PENTACARBONYL(2-FERROCENYLPYRIDINE)METAL(0) COMPLEXES OF GROUP 6

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ABSTRACT

PENTACARBONYL(2-FERROCENYLPYRIDINE)METAL(0) COMPLEXES OF GROUP 6

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Pentacarbonyl(2-ferrocenylpyridine)metal(0) complexes of Group 6 were attempted to be prepared for the first time by using both photolytic substitution of CO from the hexacarbonylmetal(0) with 2-ferrocenylpyridine (2-Fcpy) and thermal replacement of a labile-ligand in an intermediate complex. Substitution of *cis*-cyclooctene in $Cr(CO)_5$(*cis*-cyclooctene) with 2-Fcpy in n-hexane did not yield the desired complex. However, $Cr(CO)_5$(2-Fcpy) could be obtained by irradiating $Cr(CO)_6$ in the presence of 2-Fcpy in n-hexane. Since $Cr(CO)_5$(2-Fcpy) decomposed to $Cr(CO)_6$ and free 2-Fcpy during evaporation of volatiles and crystallization from n-hexane, NMR data could not be obtained. Similarly, $Mo(CO)_5$(2-Fcpy) was formed from irradiation of $Mo(CO)_6$ in the presence of 2-Fcpy in n-hexane, but the conversion of $Mo(CO)_6$ to $Mo(CO)_5$(2-Fcpy) was low, therefore, $Mo(CO)_5$(2-Fcpy)

could not be isolated. Thermal substitution of *cis*-$Mo(CO)_4(pip)_2$ (pip: piperidine) with 2-Fcpy afforded a mixture of $Mo(CO)_5$(2-Fcpy) and $Mo(CO)_5$(pip), which could not be separated from each other. $W(CO)_5$(2-Fcpy) was prepared both by irradiation of $W(CO)_6$ with 2-Fcpy in n-hexane and by thermal substitution of THF in $W(CO)_5$(THF) by 2-Fcpy. Although the latter reaction gave approximately complete conversion of $W(CO)_5$(THF) to $W(CO)_5$(2-Fcpy) as estimated from the IR spectrum, most of $W(CO)_5$(2-Fcpy) decomposed to $W(CO)_6$ and free 2-Fcpy during evaporation under vacuum. Thus, it is concluded that the $M(CO)_5$(2-Fcpy) complexes are not stable enough to be isolated. The main reason behind their instability is the weak π-accepting ability of 2-Fcpy. The complexes were identified by IR spectroscopy and partially by ^{1}H- and ^{13}C-NMR spectroscopic techniques for $M(CO)_5$(2-Fcpy) (M: Mo, W).

ÖZ

GRUP 6 PENTAKARBONİL(2-FERROSENİLPİRİDİN)METAL(0) KOMPLEKSLERİ

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Grup 6 pentakarbonil(2-ferrosenilpiridin)metal(0) kompleksleri, ilk kez hekzakarbonilmetal(0) de bir CO ligandının 2-ferrosenilpiridin (2-Fcpy) ile fotolitik yerdeğiştirmesinden ve ara bir kompleksteki zayıf bir ligandın 2-Fcpy ile ısıl yerdeğiştirmesiyle elde edildi. $Cr(CO)_5$(*cis*-siklookten) kompleksinde *cis*-siklooktenin 2-Fcpy ile n-hekzandaki tepkimesi istenen kompleksi üretmedi. Ancak, $Cr(CO)_5$(2-Fcpy), n-hekzanda $Cr(CO)_6$ ile 2-Fcpy nin ışınlanmasından elde edilebildi. $Cr(CO)_5$(2-Fcpy), çözücü uçurma işlemi ve kristallendirme sırasında $Cr(CO)_6$ ve serbest 2-Fcpy ayrıştığından NMR verileri alınamadı. Benzer şekilde, $Mo(CO)_5$(2-Fcpy) kompleksinin n-hekzanda $Mo(CO)_6$ ile 2-Fcpy nin ışınlanmasından oluştuğu gözlendi, fakat $Mo(CO)_6$ nin $Mo(CO)_5$(2-Fcpy) kompleksine dönüşümü düşük olduğundan, $Mo(CO)_5$(2-Fcpy) izole edilemedi. *cis*-

$Mo(CO)_4(pip)_2$ (pip: piperidin) nin 2-Fcpy ile yerdeğiştirme tepkimesi $Mo(CO)_5$(2-Fcpy) ve $Mo(CO)_5(pip)$ karışımını verdi, bu kompleksler birbirinden ayrılamadı. $W(CO)_5$(2-Fcpy), hem $W(CO)_6$ nin 2-Fcpy ile n-hekzanda ışınlamasından hem de $W(CO)_5(THF)$ deki THF in 2-Fcpy ile ısıl yerdeğiştirmeisnden elde edildi. Son tepkime hemen hemen $W(CO)_5(THF)$ nin $W(CO)_5$(2-Fcpy) ye tam dönüşümünü vermesine karşın (IR spektrumundan izlendiği gibi), $W(CO)_5$(2-Fcpy) kompleksinin çoğu vakumda uçurma işlemi sırasında $W(CO)_6$ ve serbest 2-Fcpy ye ayrıştı. $M(CO)_5$(2-Fcpy) kompleksleri izole edilebilecek kadar kararlı değildir. Bunların kararsızlığının ana nedeni, 2-Fcpy ligandının zayıf bir π-alıcısı olmasıdır. Kompleksler ancak IR spektroskopisi ile ve $M(CO)_5$(2-Fcpy) (M: Mo, W) için kısmen de ^{1}H- ve ^{13}C-NMR spektroskopi teknikleriyle tanımlandı.

To My Parents

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CHAPTER 1

INTRODUCTION

Organometallic compounds are those in which there is a metal-carbon bond. According to this definition, in the case of transition metals, the organometallic compounds include not only metal carbonyls, olefin complexes, cyclopentadienyl, and other π-complexes, but also cyanide and fulminate compounds. In organometallic compounds, the bond is generally polarized as follows: $M^{\delta+}–C^{\delta-}$. Consequently, the metal atom will be susceptible to nucleophilic attack while the carbon atom will be susceptible to electrophilic attack. Metal-carbon bond in most organometallic compounds has, to a significant degree, covalent character. Definite ionic character of this bond is generally manifested only in compounds of the alkali and alkaline earth metals. The ionic or covalent contribution to the bond depends on ionization potential of the metal, the size of a resulting ion, the ratio of the ionic charge to its radius, and σ-donor, π- donor, and π- acceptor properties of ligands and their structure.[1]

Although the first recognized organometallic complex, Zeise's salt, $K[PtCl_3(C_2H_4)]$,[2] was prepared in 1827, significant interest in such compounds did not develop until the structure of ferrocene was determined in 1952[3] and it was subsequently realized that the transition metals possessed the capability of forming a wide variety of isolable organometallic compounds. Much earlier attempts to prepare these compounds had met with failure because the stabilities of the compounds are very dependent on the particular groups attached to the metal and stable combinations were not found.[4] In presenting the structural chemist with extraordinary geometrical insights into chemical bonding (sandwich and bridging features), these compounds thereby have allowed theoreticians to gain a more profound understanding of the role of d-orbitals in determining molecular structure and properties. The accelerated advances possible in this area undoubtedly owe a large debt to the early flourishing of transition metal carbonyl chemistry.[5]

The development of organometallic chemistry occurred unusually rapidly in recent years. This development could be attributed to the relation between general theory of the 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. Moreover, selectivities in metal mediated organic reactions are now competing with those of enzymes.

The reactions of primary importance that transition metal complexes bring about at moderate temperatures (usually below 200 °C) are combination reactions of various unsaturated molecules (such as olefins, acetylenes, and carbon monoxide) with each other and with other reagents in various specific ways to form products containing new carbon-carbon bonds. Complexing of the transition metal with the unsaturated molecules, in most instances, apparently is the key to getting the unsaturated groups to react. The great value of transition-metal organometallic chemistry is that often by its use organic reactions can be brought about very much more easily than would be possible by conventional organic chemistry.

Almost all of the transition metals form compounds in which carbon monoxide acts as a ligand. There are three points of interest 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.[6]

Metal carbonyls have various applications, the most important being in catalysis, particularly in the oxo synthesis. Carbonyls may also be utilized as catalysts in many other processes such as teleomerization of unsaturated compounds by polyhalogenated alkanes, hydrosilylation, hydrogenation of carbon-carbon multiple bonds, reduction of selected organic compounds, isomerization of unsaturated compounds, oligomerization and polymerization of hydrocarbons, hydrocyanation and preparation of optically active compounds from hydrogenation and hydroformylation reactions. Metal carbonyls and their derivatives are also commonly utilized in other areas. High purity metals, their metallic layers for electronics, and other technologies may be obtained from metal carbonyls.

Additionally, metal carbonyls may be used for preparation of other transition metal complexes, and may also be useful in organic synthesis.

Infrared spectroscopy is especially useful method for carbonyl complexes because the C=O stretching vibration appears at 1700-2100 cm^{-1}, a region usually free of other ligand vibrations. The intensity is large because $d\mu / dr$, the dipole moment change during vibration, is large, thanks to the polarization of the CO on binding to the metal. In complexes with more than one CO, the carbonyls do not usually vibrate independently, but instead vibrate in concert, and are therefore said to be coupled together in a way that depends on the symmetry of the $M(CO)_n$ fragment.[7] As a result, the number and intensities of carbonyl stretching bands in the vibrational spectra largely depend on the local symmetry around the central atom. Quite often, the symmetry of a metal carbonyl complex is determined simply by counting the number of infrared bands. The expected number of IR-active bands can be derived by means of group theory.[8]

The octahedral complexes of the type $M(CO)_6$ (M = Cr, Mo, W) are air-stable, hydrophobic white crystalline solids which readily sublime under vacuum. They are very slightly soluble in non-polar solvents and are soluble in polar solvents such as THF and $CHCl_3$.[9]

The metal hexacarbonyls are extremely useful starting materials for the preparation of organometallic compounds of chromium, molybdenum, and tungsten. Most of the reactions of the metal hexacarbonyls involve the nucleophilic replacement of one or more carbonyl groups with other ligands. In most cases replacement of some of the carbonyl groups in the metal hexacarbonlys markedly increases the resistance of the remaining carbonyl groups towards substitution. Thus, it is often relatively easy to control the degree of substitution of the metal hexacarbonyls by controlling the reaction conditions.[10] A complete substitution of all carbonyl groups is rarely accomplished.

The types of substituted carbonyl complexes that a metal forms is generally characteristic of its group. Group 6 metal hexacarbonyls undergo extensive ligand substitution thermally as well as photochemically according to the following equation:

$$M(CO)_6 + nL \xrightarrow[\text{solvent}]{h\nu} M(CO)_{6-n}L_n + nCO$$

Numerous substituted octahedral metal carbonyls of group 6 metals can be obtained in which one or more carbonyl groups are replaced by other Lewis base ligands including tertiary phosphines, tertiary arsines, tertiary stibines, amines, pyridines, isonitriles, etc. Since CO is a good π-accepting ligand, good σ-donors such as tertiary phosphines, amines or ethers usually displace at most three CO groups for $M(CO)_6$. Many such compounds can be prepared by heating the metal hexacarbonyl with the ligand in an inert solvent or in a sealed tube. Such reactions are generally carried out in the temperature range 100-150 °C, but in special cases they can be carried out at temperatures as low as 50 °C or as high as 250 °C. Photosubstitution of group 6 metal hexacarbonyls has been established to occur with high quantum yield and has found a wide range of applications, mainly with π-donor ligands.[11] In many cases ultraviolet irradiation may be used to effect reaction between the metal and a Lewis base ligand; this is particularly useful for thermally unstable compounds.

One variant frequently employed is the intermediate introduction of a ligand whose bond to the metal is labile. This ligand can then be replaced by other ligands under mild conditions:

$$M(CO)_{6-n}L_n + nL' \xrightarrow{\Delta} M(CO)_{6-n}L'_n + nL$$

L: cis-cyclooctene, tetrahydrofuran, acetonitrile, piperidine, and dichloromethane.

L': trialkyl phosphite, trialkyl phosphine, pyridine and its derivatives, diimine, olefin, diolefin, triolefin, and dialkyl phosphinoalkane.

Ferrocene has become a versatile building block for the synthesis of compounds with tailor-made properties in many fields, such as organic synthesis homogeneous catalysis, materials chemistry, and production of fine chemicals, due to its high stability and powerful electron-releasing ability and well-established methods for its incorporation into more complex structures.[12] In general, three properties distinguish ferrocenyl substituents from other, purely organic moieties: (i) unique steric bulk with special steric requirements due to the cylindrical shape, (ii) electronic stabilization of adjacent electron-deficient centers due to participation of the iron atom in the dispersal of the positive charge,[13, 14] and (iii) chemical stability and reversibility of the ferrocene/ferrocenium redox couple,[15] which has made ferrocene one of the most classical redox agents of the organometallic chemistry since its first appearance on the chemical stage. [16]

Beyond the well-known interest in the study of mixed-valent complexes, the incorporation of redox-active ferrocene molecules into transition metal fragments is now opening promising fields of research.[12] Heterobimetallic complexes able to undergo sequential electron-transfer steps have been shown to display following:

1. to exhibit unusual catalytic activity,[17] likely because of the availability of different, but cooperatively conjugated metal sites ;
2. to offer the unique opportunity to control the chemical, physico-chemical and structural variations in the coordination sphere of the central transition metal fragment through change of the oxidation state of the remote ferrocene subunit(s);[18]
3. to exhibit non-linear optical properties, which are of great relevance in molecular materials for optical data transmission in the telecommunication industry;[19]
4. to add synergically the antitumor activity of platinum[20] or gold[21] complexes to that of metallocene[22] derivatives.

The ferrocenyl moiety has been playing a useful role as backbone or substituent in ancillary ligands. Numerous derivatives have been described in which ferrocene unit is bound to a fragment containing one or more donor atoms conjugated with the cyclopentadienyl ring. Studies of these ligands are important because the complexes thus obtained may have interesting redox properties and unusual structure.[23] As part of the ongoing interest in electronically communicating metal centers linked by conjugated bridge, we thought that synthesis of the metal-carbonyl complexes of group 6 with a ferrocene-functionalized imine ligand would be very challenging to study long-range metal-metal interactions in these dinuclear complexes. Ferrocenylpyridines, which can be considered as an imine ligand in bonding to a transition metal, represent a class of ligands carrying independent redox activity.[16] They have a potential nitrogen ligating atom which is in conjugation with the cyclopentadienyl ring of the ferrocenyl moiety. The nitrogen atom can bind a transition metal center through both σ and π interactions using its filled σ orbital (HOMO) and empty π^* orbital (LUMO), respectively, thus providing a through-bond interaction between the iron atom and the transition metal. The ferrocenylpyridines (henceforth abbreviated as Fcpy) were synthesized some years ago,[16, 24] but their coordination properties have not been intensively described. To date, only some rhenium complexes with the 4-Fcpy[18] and platinum,[16] gold and silver derivatives[23] with 3-Fcpy have been described.

In this study, we attempted to synthesize three novel dinuclear metal-carbonyl complexes of 2-Fcpy with M = Cr, Mo, W. In the first place, the synthesis of $Cr(CO)_5$(2-Fcpy) was performed by irradiation of $Cr(CO)_6$ in the presence of 2-Fcpy in n-hexane solution.

$$Cr(CO)_6 + \text{2-Fcpy} \xrightarrow[\text{n-hexane}]{h\nu,\ 7h} Cr(CO)_5(\text{2-Fcpy}) + CO$$

In the second place, $Mo(CO)_5$(2-Fcpy) was prepared by the labile-ligand exchange reaction of *cis*-$Mo(CO)_4(pip)_2$ with 2-Fcpy according to the following route:

$$Mo(CO)_6 + \text{pip (excess)} \xrightarrow[\text{n-heptane}]{\text{Reflux, 4h}} cis\text{-}Mo(CO)_4(pip)_2$$

$$2\ cis\text{-}Mo(CO)_4(pip)_2 + \text{2-Fcpy} \xrightarrow[CH_2Cl_2]{\text{At room T, 48 h}} Mo(CO)_5(\text{2-Fcpy}) + Mo(CO)_5(pip) + \ldots$$

In the third place, $W(CO)_5$(2-Fcpy) was synthesized either by irradiation of $W(CO)_6$ in the presence of 2-Fcpy in n-hexane solution or by thermally reacting photogenerated $W(CO)_5$(THF) with 2-Fcpy in THF solution.

$$W(CO)_6 + \text{2-Fcpy} \xrightarrow[\text{n-hexane}]{h\nu,\ 16h} W(CO)_5(\text{2-Fcpy}) + CO$$

or

$$W(CO)_6 \xrightarrow[\text{THF}]{h\nu,\ 2h} W(CO)_5(\text{THF}) + CO$$

$$W(CO)_5(\text{THF}) + \text{2-Fcpy} \xrightarrow{\Delta,\ 22\ h} W(CO)_5(\text{2-Fcpy})$$

These new complexes were characterized by IR spectroscopy. The IR data were also supported by ^{1}H- and ^{13}C-NMR spectroscopic techniques for the $M(CO)_5$(2-Fcpy) complexes (M: Mo, W).

CHAPTER 2

BONDING

2.1.Metal-Carbonyl Bonding

Coordination of the ligand to the metal [9] usually increases the electron density of the central metal, if only electron donation is considered. This apparently contradicts the electroneutrality principle of atoms in molecules, when ligands coordinate to the electron-rich low-valent metals. Typical examples are metal carbonyls in which the metal atom is frequently zero-valent.

When CO is bonded to a single transition metal, the M–C–O linkage is invariably linear. The metal carbonyl bond can be described by the following resonance structures:

$$M^{-}\!-\!C^{+}\!\equiv\!O: \longleftrightarrow M\!=\!C\!=\!\ddot{\underset{\cdot\cdot}{O}}$$

However, a more accurate description of this bonding comes from molecular orbital theory.

Carbon monoxide has a filled σ bonding molecular orbital and two filled π bonding molecular orbitals localized mainly between carbon and oxygen. It also possesses two lone pairs of electrons, one on the carbon and the other on oxygen atoms. They reside in the nonbonding molecular orbitals directed away from the molecule. Because of electronegativity difference between carbon and oxygen, the spatial extent of the carbon lone pair is greater than that of the oxygen lone pair. Carbon monoxide also possesses two mutually perpendicular π-antibonding (π^*) orbitals directed away from the CO internuclear region, and these two orbitals are empty in the ground state. Since oxygen is more electronegative than carbon, the filled orbitals are localized to a greater extent on oxygen than carbon, and the empty π^* orbitals are more localized on carbon.[25]

A ligand interacts with a transition metal by its frontier orbitals. Since both HOMO and LUMOs are at the carbon atom of CO, carbon monoxide is attached to a transition metal atom through C atom.[26] Thus, the metal-CO bond is formed as a result of an overlap between a weakly antibonding σ orbital at carbon (HOMO) and empty hybridized metal orbitals, as well as a result of the formation of back-bonding due to an interaction between filled dπ metal orbitals and antibonding π orbitals of CO (LUMOs).[1]

The net effect of the bonding is that carbon monoxide donates some electron density to the metal through σ-interaction from its carbon lone pair ($M \leftarrow CO$) and accepts electron density from the metal through π-interaction into its π^* orbitals ($M \rightarrow CO$). Carbon monoxide is hence classified as a σ-donor, π-acceptor ligand.

The formation of the σ M-C bonds should lead to concentration of electron density on the metal atom. The π back-bonding prevents this concentration, since a reverse process take place- there is donation of electron density back into the π^* orbitals of CO. Thus, the π-bond enhances the σ-acceptor properties of the metal, as well as the σ-donor properties of CO. This situation leads to a synergic effect: the increase in stability of σ bond strengthens the π bonding, and vice versa. It is this ability of carbon monoxide to accept electron density from the metal which allows it to stabilize metals in zero or negative oxidation states.

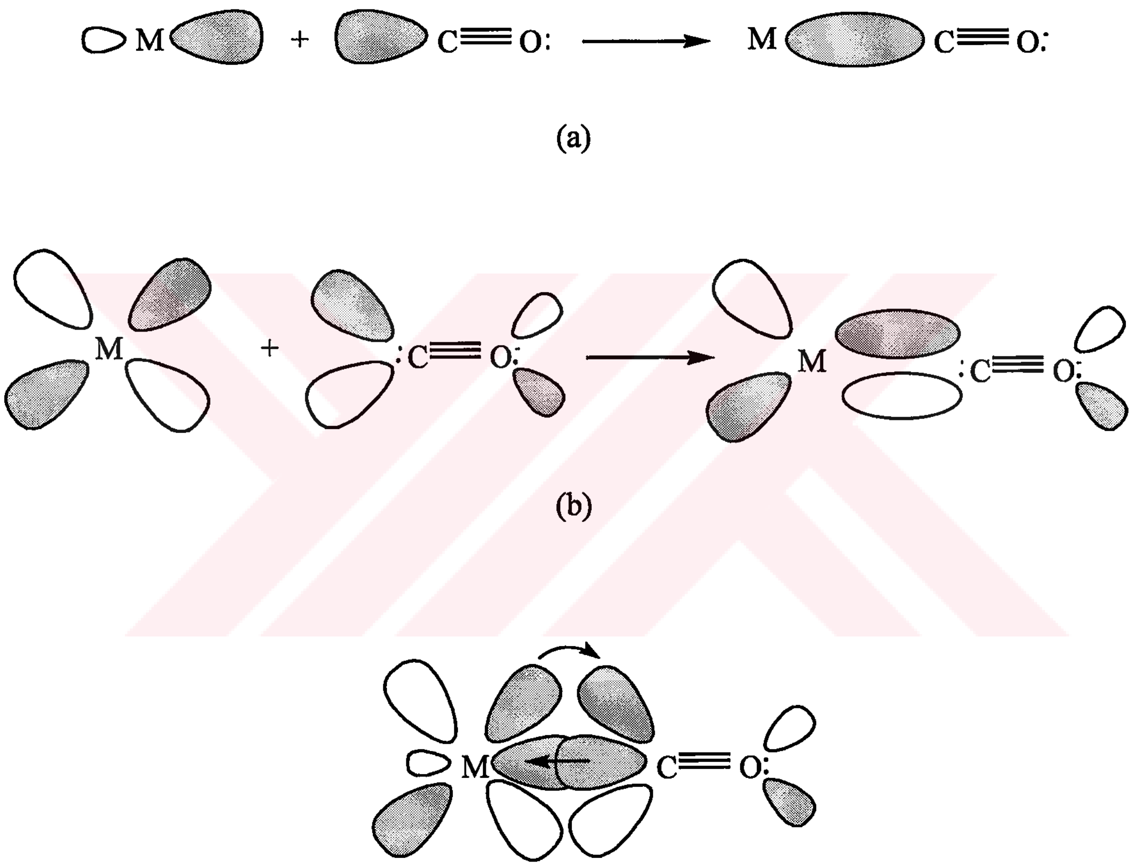


Figure 2.1. Molecular orbital description of metal-carbonyl interaction

(a) Metal←carbon σ-bond: σ-bonding

(b) Metal→carbon d_π-π^* bond: back-bonding

(c) Synergic effect

The CO molecule has a stretching frequency of 2143 cm^{-1}.[27] The relative degree to which back bonding may occur varies significantly from compound to compound and has been estimated from the carbon-oxygen infrared stretching frequencies of a series of metal carbonyl complexes. The range of absorptions varies from about 2125 cm^{-1} for carbonyl with presumed little back bonding to 1700 cm^{-1} in presumed strongly back-bonded examples.[4] The usefulness of the C–O stretching frequency as a measure of C–O bond strength (and hence of the extent of metal-carbonyl π bonding) derives from the sensitivity of this absorption to the electron population of the CO π^* orbitals.[6]

The extent of the M-CO back bonding mainly depends upon the electron density on the metal atom which is affected by two factors:

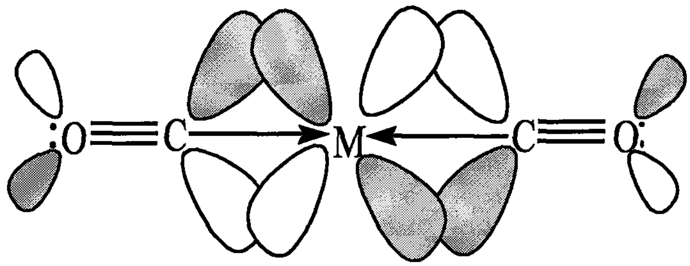
i) Effect of the charge on the metal carbonyl species: Table 2.1 lists CO stretching frequencies for two isoelectronic series of the metal carbonyls. On the basis of the absorption maxima, the C–O bond strengths in these two series decrease in the order $[Mn(CO)_6]^+$ > $[Cr(CO)_6]$ > $[V(CO)_6]^-$ > $[Ti(CO)_6]^{2-}$ and $[Ni(CO)_4]$ > $[Co(CO)_4]^-$ > $[Fe(CO)_4]^{2-}$. These qualitative results are consistent with the π-bonding model described earlier: As M–C π bonding increases, the C–O bond becomes weaker and the C–O stretching frequency decreases. The greater the positive charge on the central metal atom, the less readily the metal can donate electron density into the π^* orbitals of the carbon monoxide ligands to weaken the C–O bond. In contrast, in the carbonylate anions the metal has a greater electron density to be dispersed, with the result that M–C π bonding is enhanced and the C–O bond is diminished in strength.

Table 2.1. Infrared absorptions of some metal carbonyl complexes

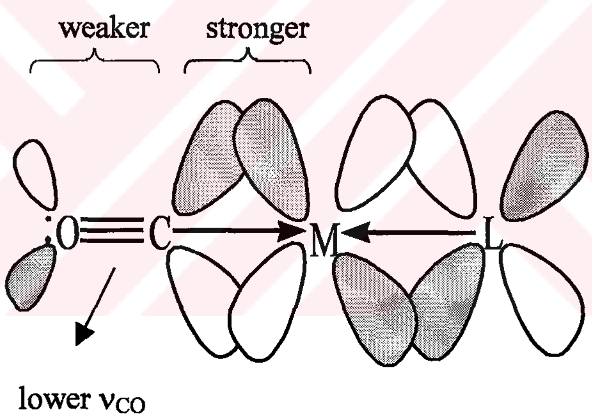
Compound	Frequency (cm^{-1})
$[Mn(CO)_6]^+$	2090
$[Cr(CO)_6]$	2000
$[V(CO)_6]^-$	1860
$[Ti(CO)_6]^{2-}$	1748
$[Ni(CO)_4]$	2060
$[Co(CO)_4]^-$	1890
$[Fe(CO)_4]^{2-}$	1790

ii) Effect of the other ligands attached to the metal atom: In unsubstituted metal-carbonyl complexes, the two trans carbonyl groups compete equally for the electron density on the metal via π interaction. Whereas, substitution of CO with a ligand L generally alters the CO stretching frequencies of the remaining carbonyl ligands in a manner that reflects the net electron density transmitted by L to the central metal atom. This in turn depends both on the σ-donating capacity and the π acidity of L. Especially, the CO group lying opposite the ligand L competes most directly with L for available metal dπ electrons. For ligands having little or no back-accepting ability, the CO in a trans position can absorb significant electron density from the filled dπ orbitals of the metal into its antibonding π orbitals and relatively low C–O stretching frequencies are observed. That is, the M–C bond becomes stronger and the C≡O bond becomes weaker as illustrated in Figure 2.2. However, as a weaker σ-donor and stronger π-acceptor ligand, such as $N{\equiv}O^+$ and CS, in trans position to CO group competes for the use of the same dπ orbital of the metal, it will cause the CO stretching frequency to increase.

The π-accepting ability is affected by the electronegativity of the substituents on the donor ligand. In the case of phosphorous ligands, the π acidity increases as the electronegativity of any substituent on P increases. As these ligands become more and more competitive for π electrons on the metal, CO receives less and less π electron density, the M–CO bond directly weakens, the C–O bond strengthens, and the C–O stretching frequency increases accordingly. For example, the most electronegative substituent, F in PF_3 reduces substantially the σ-donor character and increases the π accepting ability, so the very high C–O stretching frequency for the PF_3-substituted metalcarbonyls indicates that this ligand is comparable in its π acidity to carbon monoxide itself.



(a)



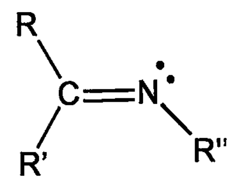
(b)

Figure 2.2. Competition of two ligands for the use of the same dπ orbital of the central metal atom

(a) Two carbonyl ligands; equal M–CO π interactions

(b) Carbonyl ligand and a weaker π-acceptor ligand, L; stronger M–CO π-bonding

2.2.Metal-Imine Bonding



R: H, alkyl, or aryl group

R′: H, alkyl, or aryl group

R″: H, alkyl, or aryl group

Figure 2.3. The structure of an imine molecule

The carbon-nitrogen double bond in an imine molecule consists of a σ bond and a π bond as shown in Figure 2.3. In the MO energy level diagram there will be two σ orbitals (bonding and antibonding) and two π orbitals (bonding and antibonding) for C=N: moiety (Figure 2.4). The bonding orbitals are mainly localized on the nitrogen atom, while antibonding orbitals belong mainly to the carbon atom, considering the fact that nitrogen is more electronegative than carbon. Moreover, there should be one nonbonding σ orbital localized on the nitrogen atom because there are two lone-pair electrons on the nitrogen atom as seen from the structure of the molecule. Totally six electrons (2 from the carbon and 4 from the nitrogen) are available to occupy molecular orbitals of the C=N: moiety of the imine molecule.

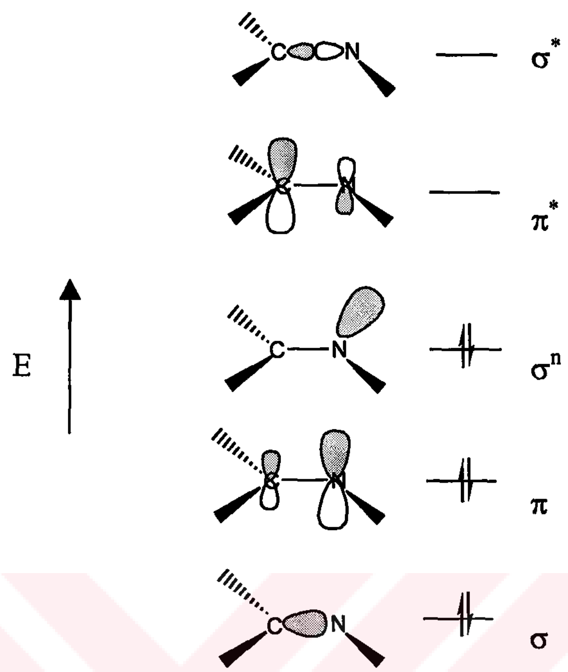
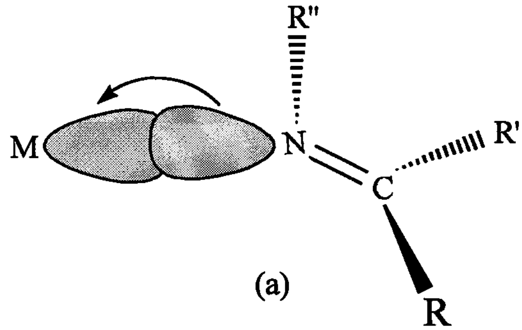
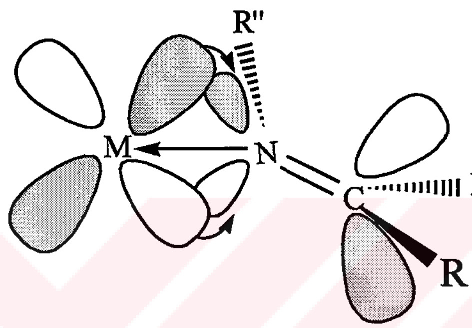


Figure 2.4. The molecular orbital diagram of an imine molecule

The HOMO of the imine molecule is the nonbonding σ orbital, and the LUMO is the antibonding π^* orbital. A strong σ interaction between metal and the imine ligand should be expected because the HOMO, the sigma-symmetry orbital completely localized on the nitrogen, is directed to the dσ orbital of the metal along the bond-axis (Figure 2.5.a). On the other hand, the π bonding takes place to the lower extent in comparison with the σ-bonding because the π* orbital (LUMO) of imine is mainly localized on the carbon atom, that is, the LUMO has its smaller amplitude on the nitrogen (Figure 2.5.b).



(a)



(b)

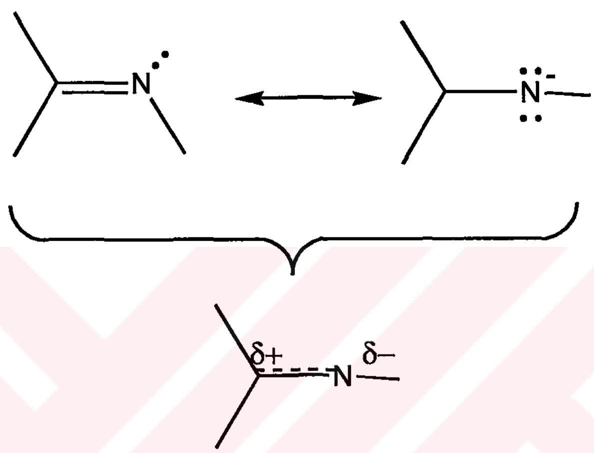
Figure 2.5. Molecular orbital description of the metal-imine bonding

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

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

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

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



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

It is generally found that imines are stabilized by coordination to a π-bonding transition metal. Of course, in the absence of significant π-bonding interactions, ligand polarization is expected to activate the imine ligand towards nucleophilic attack.[28] When imines are coordinated to a transition metal, polarization of the C=N: bond is inverted: The nitrogen donates its nonbonding electron-pair to the metal via σ interaction so that the electron density on the nitrogen is reduced. In addition, the electrons backdonated from the dπ orbital of metal to the π* orbital of the imine ligand are localized on the nitrogen very little, so the nitrogen atom bears a partial positive charge; that is, the electron density on the nitrogen lost by σ-bonding cannot be compensated by backbonding. Because the π* orbital of the imine mainly belongs to the carbon atom, upon coordination to the transition metal, this π* orbital becomes more populated by electrons, the C=N bond is weakened and the electron density on the carbon atom will increase with respect to the carbon atom of an uncoordinated imine molecule. Consequently, the carbon atom bears a substantial negative charge. On account of this inversion of polarization of the C=N bond, the reactivity of imines in nucleophilic addition reactions, where the nucleophile (Nu:$^-$) attacks the carbon atom of the C=N: moiety, is reduced upon coordination to a transition metal. However, they might undergo a nucleophilic attack on the nitrogen atom bearing a partial positive charge as long as the transition metal and the substituent on the nitrogen do not create a significant steric crowding as shown in Figure 2.6.

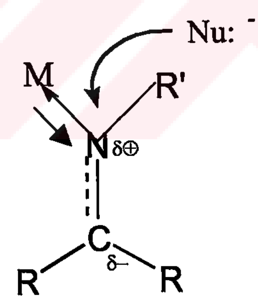


Figure 2.6. A nucleophile attacks the nitrogen atom of the coordinated imine.

CHAPTER 3

EXPERIMENTAL

3.1. Basic Techniques

Due to air-and-moisture sensitivity of organometallic compounds, all synthetic procedures and manipulations were routinely carried out under an atmosphere of oxygen-free dry argon or dinitrogen by using an inert gas line. To remove any trace of air in these gases, drying column and deoxygenation columns were used. The inert gas is firstly allowed to pass through P_2O_5 and then through molecular sieves to be dried up from its moisture. Finally, it is deoxygenated by a catalyst, which is in the form of pellets of activated copper supported on diatomite, operating at 180 °C by means of an electrical resistance. This catalyst, purchased from BASF (Ludwighafen, Germany), is reusable and can be reduced periodically at the same temperature with hydrogen.

Apparatus for handling air-sensitive compounds varies, depending on how stable the compounds are in air, how much purity is required, the scale, and the physical state of the compounds: solid, liquid, or gas. In order to perform experiments with exclusion of glass apparatus from air, vacuum line and Schlenk techniques were used. In use, the air in a Sclenk flask was replaced at least three times by inert gas using a vacuum pump, and procedure and all subsequent handling were carried out under argon or nitrogen flow.

Except for diethylether, which was obtained from Merck (Darmstadt), all solvents were purchased from Aldrich. Since solvents are usually in large excess relative to reagents, even minor contaminations with water or oxygen can result in reduced or, in the worst case, in no yields at all of the desired product. For this reason, the solvents, n-hexane, cyclohexane, THF, diethylether, and toluene were kept under reflux over Na for a few days and carefully distilled off in a stream of nitrogen before use. Whereas, CH_2Cl_2 was purified by distillation over P_2O_5 under an atmosphere of nitrogen.

Hexacarbonylchromium(0), hexacarbonylmolybdenum(0), hexacarbonyltungsten(0), n-butyllithium (2.5 M solution in n-hexane), and Na_2SO_4 were purchased from Aldrich and used without any further purification. NaOH was obtained from Merck and used as obtained. Pyridine, also obtained from Aldrich, was distilled from CaH_2 under an atmosphere of argon prior to use. Neutral aluminumoxide (70-230 mesh, Merck) was used for column chromatography in the purification of 2-ferrocenylpyridine.

The photochemical reactions were conducted by means of a special glass apparatus which had two pats: the inner part and the outer part shown in Figure 3.1. A UV lamp (b) (Hg-Tauch Lampe TQ 150 Quartslampen GmBH, Hanau, West Germany) was immersed in the inner part (a). In order to perform the photochemical reactions, the solution was filled into the outer part (c) and cooled by circulating water through (d) to (e), then irradiated by the UV lamp.

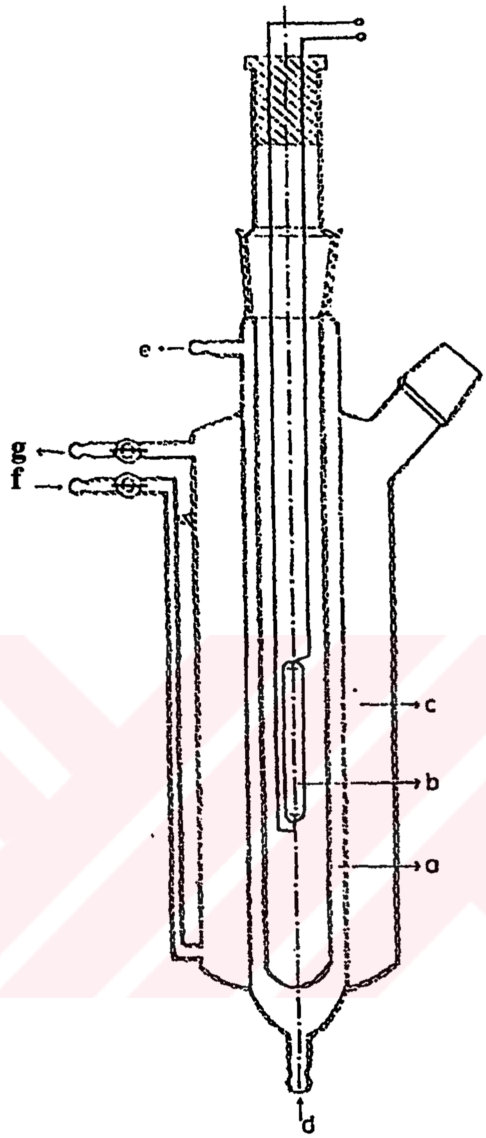


Figure 3.1. The apparatus employed for photochemical reactions

a) Inner part,

b) Mercury lamp,

c) Outer part,

d) Water inlet,

e) Water outlet,

f) Argon or nitrogen gas inlet,

g) Argon or nitrogen gas outlet.

3.2. Physical Measurements

3.2.1 Infrared Spectra

The infrared spectra of the complexes were recorded from their n-hexane, CH_2Cl_2 or THF solutions in the Specac IR-Liquid cell with CaF_2 windows by use of a Nicolet 510 FTIR Spectrometer with OMNIC software.

3.2.2 NMR Spectra

The ^{1}H-NMR and ^{13}C-NMR spectra of complexes and other compounds were recorded from their d-chloroform solutions on a Bruker-Spectrospin DPX 400 Spectrometer. Samples of the complexes were particularly prepared under an atmosphere of nitrogen. All the chemical shift values were given relative to the signal of TMS used as an internal reference.

3.3 Syntheses

3.3.1 2-Ferrocenylpyridine:

The ligand, 2-ferrocenylpyridine was prepared by the literature procedure.[24] Under an argon atmosphere, 36 ml of a 2.5 M n-butyllithium solution in n-hexane (0.09 mol) was added via syringe to a stirred solution of 5.60 g (0.03 mol) ferrocene in 100 ml of dry diethylether. The resulting mixture was stirred for three days at room temperature. After addition of 50 ml of dry cyclohexane, a solution of 4 ml of absolute pyridine in 25 ml of cyclohexane was added with efficient stirring under an Ar atmosphere. Upon removal of diethylether under vacuum, the final mixture was refluxed for 48 h. The dark mixture was allowed to cool gradually to room temperature, and 15 ml of distilled water was added slowly with efficient stirring in order to destroy the unreacted n-butyllithium. The organic phase was then washed with 10 N HCl twice (10ml*2). The aqueous solution of the collected acid extracts were made strongly basic with concentrated NaOH solution until the crude brown product was precipitated out, and extracted with diethylether (50, 25, and 25 ml). After the combined ether extracts were dried over Na_2SO_4, diethylether was evaporated on a rotary evaporator, and then the unreacted pyridine was removed under vacuum. The final residue was purified by column chromatography on Al_2O_3 using CH_2Cl_2 as eluent. The first orange fraction was 2-ferrocenylpyridine which was recrystallized from n-hexane-ether (4:1), to afford 2.5 g, 32% calculated based on ferrocene (mp. 92-93 °C). ^{1}H-NMR ($CDCl_3$): δ 3.98 (s, 5H, $Cp_{unsusbst}$), 4.34 (t, < 1Hz, H3/H4, Cp_{subst}), 4.88 (t, < 1Hz, H2/H5, Cp_{subst}), 6.96 (t, 5.99 Hz, H5, py), 7.35 (d, 7.93 Hz, H3, py), 7.48 (t, 7.68 Hz, H4, py), 8.45(d, 4.55 Hz, H6, py). ^{13}C-NMR ($CDCl_3$): δ 67.6 (C3/C4, Cp_{subst}), 70.0 ($Cp_{unsubst}$), 70.3 (C2/C5, Cp_{subst}), 84.1 (C1, Cp_{subst}), 120.4 (C5, py), 120.9 (C3, py), 136.3 (C4, Cpy), 149.7 (C6, py), 159.6 (C2, py).

While the second red-orange band belonged to the side product 1,1'-dipyridylferrocene which was recrystallized from CH_2Cl_2 to yield 0.3g, 3% as red needles (mp.188-189 °C). ^{1}H-NMR ($CDCl_3$): 4.26 (s, H3/H4 (4H), Cp_{subst}), 4.76 (s, H2/H5 (4H), Cp_{subst}), 6.91 (m, H5 (2H), py), 6.98 (m, H3 (2H), py), 7.28 (m, H4 (2H), py), 8.32 (m, H6 (2H), py). ^{13}C-NMR ($CDCl_3$): δ 68.4 (C3/C4, Cp_{subst}), 71.1 (C2/C5, Cp_{subst}), 85.0 (C1, Cp_{subst}), 120.1 (C5, py), 120.2 (C3, py), 135.7 (C4, py), 149.2 (C6, py), 157.4 (C2, py).

3.3.2 Pentacarbonyl(2-ferrocenylpyridine)chromium(0), $Cr(CO)_5(2\text{-}Fcpy)$:

To a stirred solution prepared by dissolving 220 mg (1mmol) of $Cr(CO)_6$ in Ar-purged 150 ml n-hexane was added 263 mg (1 mmol) of 2-Fcpy. The solution was irradiated and the course of the reaction was followed by taking an IR spectrum for every hour. During irradiation process additionally 1 mmol 2-Fcpy was added so as to improve the conversion from $Cr(CO)_6$ to $Cr(CO)_5(2\text{-}Fcpy)$. However, this addition did not cause the expected increase in the conversion. Ultimately, 40% conversion was achieved as determined by the IR spectrum of the final solution. At the end of 7 h photolysis, this solution was transferred from the irradiation apparatus to a Schlenk tube. While the solvent was being evaporated to approximately 10 ml for crystallization, most of the unreacted $Cr(CO)_6$ precipitated. After filtering the solution, it was allowed to cool down to –35 °C for crystallization. Most of the free ligand precipitated and was separated by inverse filtration under N_2 atmosphere. The IR spectrum of the mother liquor showed that the amount of $Cr(CO)_5(2\text{-}Fcpy)$ was reduced to 1/8 of the initial amount. NMR data of $Cr(CO)_5(2\text{-}Fcpy)$ could not be obtained due to instability of this complex. For $Cr(CO)_5(2\text{-}Fcpy)$, IR $\nu_{C\equiv O}$ (n-hexane): 2066 (w), 1936 (s), and 1912 (m), cm^{-1}.

3.3.3 Pentacarbonyl(2-ferrocenylpyridine)molybdenum(0), $Mo(CO)_5(2\text{-}Fcpy)$:

Firstly, the starting complex *cis*-$Mo(CO)_4(pip)_2$ was prepared by the literature procedure.[29] For that purpose, 10 g (0.0378 mol) of $Mo(CO)_6$ and 25 ml (0.253 mol) of piperidine were refluxed in 120 ml of heptane for 4 h during which the bright yellow product precipitated from solution. The reaction mixture was filtered hot to remove any heptane-soluble $Mo(CO)_5(pip)$. The isolated yellow solid was washed with cold heptane and dried under vacuum to afford a yield of 13.1 g (91%) of *cis*-$Mo(CO)_4(pip)_2$.

Then, $Mo(CO)_5$(2-Fcpy) was synthesized by the ligand exchange reaction of *cis*-$Mo(CO)_4(pip)_2$ with 2-ferrocenylpyridine at room temperature as follows: Under an atmosphere of N_2, 200 mg (0.529 mmol) of *cis*-$Mo(CO)_4(pip)_2$ was dissolved in 20 ml of CH_2Cl_2 at room temperature, and 278 mg (1.057 mmol) of 2-ferrocenylpyridine was added with efficient stirring. The course of the reaction was monitored by taking IR spectrum of the reaction mixture for every two hours. The resulting mixture was stirred for 48 h, so that the starting complex was completely consumed. The solvent was removed under vacuum, and the residue was dissolved in n-hexane for recrystallization. Although unreacted 2-ferrocenylpyridine was thoroughly crystallized and separated, $Mo(CO)_5$(2-Fcpy) was still contaminated with $Mo(CO)_5$(pip) and it could not be further purified. From the NMR spectra it was determined that $Mo(CO)_5$(2-Fcpy) and $Mo(CO)_5$(pip) were obtained in the ratio 2:1. For $Mo(CO)_5$(2-Fcpy), IR $\nu_{C=O}$ (n-hexane): 2073 (w), 1939 (s), 1920 (m), cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.98 (s, 5H, $Cp_{unsubst}$), 4.34 (s, H3/H4, Cp_{subst}), 4.87 (s, H2/H5, Cp_{subst}), 6.99 (t, 5.51 Hz, H5, py), 7.36 (d, 7.86 Hz, H3, py), 7.50 (t, 7.21 Hz, H4, py), 8.43 (d, H6, py). ^{13}C-NMR ($CDCl_3$): δ 66.2 (C3/C4, Cp_{subst}), 68.6 ($Cp_{unsubst}$), 68.9 (C2/C5, Cp_{subst}), 82.7 (C1, Cp_{subst}), 119.0 (C5, py), 119.5 (C3, py), 134.9 (C4, py), 148.3 (C2, py), 158.2 (C6, py), 203.2 (C=O, 4), 212.3 (C=O, 1).

3.3.4 Pentacarbonyl(2-ferrocenylpyridine)tungsten(0), $W(CO)_5$(2-Fcpy):

A solution of 352 mg (1 mmol) of $W(CO)_6$ and 263 mg (1 mmol) of 2-ferrocenylpyridine in 150 ml of n-hexane was irradiated under an atmosphere of Ar at room temperature. The course of the reaction was followed by taking IR spectrum of the solution for every two hours. At the end of 16 h, it was certain that no more than 25 % conversion of $W(CO)_6$ to $W(CO)_5$(2-Fcpy) could be obtained. Then irradiation was stopped, and the solution was brought to dryness. Sublimation under vacuum removed $W(CO)_6$ and the residue was tried to be recrystallized from n-hexane, but $W(CO)_5$(2-Fcpy) was so unstable that it completely decomposed in solution even at low temperature. When this synthesis was repeated under the same conditions, ^{1}H- and ^{13}C-NMR spectra of the crude product consisting of $W(CO)_6$, $W(CO)_5$(2-Fcpy), and free 2-ferrocenylpyridine in $CDCl_3$ were taken immediately after n-hexane was removed under vacuum. For $W(CO)_5$(2-Fcpy), IR $\nu_{C=O}$ (n-hexane): 2070 (w), 1930 (s), 1911 (m), cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 4.07 (s, 5H, $Cp_{unsubst}$), 4.39 (s, H3/H4, Cp_{subst}), 4.64 (s, H2/H5, Cp_{subst}), 6.91 (t, < 1Hz, H5, py), 7.62 (t, 7.41 Hz, H4, py), 8.00 (d, 7.70 Hz, H3, py), 8.96 (d, 5.10 Hz, H6, py). ^{13}C-NMR ($CDCl_3$): δ 69.6 (C3/C4, Cp_{subst}), 70.5 ($Cp_{unsubst}$), 72.2 (C2/C5, Cp_{subst}), 90.6 (C1, Cp_{subst}), 121.9 (C5, py), 129.8 (C4, py), 137.5 (C3, py), 156.8 (C6, py), 164.6 (C2, py), 199.6 (C=O, 4), 203.2 (C=O, 1).

$W(CO)_5$(2-Fcpy) was also synthesized by thermal replacement of THF in the photochemically generated substitution-labile $W(CO)_5$(THF) by 2-Fcpy in THF. Even though this reaction results in approximately complete conversion of $W(CO)_5$(THF) to $W(CO)_5$(2-Fcpy) as estimated from the IR spectrum taken at the end of the reaction, most of $W(CO)_5$(2-Fcpy) decomposed to $W(CO)_6$ and free 2-Fcpy evaporation of THF under vacuum.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Synthesis of 2-Ferrocenylpyridine

The ligand, 2-ferrocenylpyridine (2-Fcpy), was prepared by the long but convenient literature procedure[24]. Firstly, lithioferrocene forms by the reaction of n-butyllithium and ferrocene in diethylether. Then, cyclohexane and pyridine are added into the solution and diethylether is removed by vacuum distillation, so that the reaction mixture is refluxed at the boiling point of cyclohexane by changing the solvent from diethylether to cyclohexane. After 48 h reflux, a mixture of crude products including 2-Fcpy is obtained and is worked up as follows: First, the unreacted n-butyllithium is destroyed by adding H_2O. Then a 10 N HCl solution is added, so that 2-Fcpy passes into the aqueous phase as 2-ferrocenylpyridinium chloride while the unreacted ferrocene remains in the organic phase. After the organic phase is washed with the HCl solution once more, the aqueous phase consisting of the combined acid extracts is made strongly basic by adding concentrated NaOH solution, whereby 2-ferrocenylpyridinium is deprotonated to release the free 2-Fcpy which is then extracted into diethylether. The whole procedure is illustrated in Figure 4.1.

This procedure also yields 1,1'-dipyridylferrocene (Figure 4.2) as a minor product, but both products can easily be separated from each other by column chromatography on alumina as described in the experimental section.

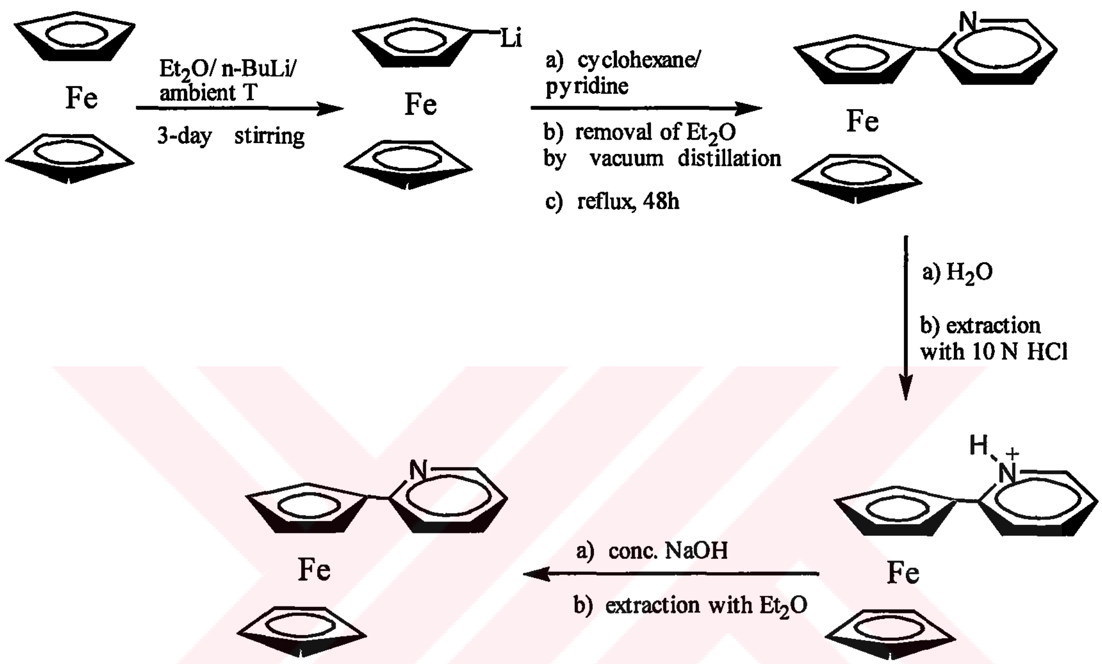


Figure 4.1. Synthesis of 2-ferrocenylpyridine

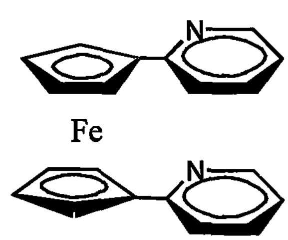


Figure 4.2. 1,1'-Dipyridylferrocene

Although 2-Fcpy has already been synthesized before[24], its spectroscopic identification has not been reported yet. Therefore, it is worth to give a brief discussion of its NMR data. The orthosubstituted pyridine ring in 2-Fcpy has four different hydrogen atoms and five different carbon atoms as evidenced by ^{1}H- and ^{13}C-NMR spectra, respectively (Figure 4.3 and 4.4). In 2-Fcpy, the electronegative nitrogen atom has a strong electron-withdrawing effect on the pyridine ring. According to the ^{1}H-NMR spectrum, the hydrogen atom H6, which is in ortho position to the nitrogen atom, is the most deshielded hydrogen atom of the pyridyl moiety, giving a doublet at 8.45 ppm (J = 4.55 Hz). A doublet at 7.35 ppm (J = 7.93 Hz), a triplet at 7.48 ppm (J = 7.68 Hz), and a triplet at 6.96 ppm (J = 5.99 Hz) belong to H3, H4, and H5, respectively. Moreover, the five signals of the pyridine ring in the ^{13}C-NMR are assigned as follows: 120.4 (C5), 120.9 (C3), 136.3 (C4), 149.7 (C6), and 159.6 ppm (C2). Similarly, the ^{1}H-NMR spectrum shows the characteristic ferrocenyl pattern with a singlet at 3.98 ppm for the five equivalent hydrogens of the unsubstituted cyclopentadienyl (Cp) ring and two virtual triplets at 4.88 and 4.34 ppm (J < 1 Hz) corresponding to the hydrogens H2/H5 and H3/H4 of the monosubstituted cyclopentadienyl ring, respectively, with an intensity ratio of 5:2:2. As expected for ferrocenyl compounds containing electron-withdrawing substituents, the triplets of the protons H2/H5 and H3/H4 are expected at lower field than the singlet of the protons of the unsubstituted cyclopentadienyl ring. The reason for assigning the triplet at 4.88 ppm to the hydrogens H2/H5 is that these hydrogens are closer to the electron-withdrawing pyridyl ring and thus more deshielded than the hydrogens H3/H4 resonating at 4.34 ppm. The ^{13}C-NMR spectrum exhibits three signals for the substituted cyclopentadienyl ring and one signal for the unsubstituted cyclopentadienyl ring in a ratio of 1:2:2:5 at 84.1, 70.3, 67.6, and 70.0 ppm, respectively. Both the hydrogen and carbon atoms of the unsubstituted cyclopentadienyl ring are actually not equivalent, but they are equalized by free rotation of the cyclopentadienyl ring about the Fe-Cp bond axis, as observed for the ferrocene itself. Ferrocene has only one singlet at 4.07 ppm in the ^{1}H-NMR spectrum and a signal at 68.3 ppm in the ^{13}C-NMR spectrum taken in d-chloroform.

Secondly, the ^{1}H- and ^{13}C-NMR spectra of the minor product indicate that both of the cyclopentadienyl rings are monosubstituted, thus confirming the formula 1,1'-dipyridylferrocene. The ^{1}H-NMR spectrum gives two singlets with equal intensity for eight hydrogens of the two monosubstituted cyclopentadienyl rings at 4.76 (H2/H5) and 4.26 ppm (H3/H4), and four multiplets with equal intensity for the eight ortho-substituted pyridyl hydrogens at 8.32 (H6), 7.28 (H4), 6.98 (H3), and 6.91 ppm (H5). Similarly, the ^{13}C-NMR spectrum exhibits three signals at 85.0 (C1), 71.1 (C2/C5), and 68.4 ppm (C3/C4) for the 1-1'-disubstituted ferrocenyl moiety and five signals for the two ortho-substituted pyridyl rings at 157.4 (C2), 149.2 (C6), 135.7 (C4), 120.2 (C3), and 120.1 ppm (C5).

The ^{1}H-NMR spectrum of the unsubstituted pyridine taken in d-chloroform gives three multiplets at 8.60, 7.64 and 7.25 ppm for the hydrogens H2/H6, H4, and H3/H5, respectively, and the ^{13}C-NMR spectrum gives three signals at 150, 138 and and 124 ppm attributed to C2/C6, C4, and C3/C5, respectively. When the ^{1}H-NMR chemical shifts of the unsubstituted pyridine are compared with those of the pyridyl fragments in 2-Fcpy and 1,1'-dipyridylferrocene, it is easily seen that the pyridyl protons are shielded by the electron-donating ferrocenyl ring. This shielding effect is reflected more in 1,1'-pyridylferrocene than in 2-Fcpy.

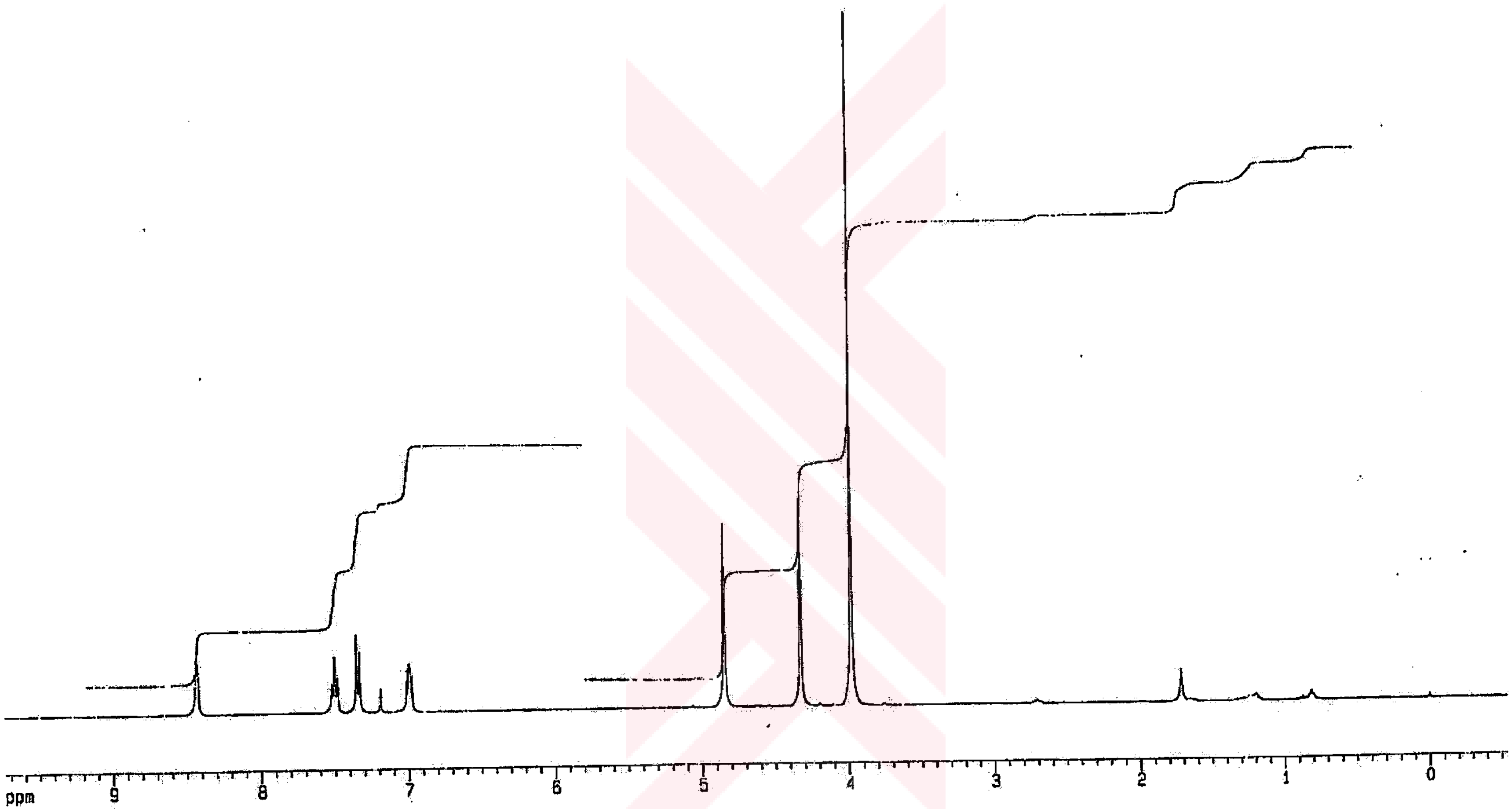


Figure 4.3. ^{1}H-NMR spectrum of 2-Fcpy taken in d-chloroform

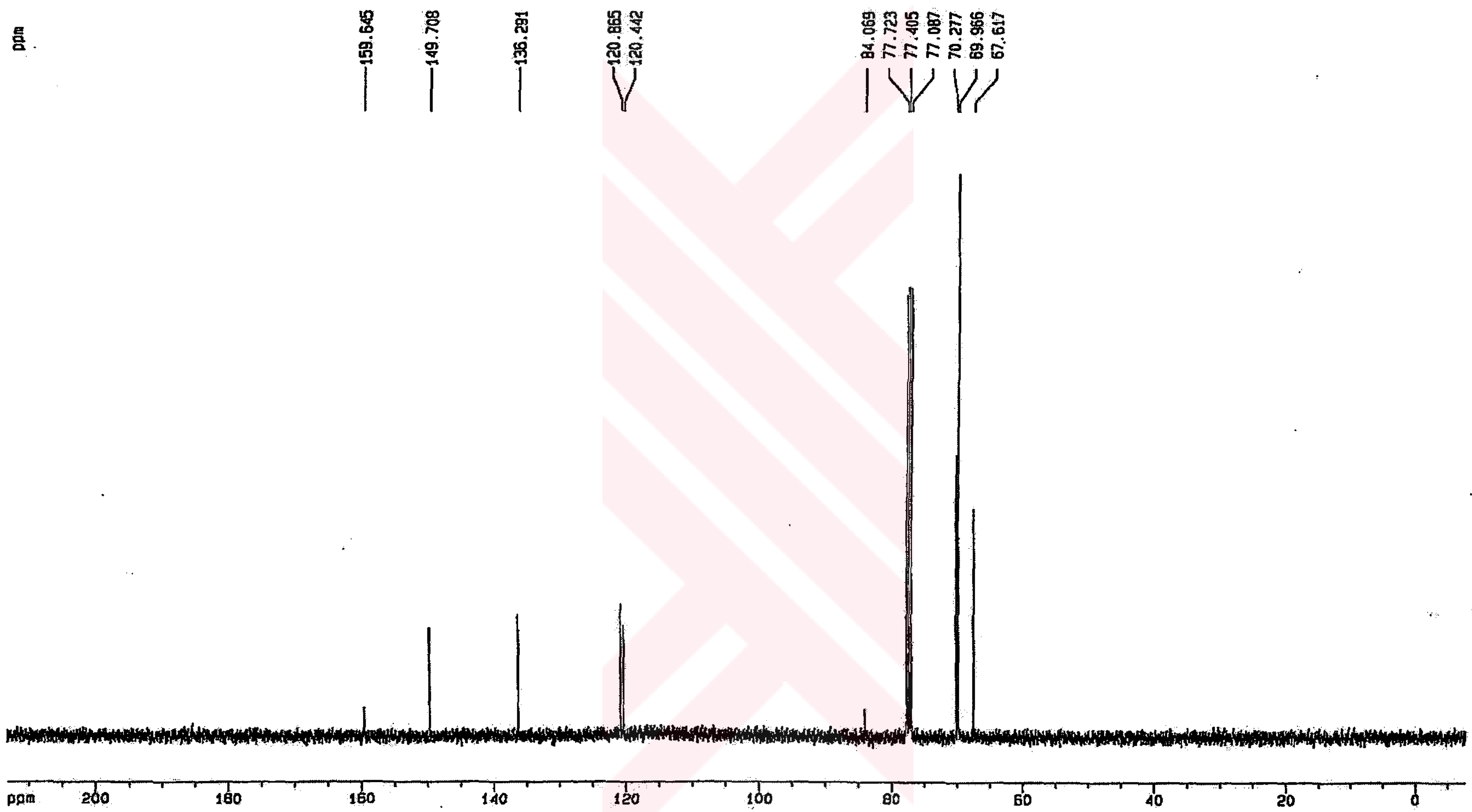


Figure 4.4. ^{13}C-NMR spectrum of 2-Fcpy taken in d-chloroform

4.2. Complex formation of 2-Fcpy with Group 6 Metal Carbonyls

A series of attempts were made to bind 2-Fcpy to a metal carbonyl moiety of Group 6 elements by using both photolytic and thermal ligand substitution.

cis-Cyclooctene (ZCO) is used as a weakly bound stand-in ligand, which has the advantage that its $Cr(CO)_5$ complex is readily accessible on a preparative scale as a pure, crystalline substance through a ligand exchange reaction:

$$Cr(CO)_6 + ZCO \xrightarrow{h\nu} Cr(CO)_5(ZCO) + CO$$

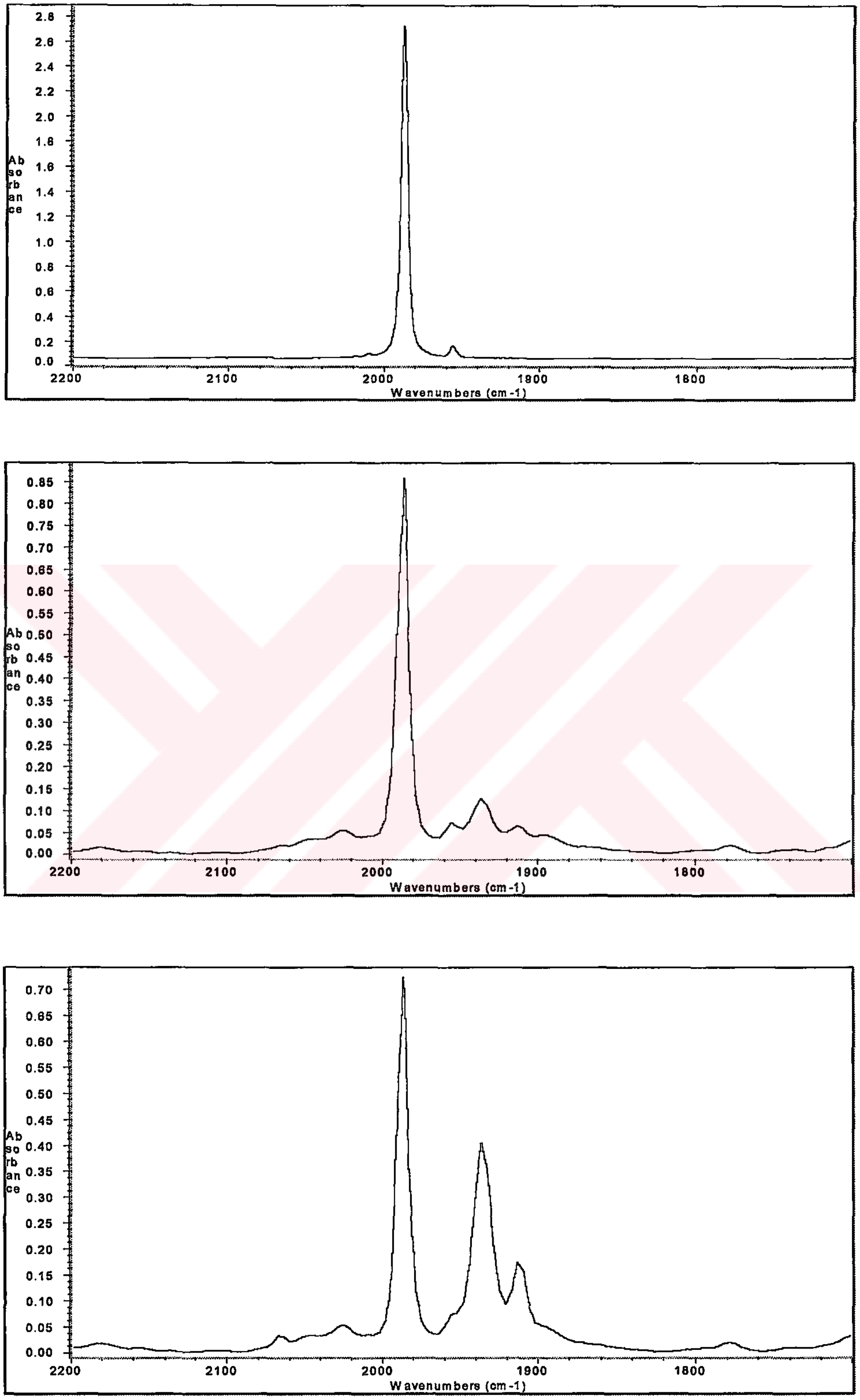
The solid material is stable enough for handling at ambient temperature, while in solution $Cr(CO)_5(ZCO)$ is rather labile and thus serves as a versatile source of the $Cr(CO)_5$ unit.[11,30] Keeping this in mind, the substitution of ZCO in $Cr(CO)_5(ZCO)$ with 2-Fcpy in 5 % ZCO solution in n-hexane was used for the preparation of $Cr(CO)_5$(2-Fcpy). However, the reaction did not yield the desired complex.

$$Cr(CO)_5(ZCO) + \text{2-Fcpy} \xrightarrow[\text{5 \% ZCO soln in n-hexane}]{\Delta} Cr(CO)_6 + \text{2-Fcpy} + ZCO + \ldots$$

Fortunately, it was observed that the continuous irradiation of $Cr(CO)_6$ in the presence of 2-Fcpy in n-hexane solution yields $Cr(CO)_5$(2-Fcpy):

$$Cr(CO)_6 + \text{2-Fcpy} \xrightarrow[\text{n-hexane}]{h\nu,\ 7\ h} Cr(CO)_5(\text{2-Fcpy}) + CO$$

As the IR spectra show (Figure 4.5), the absorption band for CO stretching in $Cr(CO)_6$ at 1986.9 cm^{-1} decreases while three new features grow in at 2066.0, 1935.6, and 1911.9 cm^{-1} during the irradiation. According to the IR spectrum taken at the end of this reaction (Figure 4.5.c), about 40 % conversion of $Cr(CO)_6$ to $Cr(CO)_5$(2-Fcpy) was estimated from the relative ratio of the CO absorption bands of $Cr(CO)_5$(2-Fcpy) at 2066.0, 1935.6, and 1911.9 cm^{-1} to those of the starting complex, $Cr(CO)_6$, at 1986.9 (vs) and 1955.6 cm^{-1}. While the solvent was being evaporated under vacuum, a large amount of $Cr(CO)_6$ precipitated out. After filtering the solution under N_2 atmosphere, the solution was concentrated to 10 ml and allowed to cool down to –35 °C for crystallization, whereby some of the free ligand precipitated. As soon as the precipitated 2-Fcpy was removed by inverse filtration, the IR spectrum of the filtrate was taken (Figure 4.6), indicating that $Cr(CO)_5$(2-Fcpy) so much decomposed that the amount decreased to approximately 1/8 of the initial amount estimated at the end of the reaction. At this point, it is obvious that the $Cr(CO)_6$ precipitating during the evaporation of n-hexane under vacuum has two sources. One is the unreacted $Cr(CO)_6$, and the other is the $Cr(CO)_6$ formed due to decomposion of $Cr(CO)_5$(2-Fcpy). Unfortunately, NMR data of $Cr(CO)_5$(2-Fcpy) could not be obtained due to its instability.



(a)

(b)

(c)

Figure 4.5. The IR spectra taken during the irradiation of $Cr(CO)_6$ in the presence of 2-Fcpy in n-hexane: a) Prior to the irradiation, b) 3 h later, c) 7h later.

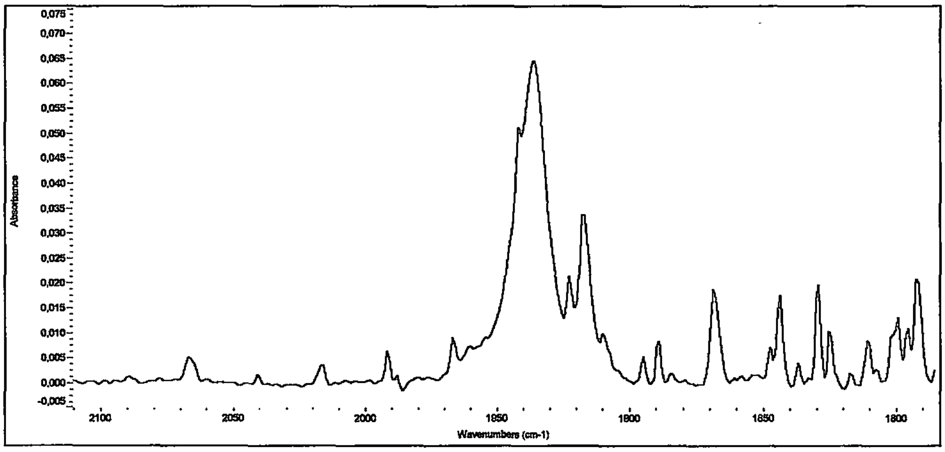


Figure 4.6. The IR spectrum of $Cr(CO)_5$(2-Fcpy) taken in n-hexane after removal of $Cr(CO)_6$

Similar to the chromium homolog, the pentacarbonyl(2-ferrocenylpyridine)molybdenum(0) was attempted to form photochemically from hexacarbonylmolybdenum(0). Figure 4.7 illustrates the IR spectra taken from the reaction mixture during the irradiation of $Mo(CO)_6$ and 2-Fcpy in n-hexane. Prior to the irradiation, only the strong CO absorption band of $Mo(CO)_6$ at 1988,97 cm^{-1} is seen (Figure 4.7.a). Upon one hour irradiation of the reaction mixture, a very small decrease in the intensity of this strong CO band is observed while the three barely discernable characteristic CO absorption bands of $Mo(CO)_5$(2-Fcpy) appear at 2072.8, 1938.9, and 1919.9 cm^{-1} (Figure 4.7.b). However, no further conversion of $Mo(CO)_6$ to $Mo(CO)_5$(2-Fcpy) was attained continuing irradiation, and the irradiation was ended after 13 hours (Figure 4.7.c). Due to this very low conversion (less than 5 %) of $Mo(CO)_6$ to $Mo(CO)_5$(2-Fcpy), isolation of $Mo(CO)_5$(2-Fcpy) is practically impossible.

$$Mo(CO)_6 + \text{2-Fcpy} \xrightarrow[\text{n-hexane}]{h\nu,\ 13\ h} Mo(CO)_5(\text{2-Fcpy}) + CO$$

$$< 5\ \%$$

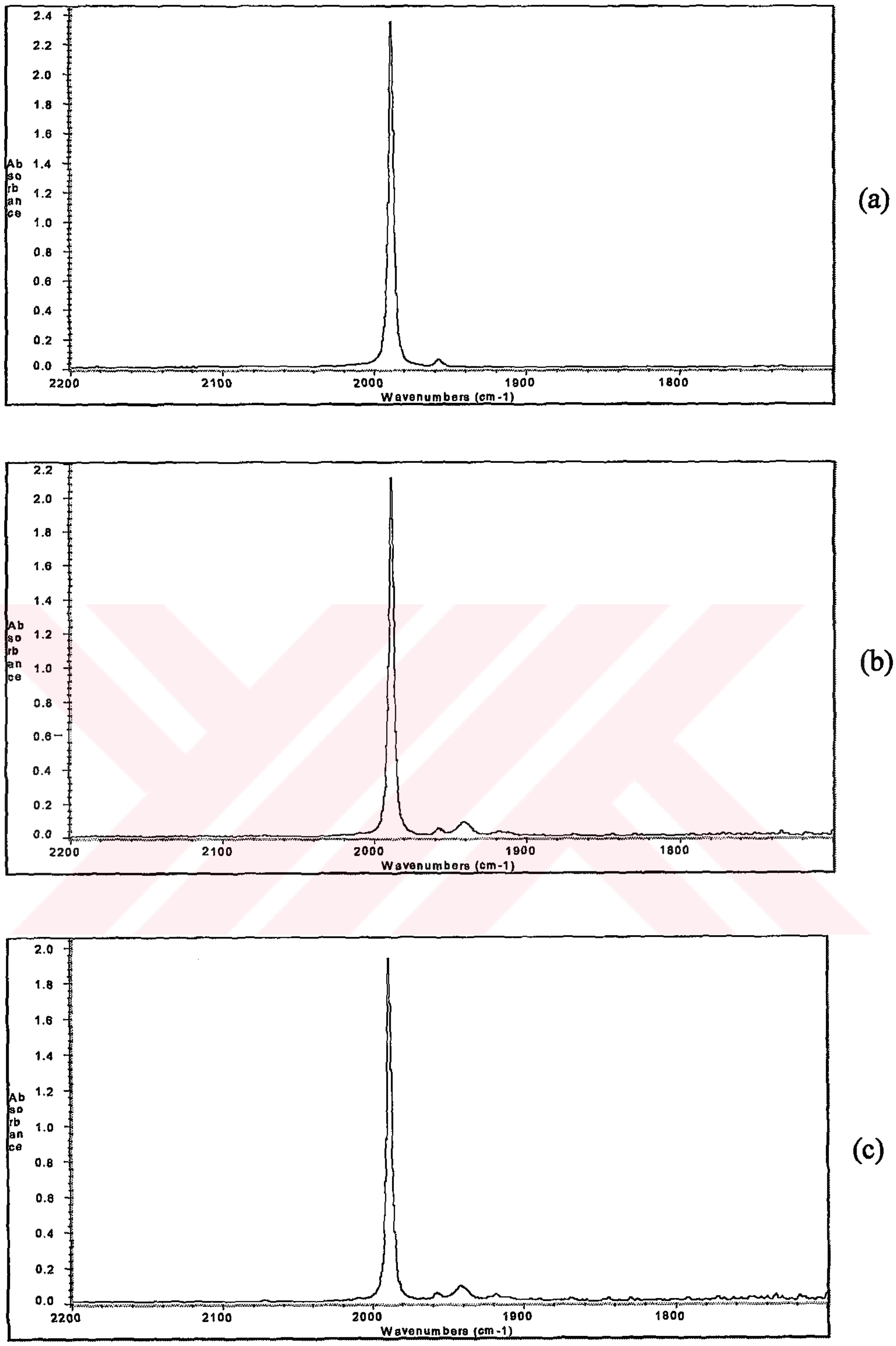


Figure 4.8. The IR spectra taken during the irradiation of $Mo(CO)_6$ in the presence of 2-Fcpy in n-hexane: a) Prior to the irradiation, b) 1 h later, c) 13h later.

Since the direct photosubstitution of CO in $Mo(CO)_6$ by 2-Fcpy gives $Mo(CO)_5$(2-Fcpy) in very low conversion, we searched for an accessible intermediate containing a labile ligand which would be replaced thermally by 2-Fcpy. Unfortunately, there exist no such a complex of the type $Mo(CO)_5L$ with a labile ligand L. Nevertheless, there are two known tetracarbonylmolybdenum(0) complexes, $Mo(CO)_4$(NBD)[31] and *cis*-$Mo(CO)_4(pip)_2$,[29] which have been used as $Mo(CO)_4$ transfer reagent for the synthesis of many tetracarbonylmolybdenum(0) complexes.[32] Both of them were used in thermal replacement of the labile ligand, NBD or pip, by 2-Fcpy, but only one of them gives a substitution product. The tetracarbonyl($\eta^{2:2}$-norbornadiene)molybdenum(0) complex does not give any thermal substitution with 2-ferrocenylpyridine at ambient temperature. Refluxing in n-hexane results in the formation of $Mo(CO)_6$ and free norbornadiene, but no complex containing 2-Fcpy is formed.

$$cis\text{-}Mo(CO)_4(NBD) + 2\text{-Fcpy} \xrightarrow[\text{n-hexane}]{\text{At ambient T}} Mo(CO)_6 + NBD + 2\text{-Fcpy} + \ldots$$

Fortunately, the thermal ligand substitution reaction of *cis*-$Mo(CO)_4(pip)_2$ with 2-Fcpy in 1:2 molar ratio in CH_2Cl_2 does give a substitution reaction. However, this substitution does not yield the expected $Mo(CO)_4(2\text{-Fcpy})_2$ complex, either. Instead, one obtains a mixture of $Mo(CO)_5$(2-Fcpy) and $Mo(CO)_5$(pip).

$$cis\text{-}Mo(CO)_4(pip)_2 + 2\text{-Fcpy} \xrightarrow[CH_2Cl_2]{\text{At room T, 48 h}} Mo(CO)_5(2\text{-Fcpy}) + Mo(CO)_5(pip) + \ldots$$

$Mo(CO)_5$(2-Fcpy) is thoroughly separated from the free 2-Fcpy by recrystallization from CH_2Cl_2 but cannot be freed from $Mo(CO)_5$(pip). Even after repeated recrystallization, the $Mo(CO)_5$(2-Fcpy) is contaminated by $Mo(CO)_5$(pip) in significant amount. The IR spectrum of this mixture taken in n-hexane solution (Figure 4.8) displays two sets of bands. One set, which consists of three CO absorption bands at 2072.8 (w), 1938,9 (vs), and 1919.9 cm^{-1} (m), belongs to $Mo(CO)_5$(2-Fcpy), while the other, which consists of a weak CO absorption band at 2066.4 cm^{-1} and a moderately intense CO absorption band at 1934.6 cm^{-1} seen as a shoulder of the strong CO absorption band of $Mo(CO)_5$(2-Fcpy), is attributed to $Mo(CO)_5$(pip). The third CO absorption band of $Mo(CO)_5$(pip) is presumably hidden by the moderately intense CO absorption band of $Mo(CO)_5$(2-Fcpy) at 1919.9 cm^{-1}. One important point emerging from the inspection of the IR spectra is that $Mo(CO)_5$(2-Fcpy) does not decompose to $Mo(CO)_6$ and free 2-Fcpy during evaporation of CH_2Cl_2 and repeated recrystallizations from CH_2Cl_2 or n-hexane.

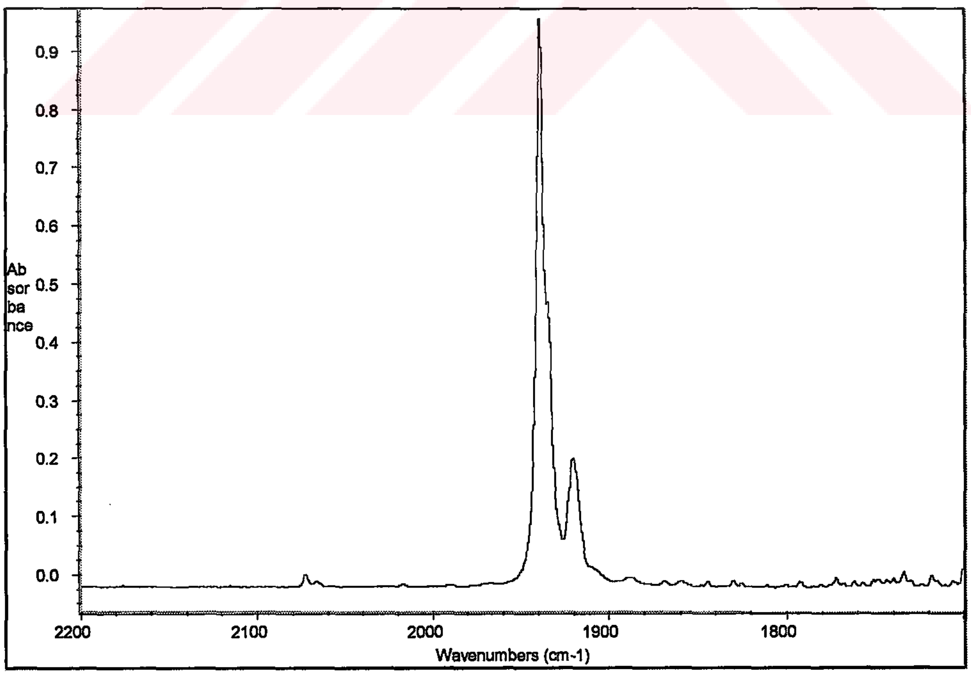


Figure 4.8. The IR spectrum of a mixture of $Mo(CO)_5$(2-Fcpy) and $Mo(CO)_5$(pip) taken in n-hexane.

The ^1H- and ^{13}C-NMR spectra reveal that the final solid material after repetitive recrystallization contains $Mo(CO)_5$(2-Fcpy) and $Mo(CO)_5$(pip) in the ratio 2:1, respectively (Figure 4.9 and 4.10). The ^1H-NMR spectrum of the mixture gives also two sets of signals, one for each compound. One set of signals for $Mo(CO)_5$(2-Fcpy) contains three singlets at 4.87 (H2/H5), 4.34 (H3/H4) and 3.98 ppm (five hydrogens of the unsubstituted cyclopentadienyl ring) with an intensity ratio of 2:2:5 for the ferrocenyl moiety of the coordinated 2-Fcpy. In addition, one observes a doublet at 8.43 ppm (J = 3.82 Hz), a triplet at 7.50 ppm (J = 7.21 Hz), a doublet at 7.36 ppm (J = 7.86 Hz) and a triplet at 6.99 ppm (5.51 Hz) with equal intensities, attributed to the four pyridyl hydrogens H6, H4, H3 and H5 of $Mo(CO)_5$(2-Fcpy), respectively. The second set of signals in the ^1H-NMR spectrum spectrum consists of a doublet at 3.12 ppm, a multiplet at 1.67 ppm and a multiplet at 1.60 ppm, which can be assigned to the coordinated piperidine of $Mo(CO)_5$(pip) by comparing the ^1H-NMR chemical shifts of free piperidine in d-chloroform (2.7, 1.5 and 1.5 ppm with an intensity ratio of 2:2:1).[33] There are also other weak signals between 1.35 and 3.00 ppm attributable to the hydrogens of *cis*-$Mo(CO)_4(pip)_2$, which cannot be resolved in the IR spectrum.

The ^{13}C-NMR spectrum of the mixture of $Mo(CO)_5$(2-Fcpy) and $Mo(CO)_5$(pip) (Figure 4.10) displays three signals at 82.7, 68.9 and 66.2 ppm for the substituted cyclopentadienyl ring, and one signal at 68.6 ppm for the unsubstituted cyclopentadienyl ring. The five pyridyl carbons C2, C6, C4, C3, and C5 resonate at 158.2, 148.3, 134.9, 119.5, and 119.0 ppm, respectively. Both ^1H- and ^1C-NMR signals of the coordinated 2-Fcpy in $Mo(CO)_5$(2-Fcpy) have the same relative positions as those of the free 2-Fcpy. The only difference is that hydrogens and carbons of 2-Fcpy in $Mo(CO)_5$(2-Fcpy) are slightly shielded, except for C2 of the pyridyl ring which is deshielded by about 1.5 ppm upon coordination. The ^{13}C-NMR spectrum of free piperidine shows three signals at 47.9, 27.8, and 25.9 ppm with an intensity ratio of 2:2:1.[35] Similar to the ^{1}H-NMR spectrum (Figure 4.9), the ^{13}C-NMR spectrum (Figure 4.10) gives three signals at 57.1, 27.3 and 21.8 ppm attributable to the carbon atoms of the coordinated piperidine in $Mo(CO)_5$(pip). The less intense signals at 57.4, 27.6 and 21.9 are due to the carbon atoms of the coordinated piperidine in *cis*-$Mo(CO)_4(pip)_2$. Furthermore, the ^{13}C-NMR spectrum shows two sets of carbonyl signals for $Mo(CO)_5$(2-Fcpy) and $Mo(CO)_5$(pip). On the one hand, the signals at 212.4 and 203.2 ppm with an intensity ratio of 1:4 belong to the CO groups of $Mo(CO)_5$(2-Fcpy). On the other hand, the signals at 218.9 and 213.0 ppm belong to the CO groups of $Mo(CO)_5$(pip). However, no carbonyl signals are observed for *cis*-$Mo(CO)_4(pip)_2$, indicating that *cis*-$Mo(CO)_4(pip)_2$ is found in very small amount.

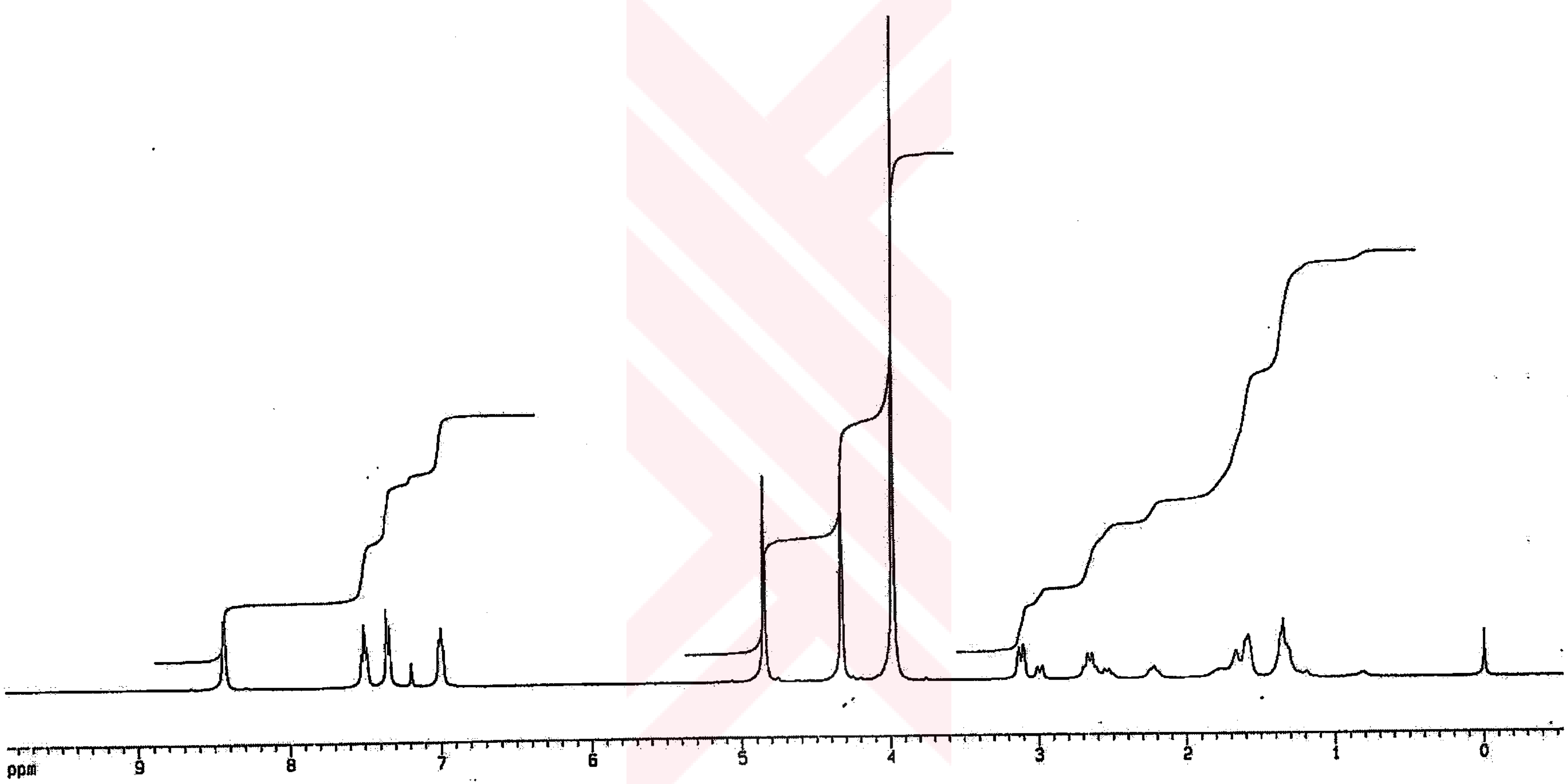


Figure 4.9. ^{1}H-NMR spectrum of a mixture of $Mo(CO)_5(2\text{-}Fcpy)$ and $Mo(CO)_5(pip)$ taken in d-chloroform

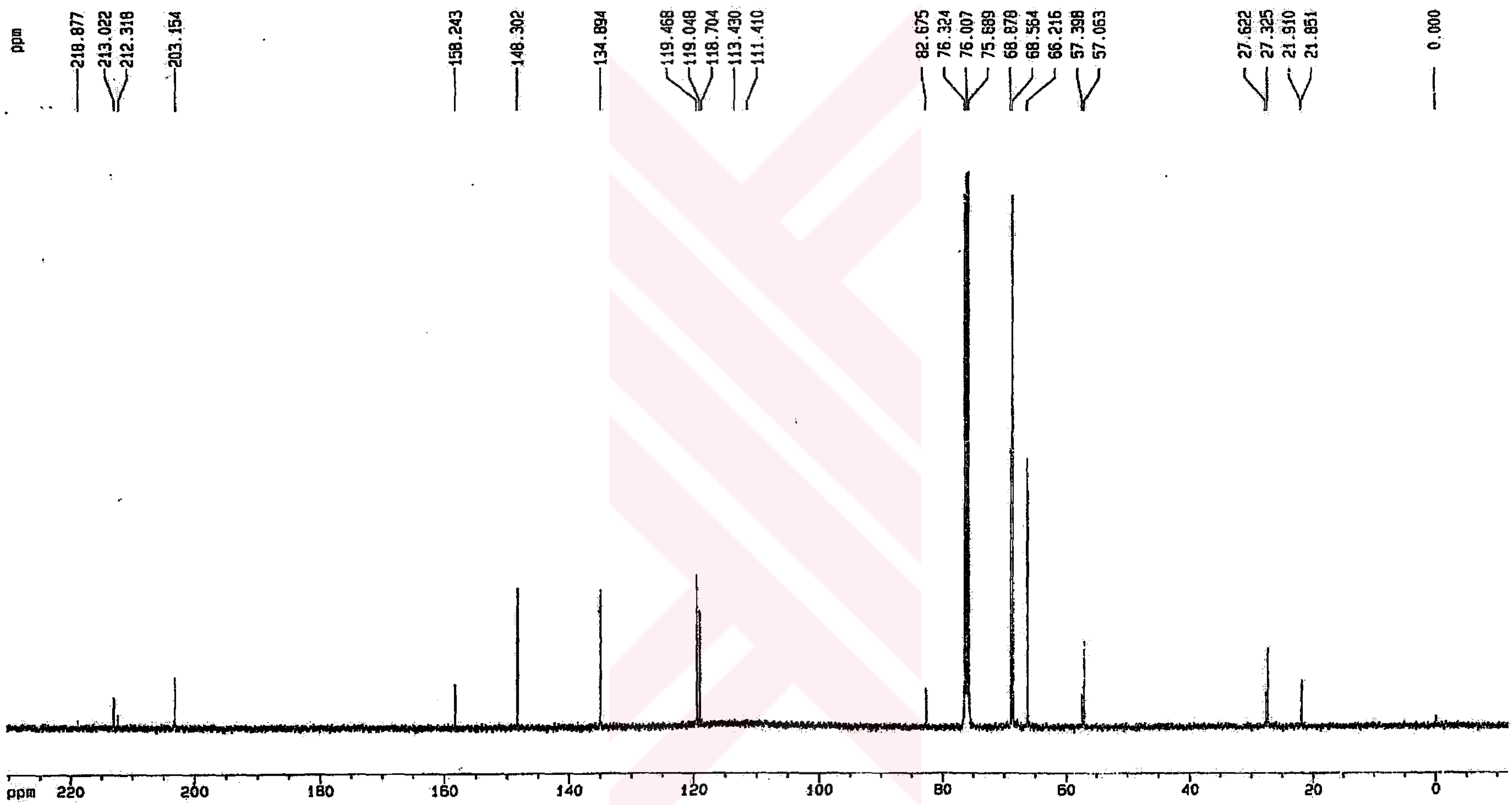


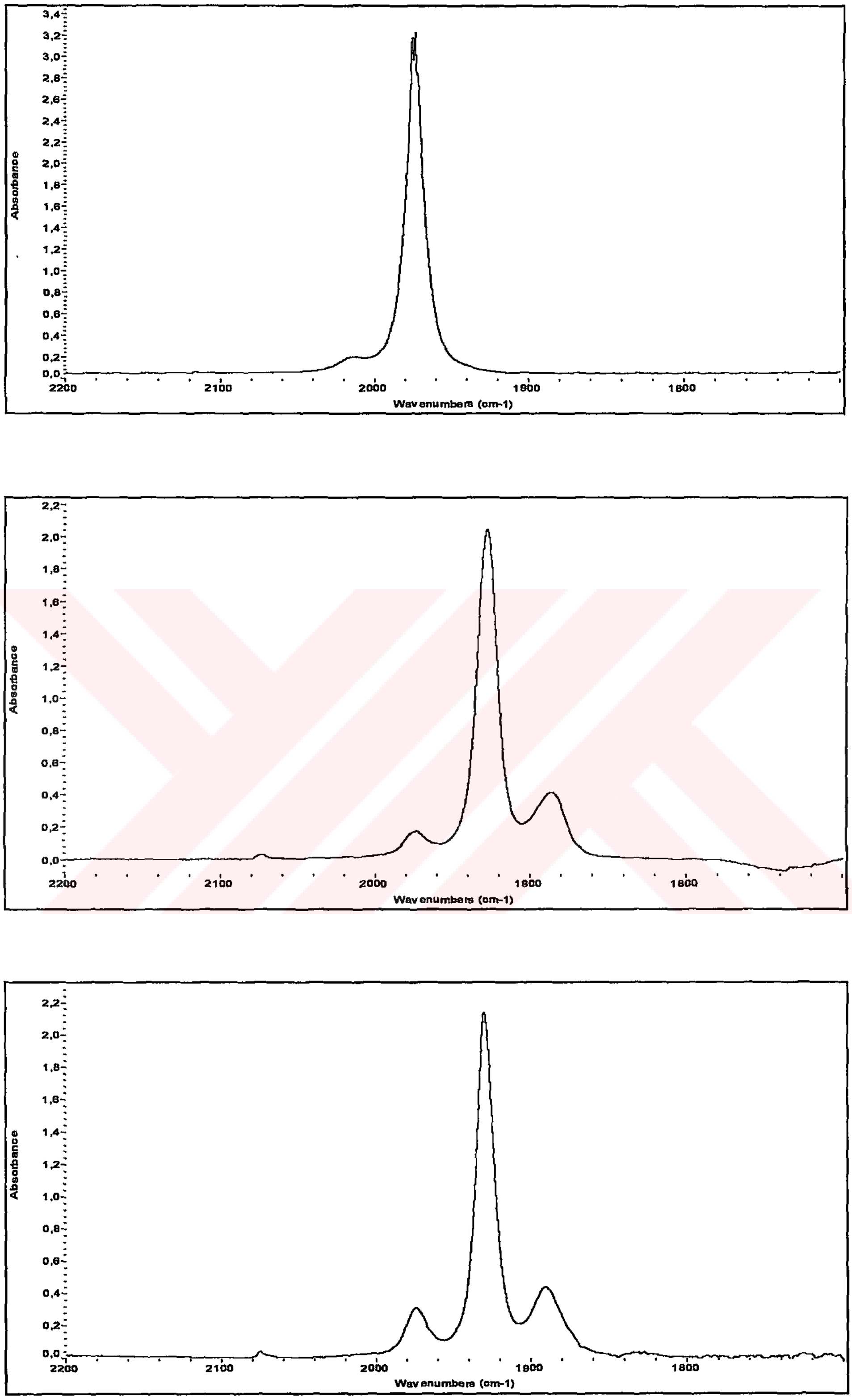
Figure 4.10. ^{13}C-NMR spectrum of a mixture of $Mo(CO)_5$(2-Fcpy) and $Mo(CO)_5$(pip) taken in d-chloroform

$W(CO)_5$(2-Fcpy) was firstly prepared by the thermal exchange of THF in the photochemically generated substitution-labile $W(CO)_5$(THF) by 2-Fcpy in THF solution:

$$W(CO)_6 \xrightarrow[\text{THF}]{h\nu,\ 2\ h} W(CO)_5(\text{THF}) + CO$$

$$W(CO)_5(\text{THF}) + \text{2-Fcpy} \xrightarrow{\Delta,\ 22\ h} W(CO)_5(\text{2-Fcpy})$$

As the IR spectra (Figure 4.11) show, after 2 h irradiation of $W(CO)_6$ in THF, the strong CO absorption band of $W(CO)_6$ at 1975.6 cm^{-1} is replaced by the three CO absorption bands of $W(CO)_5$(THF) at 2073.2 (w), 1927.6 (vs), and 1886.0 (m) cm^{-1}. After adding 2-Fcpy to the reaction solution, three CO absorption bands of $W(CO)_5$(2-Fcpy) are observed at 2075.0 (w), 1930.1 (vs), and 1891.0 cm^{-1}. Although the thermal replacement of THF in $W(CO)_5$(THF) by 2-Fcpy takes place to a very large extent as illustrated by the IR spectrum taken at the end of the reaction 4.11.c), $W(CO)_5$(2-Fcpy) significantly decomposes to $W(CO)_6$ and free 2-Fcpy during evaporation of THF under vacuum as evidenced by the IR spectrum of the solid material taken in n-hexane (Figure 4.12)



(a)

(b)

(c)

Figure 4.11. The IR spectra taken during the thermal replacement of THF in $W(CO)_5(THF)$ by 2-Fcpy in THF: a) Prior to the irradiation of $W(CO)_6$, b) 1 h later, c) 22 h after adding 2-Fcpy

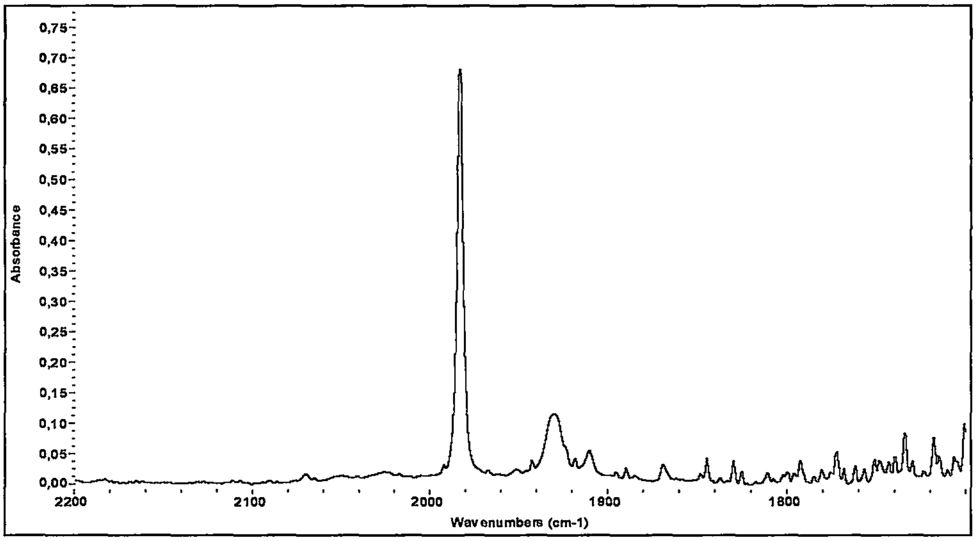


Figure 4.12. The IR spectrum of the solid material from the thermal replacement of THF in $W(CO)_5(THF)$ by 2-Fcpy after evaporation of THF under vacuum

Then, $W(CO)_5$(2-Fcpy) was prepared by irradiation of $W(CO)_6$ in the presence of 2-Fcpy in n-hexane:

$$W(CO)_6 + \text{2-Fcpy} \xrightarrow[\text{n-hexane}]{h\nu,\ 16h} W(CO)_5\text{(2-Fcpy)} + CO$$

Prior to the irradiation, the strong CO absorption band of $W(CO)_6$ at 1983,14 cm^{-1} is observed (Figure 4.13.a). During irradiation, the intensity of this band decreases very slowly while the three characteristic CO absorption bands of $W(CO)_5$(2-Fcpy) gradually develop at 2070.1 (w), 1929.4 (vs), and 1910.5 cm^{-1} (m). For example, as seen from the IR spectra of the reaction mixture after 9 and 16 h irradiation (Figure 4.13.b and c), improvement in the conversion of $W(CO)_6$ to $W(CO)_5$(2-Fcpy) is not noticeable. As estimated from the final IR spectrum of the reaction mixture (Figure 4.13.c), approximately 25 % conversion can be achieved by the UV-irradiation of an n-hexane solution of $W(CO)_6$ and 2-Fcpy. In our first trial of this reaction, we removed the solvent under vacuum immediately after the reaction was complete.

$W(CO)_5$(2-Fcpy) was separated thoroughly from $W(CO)_6$ by sublimation and partially from unreacted 2-Fcpy by recrystallization from n-hexane, respectively. After that, the IR spectrum of the mother liquor showed only the characteristic CO vibrational stretching bands of $W(CO)_5$(2-Fcpy) at 2070.14, 1929.42, and 1910.49 cm^{-1} (m), that is, the CO absorption band of $W(CO)_6$ at 1983,14 cm^{-1} disappeared (Figure 4.14). Due to very low concentration of $W(CO)_5$(2-Fcpy) with respect to the free ligand, and decomposition of $W(CO)_5$(2-Fcpy) during overnight NMR measurements, NMR signals of this complex could not be obtained at this time. Then, the same reaction was repeated. In the light of the low yield and poor stability of $W(CO)_5$(2-Fcpy) as faced in the previous experiment, the ^{1}H- and ^{13}C-NMR spectra of this complex were taken even though it was contaminated with $W(CO)_6$ (Figure 4.13.c) and free 2-Fcpy as soon as the solvent was shortly evaporated under vacuum. Because $W(CO)_5$(2-Fcpy) previously decomposed during the long-term NMR measurements, the sample was prepared very concentrated, so that the measurements took 2-3 h, and $W(CO)_5$(2-Fcpy) was characterized by its ^{1}H- and ^{13}C-NMR data.

Column chromatography was not used for purification of the complexes because it appeared to induce decomposition even conducted under an inert atmosphere.

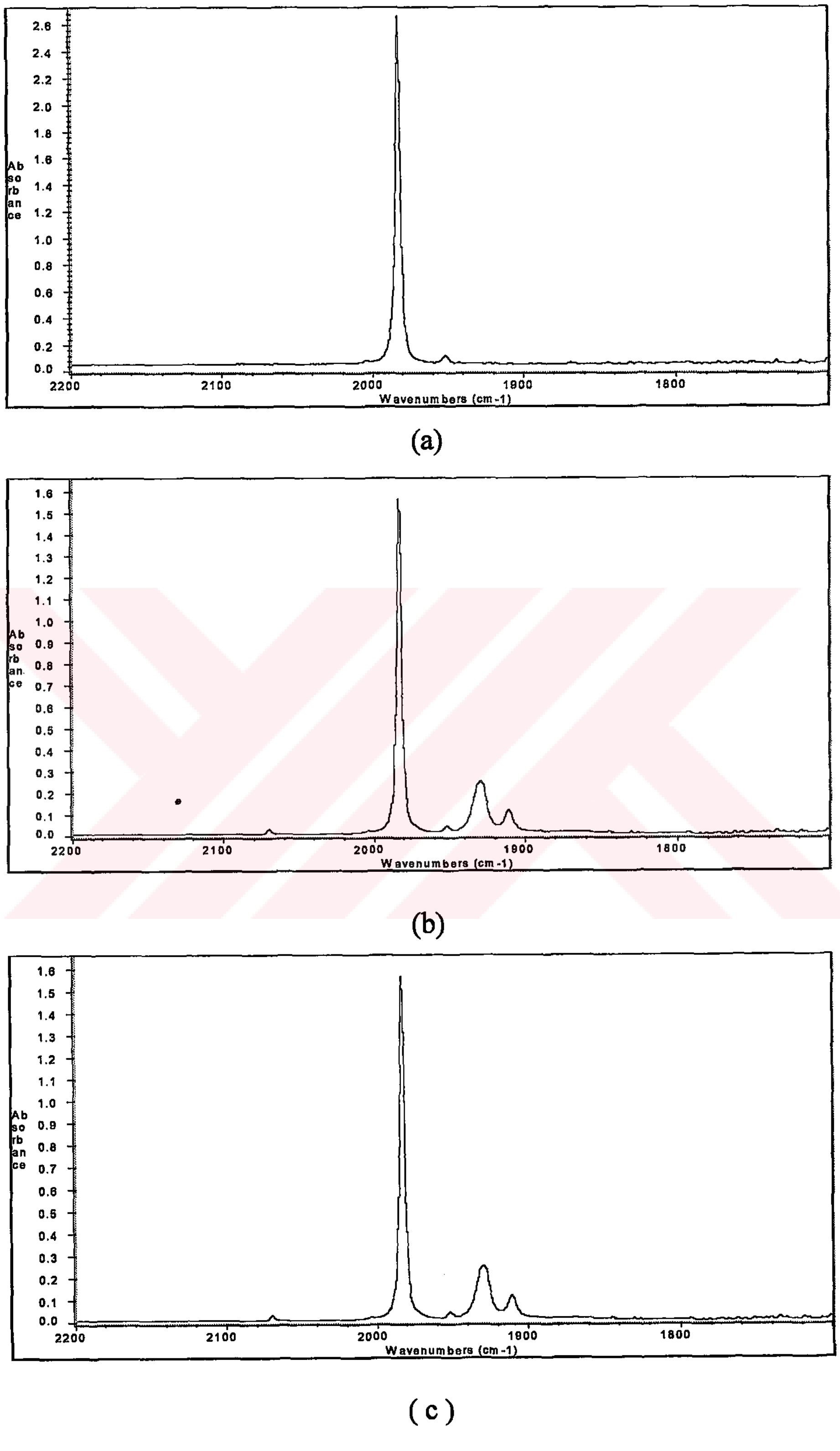


Figure 4.13. The IR spectra taken during the irradiation of $W(CO)_6$ in the presence of 2-Fcpy in n-hexane: a) Prior to the irradiation, b) 9 h later, c) at the end of the irradiation (16 h)

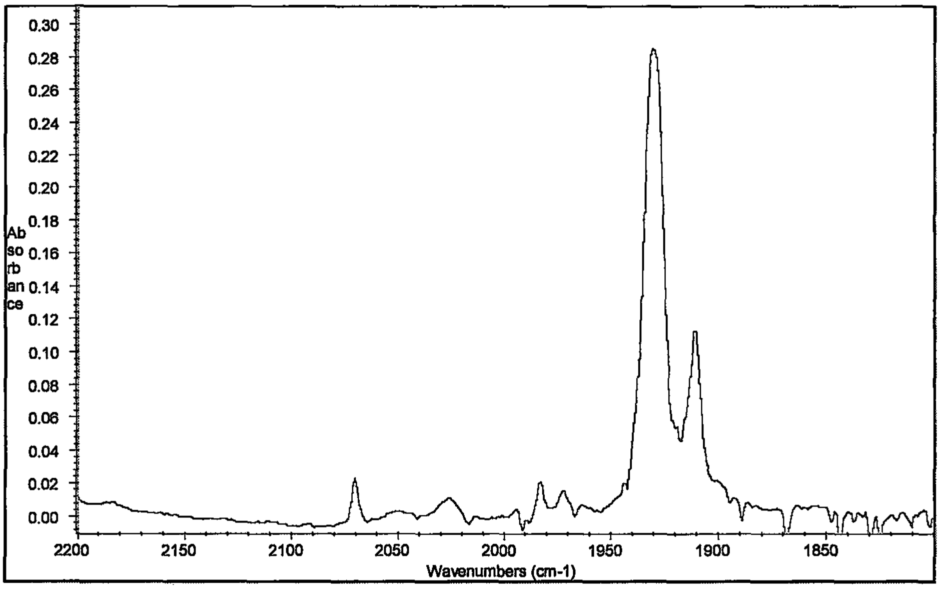


Figure 4.14. The IR spectrum of $W(CO)_5$(2-Fcpy) taken in n-hexane after sublimation of $W(CO)_6$

The ^{1}H-NMR spectrum (Figure 4.15) shows two sets of signals for $W(CO)_5$(2-Fcpy) and free 2-Fcpy. The set of signals with the higher intensity has the same chemical shifts assigned to free 2-Fcpy (Figure 4.3). The set of signals with lower intensity is attributed to the coordinated 2-Fcpy of $W(CO)_5$(2-Fcpy): The hydrogen atoms H2/H5 and H3/H4 of the substituted cyclopentadienyl ring resonate at 4.64 and 4.39 ppm, so do the hydrogen atoms of the unsubstituted cyclopentadienyl ring at 4.07 ppm. The four pyridyl hydrogens of $W(CO)_5$(2-Fcpy) give a doublet at 8.96 ppm (H6, J = 5.10 Hz), a doublet at 8.00 ppm (H3, J = 7.70 Hz), a triplet at 7.62 ppm (H4, J = 7.41 Hz) and a triplet at 6.91 ppm (H5, J < 1 Hz). The ^{13}C-NMR spectrum (Figure 4.15) gives three signals at 90.6, 72.2, and 69.6 ppm for the carbons C1, C2/C5, and C3/C4 of the substituted cyclopentadienyl ring, and one signal at 70.5 ppm for the unsubstituted cyclopentadienyl ring of the coordinated 2-Fcpy in $W(CO)_5$(2-Fcpy). The five signals at 164.6, 156.8, 137.5, 129.8, and 121.9 ppm belong to the carbons C2, C6, C3, C4, and C5 of the pyridyl ring of $W(CO)_5$(2-

Fcpy), respectively. As both the ^{1}H- and ^{13}C-NMR spectra of $W(CO)_5$(2-Fcpy) show, the order of signals of the pyridyl ring in $W(CO)_5$(2-Fcpy) is different from those in free 2-Fcpy. That is, the H3 and C3 are highly deshielded and their ^{1}H- and ^{13}C-NMR signals come at lower field than those of H4 and C4 in comparison with the signals of H3/C3 and H4/C4 of the pyridyl ring in free 2-Fcpy.

The ^{13}C-NMR spectrum (Figure 4.16) gives three CO signals. The signals at 203.2 and 199.6 ppm in an intensity ratio of 1:4 are attributed to $W(CO)_5$(2-Fcpy). A more intense signal at 191.5 ppm is due to carbonyl ligands of $W(CO)_6$. This signal is accompanied by two small peaks which are symmetrically positioned on both sides of the main peak. These small peaks are called tungsten satellites arising from the spin-spin coupling of ^{13}C with ^{183}W having a natural abundance of 14.4 % and nuclear spin of ½.

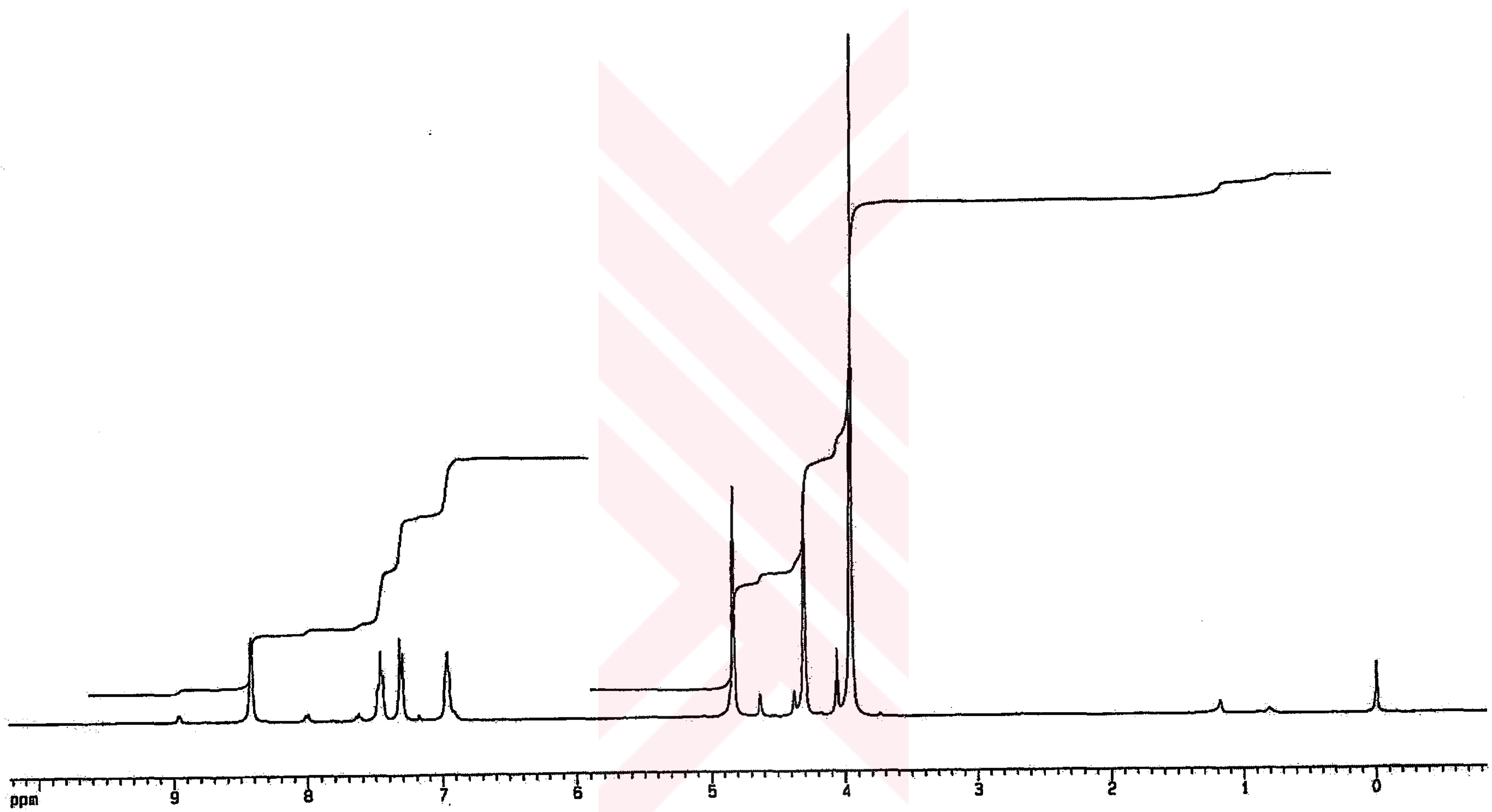


Figure 4.15. ^{1}H-NMR spectrum of $W(CO)_5$(2-Fcpy) taken in d-chloroform

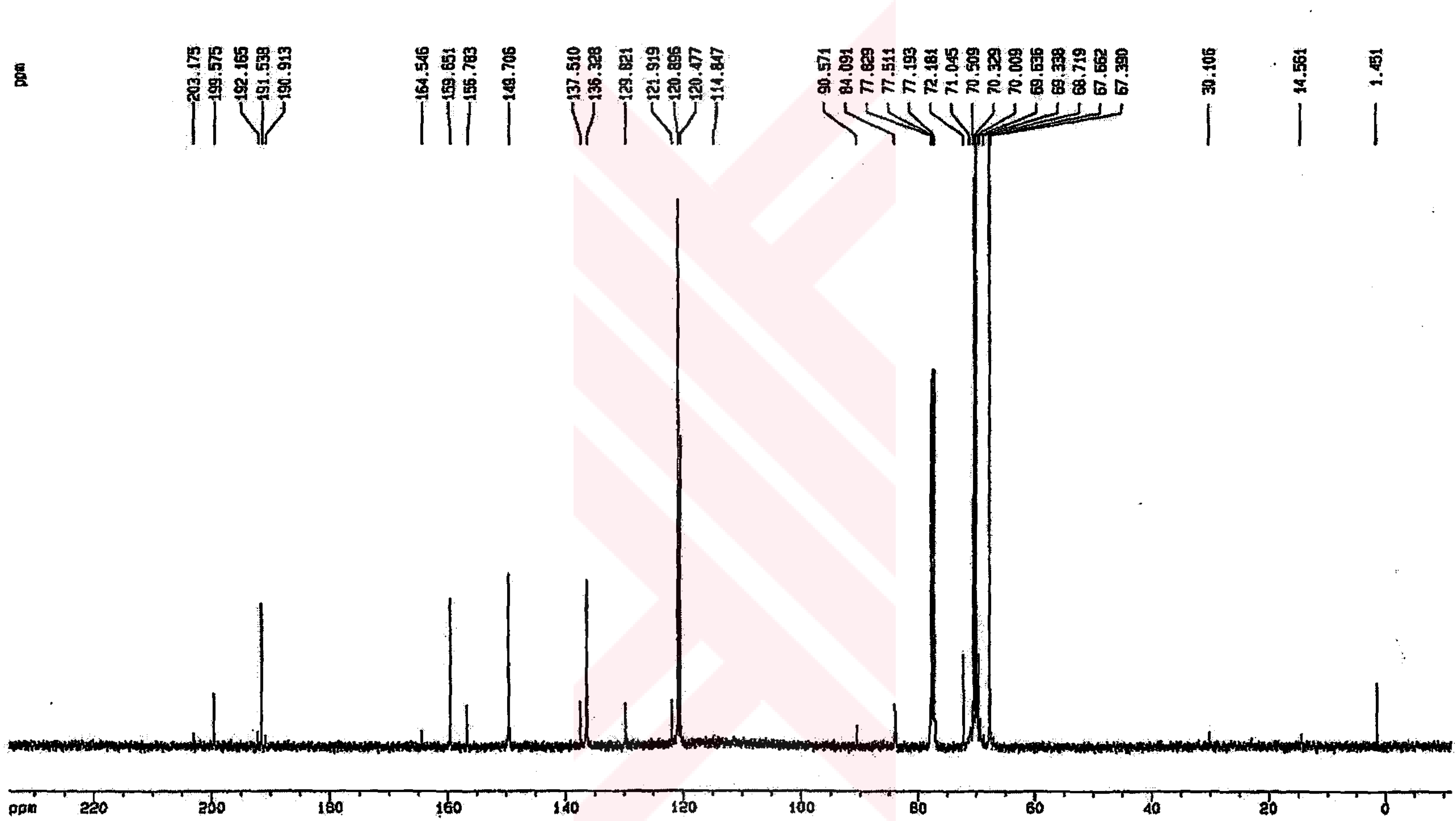


Figure 4.16. ^{13}C-NMR spectrum of $W(CO)_5$(2-Fcpy) taken in d-chloroform

Pyridine is a weak π-acceptor ligand.[8] It is bound to a transition metal through the nitrogen atom. The HOMO is the sigma symmetry orbital oriented away from the nitrogen atom. It is through this orbital, occupied by an electron pair, that pyridine exerts its σ-donor function, donating electron density toward an empty dσ or a hybrid orbital of the metal (Figure 4.17.a). However, nitrogen makes the second largest contribution to the LUMO because C4 (carbon atom in para position to nitrogen) of the pyridine possesses the largest lobe of the LUMO (Figure 4.17.b).[34] Metal backdonates the electron density from its filled dπ orbital into this empty π^* orbital on nitrogen (Figure 4.17.c). This explains why pyridine has poor π-acceptor character. That is, if the largest contribution to the LUMO had come from nitrogen, pyridine would have been stronger π-acceptor. Similar to pyridine, an aliphatic imine is bound to a transition metal through nitrogen. In an aliphatic imine the HOMO is mostly on the nitrogen atom of the C=N: moiety, but the LUMO has much more carbon than nitrogen character. The difference in contributing to the LUMO between C and N in an aliphatic imine is much greater than that between C4 and N in pyridine. As a consequence, the π-acceptor strength of pyridine is superior to that of an aliphatic imine, implying that metal carbonyl complexes of pyridine may be more stable than those of aliphatic imines due to stronger backbonding.

2-Ferrocenylpyridine in which a good electron-donating ferrocenyl group is substituted to the pyridine ring in ortho position is expected to behave as a stronger σ-donor and weaker π-acceptor than pyridine. As a consequence, poor stability of the $M(CO)_5$(2-Fcpy) complexes synthesized in this study may be attributed to the weak M→ N backbonding.

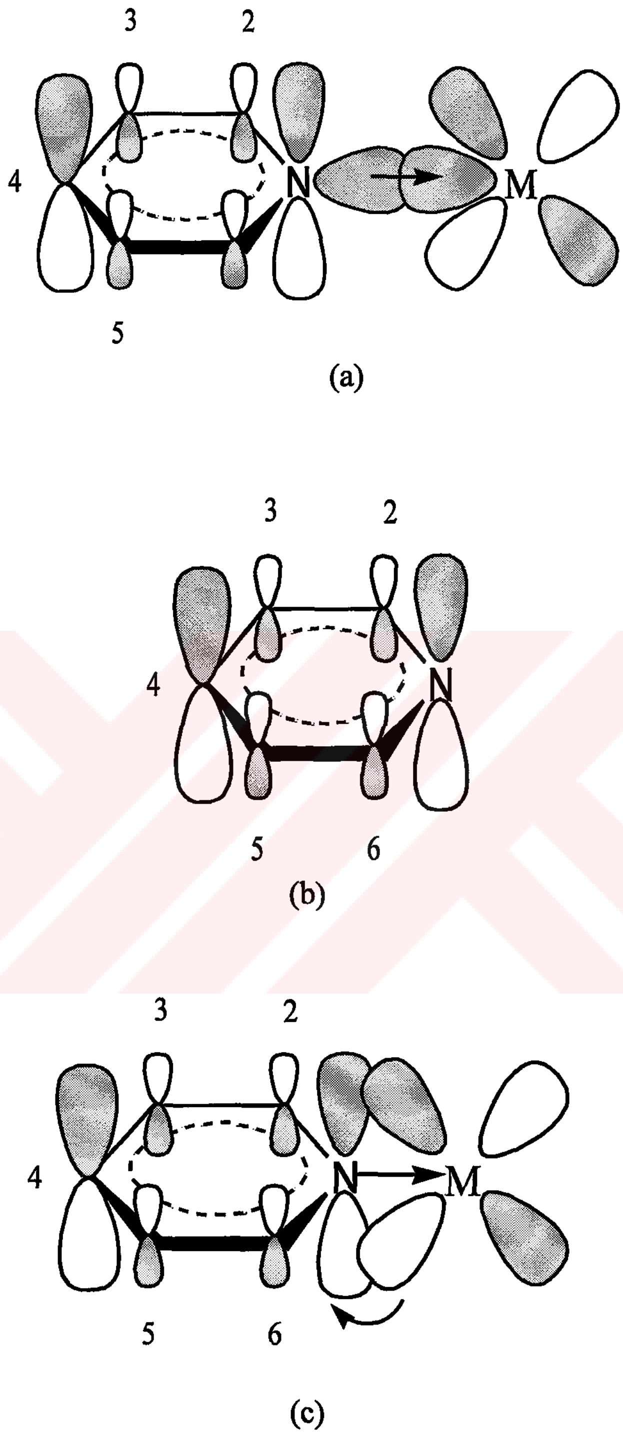


Figure 4.17. Molecular orbital description of the metal-pyridine bonding

a) M←N σ bonding

b) LUMO of pyridine

c) M→N backbonding

The IR spectra of the $M(CO)_5$(2-Fcpy) complexes display three absorption bands with $2A_1$+E CO vibrational stretching modes in the region 2200-1700 cm^{-1} (Table 4.1) indicating a square pyramidal arrangement of five CO groups in the pseudo-octahedral coordination sphere of the metal (Figure 4.18). Accordingly, the $M(CO)_5$ moiety in these complexes has a local C_{4v} symmetry.

Table 4.1. Carbonyl stretching band frequencies (cm^{-1}) of $M(CO)_5$(2-Fcpy) complexes (M: Cr, Mo, W) recorded in n-hexane.

	A_1^1	E	A_1^2
$Cr(CO)_5$(2-Fcpy)	2066.0	1935.6	1912.0
$Mo(CO)_5$(2-Fcpy)	2072.8	1938.9	1919.9
$W(CO)_5$(2-Fcpy)	2070.1	1929.4	1910.5

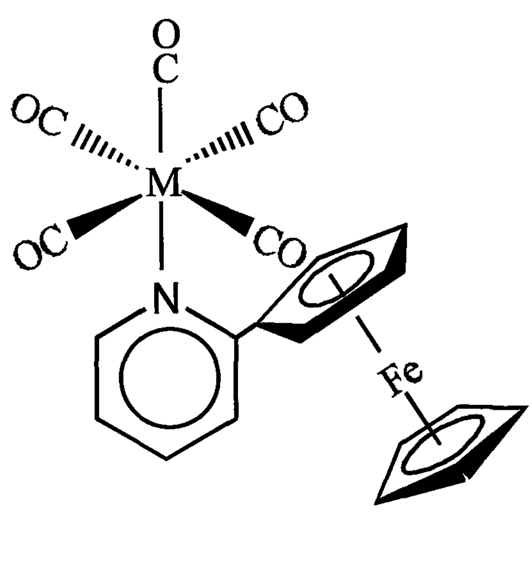


Figure 4.18. $M(CO)_5$(2-Fcpy) complexes (M: Cr, Mo, W)

The C_{4v} symmetry of $M(CO)_5$ fragment is also confirmed by ^{13}C-{^1H}-NMR spectra of the $M(CO)_5$(2-Fcpy) complexes (M: Mo, W), each of which displays two carbonyl signals with an intensity ratio of 1:4 (Figure 4.11 and 4.16, Table 4.2). The ^{13}C signal of the CO ligand *trans* to 2-Fcpy is in lower field than that of four *cis* CO ligands: While the *trans* CO competes with the 2-Fcpy ligand for the electrons of two dπ orbitals of the metal, *cis* ones compete for use of the electron density in the metal through only one dπ orbital. Thus, the *trans* CO is affected twice by M-N bonding with respect to the *cis* ones.

Table 4.2. ^{13}C-NMR chemical shifts (ppm) of CO groups in $M(CO)_5$(2-Fcpy) (M: Mo, W) recorded in d-chloroform.

	CO (*trans*)	**CO (*cis*)**
$Mo(CO)_5$(2-FcPy)	212.318	203.154
$W(CO)_5$(2-Fcpy)	203.175	199.575

According to the ^1H- and ^{13}C-NMR data of $Mo(CO)_5$(2-Fcpy), chemical shifts of the hydrogens and carbons of 2-Fcpy are slightly shifted to the higher magnetic field upon coordination to molybdenum. In contrast, ^1H- and ^{13}C-NMR data of $W(CO)_5$(2-Fcpy) reveal that chemical shifts of the carbons and hydrogens of the 2-Fcpy, except for that of C4 of the pyridyl ring, are significantly shifted to the lower magnetic field upon coordination to tungsten, which indicates that the $W(CO)_5$ fragment exerts a significant electron-withdrawing effect on the 2-Fcpy frame (Table 4.3 and 4.4).

Table 4.3. ^{13}C-NMR chemical shifts of free 2-Fcpy and coordinated 2-Fcpy in $M(CO)_5$(2-Fcpy) complexes (M: Mo, W)

	C2 (Py)	**C3 (Py)**	**C4 (Py)**	**C5 (Py)**	**C6 (Py)**	**C1 (Cp_{subst})**	**C2/ C5 (Cp_{subst})**	C3/ C4 **(Cp_{subst})**	5C ($Cp_{unsub st}$)
Free 2-Fcpy	159.645	120.865	136.291	120.442	149.708	84.068	70.277	67.617	69.966
$Mo(CO)_5$(2-Fcpy)	158.243	119.468	134.894	119.048	148.302	82.675	68.878	66.216	68.564
$W(CO)_5$(2-Fcpy)	164.546	137.510	129.821	121.919	156.783	90.571	72. 181	69.636	70.509

Table 4.4. ^{1}H-NMR chemical shifts of free 2-Fcpy and coordinated 2-Fcpy in $M(CO)_5(2\text{-Fcpy})$ complexes (M: Mo, W)

	H3 (Py)	**H4 (Py)**	**H5 (Py)**	**H6 (Py)**	**H2/ H5 (Cp_{subst})**	H3/ C4 **(Cp_{subst})**	5H ($Cp_{unsub st}$)
Free 2-Fcpy	7.35	7.48	6.96	8.45	4.88	4.34	3.98
$Mo(CO)_5(2\text{-Fcpy})$	7.36	7.50	6.99	8.43	4.87	4.34	3.98
$W(CO)_5(2\text{-Fcpy})$	8.00	7.62	6.91	8.96	4.64	4.39	4.07

CHAPTER 5

CONCLUSIONS

- Pentacarbonyl(2-ferrocenylpyridine)metal(0) complexes of Group 6, were attempted to be prepared for the first time by using both photolytic substitution of CO from the hexacarbonylmetal(0) complex with 2-Fcpy and thermal replacement of a labile-ligand in thermally or photochemically generated intermediate complex.

- Due to instability of these complexes, they can be prepared in low yields, and thus they could not be isolated as pure substances.

- The complexes were identified by IR spectroscopy and partially by ^{1}H- and ^{13}C-NMR spectroscopic techniques for $M(CO)_5(2\text{-Fcpy})$ (M: Mo, W).

- The IR spectra of the $M(CO)_5(2\text{-Fcpy})$ complexes display three CO absorption bands ($2A_1+E$) in the region 2200-1700 cm^{-1}, indicating that $M(CO)_5$ moiety of these complexes has a local C_{4v} symmetry.

- The C_{4v} symmetry of $M(CO)_5$ fragment was also confirmed by the ^{13}C-NMR data of $Mo(CO)_5(2\text{-Fcpy})$ and $W(CO)_5(2\text{-Fcpy})$. Each complex possesses two ^{13}C-NMR signals with an intensity ratio of 1:4 for the carbonyl ligands.

• The main reason for the instability of $M(CO)_5$(2-Fcpy) complexes is the weak π-accepting ability of the 2-Fcpy ligand. More stable pyridine-coordinated complexes of group 6 can be achieved by two ways:

i) increasing the oxidation state of the metal, so that the electron density on the metal decreases, thus the need for backdonation to the ligand through π interaction decreases as well, or

ii) using a pyridine ligand containing electron-withdrawing groups instead of the electron-releasing ferrocenyl group, so that the LUMO of the pyridine is lowered in energy and this substituted pyridine becomes a stronger π-acceptor ligand than 2-Fcpy.

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