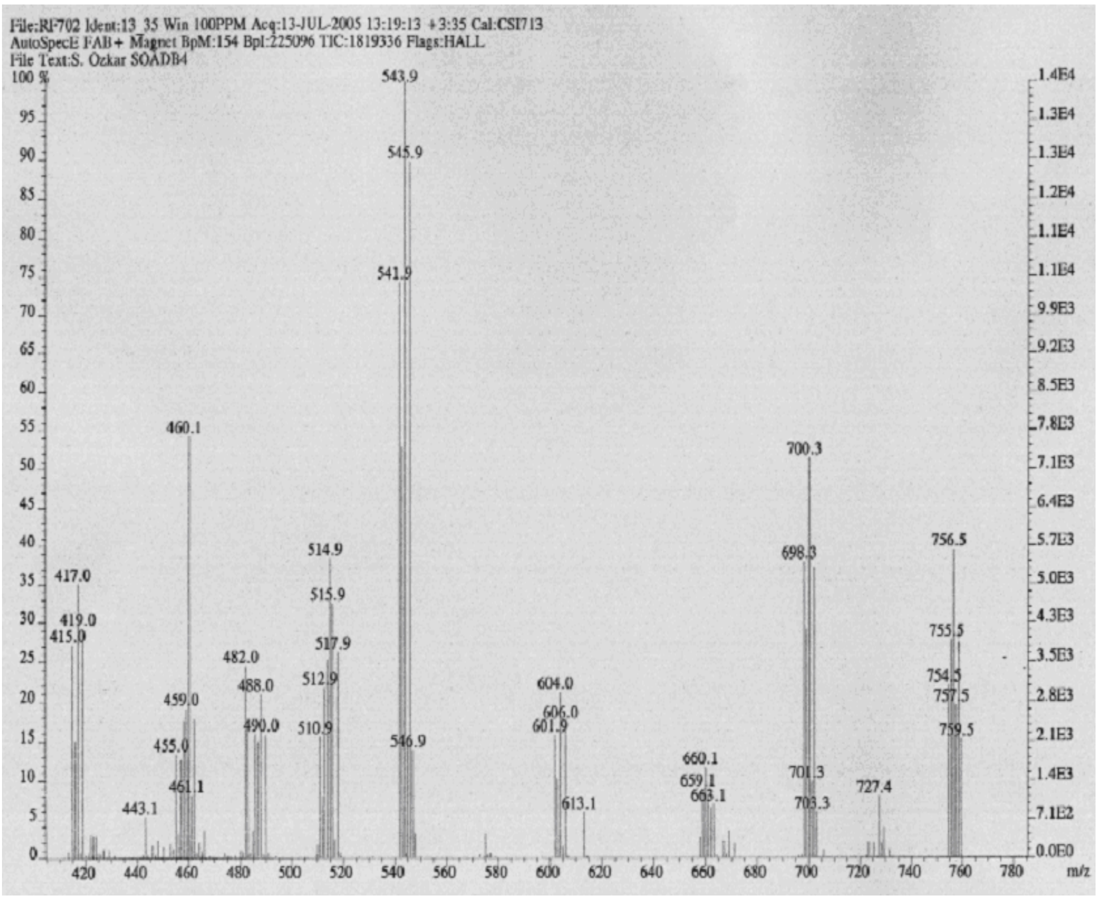

Figure 4.19. Mass spectrum of cis-$W(CO)_4[P(OCH_3)_3](\eta^2$-acfc)

CHAPTER 5

CONCLUSION

UV irradiation of hexacarbonyltungsten(0), $W(CO)_6$, in n-hexane solution in the presence of acryloylferrocene, acfc, gives the pentacarbonylacryloylferrocenetungsten(0) complex, $W(CO)_5(\eta^2\text{-acfc})$, as the sole product of photosubstitution reaction.

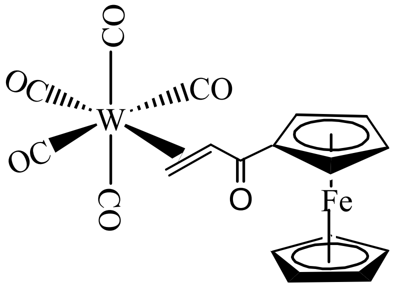

Figure 5.1. $W(CO)_5(\eta^2\text{-acfc})$

Different from the general scheme of sequential photosubstitution of hexacarbonylmetal(0) with olefin,[16] photolysis of $W(CO)_6$ in the presence of acryloylferrocene gives only the monosubstitution product, $W(CO)_5(\eta^2\text{-acfc})$. Prolonged irradiation doesn't give any further CO substitution reaction, contrarily it results in backward reaction of the product, $W(CO)_5(\eta^2\text{-acfc})$ complex, to decompose into hexacarbonyltungsten(0) complex and free acryloylferrocene. The formation of the complex was monitored by FT-IR spectroscopy. After the reaction was completed, the resulting complex was isolated and characterized by the techniques of IR, Raman, NMR spectroscopy and mass Spectrometry and elemental analysis. The $W(CO)_5(\eta^2$-acfc) complex was found not to be stable in solution and decomposed into hexacarbonyltungsten(0) complex and free acryloylferrocene.

In order to stabilize the tungsten-olefin bond with the acryloylferrocene, a donor ligand was introduced into the complex. For this purpose, trimethylphosphite was used as donor ligand and a tungsten carbonyl complex containing a donor ligand and an olefinic ligand was designed. Starting with $W(CO)_6$, $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) was synthesized and characterized by IR, NMR spectroscopies and mass spectrometry. This complex was shown to have a cis arrangement of the $W(CO)_4$ unit in the octahedral $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) molecule. The ^{13}C-NMR spectrum shows that all of the four carbonyl ligands are different. The $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc) was found to be even less stable than $W(CO)_5(\eta^2$-acfc). Thus, introducing a donor ligand into the molecule doesn't provide additional stability for the tungsten-olefin bond in the case of acryloylferrocene.

In general, the metal-carbonyl complexes of acryloylferrocene are not stable. Attempts to prepare the chromium and molybdenum analogs failed, presumably because of the instability of the metal-olefin bond. Together with the large coordination shifts of olefinic carbon and proton signals in both complexes $W(CO)_5(\eta^2$-acfc) and $W(CO)_4[P(OCH_3)_3](\eta^2$-acfc), this instability may be considered as an indication for the activation of the acryloylferrocene C=C bond upon coordination to a transition metal.

REFERENCES

[1] Bochman M.; *Organometallics 1-Complexes with Transition Metal-Carbon σ-bonds*; Oxford University Press, Oxford , 1994

[2] Zeise, W.C; *Ann. Phys*. (Leipzig) (2) 9 (1827) 632

[3] Wilkinson G., Rosenblum M., Whiting M.C., Woodward R.B.; *JACS* , 74 (1952) 2125

[4] Heck, R.F.; *Organotransition Metal Chemistry A Mechanistic Approach ;* Academic Press, New York and London, 1974

[5] Pruchnik, F.P.; *Organometallic Chemistry of the Transition Elements* ; Plenum Press, New York and London, 1990

[6] Tsutsui, M., Morris, N.L., Nakamura, A., Ichikawa, M., Mori, K.; *Introduction to Metal π-Complex Chemistry* ; Plenum Press, New York-London , 1970

[7] Elschenbroich, C., Salzer A.; *Organometallics A Concise Introduction* ; VCH Publishers, Inc., 1992

[8] Bratermann, P.S.; *Metal Carbonyl Spectra*; Academic Press, Lomdon, New York, San Francisco, 1975

[9] Jones, L.H.; *Advances in the Chemistry of the Coordination Compounds* ; Macmillan, New York, 1961

[10] Cotton, F. A.; *Modern Coordination Chemistry*, Interscience, New York, 1960

[11] Mond, L., Langer C., Quincke, F.; *J. Chem. Soc.* (1980) 749

[12] Wender, I., Pino, P.; *Organic Synthesis via Metal Carbonyls*, Vol. 1 ; Interscience, New York, 1968

[13] Huheey, J.E., Keiter, E.A., Keiter, R.L.; *Inorganic Chemistry Principles and Structure and Reactivity*; 4th Edition, Harper Collins College Publishers, New York, 1993

[14] Strohmeier, W., Von Hobe D.; *Chem. Ber.*, 94, 1964, 761; Nasielski J., Colas, A.; *Inorg. Chem.* 17 (1978) 237

[15] Strohmeier W.; *Angew. Chem.*, 76 (1964) 873; *Angew. Chem., Int., Ed., Engl.*, 3, (1964) 730; Koerner, G.E., Grewels, F.W.; *Top. Curr. Chem.*, 13 (1969) 366; Geoffroy, G.L., Wrighton, M.S.; *Organometallic Photochemistry*; Academic Press, New York, 1979

[16] Grevels, F.W., Jacke, J., Klotzbücher, W.E., Mark, F., Skibbe, V., Schaffner, K., Özkar S.; *Organometallics*, 18 (1999) 3278

[17] *Gmelin Handbook of Inorganic and Organometallic Chemistry, Fe Organic Compounds*, 8th ed., vol. A10, Springer, Berlin, 1991

[18] Togni, A.; Hayashi, T.; *"Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science",* VCH, Weinheim, 1995

[19] Bear, P.D., Smith, D.K.; *Prog. Inorg. Chem.*, 46 (1997) 1

[20] Miller, J.S., Epstein, A.J.; *Angew. Chem. Int. Ed. Engl*, 34 (1994) 385

[21] Long, N.J.; *Angew. Chem. Int. Ed. Engl.*, 35 (1995) 21

[22] Coles, H.J., Meyer, S., Lehmann, P., Deschenaux, R., Juaslin, I.; *J. Mater. Chem.*, 9 (1999) 1085

[23] Astruc, D.; *New. J. Chem.,* 16 (1992) 305

[24] Özkar, S., Kayran, C., Demir, N.; *J. Organomet. Chem.* **;** 688 (2003) 62

[25] Doğan, Ö., Şenol, V., Zeytinci, S., Koyuncu, H., Bulut, A.; *J. Organomet. Chem.*, 691 (2005) 430

[26] Grevels, F.W., Jacke, J., Özkar, S., Saldamlı, S.; *Organometallics*, 24 (2005) 4613

[27] Shriver D.F., Atkins P.W., Langford S.H.; *Inorganic Chemistry 2nd edition*; Oxford University Press , Oxford , 1994

[28] Özkar, S., Tunalı, N.K. ; *Anorganik Kimya*, Gazi Üniversitesi, yayın no: 185, Ankara, 1993

[29] Templeton, J.L.; *Advanced Organometallic Chemistry, Four-Electron Alkyne Ligands in Molybdenum(II) and Tungsten(II) Complexes*, Academic Press Inc., 29 (1989) 1-100

[30] King, R.B., Eisch, J.; *Organometallic Syntheses*, Transition Metal Compounds, (1965) 1

[31] Mathieu, R., Lenzi, M., Poilblanc, R. ; Inorg. Chem. 9 (1970) 2030

[32] Bodner, G. M., Inorg. Chem., 14 (1975) 2694

[33] Braterman, P.S., Milne, D.W., Randall, E.W., Rosenberg, E.; *J. C. S. Dalton*, (1973) 1027