

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES

PHOTO-SUBSTITUTION REACTIONS OF SOME
TRANSITION METAL ORGANOMETALLICS
AND THEIR SPECTROSCOPIC
CHARACTERIZATIONS

by
Salih ÇETİN

July, 2010
İZMİR

**PHOTO-SUBSTITUTION REACTIONS OF SOME
TRANSITION METAL ORGANOMETALLICS
AND THEIR SPECTROSCOPIC
CHARACTERIZATIONS**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Master of Science
in
Chemistry**

**by
Salih ÇETİN**

**July, 2010
İZMİR**

MSc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**PHOTO-SUBSTITUTION REACTIONS OF SOME TRANSITION METAL ORGANOMETALLICS AND THEIR SPECTROSCOPIC CHARACTERIZATIONS**” completed by **SALİH ÇETİN** under supervision of **ASSOC. PROF. DR. ELİF SUBAŞI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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Salih ETİN

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ABSTRACT

A series of metal carbonyl complexes of **VI B** and **VII B** groups having the general compositions *cis*-[M(CO)₄(η²-*N,S*-TSC)], [M= Cr; **1**, Mo; **2**, W; **3**] and *fac*-[ReBr(CO)₃(η²-*N,N*-TSC)], **4** and [(η⁵-Cp)Mn(CO)(η²-*N,N*-TSC)], **5** with thiosemicarbazide (**TSC**) have been prepared and characterized by elemental analysis, LC-mass spectrometry, FTIR and ¹H NMR spectroscopy. The spectral data suggest the involvement of sulfur and terminal amino nitrogen of **TSC** in coordination to the central metal ion for **VI B** metal carbonyl complexes whereas the terminal amino nitrogen and thioamide nitrogen of **TSC** in coordination to the central metal ion for **VII B** metal carbonyl complexes. On the basis of spectral studies, an octahedral geometry has been assigned for all of the complexes.

Keywords: Thiosemicarbazide; Metal carbonyls, Photochemical reactions, Schlenk technique

**BAZI GEÇİŞ METAL ORGANOMETALİKLERİN
FOTO-YERDEĞİŞTİRME TEPKİMELERİ
VE
SPEKTROSKOPİK KARAKTERİZASYONLARI**

ÖZ

Bu çalışmada tiyosemikarbazit ligandının, VIB ve VIIB grubu metal karbonil $[M(CO)_6]$ (M= Cr; **1**, Mo; **2**, W; **3**); $ReBr(CO)_5$; $[(\eta^5-Cp)Mn(CO)_3]$ kompleksleri ile fotokimyasal tepkimeleri sonucunda bir seri orjinal karbonil kompleksleri; *cis*- $[M(CO)_4(\eta^2-N,S-TSC)]$ (M= Cr; **1**, Mo; **2**, W; **3**); *fac*- $[ReBr(CO)_3(\eta^2-N,N-TSC)]$, **4** ve $[(\eta^5-Cp)Mn(CO)(\eta^2-N,N-TSC)]$ sentezlendi. Sentezlenen komplekslerin yapıları, elemental analiz, FTIR, 1H NMR ve LC-Mass spektrometri yöntemleri ile aydınlatıldı. Spektroskopik bulgulara dayanarak, VIB grubu metal karbonil komplekslerinde (**1-3**), tiyosemikarbazit ligandının kükürt ve terminal amin azot atomundan bidentat olarak koordine olmasına rağmen, VIIB grubu metal karbonil komplekslerinde (**4-5**), ligandın terminal amin ve tiyoamid azot atomlarında bidentat olarak koordine olduğu açıklanmıştır.

Anahtar kelimeler: Tiyosemikarbazit, Metal karboniller, fotokimyasal reaksiyonlar, schlenk tekniği

CONTENTS

	PAGE
MSc THESIS EXAMINATION RESULT FORM	ii
ACKNOWLEDGEMENTS.....	iii
ABSTRACT	iv
ÖZ.....	v
CHAPTER ONE-INTRODUCTION	1
1.1 Metal Carbonyls.....	1
1.2 Chromium, Molybdenum and Tungsten Carbonyls.....	3
1.2.1 Geometrical Structure.....	3
1.2.2 Electronic Structure	4
1.2.3 Luminescence Structure.....	13
1.2.4 Photoreactions	16
1.2.4.1 Substitution reactions $M(CO)_n(L)_{6-n}$ Complexes	16
1.2.4.2 $(Cp)M(CO)_3X$ Complexes	24
1.3 Manganese and Rhenium Carbonyls.....	27
1.3.1 Geometrical Structure.....	27
1.3.2 Electronic Structure	28
1.3.3 Luminescence Structure.....	34
1.3.4 Photoreactions	35
1.3.4.1 Substitution reactions $M(CO)_n(L)_{6-n}$ Complexes	35
1.3.4.1 $(Cp)M(CO)_3X$ Complexes	37
CHAPTER TWO-THIOSEMICARBAZIDE.....	40
2.1 Thiosemicarbazide	40

CHAPTER THREE- EXPERIMENTAL	42
3.1 Experimental Techniques for Handling Air-Sensitive Compounds	42
3.2 The Vacuum-Line Technique	42
3.2.1 The double manifold.....	42
3.2.2 The schlenk technique	43
3.2.3 Immersion-well photochemical reactor	44
3.3 Materyal and metod	45
3.4 Preparation of Complexes	45
3.4.1 Reaction of $[\text{Cr}(\text{CO})_6]$ with Thiosemicarbazide(1)	45
3.4.2 Reaction of $[\text{Mo}(\text{CO})_6]$ with Thiosemicarbazide(2).....	46
3.4.3 Reaction of $[\text{W}(\text{CO})_6]$ with Thiosemicarbazide(3)	46
3.4.4 Reaction of $[\text{ReBr}(\text{CO})_5]$ with Thiosemicarbazide(4).....	47
3.4.5 Reaction of $[\text{MnCp}(\text{CO})_3]$ with Thiosemicarbazide(5)	47
CHAPTER FOUR-RESULT AND DISCUSSION	61
4.1 Results And Discussion.....	61
CHAPTER FIVE- CONCLUSION	67
5.1 Conclusion.....	67
REFERENCES	68

CHAPTER ONE

INTRODUCTION

1.1 Metal Carbonyls

Metal carbonyl complexes are among the most photoreactive transition metal complexes known, and the purpose of this article is to acquaint the reader with results related to the photochemistry of metal carbonyls and their derivatives. Reviews of metal carbonyls are numerous, (Abel and Stone, 1970) but only a few deal specifically with excited-state processes. (Koerner von Gustorf and Grevels, 1969; Balzani and Carassiti, 1970) We review here all metal carbonyl photoprocesses including electronic absorption phenomena, luminescence, nonradiative decay, energy transfer, and chemical reaction. The use of light as a synthetic tool in this field became important in the late 1950's and early 1960's, and the last substantial review of the photochemistry appeared in 1969. (Koerner von Gustorf and Grevels, 1969) This paper centers on developments since that time, but emphasis is on a critical evaluation of all published material and enough data are presented to establish some generalities.

Metal carbonyls are known for numerous low-valent metals; four-, five-, six-, and seven-coordination are found; and formal d^n configurations include largely d^4 , d^5 , d^6 , d^7 , d^8 , d^9 , and d^{10} . Table 1.1 lists the elements whose carbonyl complexes have been the object of photochemical investigations (*vide infra*). At the present time, correlations between electronic structure and reactivity are in primitive stages of development so I have organized the material according to the central metal involved. The first section describes the work with group VI metal carbonyls since this group is the most well studied and can be used to illustrate several important concepts and generalities. The subsequent sections deal with the group V, group VII, and group VIII metal carbonyls in the order found in the periodic table.

It is widely believed that the bonding between CO and a metal is a combination of σ - and π -bonding.(Abel and Stone, 1969) Delocalization of π -d electrons from the

central metal into the π^* CO orbital gives rise to π -back-bonding, and overlap of σ symmetry orbitals of the metal and CO yields a strong σ donor interaction for the CO as Figure 1.1.

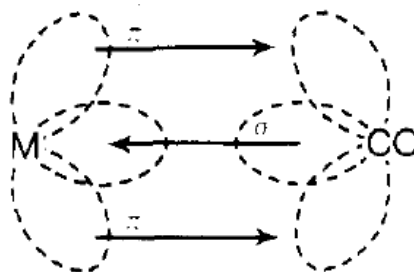


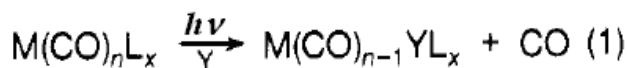
Figure 1.1 σ and π interaction of M-CO

The relative importance of σ and π interactions are difficult to assess, but one generally associates stronger π -backbonding with lower valent metals which have a greater tendency to delocalize electron density into the ligand. Thus, we associate stable carbonyl complexes with low valent metals. As a consequence of the large degree of delocalization of the electrons from the central metal into the ligand, these compounds are highly covalent. Therefore, electronic transitions involving these electrons should yield substantial changes in bonding, providing a general rationale for the extreme photosensitivity of the compounds. For d^n cases where $n = 1-9$, one expects the possibility of ligand field (LF) absorptions as well as charge-transfer (CT) transitions involving CO and the other ligands and the central metal. For some ligands one also must contend with the probability that intraligand excited states could be achieved.

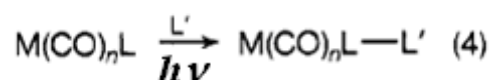
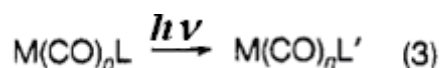
Table 1.1 Elements known to form photoreactive carbonyl complexes

GroupV	GroupVI	GroupVII	GroupVIII		
V	Cr	Mn	Fe	Co	Ni
Nb	Mo	...	Ru	Rh	...
Ta	W	Re	Os	Ir	...

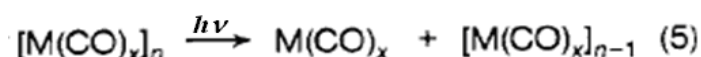
The dominant photoreaction of $M(\text{CO})_n\text{L}_x$ complexes is ligand substitution of either L or CO (eq 1 and 2).



While oxidative addition to photogenerated coordinatively unsaturated intermediates is common, there appears to be no definitive data that show that either photooxidation or photoreduction is a primary photoprocess upon uv or visible excitation. The photoassisted reaction of coordinated ligands is an area of importance, common reactions being either intramolecular rearrangements of L (eq 3) or Addition with molecules in the medium (eq 4).



One can also envision reactions involving the incorporation of CO into the ligand L. Emerging class of photoreactions of metal carbonyls is the fragmentation reactions of clusters as indicated in (eq 5).



1.2 Chromium, Molybdenum and Tungsten Carbonyls

1.2.1 Geometrical structure

The commonly known carbonyls of Cr(0), Mo(0), and W(0) are six-coordinate octahedral complexes, $\text{M}(\text{CO})_6$. Other stable complexes containing only the central metal and CO include the dimers $\text{M}_2(\text{CO})_{10}^{-2}$ having a single M-M bond. (Hieber et al., 1960) Numerous compounds of the $\text{M}(\text{CO})_n(\text{L})_{6-n}$ variety have been prepared, many photochemically. (Koerner von Gustorf and Grevels, 1969; Balzani and Carassiti, 1970)

Complexes which are formally seven-coordinated are also found. A typical example is the dimeric complex $\text{Mo}_2(\text{CO})_6(\pi\text{-C}_5\text{H}_5)_2$ (Figure 1.2). Assuming $\pi\text{-C}_5\text{H}_5$ (Cp) to have a negative charge and to be a six-electron donor occupying three coordination sites, the central metal is in the +1 oxidation state. In Figure 1.3, though, it is appropriate to identify the central metal as being in a +2 oxidation state. Other complexes involving the +2 oxidation state are clearly seven-coordinate as exemplified by species such as $[\text{W}(\text{CO})_2(\text{diars})_2(\text{I})]\text{I}$ and $\text{Mo}(\text{CO})_3(\text{L})\text{I}_2$ (L= bidentate ligand). (Cotton and Kraihanzel, 1972) Finally, seven-coordinate compounds of the type $[\text{W}(\text{CO})_3(\text{diars})\text{Br}_2]^+$ can be obtained. (Cotton and Kraihanzel, 1972) Thus, for the zerovalent metal complexes, six coordination is common while for the +1, +2, and +3 oxidation states seven-coordination is found. Important work in the area of excited-state chemistry involves the six-coordinate compounds and π -cyclopentadienyl complexes.

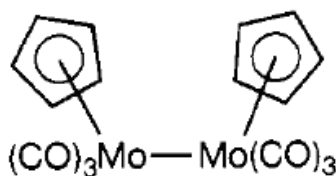


Figure 1.2 $[\text{MoCp}(\text{CO})_3]_2$

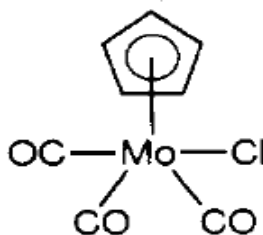


Figure 1.3 $\text{MoCp}(\text{CO})_3\text{Cl}$

1.2.2 Electronic Structure

Complexes of the general formula $\text{M}(\text{CO})_n(\text{L})_{6-n}$ have been given the most attention regarding electronic structure. The band position, intensity, and likely assignments for the electronic transitions for several types of Cr, Mo, and W

carbonyls are seen in Table 1.2 (Beach and Gray, 1968; Graham et al., 1971; Braterman and Walker, 1969; Darensbourg and Brown, 1968; Wrighton, 1971–1973; Saito et al., 1968; Carroll and McGlynn, 1968; Lundquist and Cais, 1962). Generally, the complexes exhibit a number of intense ($\epsilon > 10^2$) transition in the uv-visible region which are associated with LF and $M \rightarrow L$ and $L \rightarrow M$ CT absorptions. Intraligand absorptions are indicated in several cases. The complexes of d^6 configuration are invariably diamagnetic.

Spectra for the $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) compounds were determined early, (Gray and Beach, 1963) and the lowest energy absorption at $\sim 30,000 \text{ cm}^{-1}$ was assigned as the $^1A_{1g} \rightarrow ^1T_{1g}$ LF absorption. The band appears only as a shoulder on the more intense $M \rightarrow \pi^* \text{CO}$ CT absorption at $\sim 35,000 \text{ cm}^{-1}$. The second LF band, $^1A_{1g} \rightarrow ^1T_{2g}$, predicted for d_6 O_h complexes, can be observed in the vicinity of $\sim 37,500 \text{ cm}^{-1}$ for the $M(\text{CO})_6$ species. The most intense transition at $\sim 43,000 \text{ cm}^{-1}$ is assigned as a second component of the $M \rightarrow \pi^* \text{CO}$ CT absorption. In later studies, (Beach and Gray, 1968) including the isoelectronic $\text{V}(\text{CO})_6^-$, $\text{Mn}(\text{CO})_6^+$ and $\text{Re}(\text{CO})_6^+$ the same assignments were made except for one band at an energy below the $^1A_{1g} \rightarrow ^1T_{1g}$, absorption having $\epsilon \sim 1000$ for $\text{W}(\text{CO})_6$, $\epsilon 350$ for $\text{Mo}(\text{CO})_6$, and not present in the $\text{Cr}(\text{CO})_6$. This low-energy absorption was identified as the lowest LF spin-forbidden singlet \rightarrow triplet transition, $^1A_{1g} \rightarrow ^3T_{1g}$. Spectra of $M(\text{CO})_6$ in the low-energy region are shown in Figure 1.4 The enhanced intensity of the $^1A_{1g} \rightarrow ^3T_{1g}$ transition with increasing atomic weight of the central metal is expected owing to the larger spin-orbital coupling in the heavier metal. (Turro, 1965) The constancy of the value of IODq of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ is due to a balancing of diminishing σ -bonding and increasing π -bonding for the heavier metal system. (Beach and Gray, 1968) While it has been argued (Schreiner and Brown, 1968) that all of the bands in these complexes are CT absorptions, the LF treatment provides the best rationale for the band positions including the lowest singlet \rightarrow triplet absorption. Further, the LF approach accounts well for the observed spectral changes occurring upon substitution to yield $M(\text{CO})_5(\text{X})$ and $M(\text{CO})_4(\text{X})_2$ (vide infra). Finally, the intensities of the LF transitions are uncommonly large because of the high degree of covalency in these molecules; i.e., the molecular orbitals have substantial

contribution from both metal and ligand atomic orbitals tending to remove restrictions associated with the intensity of "d-d" transitions.

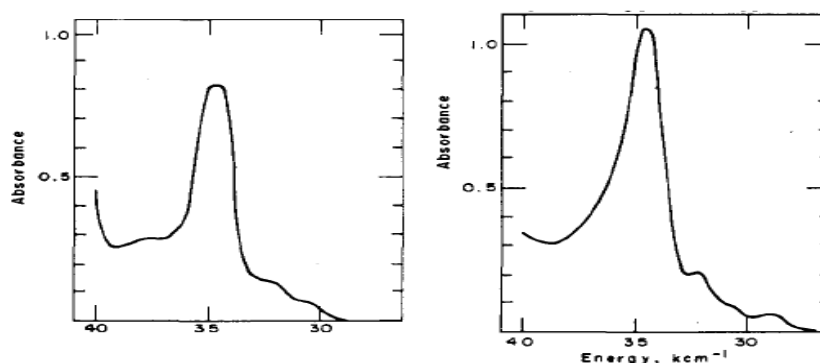


Figure 1.4 Electronic absorption spectra of 0.55×10^{-4} M $\text{Mo}(\text{CO})_6$ (top) and 0.80×10^{-4} M $\text{W}(\text{CO})_6$ (bottom) in EPA at 77^0K . Note the presence of the band at 28.900cm^{-1} in $\text{W}(\text{CO})_6$ not observed in $\text{Mo}(\text{CO})_6$ which is identified as the spin-forbidden $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g} (t_{2g} \rightarrow t_{2g}^5 e_g^1)$ transition (Beach and Gray, 1968): see table 1.1 for extinction coefficients.

The one-electron energy level diagram for $\text{M}(\text{CO})_6$ is shown in Figure 1.5. The ground electronic state, $^1\text{A}_{1g}$, has a t_{2g} electronic configuration and the one-electron excitation to $t_{2g}^5 e_g^1$ yields the $^1,3\text{T}_{1g}$ and $^1,3\text{T}_{2g}$ excited State. (Figgis, 1966) These one-electron excitations can result in dramatic changes in the substitutional lability of $\text{M}(\text{CO})_6$ least since both σ -bonding and π -bonding are diminished by causes depopulation of t_{2g} (π_b) and population of e_g (σ^*). (Wrighton et al, 1973)

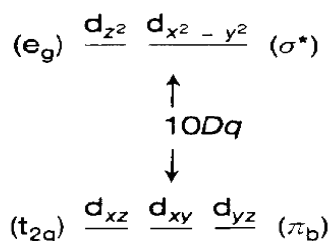


Figure 1.5 The one-electron energy level diagram for $\text{M}(\text{CO})_6$

Reducing the symmetry of the system from O_h to at least C_{4v} substitution to form $M(CO)_5(X)$ complexes causes changes in the one-electron energy levels. (Cotton, 1971) Since CO lies so high in the spectrochemical series (Gray and Benjamin, 1965) it is generally expected that substitution of CO to give $M(CO)_5(X)$ will result in a one-electron energy ordering like that shown in Figure 1.6. Naturally, if the LF treatment is to hold, the splitting of b_1 and a_1 should depend on the ligand X, and experimentally this is verified by noting (Table 1.2) that the first absorption band is sensitive to the nature of X, but for ligands having the same donor atom the first band is at about the same energy even though the ligand, X, may or may not have a low-lying excited state of its own; cf. acetone vs. ether and NH_3 vs. pyridine. For the available data the spectrochemical series is;

CO > alkene ~ PPh_3 > pyridine ~ amine ~ oxygen-donor

$\leftarrow 10Dq$

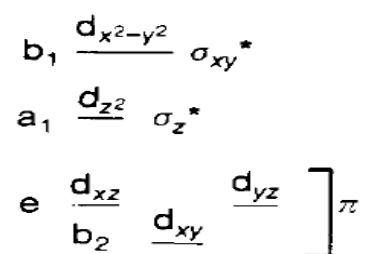


Figure 1.6 one-electron energy levels of $M(CO)_5(X)$

Table 1.2 Electronic transitions in chromium, molybdenum, and tungsten carbonyls

Complex	Bands, cm ⁻¹ (ν)	Assignment	Complex	Bands, cm ⁻¹ (ν)	Assignment
Cr(CO) ₆ ^a	29,500 (700)	¹ A _{1g} → ¹ T _{1g}	Cr(CO) ₆ (phen) ^{a,f} In cyclo- hexane In CH ₃ CN	16,950 (~5000) 21,370 (~5000) 37,370 (46,600) ^g	M → π* CT M → π* CT Intraligand π → π*
	31,550 (2670)				
	35,700 (13,100)				
	38,850 (3500)				
	43,600 (85,100)				
Mo(CO) ₆ ^a	28,850 (350)	¹ A _{1g} → ¹ T _{1g}	Mo(CO) ₆ (phen) ^a In cyclo- hexane In CH ₃ CN	18,100 (~6300) 22,630 (~6300) 37,470 (52,500) ^g	M → π* CT M → π* CT Intraligand π → π*
	30,150 (1690)				
	31,950 (2820)				
	34,600 (16,800)				
	37,200 (7900)				
W(CO) ₆ ^a	42,800 (138,000)	¹ A _{1g} → d ¹ T _{1u}	W(CO) ₆ (phen) ^a In cyclo- hexane In CH ₃ CN	17,640 (~8000) 21,980 (~8000) 37,380 (48,900)	M → π* CT M → π* CT Intraligand π → π*
	28,300 (1000)				
	29,950 (1680)				
	31,850 (3250)				
	34,650 (17,600)				
Cr(CO) ₃ ^b	37,100 (7400)	¹ A _{1g} → ¹ T _{1g}	Cr(CO) ₃ - (benzene)	~26,620 31,220	LF (?) M → arene CT M → π* CO M → π* CO
	43,750 (208,000)				
	18,450 (3200)				
	42,194 (39,500)				
	22,990 (3300)				
Mo(CO) ₃ ^b	40,820 (20,000)	M → π* CO CT	Cr(CO) ₃ - (aniline) ^f	~26,000 ~31,000 (12,600) ~38,500	LF (?) M → arene, π* CO M → π* CO
	22,727 (6300)				
	42,194 (63,500)				
	25,640 (5600)				
	41,322 (34,700)				
Cr(CO) ₃ - (pyridine) ^a	27,855 (1400)	¹ A ₁ → ¹ E(?)	Cr(CO) ₃ - C(OC ₂ H ₅) ₂ CH ₃ ^f	26,525 (5400) 31,095 (6000) 41,102 (26,700)	(?) (?) M → π* CO
	23,810 (3500)				
	40,000				
	~29,200				
	~32,260				
Mo(CO) ₃ - (PPh ₃) ^a	32,740 (3100)	?	Cr(CO) ₃ - (ethylene- diamine) ^g	23,600 (1300) 29,700 (5360) 35,500 (6300)	LF (¹ A ₁ → ¹ A ₁ , ¹ B ₁)
	25,975 (6600)				
	41,150 (58,000)				
	25,130 (5000)				
	39,680 (58,000)				
Mo(CO) ₃ - (piperidine) ^a	22,700 (630)	¹ A ₁ → ¹ E	Mo(CO) ₃ - (ethylene- diamine) ^g	32,700 (10,000) 38,300 (20,000) 43,400 (20,000)	M → π* CO CT + LF LF (¹ A ₁ → ¹ A ₁ , ¹ B ₁) M → π* CO CT + LF
	25,975 (6900)				
	22,800 (730)				
	24,875				
	24,875				
W(CO) ₃ - (pyridine) ^a	22,800 (520)	¹ A ₁ → ¹ E	W(CO) ₃ - (ethylene- diamine) ^g	22,200 (400) 25,200 (1400) 33,200 (8300)	LF (¹ A ₁ → ¹ A ₁ , ¹ B ₁) LF (¹ A ₁ → ¹ A ₁ , ¹ B ₁)
	24,875				
	22,800 (520)				
	24,875				
	24,875				
W(CO) ₃ - (cyclohexyl- amine) ^a	22,200 (910)	¹ A ₁ → ¹ E	Cr(CO) ₃ - (mesitylene) ^f	~32,000 (12,600) 38,500 45,450	M → arene, π* CO M → π* CO M → π* CO
	24,630 (5100)				
	21,930				
	23,920				
	23,920				
W(CO) ₃ - (1-pentene) ^a	~25,975 (~550)	¹ A ₁ → ¹ E	Mo(CO) ₃ - (mesitylene) ^f	31,750 (8300) 34,700 39,500 43,500	M → arene, π* CO M → π* CO M → π* CO M → π* CO
	27,780 (1530)				
	33,000 (7900)				
	?				
	?				
W(CO) ₃ (PPh ₃) ^a	27,500 (400)	¹ A ₁ → ¹ E	W(CO) ₃ - (hexamethyl- benzene) ^g	24,400 (563) 30,800 (15,000) 34,700 (6500) 42,000 (~1500)	LF (?) M → arene, π* CO M → π* CO ...
	28,800 (2200)				
	~22,800 (5670)				
	24,500 (7870)				
	31,650 (16,346)				
W(CO) ₃ (trans-4- styrylpyridine)	~22,800 (1230)	¹ A ₁ → ¹ E	(benzene)- Cr(CO) ₃ - (pyridine)	20,200	M → L CT
	25,130 (4800)				
	31,850 (17,900)				
	21,600 (4740)				
	24,200 (9370)				
cis-W(CO) ₃ - (pyridine) ₂ ^a	27,170 (7820)	Intraligand π → π*	(benzene)- Cr(CO) ₃ - (trans-4- styrylpyridine) ^f	16,340	M → L CT
	24,200 (9370)				
	(?)				

^a Acetonitrile solution, 300°K. ^b Rare gas matrices, 20°K. ^c Methanol solution, ambient. ^d Isooctane or other aliphatic hydrocarbon solution, ambient. ^e Benzene solution, ambient. ^f Ethanol solution, ambient. ^g phen = 1,10-phenanthroline.

For $\text{W}(\text{CO})_5(1\text{-pentene})$ the first band appears at $\sim 27,780\text{ cm}^{-1}$, while for $\text{W}(\text{CO})_5(\text{NH}_3)$ the corresponding band occurs at $\sim 24,875\text{ cm}^{-1}$. Thus, for the complexes studied, NH_3 and alkenes represent the extremes, consistent with alkenes being good π -acceptor ligands and amines being only σ -donor ligands. The one-electron energy levels in $\text{W}(\text{CO})_5(1\text{-pentene})$ are not substantially different from those in $\text{M}(\text{CO})_6$, while for $\text{W}(\text{CO})_5(\text{NH}_3)$ the splitting of b_1 (σ_{xy}^*) and a_1 (σ_z^*) is enough to yield "localized" antibonding character along the x and y axes or the z axis depending upon the excitation energy. As with the O_h complexes the C_{4v} complexes exhibit an intense singlet \rightarrow triplet LF band only for the W species. In Figure 1.7 a comparison of the low-energy absorptions for $\text{Mo}(\text{CO})_5(\text{diethylamine})$ and $\text{W}(\text{CO})_5(\text{diethylamine})$ is shown. Generally, the spectral features of $\text{M}(\text{CO})_5\text{X}$ are qualitatively similar to those for other d^6 , C_{4v} complexes. (Gutterman and Gray, 1971) The lowest energy transition (Wrighton et al., 1971&1972) is the ${}^1\text{A}_1(e^4 b_2^2) \rightarrow {}^{1,3}\text{E}(e^3 b_2^2 a_1^1)$, but higher energy excitations have not been assigned. Higher energy excitations should populate both $\text{M} \rightarrow \text{L}$ CT and LF states.

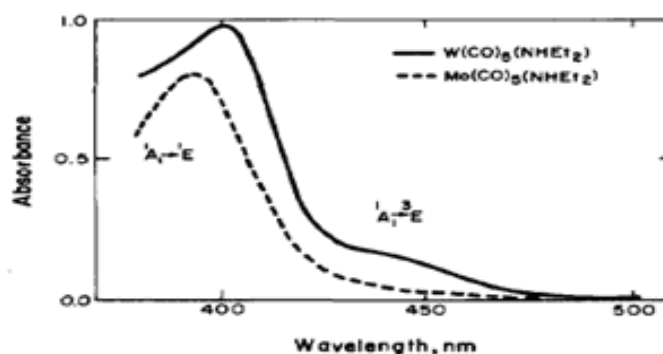


Figure 1.7 Electronic absorption spectra of $\text{W}(\text{CO})_5(\text{NHEt}_2)$ (—) and $\text{Mo}(\text{CO})_5(\text{NHEt}_2)$ (----) in aliphatic hydrocarbon solution. The intense band ($\epsilon \approx 5000$) in the vicinity of 400 nm is identified as the ${}^1\text{A}_1 \rightarrow {}^1\text{E}$ ($e^4 b_2^2 \rightarrow e^3 b_2^2 a_1^1$) spin-allowed transition and the shoulder only observed for the tungsten complex is the corresponding spin-forbidden ${}^1\text{A}_1 \rightarrow {}^1\text{E}$ transition (Wrighton et al., 1971&1972)

The C_{4v} $\text{M}(\text{CO})_5$ compounds have been studied in low-temperature matrices, (Graham et al., 1971) and the position of the first absorption band is consistent with a

LF interpretation. The band position is even lower than with nitrogen or oxygen donors since there is no ligand in the sixth coordination site. It is clear, though, that the LF splitting will be dominated by $M(\text{CO})_5$ when X is a weak field ligand in $M(\text{CO})_5\text{X}$ since the $M(\text{CO})_5$ spectra are not dramatically different from the $M(\text{CO})_5(\text{amine})$ spectra, particularly for $M = \text{W}$ or Mo .

The $M(\text{CO})_5(\text{styrylpyridine})$ illustrates a situation where an intraligand transition obtains. (Wrighton et al, 1973) In Figure 1.8 we show a comparison of the absorption of $\text{W}(\text{CO})_5(\text{pyridine})$ and $\text{W}(\text{CO})_5(\text{trans-4-styrylpyridine})$. In the vicinity of $33,000 \text{ cm}^{-1}$ the styrylpyridine complex exhibits an intense absorption with vibrational structure characteristic of the trans-stilbene-like chromophor. The red-shifted $^1\text{A}_1 \rightarrow ^{1,3}\text{E}$ absorption in the styrylpyridine complex may reflect some contribution from a $M \rightarrow L$ CT absorption.

A final class of C_{4v} complexes merits attention. The "carbene" complexes $M(\text{CO})_5\text{C}(\text{OC}_2\text{H}_5)\text{R}$ have low-lying absorption (Darensbourg, 1970) near that for the $M(\text{CO})_5(\text{amine})$ complexes, and the assignment of the lowest transition as the $^1\text{A}_1 \rightarrow ^{1,3}\text{E}$ is attractive. However, a carbon donor is usually found high in the spectrochemical series. If the LF assignment is correct, the fact that the first band is at such low energies reveals that the carbene is surprisingly weak in LF strength. The $M \rightarrow L$ CT assignment is, thus, possible here.

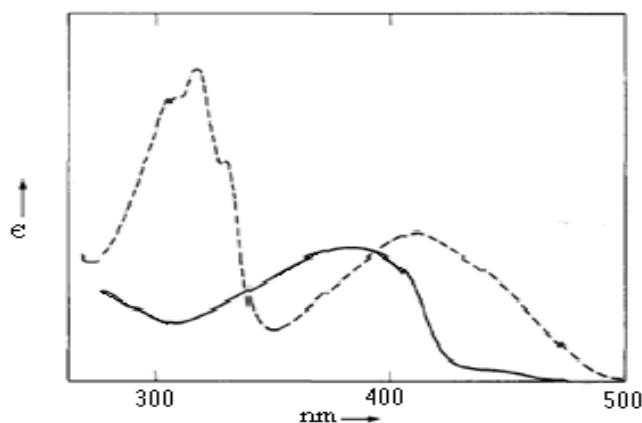


Figure 1.8 Comparison of electronic absorption spectra of $W(CO)_5(\text{pyridine})$ (—) and $W(CO)_5(\text{trans-4-styrylpyridine})$ (---). See table 1.1 for extinction coefficients. (Wrighton et al, 1973)

Disubstituted complexes $M(CO)_4(X)_2$ have also been investigated. Data for only the cis geometry are available, and the lowest energy bands are again given the LF assignments. The lowering of the energy for the first LF band (compared to $M(CO)_6$) in cis- $M(CO)_4(X)_2$ should be only slightly more than that of $M(CO)_5(X)$, while the shift for trans- $M(CO)_4(X)_2$ should be substantially larger. (Figgis, 1966; Wentworth and Piper, 1965; Ballhausen, 1962) This fact may be used to rationalize differences in trans- and cis- $M(CO)_4X_2$ complexes. For example, cis- $Mo(CO)_4(PEt_3)_2$ is colorless while the trans isomer is yellow. (Wender and Pino, 1968) The data for amine complexes in Table 1.2 strongly support the notion that the first band in cis- $M(CO)_4(X)_2$ and $M(CO)_5X$ should occur at similar energies, and the lowest bands have been assigned as LF. (Saito et al, 1968) Only the W complexes exhibit the familiar shoulder associated with the lowest singlet \rightarrow triplet absorption. Like the $M(CO)_6$ (Beach and Gray, 1968) and many $M(CO)_5(X)$ complexes, the bands for cis- $M(CO)_4(X)_2$ exhibit only a very modest solvent dependence. (Saito et al, 1968) For the $M(CO)_4(\text{phenanthroline})$ complexes though, a very large solvent effect on the first transition is observed. (Saito et al, 1968) The lowest energy absorption band in these cases is identified as the M-L π^* CT band with LF transitions appearing only as shoulders at higher energy. The cis- $M(CO)_4(\text{pyridine})_2$ spectra (Wrighton et al,

1973) more closely resemble the $M(CO)_4(\text{ethylenediamine})$ spectra, rather than the $M(CO)_4(\text{phenanthroline})$ spectra. (Saito et al, 1968)

The $(\text{arene})M(CO)_3$ complexes represent a final mononuclear system where some effort has been directed toward understanding electronic structural features. These complexes were recognized early (Lundquist and Cais, 1962) as having an absorption band in the vicinity of $\sim 38,500\text{ cm}^{-1}$ which was said to be characteristic of the M-C bond in metacarbonyl-sandwich compounds. This band was later assigned as the $M \rightarrow \pi^*CO$ CT absorption, while the lower energy absorption maximum in the vicinity of $\sim 31,000\text{ cm}^{-1}$ is assigned as a $M \rightarrow \text{arene}$ CT. (Carroll and McGlynn, 1968) Some qualitative evidence in support of such an assignment can be gained by examination of the colors of the $(\text{arene})M(CO)_3$ complexes. (Wender and Pino, 1968) For example, $(\text{benzene})Cr(CO)_3$ is yellow, $(\text{trans-stilbene})Cr(CO)_3$ is red, and $(\text{anthracene})Cr(CO)_3$ is violet-black. The energy of the onset of absorption in these compounds seems to be related to the energy of the first $\pi \rightarrow \pi^*$ absorption (Calvert and Pitts, 1966) in the arene group. Further, $(\text{cis-stilbene})Cr(CO)_3$ is only yellow while the trans-stilbene complex is red, again consistent with the ordering of the arene $\pi \rightarrow \pi^*$ energies (Calvert and Pitts, 1966) Little work has been carried out with the Mo and W complexes, but examination of a published spectrum (Lang, 1967) of $(\text{hexamethylbenzene})W(CO)_3$ reveals enhanced absorption in the $\sim 25,000\text{ cm}^{-1}$ region, perhaps reflecting the importance of direct singlet \rightarrow triplet absorption due to the large spin-orbital coupling associated with the central metal. Finally, one may suspect that LF absorption is important on the low-energy side of the $M \rightarrow \text{arene}$ CT band in $(\text{benzene})M(CO)_3$ since this is the region of the lowest LF bands in $M(CO)_6$. (Beach and Gray, 1968)

The monosubstituted complexes $(\text{arene})Cr(CO)_2(X)$ are often highly colored with the first absorption energy being very sensitive to the ligand X. The $\sim 4000\text{ cm}^{-1}$ red shift by changing X from pyridine to $\text{trans-4-styrylpyridine}$ is consistent with a $M \rightarrow X \pi^*$ CT absorption. Even for X = acetylenic group the complexes are highly colored, (Strohmeier and Hellmann, 1965) reflecting the ease of the $M \rightarrow L$ CT absorption in these systems. One expects relatively low energy $M \rightarrow L$ CT in these

systems because only two CO groups remain coordinated to the central metal to accept electron density and stabilize the low oxidation state. In this regard we note that (arene)Cr(CO)₂X complexes for X = σ -donor, π -donor are not particularly stable.

1.2.3 Luminescence Studies

Only a few papers dealing with luminescence of Cr, Mo, and W carbonyls have been published. It was found (Wrighton et al., 1971&1972) that complexes of the formula W(CO)₅(X), where X is an n-electron donor, will luminesce at 77 °K either as the pure solid or in rigid glasses. The corresponding Cr and Mo complexes did not luminesce, or, at least, emission was not detectable under conditions used to determine spectra for the W complexes. The typical, structureless emission of W(CO)₅(X) is exemplified in Figure 1.9. The lack of luminescence of the Cr and Mo complexes was correlated with the lack of an identifiable $^1A_1(e^4b_2^2) \rightarrow ^3E(e^3b_2^2a_1^1)$ transition in absorption (cf. Table 1.2). Emission maxima, lifetimes, and some relative yields are set out in Table 1.3 for some W(CO)₅(X) complexes. Since the emission overlaps the low-energy absorption band and the lifetime is $\sim 10^{-6}$ sec, it seems reasonable that the emission be assigned as the $^3E(e^3b_2^2a_1^1) \rightarrow ^1A_1(e^4b_2^2)$ transition. Microsecond lifetimes are fairly typical of heavy transition metal complexes for spin-forbidden emission. (Watts and Crosby, 1972; Demas and Crosby, 1970; Ryskin et al., 1965; Fleischauer, 1970)

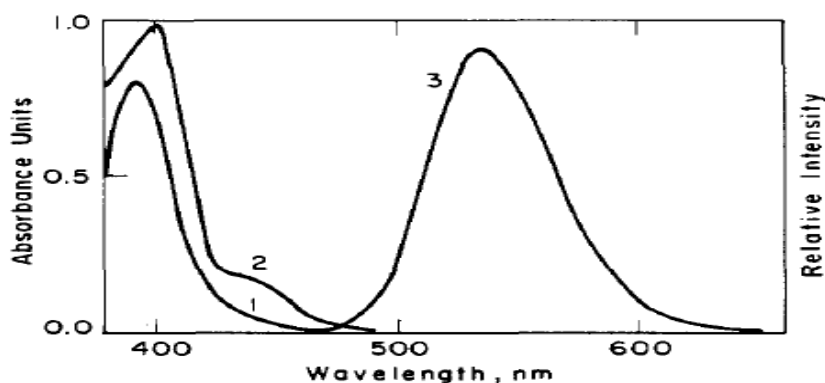


Figure 1.9 Electronic absorption spectra of $\text{Mo}(\text{CO})_5(\text{cyclohexylamine})$ (curve 1) and $\text{W}(\text{CO})_5(\text{cyclohexylamine})$ (curve 2) in aliphatic hydrocarbon solution and emission spectrum (curve 3) of the tungsten complex at 77°K . The molybdenum complex exhibited no luminescence (Wrighton et al., 1971, 1972).

The emission quantum yield, ϕ_e , and the emission lifetime, τ_e are related using (eq 6 and 7). Using the Einstein equation, (Turro, 1965) the radiative rate constant can be estimated from the integrated absorption to the state from which emission occurs. Since the absorptivity only changes by small amounts while emission lifetimes vary over a wide range, large changes in $k_{\text{nonradiative}}$ are implicated for the $\text{W}(\text{CO})_5(\text{X})$ species. Unfortunately, these complexes do not luminesce in room-temperature fluid solution, clouding the relationship of the emission data and photoreactivity.

$$\tau_e = \frac{1}{k_{\text{nonradiative}} + k_{\text{radiative}}} \quad (6)$$

$$\Phi_e = \frac{k_{\text{radiative}}}{k_{\text{nonradiative}} + k_{\text{radiative}}} \quad (7)$$

Table 1.3 Luminescence of tungsten and molybdenum carbonyl derivatives

A. C ₁₈ Complexes					B. C ₂₁ Complexes				
Complex	Emission max, nm	Rel Φ_{e}	$\tau_{\text{e}} \times 10^6$, sec		Complex	EPA, 77°K	Solid, 298°K	$\Phi_{\text{e}} \pm 20\%$	$\tau_{\text{e}} \times 10^6$, sec
W(CO) ₆	533				Mo(CO) ₆ (2,2'-bipyridine)		14.95		
W(CO) ₅ (EtNH ₂)	533		0.92		Mo(CO) ₆ (1,10-phenanthroline)	16.08	15.45	0.087	11.6
W(CO) ₅ (<i>i</i> -BuNH ₂)	533		1.2		Mo(CO) ₆ (5-methyl-1,10-phenanthroline)	15.62	15.15	0.081	13.2
W(CO) ₅ (<i>i</i> -PrNH ₂)	533		0.65		Mo(CO) ₆ (5-chloro-1,10-phenanthroline)	15.10	14.66	0.035	13.3
W(CO) ₅ (<i>c</i> -HxNH ₂)	533	1.0	1.1		W(CO) ₆ (2,2'-bipyridine)		14.70		
W(CO) ₅ (Et ₃ NH)	533	6.0	5.1		W(CO) ₆ (1,10-phenanthroline)		14.84	0.054	11.6
W(CO) ₅ (Me ₂ NH)	533		2.6		W(CO) ₆ (5-methyl-1,10-phenanthroline)	15.31	14.93	0.036	12.5
W(CO) ₅ (piperidine)	533		3.1		W(CO) ₆ (5-chloro-1,10-phenanthroline)	14.82	14.83	0.022	7.9
W(CO) ₅ (Et ₃ NMe)	533		25.5		<i>cis</i> -W(CO) ₆ (<i>n</i> -PrNH ₂)	18.52	<i>d</i>		0.85
W(CO) ₅ (Et ₃ N)	533		9.7		<i>cis</i> -W(CO) ₆ (piperidine) ₂	18.35	<i>d</i>		28.5
W(CO) ₅ (<i>n</i> -Bu ₃ N)	533		6.9		<i>cis</i> -W(CO) ₆ (pyridine)	18.32	<i>d</i>		48.3
W(CO) ₅ (Me ₂ NCH(CH ₃)Ph)	533	12.0	15.5		W(CO) ₆ (ethylenediamine)	18.31	<i>d</i>		23.5
W(CO) ₅ (EtOH)	~535		11.7						
W(CO) ₅ (<i>i</i> -PrOH)	~535		6.6						
W(CO) ₅ (<i>i</i> -BuOH)	~535		6.3						
W(CO) ₅ (Et ₂ O)	533		7.1						
W(CO) ₅ (acetone)	538		5.3						
W(CO) ₅ (acetone- <i>d</i> ₆)	~535		5.7						
W(CO) ₅ (cyclohexanone)	~535		3.6						
W(CO) ₅ (pyridine)	510		2.5						
W(CO) ₅ (2-methylpyridine)	~520		1.7						
W(CO) ₅ (2,4,6-trimethylpyridine)	~520		11.7						

Data for C₁₈ complexes are for methylcyclohexane solutions at 77°K. Quantum yields measured in EPA at 77°K. Not detectable.

The luminescence data for the W(CO)₅(N-donor) (N-donor = NR₃, HNR₂, H₂NR) are particularly interesting. It is observed that for the H₂NR ligands the lifetimes are grouped in the vicinity of 1x10⁻⁶ sec, HNR₂ complexes fall between 2.6 and 5.1x10⁻⁶ sec, and the NR₃ systems yield lifetimes in the range of 6.9-25.5x10⁻⁶sec. More hydrogens on the donor nitrogen yield the complexes having the shortest lifetimes and fastest rates of nonradiative decay. This effect is consistent with the general theory of Robinson and Frosch (Robinson and Frosch, 1962) states that the highest energy vibrational modes in a molecule are the key to fast nonradiative decay. Removal of the highenergy N-H stretching modes in the series H₂NR, HNR₂, NR₃ thus reduces the rate of nonradiative decay. The fact that the N-H stretches seem to be particularly effective is reminiscent of the specific effect of replacing the hydrogens in acetone with alkyl groups where it was found that non radiative decay from both the singlet and the triplet state (O'Sullivan and Testa, 1972) is slowed by the loss of the C-H stretching modes. Finally, in this regard it is to be pointed out that for certain Cr(III) complexes (Chatterjee and Forster, 1964) there seems to be a correlation of nonradiative decay rates and the number of high energy vibrational modes.

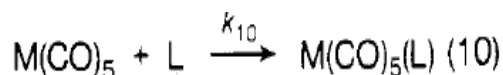
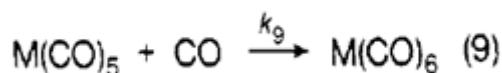
For the $W(CO)_5(O\text{-donor})$ complexes, importance of the O-H stretching mode as a nonradiative decay path is much less than in the N-donor cases. For example, the lifetime of $W(CO)_5(EtOH)$ is actually longer than the lifetime of $W(CO)_5(Et_2O)$. The explanation of this result requires further quantitative investigation of the relative emission quantum yields.

Optical luminescence has been recently observed (Kaizu et al, 1972) from a large number of bis-nitrogen donor tetracarbonylmolybdenum(0) and -tungsten(0) complexes. Data for these complexes of $\sim C_{2v}$ symmetry are included in Table 1.3 For the complexes where the bis-nitrogen donor is 1,10-phenanthroline (and related ligands), both the Mo and W (but not Cr) species emit as solids at 298 °K or in glassy solvents at 77 °K. The position of the luminescence maximum correlates well with the position of the lowest $M \rightarrow \pi^*CT$ absorption. For complexes where the bis-nitrogen donor is an aliphatic amine or pyridine, luminescence was only detectable from the W species at low temperatures. The luminescence features of bis-aliphatic amine and -pyridine complexes parallels observations for the C_{4v} complexes, and thus, a LF triplet \rightarrow singlet emission assignment is appropriate. The facts that for the 1,10-phenanthroline complexes room-temperature emission is seen, the Mo complexes emit, and the position of the band varies with the position of the lowest $M \rightarrow \pi^*CT$ absorption suggest a CT assignment for the luminescence in these complexes. The similar lifetimes and quantum efficiencies for the Mo and W species is seemingly inconsistent with a totally spin-forbidden transition.

1.2.4 Photoreactions

1.2.4.1 Substitution Reactions $M(CO)_n(L)_{6-n}$ Complexes

Chemistry involving ligand exchange and substitution dominates the excited-state processes of $M(CO)_6$ complexes. It appears certain that the photochemical formation of $M(CO)_5(L)$ is obtained by the sequence outlined in (eq 8–10). Several lines of evidence support very efficient generation of the coordinatively unsaturated intermediate, $M(CO)_5$, which has a substantial lifetime.



It was found that a reversible photoreaction occurs upon photolysis of $\text{M}(\text{CO})_6$ in a methyl methacrylate polymer. (Massey and Orgel, 1961) The slow thermal bleaching of the yellow intermediate formed during photolysis is thought to be due to reaction 9. Infrared characterization of the $\text{M}(\text{CO})_5$ intermediate was first gained by Sheline and coworkers (Stolz et al, 1962) who obtained ir spectra after photolysis of $\text{M}(\text{CO})_6$ at 77 °K in methylcyclohexane glasses. The ir spectra supported assignment of the primary photoproduct as a C_{4v} $\text{M}(\text{CO})_5$. However, evidence obtained upon thawing the $\text{Mo}(\text{CO})_5$ sample implicated isomerization from a species of C_{4v} symmetry to one of D_{3h} symmetry. Strohmeier and his colleagues advanced chemical evidence supporting the mechanism in (eq 8–10). The initial quantum yield of 1.0 for $\text{M}(\text{CO})_5\text{L}$ formation was found to be independent of M (M = Cr, Mo, W) and L. If a substantial contribution to the substitution process is an associative mechanism, one expects a dependence on the entering group L. It should be emphasized, however, that the lack of an effect by the entering group is not itself conclusive proof of the dissociative mechanism.

Later work by Turner and his associates has been carried out irradiating the group VI hexacarbonyls in lowtemperature matrices. (Graham et al, 1971) Photolysis of $\text{M}(\text{CO})_6$ in argon at 20 °K yields the formation of $\text{M}(\text{CO})_5$ having C_{4v} symmetry. Both ir and uv-visible spectral changes were monitored which appear to be consistent with the formation of C_{4v} $\text{M}(\text{CO})_5$ which may subsequently thermally react with the photoreleased or added CO. In room-temperature fluid solutions, though, in the absence of any coordinating agent, species like Figure 1.10 are speculated (Graham et al, 1971) to exist. Such an intermediate seems likely in light of the fact that the irradiated solutions of $\text{M}(\text{CO})_6$ have a persistent yellow color even when CO is bubbled through them. The yellow color, however, could be due to $\text{M}(\text{CO})_5\text{X}$ where X is an impurity nucleophile in the solvent. An earlier suggestion (Dobson, 1965)

that N_2 could be weakly bound to $M(CO)_5$ is substantiated by results (Graham et al., 1971) of photolysis of $M(CO)_5$ in matrices of pure nitrogen or mixed argon-nitrogen at $20^\circ K$.



Figure 1.10 Reaction intermediate

Flash photolysis of $M(CO)_6$ at room temperature has produced some conflicting conclusions. The first solution flash photolysis (Nasielski et al., 1971) indicated two intermediates which were identified as the C_{4v} and D_{3h} forms of $Cr(CO)_5$. Later work led to conclusion that the second intermediate is actually a $M(CO)_5(L)$ complex, where L is an impurity in the solvent, unreacted $M(CO)_6$, etc. None of the workers (Nasielski et al., 1971) agree on the absorption maximum in the uv-visible or the lifetime of the $Cr(CO)_5$, but it seems clear that an intermediate of this type is formed which is highly susceptible to attack by the poorest of nucleophiles. It is still possible that the isocarbonyl Figure 1.11, formed by linkage photoisomerization of CO is the primary photo product. The O-bound CO would have a ligand field strength like other oxygen donors such as ethers, alcohols, and ketones and is likely to be very weakly bound, decaying rapidly to the free $M(CO)_5$ intermediate by thermal dissociation.

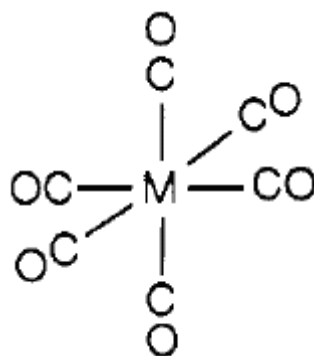


Figure 1.11 Geometrical structure of $M(CO)_6$

The question of whether the $M(CO)_5$ is rigidly C_{4v} , D_{3h} , or easily interconvertible remains unresolved. One predicts a change in the d-orbital ordering like that indicated in Figure 1.12 for a $C_{4v} \rightarrow D_{3h}$ conversion. One important physical property that undergoes a substantial change is the spin multiplicity. A d^6 configuration for the

C_{4v} form is predicted to be diamagnetic, having a singlet ground state, while the D_{3h} form should have two unpaired electrons being a ground-state triplet. The likelihood that a triplet electronically excited state is responsible for loss of CO from $M(CO)_6$ makes the triplet ground state an attractive one since excited state decay would not be dampened by slow intersystem crossing. The large degree of spin-orbital coupling implicated by absorption data, however, makes such an argument of dubious value.

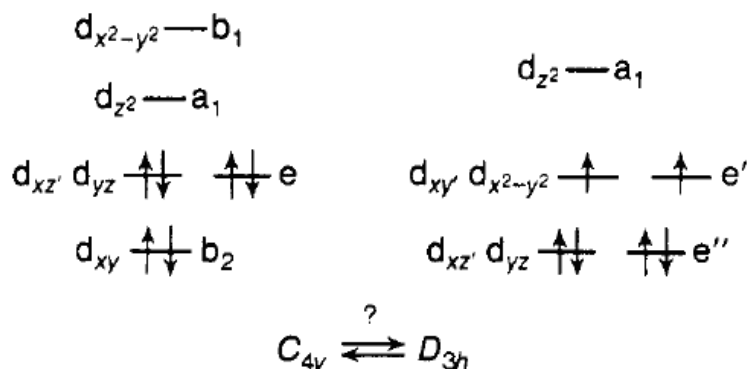
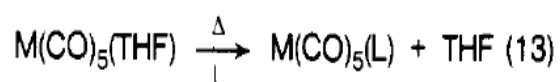
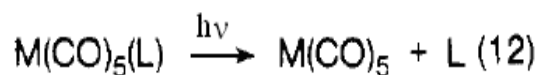


Figure 1.12 $C_{4v} \rightarrow D_{3h}$ conversion

Identification and characterization of the reactive excited state in $M(CO)_6$ complexes has not been pursued, probably because it suffices to say that the only decay path is dissociative loss of CO. The $M(CO)_6$ species have not been found to luminesce, and it is likely that spectroscopic excited states are extremely short-lived. The triplet-sensitized reaction of $Cr(CO)_6$ has been carried out and the reaction to yield loss of CO was found to be unity. The fact that the direct irradiation and triplet-sensitized yields are the same is consistent with decay of the excited states proceeding through a low-lying triplet state, but this point is clearly not proven. The $t_{2g}^6 \rightarrow t_{2g}^5 e_g$ one-electron excitation in these systems gives rise to the $^1T_{1g}$, $^3T_{1g}$, $^1T_{2g}$, and $^3T_{2g}$ excited states, all of which should be substantially more reactive than the ground state, since depopulation of the t_{2g} level diminishes π -back-bonding and concomitant population of e_g diminishes σ -bonding regardless of the spin multiplicity of the excited state achieved. Our ability to resolve the question of relative reactivity of different spin states involved in these reactions may ultimately depend on our ability to observe the reactive state prior to its decay.

The synthetic utility of the sequence 8–10 has had considerable impact on systematic studies of chemical properties of the $M(\text{CO})_n(\text{L})_{6-n}$ complexes. From numerous early successes we conclude that derivatives of $M(\text{CO})_6$ can be prepared by irradiation in the presence of almost any coordinating agent, (Koerner von Gustorf and Grevels, 1969; Balzani and Carassiti, 1970) Our objective here is to attempt to generally account for the degree of substitution ultimately obtained, and how to control it. It was recognized from the outset that photolysis of $M(\text{CO})_5\text{L}$ could result in the loss of another CO molecule (reaction 11) or loss of L (reaction 12). Reaction 11 leads to potentially two geometrical isomers of $M(\text{CO})_4(\text{L})_2$, and reaction 12 leads simply to ligand exchange in the presence of added L. The relative efficiencies of processes 11 and 12 were found to be very sensitive to the nature of L. In fact, for certain L, such as tetrahydrofuran (THF), process 12 is fairly insignificant, and nearly complete conversion of $M(\text{CO})_6$ to $M(\text{CO})_5(\text{THF})$ can be achieved.

The THF is weakly bound and a pure $M(\text{CO})_5\text{L}$ species is obtained by addition of L to the solution of $M(\text{CO})_5(\text{THF})$, reaction 13.



The relative importance of reaction 11 was found to increase with increasing strength of the M-L bond. It is not obvious that such a correlation should exist since the excitation energies are high enough to yield loss of either the CO or L. If a common excited state is responsible for both reaction 11 and 12, the correlation could be rationalized by merely assuming that photoexcitation causes the same relative increase in substitution rate for L and CO. In such a case comparison of ground-state binding strength may yield the correlation observed: when L and CO are more comparable in binding strength release of CO is competitive with release of L, though in the ground state both undergo substitution slowly.

A second parameter was found to effect the relative efficiency of reactions 11 and 12. The reaction quantum yield for (eq.11) was found to be sensitive to the wavelength of the exciting light as evidenced by data like those shown in Table 1.4 Higher energy irradiation yields more efficient loss of CO. Such an effect can be attributed to at least two reactive excited states or to differences in the reactivity of one excited state depending on the vibrational level directly achieved. The latter alternative is not likely since the reactions are carried out in condensed media. Additional data, (Wrighton et al, 1973) Table 1.5, reveals that both reaction 11 and 12 are wavelength dependent, with reaction 12 having attenuated importance upon higher excitation energy. The opposite wavelength dependence for the two processes can be rationalized by invoking two reactive LF excited states. The situation is detailed in figure 1.13 Low-energy excitation yields population of the d_z^2 (σ_z^*) orbital with σ -antibonding character directed principally along the z axis strongly labilizing the σ donor, pyridine. Higher energy excitation populates the dx^2-y^2 (σ_{xy}^*) orbital with strong labilizing effects for the equatorial CO's. Internal conversion of the upper state to the lower state with rate constant k_{nd} adequately accounts for the fact that reaction 12 occurs upon highenergy excitation. Impressive support of the rationale of the reactivity of $W(CO)_5(\text{pyridine})$ is found in the recent claim of selective incorporation of ^{13}CO into equatorial positions in $Mo(CO)_5(\text{piperidine})$ upon photolysis in the presence of ^{13}CO , and later similar evidence was obtained for the W analog.

Table 1.4 Wavelength dependence for quantum efficiency of $M(CO)_5(\text{pyridine})$ to $M(CO)_4(\text{pyridine})_2$ conversion

Central metal	Solvent	$\Phi_{356 \text{ nm}}$	$\Phi_{436 \text{ nm}}$
Cr	C_6H_6	0.21	0.13
Cr	THF	0.28	0.17
Mo	C_6H_6	0.16	0.11
Mo	THF	0.35	0.22
W	C_6H_6	0.11	0.08
W	THF	0.06	0.02

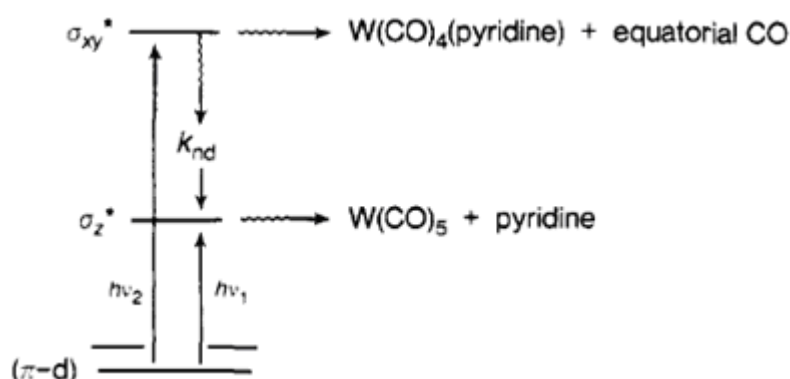


Figure 1.13 An internal conversion associated with the rate constant k_{nd}

In Figure 1.13 the internal conversion associated with the rate constant k_{nd} is key to whether a wavelength-dependent reaction will obtain. In these cases we do find reaction from the upper state which means that k_{nd} is only competitive with the rate constant for chemical change. Consequently, modest changes in k_{nd} , say a factor of 5, will have a real bearing on the chemical reactions, and thus studies directed toward elucidating factors controlling k_{nd} should be quite fruitful.

Table 1.5 Wavelength dependence for processes 11 and 12 for $M=W$ and $L=Pyridine$

Irrdn, λ , nm	$\Phi_{eq 11}$	$\Phi_{eq 12}$
436	0.002	0.53
366	0.013	0.50
313	0.039	0.38
254	~ 0.04	0.34

Quantum yields may depend on conditions used;

The metal and solvent dependence on reaction 11 revealed by the data in Table 1.4 are not easily explained. A clear explanation probably awaits results from reaction 12 and experiments designed to probe the point at which the solvent effect occurs.

Photolysis of $M(CO)_6$ has recently been used to produce tetra-, penta- and hexasubstituted derivatives (Table 1.6). (Matheiu and Poilblanc, 1972&1970; Stolz et al, 1963) A combination of factors makes such highly substituted complexes possible including final product stability and the photolabilization of the CO at intermediate stages of substitution. All of the cases for which ML_6 , $M(CO)L_5$, and $M(CO)_2L_4$ are found have L being a good π -acceptor ligand. That is, the loss of CO to yield stable low-valent complexes requires entering ligands capable of stabilizing the low-valent metal. Ligands having this quality should also tend to make possible the photolabilization of the CO. The substitution of CO by ligands which are like CO will not lead to substantial changes in the electronic structure, and thus, even though the symmetry may be quite low, the excited states are likely to be O_h -like. Consequently, CO photosubstitution can occur since the $t_{2g}^6 \rightarrow t_{2g}^5 e_g$ -type excitation is indiscriminate when all six ligands are good π acceptors. This situation is to be contrasted to situations like $W(CO)_5(\text{pyridine})$ where there are excited states which yield labilization of either the z axis or x-y axes. Empirically, for $W(CO)_5(\text{pyridine})$ z-axis excitation tends to preclude further CO substitution. Higher energy excitation yields more efficient loss of CO in $W(CO)_5(\text{pyridine})$ and the *cis*- $W(CO)_4(\text{pyridine})_2$ is formed. Higher substitution involving entrance of principally σ -donor ligands is not common, perhaps, owing in part to the fact that for *cis*- $M(CO)_4(\sigma \text{ donor})_2$ there is only one remaining axis of the OC-M-CO type. Experiments to determine substitution yields of *cis*- $M(CO)_4(\sigma \text{ donor})_2$ are necessary to speculate further on this possibility; however, the stability of $M(CO)_n(\sigma \text{ donor})_{6-n}$, for $n \leq 3$ is likely to be relatively low.

Table 1.6 Photosubstitution of chromium, molybdenum, and tungsten carbonyl by capable of stabilizing low-valent metals

Starting complex	Entering ligand, L	Product(s)
Cr(CO) ₆	(<i>n</i> -C ₃ H ₇)OPF ₂	CrL ₆
	P(OCH ₃) ₂ F	CrL ₅
	P(OCH ₃) ₃	Cr(CO)L ₅ <i>cis</i> -Cr(CO) ₂ L ₄
Mo(CO) ₆	(CH ₃)P(OCH ₃) ₂	Cr(CO)L ₅
	(CH ₃ O)P(CH ₃) ₂	Cr(CO)L ₅
	P(CH ₃) ₃	<i>cis</i> -Cr(CO) ₂ L ₄
	PF ₃	Mo(CO) ₅ L <i>cis</i> -Mo(CO) ₄ L ₂ <i>trans</i> -Mo(CO) ₄ L ₂ Isomers of Mo(CO) ₃ L ₃ <i>cis</i> -Mo(CO) ₂ L ₄ <i>trans</i> -Mo(CO) ₂ L ₄
		Mo(CO)L ₅ MoL ₆
		MoL ₅ MoL ₆ MoL ₄ Mo(CO)L ₅ <i>cis</i> -Mo(CO) ₂ L ₄
W(CO) ₆	P(OCH ₃) ₃	Mo(CO)L ₅
	(<i>n</i> -C ₃ H ₇ O)PF ₂	<i>fac</i> -W(CO) ₃ L ₃ <i>mer</i> -W(CO) ₃ L ₃ <i>cis</i> -W(CO) ₄ L ₂ W(CO) ₄ L ₂ <i>cis</i> -W(CO) ₂ L ₄ W(CO)L ₅ W(CO) ₂ L ₄
	(CH ₃)P(OCH ₃) ₂	
	P(CH ₃) ₃	
	P(OCH ₃) ₃	<i>cis</i> -W(CO) ₂ L ₄ WL ₆ WL ₅ W(CO)L ₅ Mo(CO) ₂ L ₂
	(<i>n</i> -C ₃ H ₇ O)PF ₂	
	P(OCH ₃) ₂ F	
	(CH ₃)P(OCH ₃) ₂	
	1,3-Butadiene	

1.2.4.2 (Cp)M(CO)₃X complexes

To date, very little mechanistic work has been carried out for complexes of this type, but several points can be made regarding the synthetic work carried out on these systems. The labilization of CO again appears to be the salient feature of the excited-state decay, and a high degree of substitution can be achieved as demonstrated by the photoproducts listed in Table 1.7 (King et al., 1968&1969&1971&1972; Barnett and Treichel, 1967) All three CO's can be substituted using a tridentate phosphorus donor. The restriction that the entering groups replacing CO be extremely good π -acceptor ligands may be relieved somewhat since the central metal in these cases is in either a +1 or +2 oxidation state. The loss of CO induced by photolysis can apparently be achieved regardless of X or the central metal, but the photolability of neither the cyclopentadienyl group nor X has been evaluated.

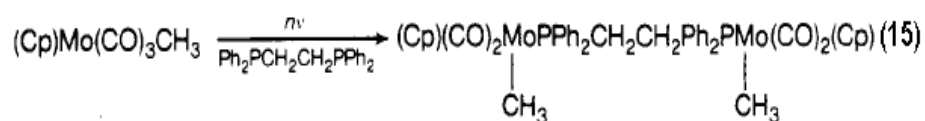
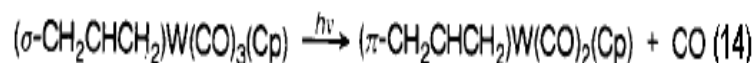
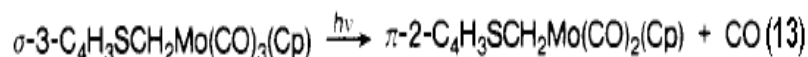
Work with these systems can be used to demonstrate other interesting consequences of CO lability. σ to π rearrangements like that in reaction 13 have

been observed, (King and Kapoor, 1969; King and Bisnette, 1965) and the primary photoprocess is probably dissociation of CO.

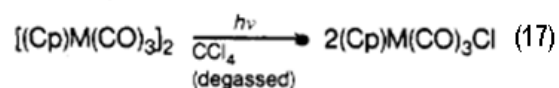
Table 1.7 Photoproducts of (Cp)M(CO)₃X

Initial complex	Entering ligand, L	Product(s)
C ₅ H ₅ Mo(CO) ₃ (Cp) (Cp)Mo(CO) ₃ Cl	Et ₃ NPF ₆ (Ph ₂ PCH ₂ CH ₂) ₂ PPh PEt ₃ Ph ₂ PCH ₂ CH ₂ PPh ₂ (Ph ₂ PCH ₂ CH ₂) ₂ PPh	C ₅ H ₅ Mo(CO)(L)(Cp) (Cp)Mo(L)Cl (Cp)Mo(CO)(L)Cl (Cp)Mo(CO)(L)Cl (Cp)Mo(CO)(L)Cl (Cp)Mo(CO)(L)Cl
(Cp)Mo(CO) ₃ I	PEt ₃ P(OPh) ₃	(Cp)Mo(CO)(L)I (Cp)Mo(CO)(L)I
[(Cp)Mo(CO) ₃ (diphos)] ⁺ Cl ⁻ [(Cp)Mo(CO) ₃] ₂	P(OC ₂ H ₅) ₃ PPh ₃	(Cp)Mo(CO)(diphos)(Cl) [(Cp)Mo(CO) ₃] ₂ Cl ₂ Mo ₂ (CO) ₂ L
(Cp)Mo(CO) ₂ Sn(CH ₃) ₂ (Cp)Mo(CO) ₂ CH ₃ (Cp)W(CO) ₂ CH ₃	P(OC ₂ H ₅) ₃ PPh ₃ PPh ₃	(Cp)Mo(CO) ₂ (L)Sn(CH ₃) ₂ (Cp)Mo(CO) ₂ (L)CH ₃ (Cp)W(CO) ₂ (L)CH ₃

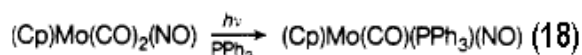
Similar reactions also occur for the tungsten complexes, (Green and Stear, 1964) reaction 14. Additionally, the (Cp)M(CO)₃X systems can be used as examples of the formation of dinuclear metal carbonyls by coordination of two metals to a bidentate ligand as in reaction 15. (Barnett and Treichel, 1967)



As indicated above, the relative importance of M-X bond cleavage has not been quantitatively investigated. However, reaction 16 (Haines et al, 1968) demonstrates the necessity of evaluating this decay mode. Preliminary results (Burkett et al, 1974) indicate that reaction 17 proceeds with high quantum efficiency ($\sim 10^{-1}$) upon either 546-nm or 366-nm irradiation with the stoichiometry shown.



Substitution of CO in $\text{CpM}(\text{CO})_2(\text{NO})$ can be achieved by irradiation (McPhail et al, 1971) as in reaction 18. Additionally, products which appear to arise from a nitrene intermediate are formed for $\text{M} = \text{Mo}$ (eq 19). In the case of $\text{M} = \text{Cr}$ only simple substitution, reaction 18, is observed while for $\text{M} = \text{W}$ the reactions like (19) obtain but give low yields. The nitrene mechanism gains some support from the fact that photolysis of an azido species gives similar product yields (McPhail et al, 1971) (eq 20).



1.3 Manganese and Rhenium Carbonyls

1.3.1 Geometrical Structure

The commonly available carbonyls of Mn and Re have the formula $M_2(CO)_{10}$ with the structure shown in Figure 1.14. The $M_2(CO)_{10}$ species are isostructural with $M_2(CO)_{10}^{-2}$ [$M = W(-1), Mo(-1), Cr(-1)$]. (Dahl and Rundle, 1963) Aside from these $M_2(CO)_{10}$ compounds having zerovalent metals, six-coordinate $M(I)$ compounds are known including $M(CO)_6^+$. Numerous substituted derivatives have been prepared including metal-carbonyl-alkyl compounds where it appears still appropriate to assign the +1 oxidation state to the central metal. The $(Cp)M(CO)_3$ complexes are stable and are again viewed as having the substitutionally inert d^6 electronic configuration.

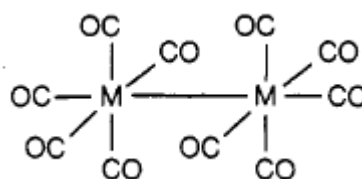


Figure 1.14 the structure of $M_2(CO)_{10}$

A number of structurally interesting Mn and Re compounds are known to exist, and some are of importance with regard to discussion of excited-state processes. The species $M_2(CO)_8X_2$ ($X = \text{halogen}$) having structure Figure 1.15 (Dahl and Rundle, 1963) does not have a direct M-M bond.

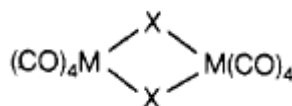


Figure 1.15 The species $M_2(CO)_8X_2$ ($X = \text{halogen}$)

Heteronuclear metal carbonyls containing Mn and Re are fairly common and include $(CO)_5Mn-Re(CO)_5$, (Nesmeyanov et al, 1963) $[(CO)_5Re]_2Fe(CO)_4$, (Evans et al, 1967) and $[(CO)_5Re][(CO)_5Mn]Fe-(CO)_4$. (Evans and Sheline, 1968) The compound $Mn_2Fe(CO)_{14}$ has the Figure 1.16 (Agron et al, 1967).

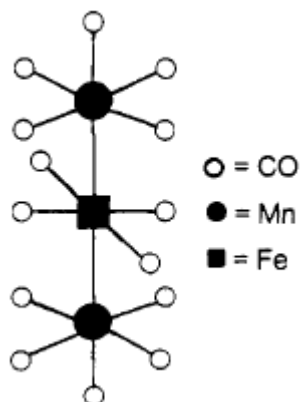


Figure 1.16 The compound of $\text{Mn}_2\text{Fe}(\text{CO})_{14}$

1.3.2 Electronic Structure

Study of the electronic structure of Mn and Re carbonyls has been carried out for several different types of complexes. Absorption band positions, intensities, and likely assignments are set out in Table 1.8 (Blakney and Allen, 1971; Gray et al, 1963; Levenson et al, 1970; Levenson, 1970)

Table 1.8 Electronic spectral data for manganese and rhenium carbonyls

Complex	Bands, cm ⁻¹ (ε)	Assignment	
[Mn(CO) ₅] ⁺ [BF ₄] ⁻	49,900 (27,000)	¹ A _{1g} → d ¹ T _{1u}	
	44,500 (16,000)	¹ A _{1g} → c ¹ T _{1u}	
	~39,600 (2200)	Vibrational components of	
	~37,300 (1100)		¹ A _{1g} → ¹ T _{1g}
	~33,250 (600)		¹ A _{1g} → ² T _{1g}
[Re(CO) ₅] ⁺ [AlCl ₄] ⁻	51,200 (77,900)	¹ A _{1g} → d ¹ T _{1u}	
	47,100 (4600)	¹ A _{1g} → ¹ T _{1g}	
	44,500 (20,000)	¹ A _{1g} → c ¹ T _{1u}	
	40,700 (2900)	Vibrational components of	
	38,500 (1500)		¹ A _{1g} → ¹ T _{1g}
	36,850 (708)		¹ A _{1g} → ² T _{1g}
CF ₃ Mn(CO) ₃ ^δ	~37,000 (~3000)	LF?	
	~46,380 (30,000)	M → π*CO	
CH ₃ Mn(CO) ₃ ^δ	>52,600 (>12,000)	M → π*CO	
	~35,500 (~3000)	LF?	
HMn(CO) ₃ ^δ	~45,050 (28,000)	M → π*CO	
	~51,020 (36,000)	M → π*CO	
	~30,000	LF?	
ClMn(CO) ₃ ^ε	~33,000		
	37,000		
	47,280	M → π*CO	
	50,630	M → π*CO	
BrMn(CO) ₃ ^ε	26,520 (600)	¹ A ₁ → ¹ E	
	37,000 (~1500)	LF?	
	45,050 (13,000)	M → CT	
	>52,600	X → π*CO	
IMn(CO) ₃ ^ε	26,070 (420)	¹ A ₁ → ¹ E	
	37,000 (1700)	LF?	
	43,950 (15,000)	M → π*CO	
	50,500 (7000)	X → π*CO	
O ₂ NOMn(CO) ₃ ^δ	25,000 (360)	¹ A ₁ → ¹ E	
	33,600 (3000)	LF?	
	36,400 (1500)	LF?	
	42,700 (20,000)	M → π*CO, X → π*CO	
	52,630 (68,000)	M → π*CO	
HRe(CO) ₃ ^δ	26,670 (1200)	¹ A ₁ → ¹ E	
	36,700	LF	
ClRe(CO) ₃ ^δ	46,510	M → π*CO	
	28,900	¹ A ₁ → ¹ E	
	~31,350	¹ A ₁ → ¹ E	
BrRe(CO) ₃ ^δ	~37,170	M → π*CO?	
	28,490 (300)	¹ A ₁ → ¹ E	
	31,060 (2260)	¹ A ₁ → ¹ E	
IRe(CO) ₃ ^δ	33,220 sh	?	
	26,460 (200)	¹ A ₁ → ¹ E	
	29,670 (1990)	¹ A ₁ → ¹ E	
	31,650 sh	?	
[Mn(CO) ₃ Cl] ^δ	23,100 (~1000)	LF	
	~29,400 (100-1000)	?	
[Mn(CO) ₃ Br] ^δ	23,100 (2300)	LF	
	~29,400 (700)	?	
[Mn(CO) ₃ I] ^δ	22,800 (100-1000)	LF	
	~28,600 (100-1000)		
[Re(CO) ₃ Cl] ^δ	~27,000 sh	LF	
ClMn(CO) ₃ (NCCH ₃) ^δ	26,600 (~1200)	LF	
BrMn(CO) ₃ (NCCH ₃) ^δ	26,500 (1500)	LF	
ClMn(CO) ₃ (Et ₂ O) ^δ	25,000	LF	
ClRe(CO) ₃ (pyridine) ^δ	~28,600 sh	LF	
ClRe(CO) ₃ (pyridine) ^ε	~29,400 sh	LF	
ClRe(CO) ₃ (5-methyl-1,10-phenanthroline) ^ε	~23,800 sh		
	26,320 (4100)	M → L _z *	
ClRe(CO) ₃ (5-bromo-1,10-phenanthroline) ^ε	37,310 (30,620)	Intraligand	
	~24,050 sh		
	25,840 (3900)	M → L _z *	
ClRe(CO) ₃ (5-nitro-1,10-phenanthroline) ^ε	36,500 (27,500)	Intraligand	
	~22,000 sh		
	25,190 (3800)	M → L _z *	
C ₅ H ₅ Mn(CO) ₂ ^γ	36,630 (27,700)	Intraligand	
	30,390 (1120)		

Table 1.8 (continued)

Complex	Bands, cm ⁻¹ (ν)	Assignment
CH ₃ COC ₂ H ₄ Mn(CO) ₂ ^f	29,590 (1640)	
C ₆ H ₅ COC ₂ H ₄ Mn(CO) ₂ ^f	28,740 (2040)	
(indenyl)Mn(CO) ₂ ^f	26,670 (1415)	
Mn ₂ (CO) ₁₀	29,400 (~20,000)	σ _b → σ*
Tc ₂ (CO) ₁₀	31,700	σ _b → σ*
Re ₂ (CO) ₁₀	32,300 (17,000)	σ _b → σ*
Mn(CO) ₅ (NO) ^e	23,360 (659)	
Mn(CO) ₅ (PPh ₃)(NO) ^e	24,450 (694)	
Mn(CO) ₅ (AsPh ₃)(NO) ^e	24,750 (696)	

^a CH₂CN, 298°K. ^b Cyclohexane, 298°K. ^c MeOH, 298°K. ^d CHCl₃, 298°K. ^e CH₂Cl₂, 298°K. ^f C₂H₅OH, 298°K. ^g Et₂O, 298°K.

The spectra of the d⁶ Mn(CO)₆⁺ and Re(CO)₆⁺ have strong similarity to the spectra of V(-I), Cr, Mo, and W carbonyls which have the same number of d electrons and are assigned accordingly. The lowest electronic transition is assigned as the ¹A_{1g}(t_{2g}⁶) → ³T_{1g}(t_{2g}⁵e_g¹) LF absorption, and the other transitions are identified with bands found in the Cr, Mo, and W carbonyls. Replacing a CO by a ligand of weaker LF strength reduces the symmetry to at least C_{4v}. The striking similarity of the electronic spectra of W(CO)₅(piperidine) and Re(CO)₅Cl is shown in Figure 1.17.

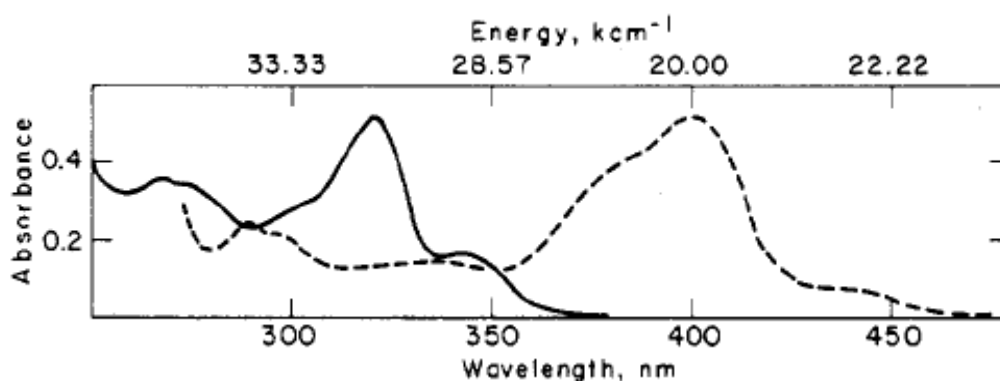
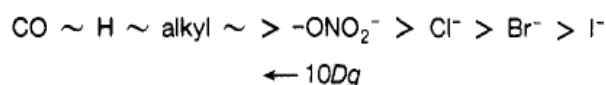


Figure 1.17 Comparison of electronic absorption spectra of W(CO)₅(piperidine)(—) and Re(CO)₅Cl(---). Maximum ε at 405 nm for the former is ≈5000 and for the latter at 320 nm ≈2000.

Thus, though the prevailing literature (Blakney and Allen, 1971) identifies the lowest bands as primarily CT in nature, it seems reasonable to assign the lowest bands in the Re(CO)₅X and Mn(CO)₅X compounds as the LF transitions ¹A₁ → ^{1,3}E as in the Cr, Mo, and W analogs. For the Mn and Re compounds the spectrochemical ordering seems to be consistent with other determinations of the series. As with the

comparisons of Cr and W, the $\text{Re}(\text{CO})_5\text{X}$ compounds appear to exhibit a more intense singlet \rightarrow triplet absorption than the corresponding Mn compounds.



The lowest absorption maximum for the dihalo-bridged compounds $\text{M}_2(\text{CO})_8\text{X}_2$ appears to be consistent with an approximately $\text{cis-M}(\text{CO})_4\text{X}_2$ chromophore. No trans-disubstituted complexes have been studied, but the shift in energy of the first electronic absorption from $\text{M}(\text{CO})_5\text{X}$ to $\text{cis-M}(\text{CO})_4\text{X}_2$ is expected to be small. The position of the first band in these compounds appears to follow the same spectrochemical ordering as in the $\text{M}(\text{CO})_5\text{X}$ complexes. The $\text{cis-ClRe}(\text{CO})_4(\text{pyridine})$ has its lowest electronic absorption band intermediate between $\text{Re}(\text{CO})_5\text{Cl}$ and $[\text{Re}(\text{CO})_4\text{Cl}]_2$ consistent with the known relative LF strengths of Cl⁻ and pyridine.

The donor atoms in the coordination sphere of $\text{ClRe}(\text{CO})_3(\text{pyridine})_2$ are the same as those of $\text{ClRe}(\text{CO})_3(1,10\text{-phenanthroline})$ but as seen in comparing Figures 1.18 and 1.19 the electronic spectra (Wrighton and Morse, 1974) of these two complexes are very different in the low-energy region. A similar relationship exists between $\text{cis-M}(\text{CO})_4(\text{pyridine})_2$ and $\text{M}(\text{CO})_4(1,10\text{-phenanthroline})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) with the 1,10-phenanthroline complex in each case exhibiting lower energy absorption which is assigned as the $\text{M} \rightarrow \pi^*$ phenanthroline CT absorption. A comparison of the CT band position for the 5-methyl-, 5-bromo-, and 5-nitro-1,10 phenanthroline shows that the more electron-withdrawing substituents gives a lower energy band maximum consistent with the $\text{M} \rightarrow \text{L}$ direction of the CT excitation.

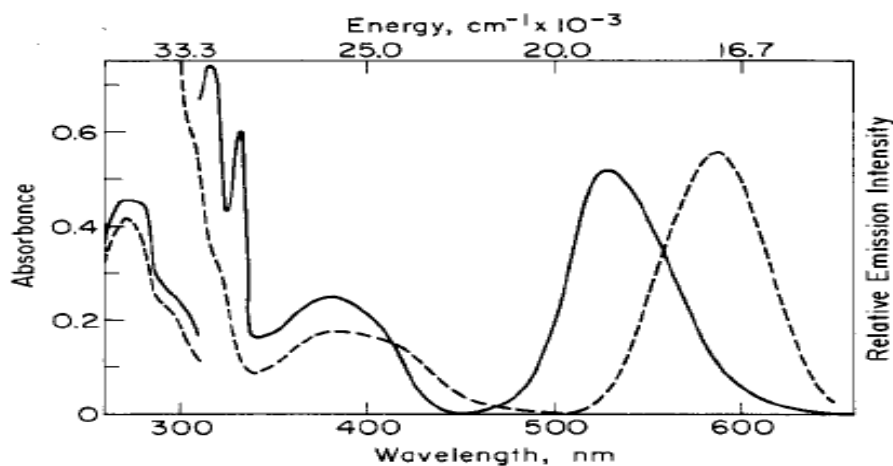


Figure 1.18 absorption (left) and emission (right) at 298⁰K(---) and 77⁰K(—) of ClRe(CO)₃(1.10-phenanthroline) in EPA. Room-temperature absorption maxima are at 26.100 cm⁻¹(ϵ 4000) and 37.030 cm⁻¹(ϵ 30.600). emission at 298 and 77⁰K were not recorded under the same sensitivity (Wrighton and Morse, 1974).

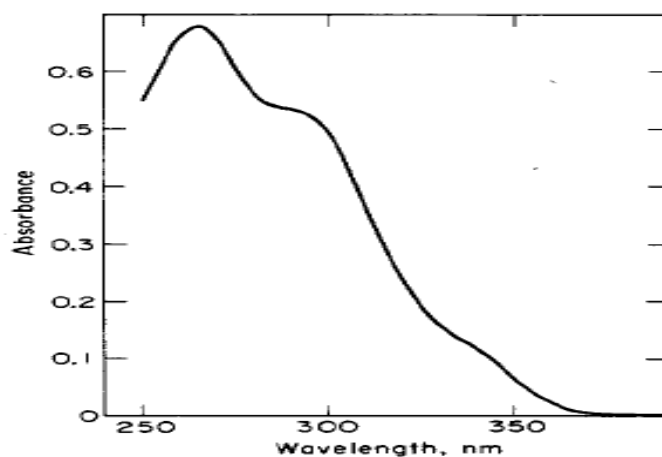


Figure 1.19 absorption spectrum of 7.8×10^{-5} M ClRe(CO)₃(pyridine)₂ at 298⁰K in CH₂Cl₂ in a 1.0-cm path length (Wrighton and Morse, 1974).

The lowest energy band maxima for several CpMn(CO)₃ complexes are included in Table 1.8, but detailed assignments have not been made. The sensitivity of the band positions to substitution in the ring implicates substantial $M \rightarrow \pi^*$ (Cp) character.

The electronic spectra of the dimeric M₂(CO)₁₀ species are dominated by an intense ($\epsilon > 10^4$) absorption band in the vicinity of 31,000 cm⁻¹. This band is not

present in the $M(CO)_6^+$ complexes, and energetic considerations (Levenson et al, 1970; Levenson, 1970) rule out a $M-\pi^*CO$ CT assignment. Assignment of the band as one associated with the M-M bond can be rationalized by a qualitative MO diagram (Figure 1.20). (Levenson et al, 1970) The dimer can be viewed as being composed of two C_{4v} $M(CO)_5$ fragments of d^7 electronic configuration with the unpaired electron being in the d_z^2 orbital. Overlap of the d_z^2 orbitals forms the σ -bonding and σ -antibonding orbitals. As indicated in the diagram, the $M_2(CO)_{10}$ species is diamagnetic and should exhibit a $\sigma_b \rightarrow \sigma_z^*$ one-electron excitation. This transition associated with the M-M bond may be quite important in interpreting the photochemistry of the M-M bonded species (vide infra).

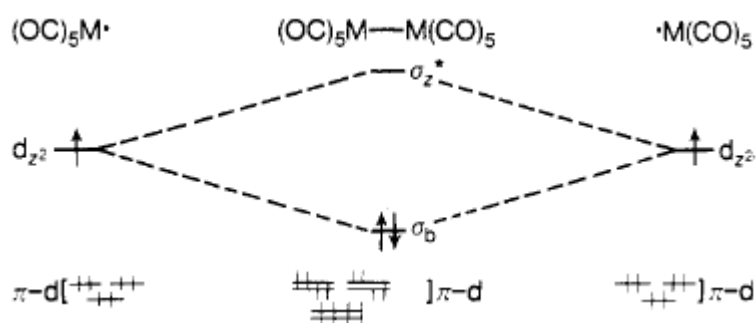
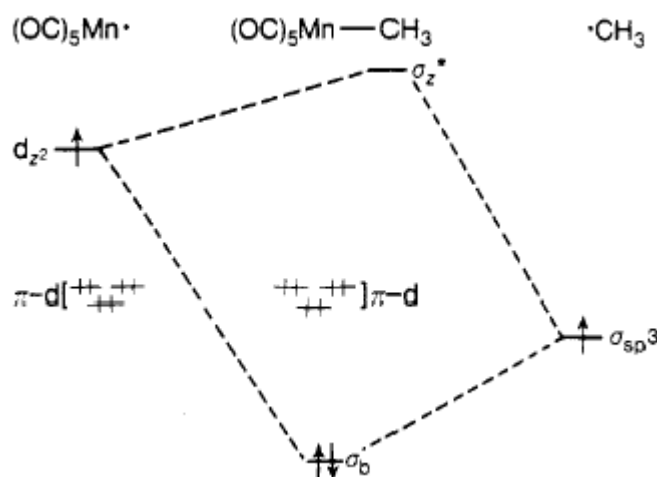


Figure 1.20 qualitative MO diagram with the M-M bond

The spectra of $M(CO)_5(X)$ ($M = Mn, Tc, Re$) can all be viewed in a similar fashion, but unless $X = M(CO)_5$ the relative orbital electronegativities will be different. Consider the MO diagram (Figure 1.21) of $Mn(CO)_5(CH_3)$, where only σ interaction with the d_z^2 orbital is shown. In these situations the $\sigma_b \rightarrow \sigma_z^*$ one-electron excitation is referred to as $L \rightarrow M$ CT. The $[\pi-d]$ level is essentially noninteracting with regard to the M- CH_3 bond. The $[\pi-d] \rightarrow \sigma_z^*$ excitations are LF transitions, and their effect on bonding interactions has already been mentioned for the isoelectronic Cr, Mo, W carbonyls. One notable point to be made here is that changes in reactivity upon LF or $L \rightarrow M$ CT excitation are due to the differences in the orbital, that is, depopulated since for both excitations the σ_z^* orbital becomes singly occupied.

Figure 1.21 MO diagram of $\text{Mn}(\text{CO})_5(\text{CH}_3)$

The complexes $\text{Mn}(\text{CO})_5(\text{X})\text{NO}$ ($\text{X} = \text{CO}, \text{PPh}_3, \text{AsPPh}_3$) are formally d^8 systems, isoelectronic with $\text{Fe}(\text{CO})_5$. A low-energy band maxima is at higher energies for $\text{X} = \text{AsPPh}_3$ or PPh_3 than for $\text{X} = \text{CO}$. (Keeton and Basolo, 1972) Detailed interpretation is not possible without further study of this system.

1.3.3 Luminescence Studies

Only one series of Re carbonyl complexes have been reported to luminesce. (Wrighton and Morse, 1974) Generally, the $\text{ClRe}(\text{CO})_3(\text{phenanthroline-X})$ complexes luminesce at either room temperature or below as solids, in fluid solutions, or in glassy media. The emission is at least partially spin-forbidden in nature as evidenced by lifetimes and quenching studies. Luminescence data for several complexes are outlined in Table 1.9

Table 1.9 Luminescence Data for $\text{ClRe}(\text{CO})_3(\text{L})$ Complexes

L	Emission max, cm^{-1}		τ , sec $\times 10^4$		$\Phi_{\pm 15\%}$ 77°K
	77°K	298°K	77°K	298°K ^b	
1,10-Phenanthroline	18.94	17.33	9.6	0.3	0.33
2,2'-Bipyridyl	18.87		3.8	0.6	
5-Methyl-1,10-phenanthroline	18.83	17.01	5.0		0.33
4,7-Diphenyl-1,10-phenanthroline	18.18	17.24	11.25	0.4	
5-Chloro-1,10-phenanthroline	18.69	17.12	6.25		
5-Bromo-1,10-phenanthroline	18.69	17.09	7.6		0.20
5-Nitro-1,10-phenanthroline	18.28		11.8		0.03 ₃
1,10-Phenanthroline-5,6-dione	18.45		2.5		

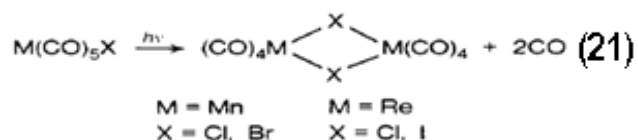
77°K measurements in EPA; 298°K measurements in CH_2Cl_2 . ^b Deoxygenated solutions.

Since the $\text{ClRe}(\text{CO})_3(\text{L})$ systems luminesce in fluid solution, this represents the first direct observation of the excited state of a metal carbonyl under conditions where photochemistry is normally carried out. The use of these as reagents for studies involving electronic energy transfer and nonradiative decay in solution has some promises. Intersystem crossing in these complexes measured by sensitized isomerization of trans-stilbene is very near unity as expected for systems involving a third row metal. (Wrighton and Morse, 1974) The order of magnitude decrease in lifetime at 298 °K compared to the 77 °K data is consistent with accelerated rates of nonchemical, nonradiative decay.

1.3.4 Photoreactions

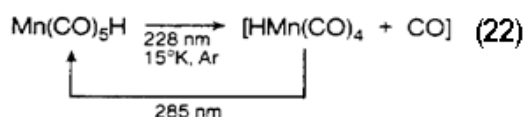
1.3.4.1 Substitution Reactions $M(\text{CO})_n(\text{L})_{6-n}$ Complexes

No detailed studies of the photoreactions of the simple d^6 six-coordinate Mn, Tc, or Re carbonyls have been reported. However, several qualitative observations have appeared in the literature and merit attention here. It was recently found that reaction 21 proceeds photochemically. (Blakney and Allen, 1972; Wrighton and Bredesen, 1973) For the $\text{Re}(\text{CO})_5\text{Cl}$ the disappearance quantum yield at 313-nm is >0.50 indicating that this reaction dominates all other excited-state pathways. It was pointed out that Mn-Cl cleavage to yield Cl does not obtain upon 436-nm photolysis of $\text{Mn}(\text{CO})_5\text{Cl}$ since $\text{Mn}_2(\text{CO})_{10}$ is not found when irradiation is carried out in the presence of 1 atm of CO. (Blakney and Allen, 1972) The lack of heterolytic M-Cl bond cleavage is consistent with the predicted (Wrighton et al., 1973) relative photolability of Cl^- vs. CO, the former being a π -donor and the latter a π -acceptor ligand. Higher energy excitation may yield $\text{L} \rightarrow \text{M}$ CT resulting in M-X cleavage.

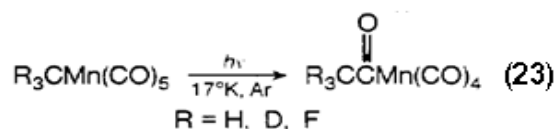


The photoreactions of a number of $\text{Mn}(\text{CO})_5(\text{L})$ ($\text{L} =$ strong σ -bonded ligand) complexes have been reported. Among these studies is the recent low-temperature

photolysis of $\text{Mn}(\text{CO})\text{H}$ which undergoes loss of CO to form a five-coordinate species of trigonal-bipyramidal structure (reaction 22). (Rest and Turner, 1969) The regeneration of the $\text{Mn}(\text{CO})_5\text{H}$ by lower energy photolysis may be due to localized softening of the environment allowing thermal recombination of the coordinatively unsaturated intermediate and the ligand. The direct observation of the five-coordinate species does serve to establish the dissociative nature of the CO photosubstitution. Additionally, the implication of the trigonal-bipyramidal structure for $\text{HMn}(\text{CO})_4$ leads to the expectation that the stereochemical significance of photoproducts $\text{HMn}(\text{CO})_4\text{L}$ will be clouded. Interestingly, the photoinduced ^{13}C O incorporation into $\text{Mn}(\text{CO})_5\text{Br}$ revealed no difference in the rate of axial vs. equatorial substitution, while the thermal reaction proceeded to give axial substitution at a rate equal to 0.74 times the equatorial rate. (Berry and Brown, 1972) These experiments provide support for different intermediates in the thermal and photosubstitution, but aside from this difference in reactivity no information is available regarding other properties of the intermediates with the exception that they are fluxional and five-coordinate. (Berry and Brown, 1972)

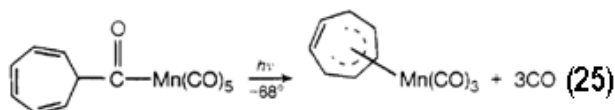
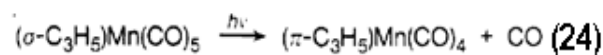


Irradiation of $\text{R}_3\text{CMn}(\text{CO})_5$ ($\text{R} = \text{H, D, F}$) at 17°K in an argon matrix has been shown to produce a five-coordinate acyl derivative (reaction 23). (Ogilvie, 1970) The role of the light in this reaction is not clear: is the primary process rupture of the $\text{Mn}-\text{CR}_3$ or the $\text{Mn}-\text{CO}$ bond.

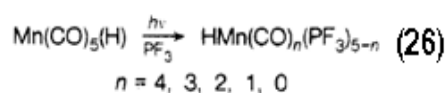


The photolysis (Green and Nagy, 1964) of $(\text{CO})_5\text{Mn}(\sigma\text{-C}_3\text{H}_5)$ represents one of the earliest reports of a reorganization of bonding between the metal and the hydrocarbon group induced by photodissociation of CO (reaction 24). The

decarbonylation reaction in 25 proceeds in 10.5 % yield at -68° , (Whitesides and Budnick, 1971) but the primary photoprocess is not obvious. Interestingly, the room-temperature photolysis yields only $\text{Mn}_2(\text{CO})_{10}$ and bitropyl, implicating $\text{Mn}(\text{CO})_5$ radical intermediates.

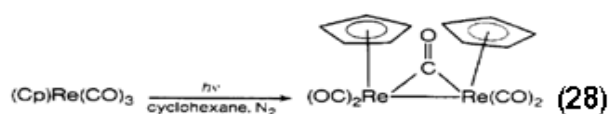


Finally, with respect to the six-coordinate $\text{M}(\text{CO})_n(\text{L})_{6-n}$ complexes, highly substituted derivatives of $\text{Mn}(\text{CO})_5\text{H}$ reformed *via* irradiation in the presence of PF_3 (reaction 26). (Miles and Clark, 1968) The PF_3 is, as usual in these cases, a strong π -acceptor ligand capable of stabilizing low oxidation states of the central metal.



1.3.4.2 $(\text{Cp})\text{M}(\text{CO})_3\text{X}$ Complexes

As with the $(\text{arene})\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) complexes the dominant photoreaction of $(\text{Cp})\text{M}(\text{CO})_3$ ($\text{M} = \text{Mn}$) is loss of CO , which leads to monosubstituted products (reaction 27). Most work has dealt with the first row Mn system though reaction 28 (Foust et al, 1971) has been recently reported which is probably initiated by loss of CO . The quantum yield for (27) is 1.0 for $\text{L} = \text{acetone}$ and diphenylacetylene (Strohmeier et al, 1963) and presumably for other ligands as well. Again it is likely that (27) will proceed for any L having any nucleophilic character at all. This fact is demonstrated by the large number of examples in Table 1.10 (King et al, 1972; Ruff, 1971; King et al, 1971; Ziegler and Sheline, 1965; Angelici and Loewen, 1967)

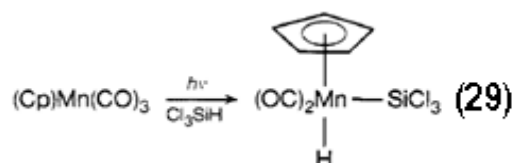


Further loss of CO from $(\text{Cp})\text{Mn}(\text{CO})_2\text{L}$ has been observed in several cases notably for L = good π -acceptor ligand as evidenced by the examples given in Table 1.10 All CO's have been displaced in the formation of $(\text{Cp})\text{Mn}(\text{benzene})$. (Fischer and Herberhold, 1964)

Table 1.10 Photosubstitution reactions of $(\text{Cp})\text{Mn}(\text{CO})_3$

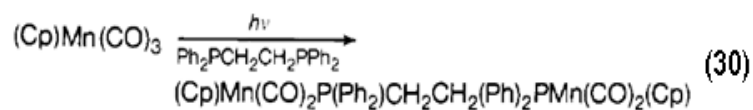
Entering group, L	Product(s)
Tetrahydrofuran	$(\text{Cp})\text{Mn}(\text{CO})_2\text{L}$
$(\text{Ph}_2\text{PCH}_2\text{CH}_2)_3\text{N}$	$(\text{Cp})\text{Mn}(\text{CO})\text{L}$
$(\text{CH}_3)_2\text{NPF}_2$	$(\text{Cp})\text{Mn}(\text{CO})\text{L}_2$
$\text{C}_6\text{H}_{10}\text{NPF}_2$	$(\text{Cp})\text{Mn}(\text{CO})\text{L}_2$
2,3-Diazabicyclo[2.2.2]-hept-2-ene	$(\text{Cp})\text{Mn}(\text{CO})_2\text{L}$
Pyridine	$(\text{Cp})\text{Mn}(\text{CO})_2\text{L}$
Piperidine	$(\text{Cp})\text{Mn}(\text{CO})_2\text{L}$
SO_2	$(\text{Cp})\text{Mn}(\text{CO})_2\text{L}$
PPh_3	$(\text{Cp})\text{Mn}(\text{CO})_2\text{L}$
	$(\text{Cp})\text{Mn}(\text{CO})\text{L}_2$
1,3-Butadiene	$(\text{Cp})\text{Mn}(\text{CO})\text{L}$
Ethylene (other alkenes)	$(\text{Cp})\text{Mn}(\text{CO})_2\text{L}$
Benzene	$(\text{Cp})\text{Mn}(\text{L})$

The coordinatively unsaturated intermediate from $(\text{Cp})\text{Mn}(\text{CO})_3$ is susceptible to oxidative addition like its $(\text{arene})\text{Cr}(\text{CO})_3$ analog (reaction 29). (Jetzand and Graham, 1971) The resulting product is a distorted square pyramid and formally seven-coordinate.



Several examples of dinuclear complexes formed *via* photolysis in the presence of a bidentate ligand have been reported. (Nyholm, 1963; King and Saran, 1971) One typical example is shown in reaction 30. Photolysis of the dinuclear complex can result in the formation of the mononuclear $(\text{Cp})\text{Mn}(\text{CO})\text{L}$. (Nyholm at all, 1963) This

may be the only example of a $(\text{Cp})\text{Mn}(\text{CO})_n\text{L}_{3-n}$ complex where the Mn-L is photolabilized, and even here it is possible that CO is lost first.



No one has claimed that substitution of the cyclopentadienyl ring is a primary photoprocess. Like with $(\text{arene})\text{Cr}(\text{CO})_3$ it is probable that the six-electron donor system is not labilized by a one-electron excitation to the degree of the two-electron donor CO groups. Finally, the only derivative of a substituted cyclopentadienyl that has been studied, $(\text{CH}_3\text{Cp})\text{Mn}(\text{CO})_3$, behaves like the parent species. (Jetzand and Graham, 1971; Nyholmet all, 1963)

CHAPTER –TWO

THIOSEMICARBAZIDE

2.1 Thiosemicarbazide

Thiosemicarbazide-based compounds have been extensively studied over the last couple of decades.(Kasuga et al, 2001; Chandra and Gupta, 2005; Demertzi et al,2001) The various Schiff bases of thiosemicarbazide (thiosemicarbazones) have attracted much attention because of the large number of potentially useful biological properties such as antibacterial, antifungal, antitumor, antimalarial, antiviral and anti-inflammatory activities. (Singh et al, 2006; Easmon et al, 2001; Seebacher et al, 2004; Du et al, 2002; Labisbal, 2003; Parmar and Kumar, 2009)Their activities has frequently been thought to be due to their ability to chelate metals. It is well known that the compounds containing $>C=S$ moiety have a strong ability to form metal complexes. Sulfur compounds have been the subject of interest in coordination and organometallic chemistry. Although many structures of thiosemicarbazone complexes have been reported, there are a few for complexes of the precursor thiosemicarbazide.(Castiñeiras,2000)

Thiosemicarbazide is an ambidentate ligand capable of forming five-membered metallocycles during coordination (**A**, **B**) or monodentate bonding through sulfur (**C**). (Koksharova et al, 2003)(figure2.1.) Thisemicarbazide usually acts as a chelating ligand for transition metal ions by bonding through the sulfur and terminal amino nitrogen atom, although in some cases they behave as monodentate ligands where bond through sulfur only.(Krishna et al,2007)

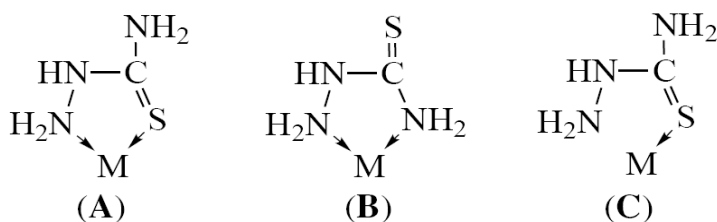


Figure 2.1 thiosemicarbazide bonding

Carbonyl compounds with sulfur and nitrogen donor ligands continue to attract considerable attention not only on account of their fascinating structural chemistry, but also because of their ability to act as electron reservoirs and their potential in catalysis. (Vahrenkamp et al, 1984) Features of the chemistry of these molecules which are currently of interest include the mechanisms and sites of substitution as well as the modification of reactivity accompanying carbonyl replacement by donor ligands. (Hogarth et al, 1988)

As a ligand, thiosemicarbazide has more than one potential donor atoms. Therefore, we tried to observe the sites of substitution of these ligands to the metal center. Along with our continued interest in the photochemical synthesis and structural aspects of group **VI B** and **VII B** metal carbonyls prompted us to make an exploratory investigation into the photolytic behaviour of the **VI B** and **VII B** metal carbonyls, $[M(CO)_6]$ $[M= Cr, Mo, W]$, $[Re(CO)_5Br]$ and $[(\eta^5-Cp)Mn(CO)_3]$ with the title ligand, **TSC**. (Subaşı et al, 2004&2006; Karahan et al, 2008; Subaşı et al, 2009) In this paper, the hitherto unknown new complexes, *cis*- $[M(CO)_4(\eta^2-N,S-TSC)]$, $[M= Cr; \mathbf{1}, Mo; \mathbf{2}, W; \mathbf{3}]$ have been prepared by the photochemically synthesized $[M(CO)_5THF]$ $[M= Cr, Mo, W]$ and *fac*- $[ReBr(CO)_3(\eta^2-N,N-TSC)]$, **4** and $[(\eta^5-Cp)Mn(CO)(\eta^2-N,N-TSC)]$, **5** have been prepared by the photochemical reactions of $[Re(CO)_5Br]$ and $[(\eta^5-Cp)Mn(CO)_3]$ with **TSC** respectively, and all of the complexes have been characterized by elemental analyses, FT-IR, 1H NMR spectroscopy and Mass spectrometry.

The spectral data suggest the involvement of sulfur and terminal amino nitrogen of **TSC** in coordination to the central metal ion for **VI B** metal carbonyl complexes whereas both terminal hydrazine and thioamide nitrogens of **TSC** in coordination to the central metal ion for **VII B** metal carbonyl complexes. On the basis of spectral studies, an octahedral geometry has been assigned for all of the complexes.

CHAPTER THREE

EXPERIMENTAL

3.1 Experimental Techniques for Handling Air-Sensitive Compounds

All reactions carried out in this study are air and moisture sensitive therefore Vacuum-line and Schlenk Technique is used for all experiments.

3.2 The Vacuum-Line Technique

3.2.1 The Double Manifold

If you wish to carry out reactions under dry and inert conditions, a double manifold is an extremely useful piece of apparatus (Figure 3.1) (Leonard et al, 1995).

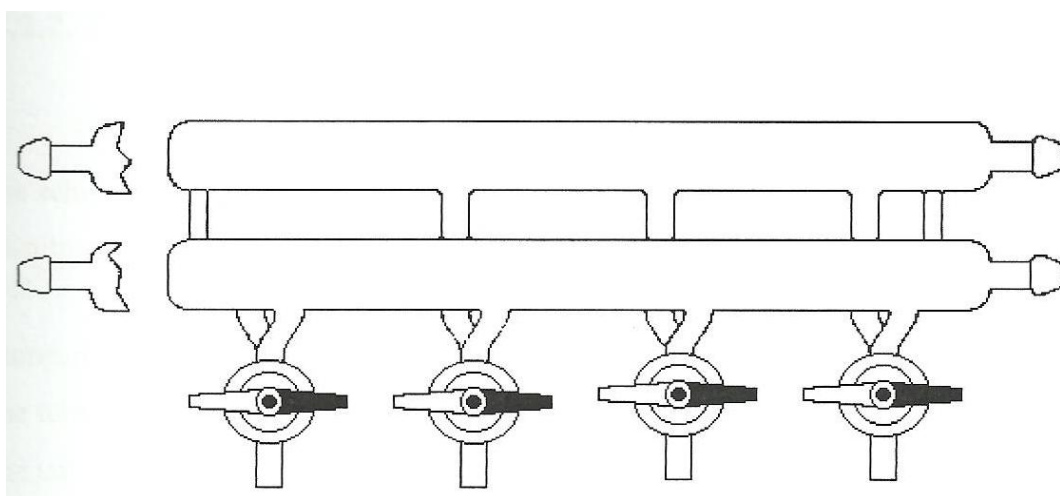


Figure 3.1 The double manifold

The manifold consists of two glass barrel. One barrel of the manifold is connected to a high vacuum pump another to dry inert gas (Figure 3.2). Thus, at the turn of the tap, equipment connected to the manifold can be alternately evacuated or filled with inert gas.

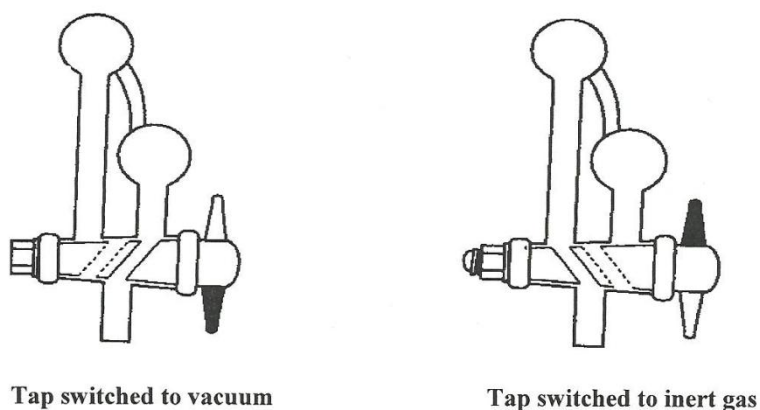


Figure 3.2 Cross section through a double oblique tap

3.2.2 The Schlenk Technique

To use a schlenk glassware provides facility during the reactions under N_2 , with the schlenk tube one can transfer a solid or liquid in an atmosphere of an inert gas, such as nitrogen or argon(Shriver, 1969; Barton, 1963).

The basic and simplest schlenk tube is shown in Figure3.3. The schlenk tube is stoppered and evacuated by pumping through D.By introducing the inert gas through the tube is filled with inert gas. The tap is turned through 90° to let gas pass through the tail part and then is turned through 90° to allow gas into the flask.



Figure 3.3 The schlenk tubes



Figure 3.4 Vacuum Line

3.2.3 Immersion-Well Photochemical Reactor



These reactors are among the most efficient for photochemical reactions since the lamps are effectively surrounded by the solution to be irradiated. The lamps are contained in double-walled immersion wells made of quartz, allowing water cooling and/or filtering of excitation radiation. Various flask designs enable reactions to be conducted under anaerobic conditions at low or constant temperature. UV irradiations were performed with a low-pressure 125 W mercury lamp through a quartz-walled immersion well reactor, which was cooled by circulating water.

Low pressure lamps emit over 90% of their radiation at 254nm.

3.3 Materials and Methods

Reactions were carried out under an oxygen-free nitrogen atmosphere using Schlenk techniques. All glassware was oven-dried at 120°C. All solvents were dried and degassed using standard techniques and stored under nitrogen until used. (Perrin et al, 1980) **TSC**, THF, petroleum ether, dichloromethane, ethanol and silica gel were purchased from Merck and $M(\text{CO})_6$ ($M = \text{Cr, Mo, W}$), $\text{ReBr}(\text{CO})_5$ and $[(\eta^5\text{-Cp})\text{Mn}(\text{CO})_3]$ from Aldrich.

Elemental analyses were performed on a Leco 932 instrument at Technical and Scientific Research Council of Turkey, TUBITAK. FT-IR spectra were recorded (KBr pellets) on a Varian 1000 FT spectrophotometer. ^1H NMR spectra were recorded in DMSO-d_6 on a 500 MHz High Performance Digital FT-NMR and chemical shifts were referenced to tetramethylsilane (TMS). LC- Mass spectra analyses were performed on Agilent 1100 MSD device at TUBITAK.

3.4 Preparation of Complexes

The complexes, *cis*- $[\text{M}(\text{CO})_4(\eta^2\text{-}N,S\text{-TSC})]$, [$M = \text{Cr}$; **1**, Mo ; **2**, W ; **3**] were prepared by the photochemical reactions of $\text{M}(\text{CO})_5\text{THF}$ ($M = \text{Cr, Mo, W}$) with **TSC** and obtained in 55-75 % yield by similar methods; the following is typical;

3.4.1 Reaction of $[\text{Cr}(\text{CO})_6]$ with Thiosemicarbazide (**1**)

A solution of $\text{Cr}(\text{CO})_6$ (0.22 g, 1 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1.30 h at room temperature. A solution of **TSC** (0.045 g, 0.50 mmol) in 20 mL of warm ethanol was added to the resulting solution of the $\text{Cr}(\text{CO})_5\text{THF}$ intermediate. The reaction mixture was stirred

at room temperature for 45 min. During stirring process, the solution changed from yellow to light brown. The solvent was then removed under vacuum afford a solid which was extracted with CH_2Cl_2 (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a light brown solid which was washed with petroleum ether and dried under vacuum, and shown to be *cis*- $[\text{Cr}(\text{CO})_4 (\eta^2\text{-}N,S\text{-TSC})]$, **1**, (60 % yield). Trace of unreacted metal carbonyl was sublimed out in vacuum on a cold finger at -20°C .

3.4.2 Reaction of $[\text{Mo}(\text{CO})_6]$ with Thiosemicarbazide (2)

A solution of $\text{Mo}(\text{CO})_6$ (0.26 g, 1 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1.30 h at room temperature. A solution of **TSC** (0.045 g, 0.50 mmol) in 20 mL of warm ethanol was added to the resulting solution of the $\text{Mo}(\text{CO})_5\text{THF}$ intermediate. The reaction mixture was stirred at room temperature for 45 min. During stirring process, the solution changed from yellow to light brown. The solvent was then removed under vacuum afford a solid which was extracted with CH_2Cl_2 (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a light brown solid which was washed with petroleum ether and dried under vacuum, and shown to be *cis*- $[\text{Mo}(\text{CO})_4 (\eta^2\text{-}N,S\text{-TSC})]$, **2**, (65 % yield). Trace of unreacted metal carbonyl was sublimed out in vacuum on a cold finger at -20°C .

3.4.3 Reaction of $[\text{W}(\text{CO})_6]$ with Thiosemicarbazide (3)

A solution of $\text{W}(\text{CO})_6$ (0.352 g, 1 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1.30 h at room temperature. A solution of **TSC** (0.045 g, 0.50 mmol) in 20 mL of warm ethanol was added to the resulting solution of the $\text{W}(\text{CO})_5\text{THF}$ intermediate. The reaction mixture was stirred at room temperature for 45 min. During stirring process, the solution changed from yellow to light brown. The solvent was then removed under

vacuum afford a solid which was extracted with CH_2Cl_2 (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a light brown solid which was washed with petroleum ether and dried under vacuum, and shown to be *cis*- $[\text{W}(\text{CO})_4(\eta^2\text{-}N,S\text{-TSC})]$, **3**, (70 % yield). Trace of unreacted metal carbonyl was sublimed out in vacuum on a cold finger at -20°C .

The complexes, *fac*- $[\text{ReBr}(\text{CO})_3(\eta^2\text{-}N,N\text{-TSC})]$, **4** and $[(\eta^5\text{-Cp})\text{Mn}(\text{CO})(\eta^2\text{-}N,N\text{-TSC})]$, **5** were prepared by the photochemical reactions of $\text{ReBr}(\text{CO})_5$ and $[(\eta^5\text{-Cp})\text{Mn}(\text{CO})_3]$ with **TSC**, respectively and obtained in 60-70 % yield by similar methods, the following is typical;

3.4.4 Reaction of $[\text{ReBr}(\text{CO})_5]$ with Thiosemicarbazide (4)

The complexes $\text{ReBr}(\text{CO})_5$ (0.203 g, 0.50 mmol) and **TSC** (0.027 g, 0.30 mmol) were dissolved in THF (80–100 mL) and the solution was irradiated for 2 h using a 125 W medium pressure mercury lamp through a quartz-walled immersion well reactor. During the irradiation, the solution changed from colourless to orange. After irradiation the solvent was evaporated under the vacuum yielding a orange solid which was extracted with CH_2Cl_2 (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a light brown solid which was washed with petroleum ether and dried under vacuum, and shown to be *fac*- $[\text{ReBr}(\text{CO})_3(\eta^2\text{-}N,N\text{-TSC})]$, **4**, (0.12 g, 73% yield). Trace of unreacted metal carbonyl was sublimed out in vacuum on a cold finger at -20°C .

3.4.5 Reaction of $[\text{MnCp}(\text{CO})_3]$ with Thiosemicarbazide (5)

The complexes $\text{MnCp}(\text{CO})_3$ (0.102 g, 0.50 mmol) and **TSC** (0.027 g, 0.30 mmol) were dissolved in THF (80–100 mL) and the solution was irradiated for 2 h using a 125 W medium pressure mercury lamp through a quartz-walled immersion well reactor. During the irradiation, the solution changed from colourless to orange. After

irradiation the solvent was evaporated under the vacuum yielding a orange solid which was extracted with CH_2Cl_2 (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a light brown solid which was washed with petroleum ether and dried under vacuum, and shown to be $(\eta^5\text{-Cp})\text{Mn}(\text{CO})(\eta^2\text{-}N,N\text{-TSC})$, 5, (0.12 g, 67% yield). Trace of unreacted metal carbonyl was sublimed out in vacuum on a cold finger at -20°C .

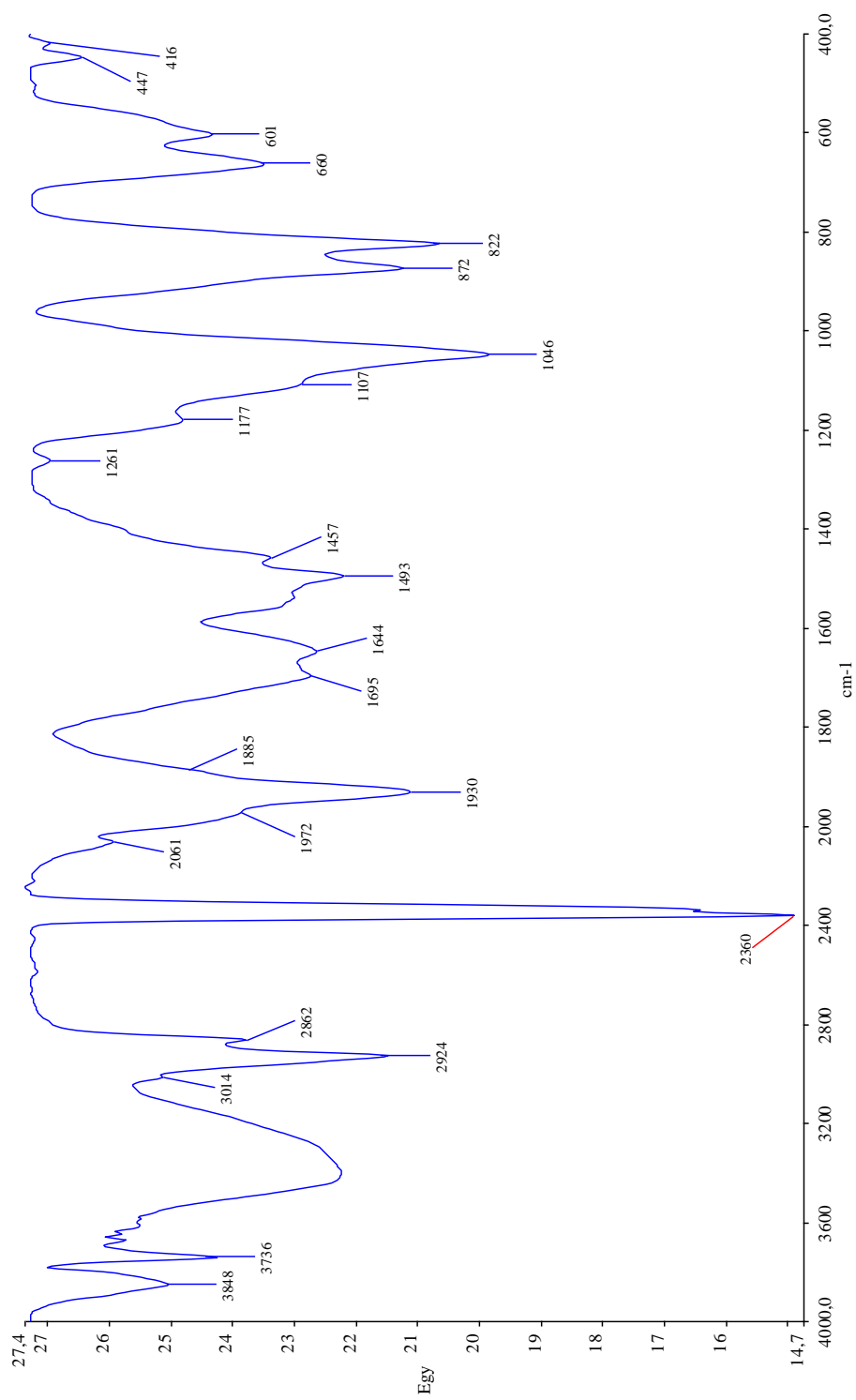
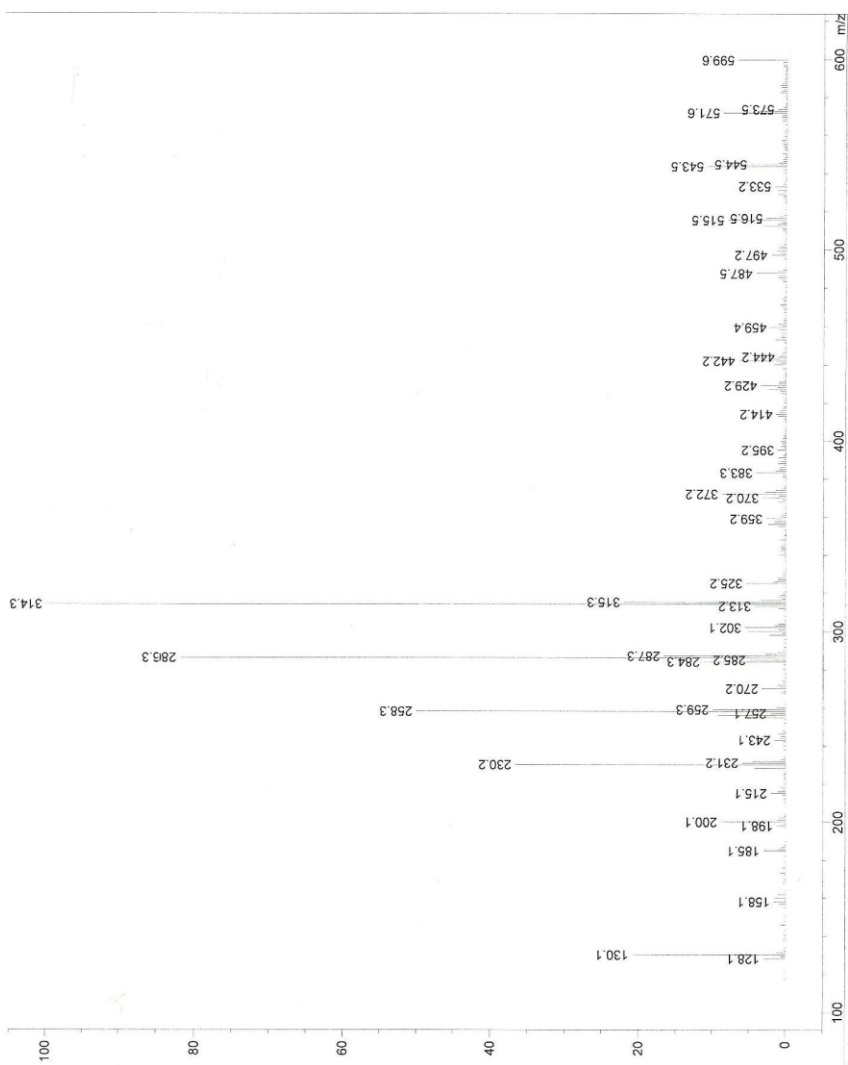


Figure 3.5 Characteristic FTIR bands (cm⁻¹) of *cis*-[Cr(CO)₄(η²-N,S-TSC)]

Figure 3.6 Mass spectroscopy data for *cis*-[Cr(CO)₄(η²-N,S-TSC)]

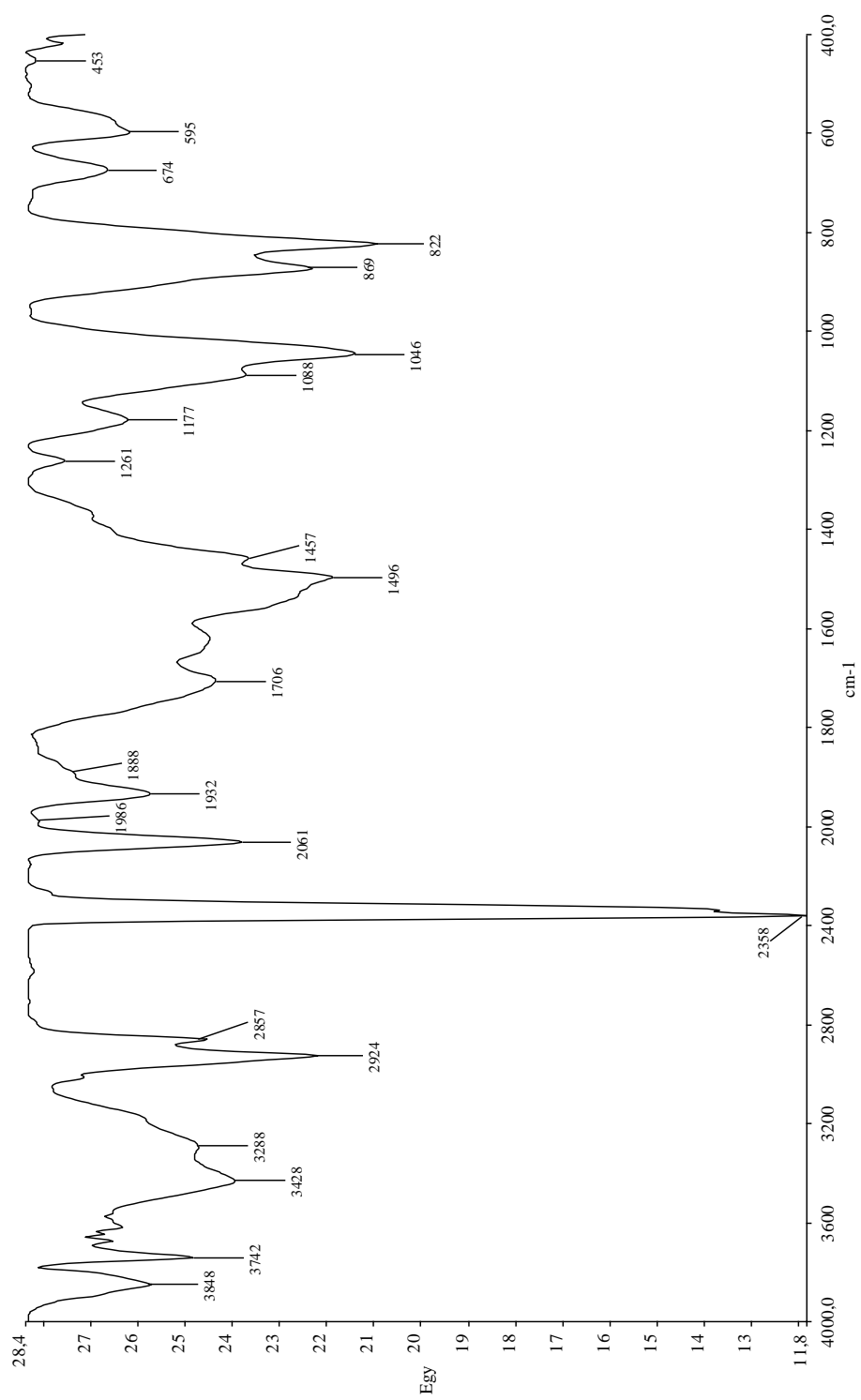


Figure 3.7 Characteristic FTIR bands (cm⁻¹) of *cis*-[Mo(CO)₄(η²-N,S-TSC)]

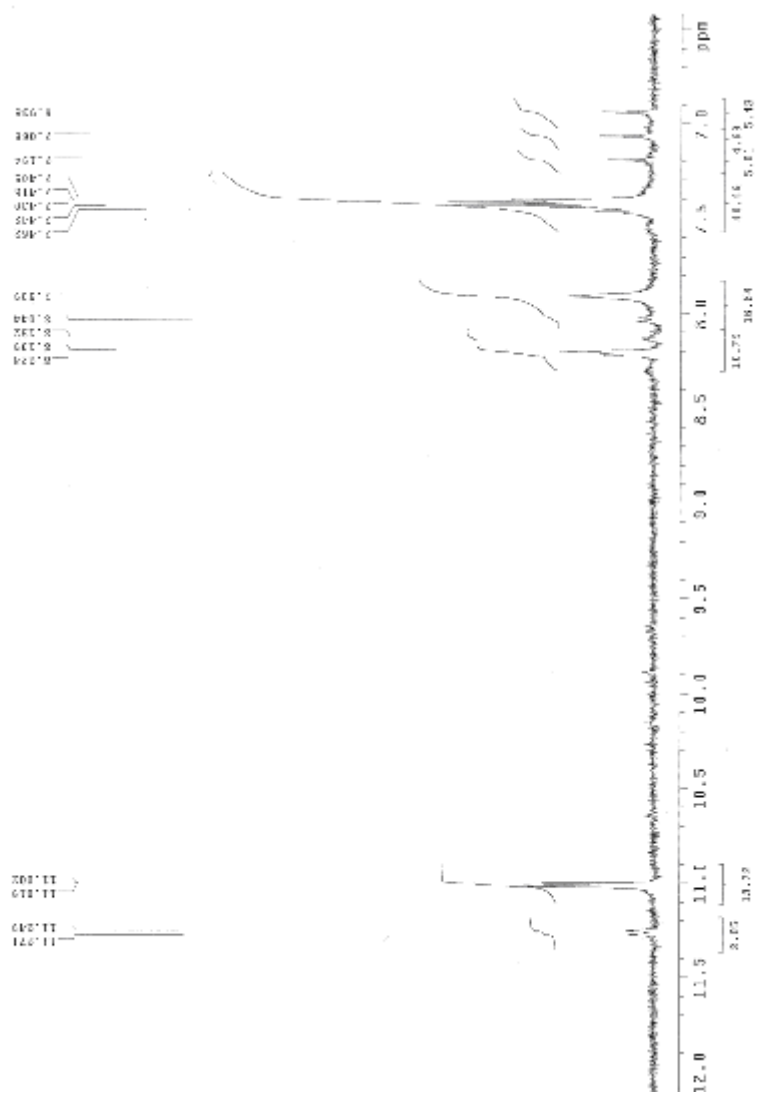
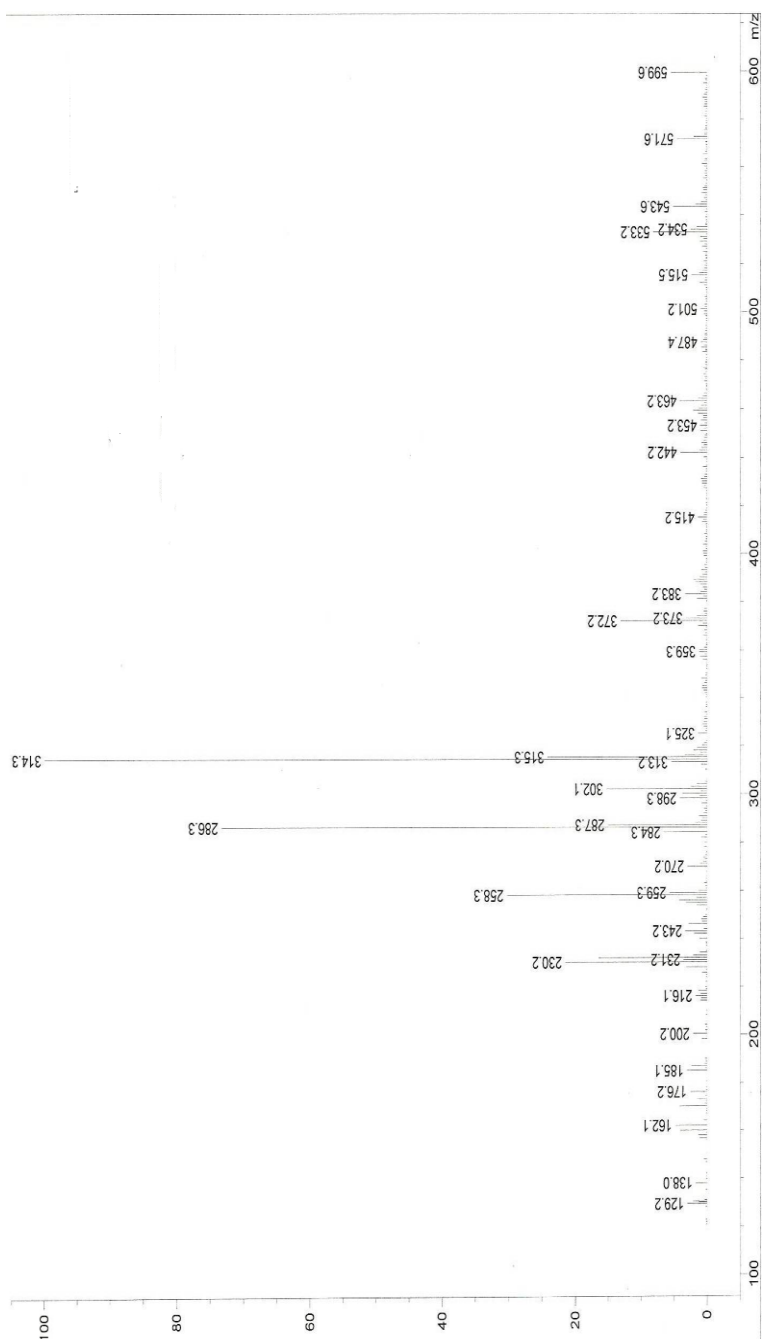


Figure 3.8 ^1H NMR data for $\text{cis-}[\text{Mo}(\text{CO})_4(\eta^2\text{-N,S-TSC})]$ in DMSO-d_6 solution

Figure 3.9 Mass spectroscopy data for *cis*-[Mo(CO)₄(η²-N,S-TSC)]

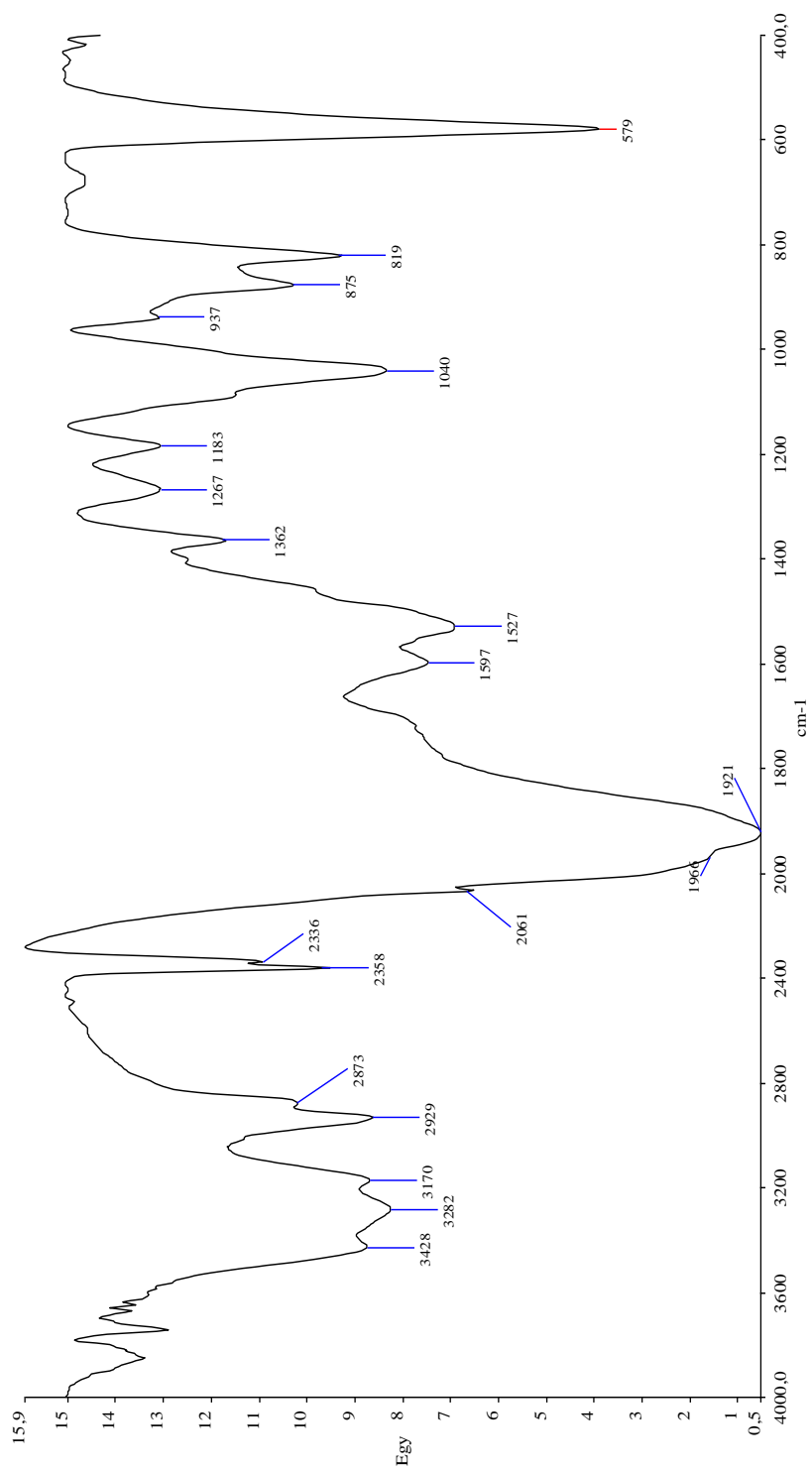


Figure 3.10 Characteristic FTIR bands (cm⁻¹) of *cis*-[W(CO)₄(η²-N,S-TSC)]

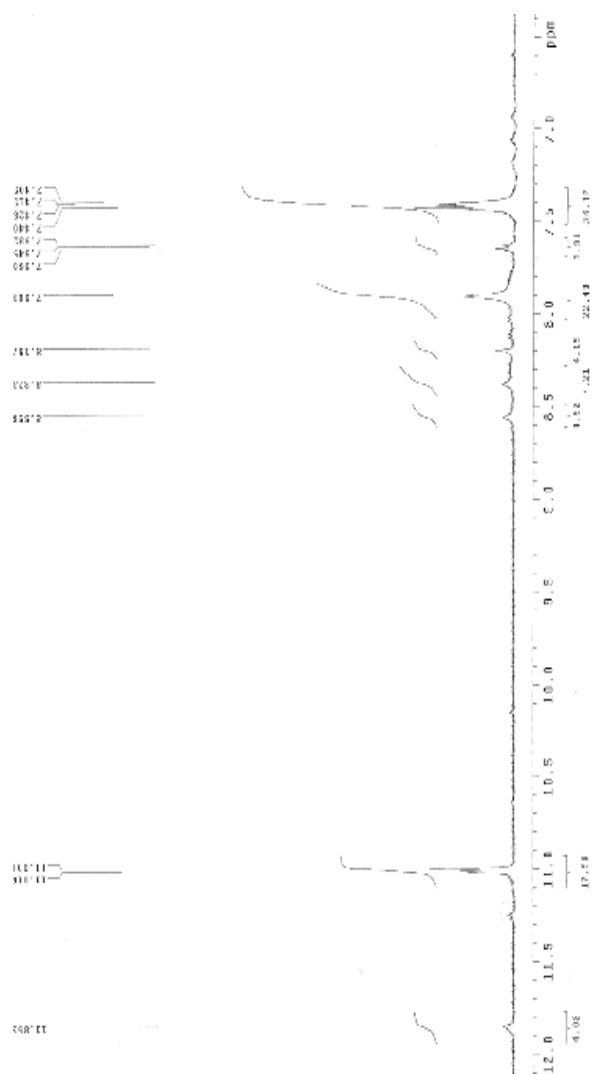
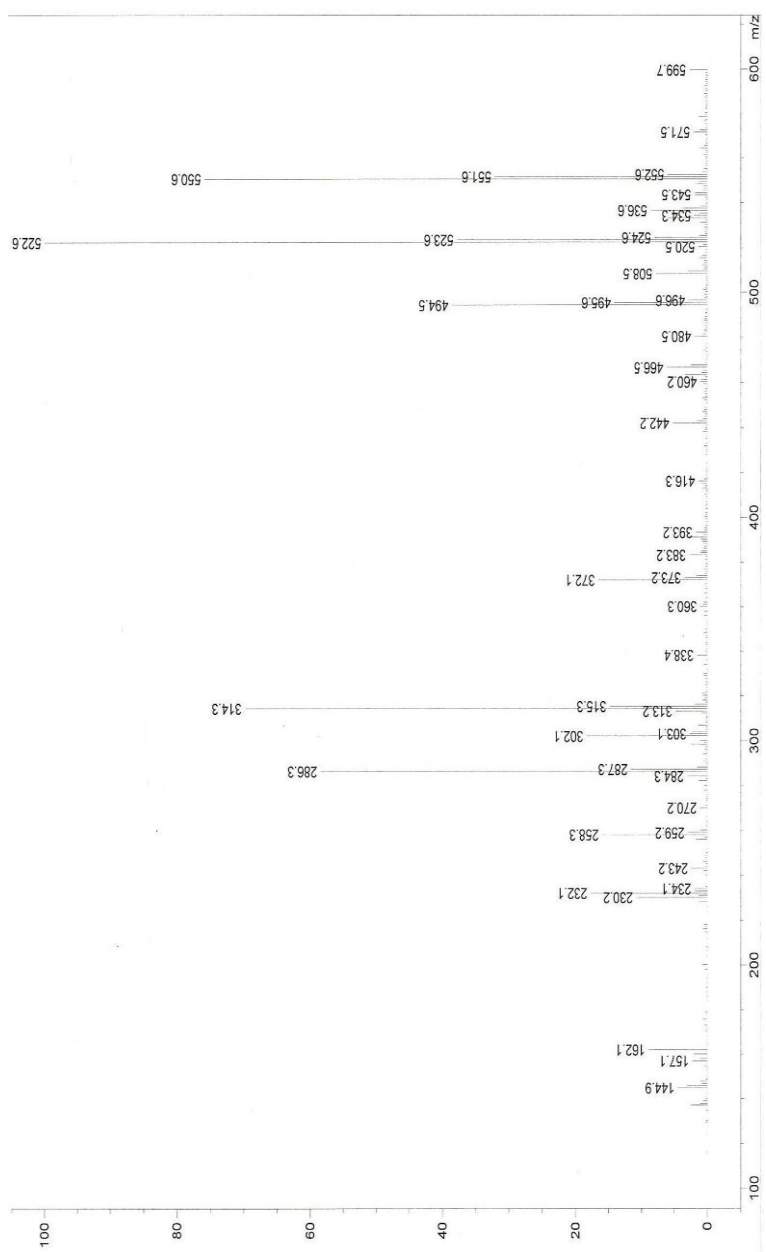


Figure 3.11 ¹H NMR data for *cis*-[W(CO)₄(η²-N,S-TSC)] in DMSO-d₆ solution

Figure 3.12 Mass spectroscopy data for *cis*-[W(CO)₄(η²-N,S-TSC)]

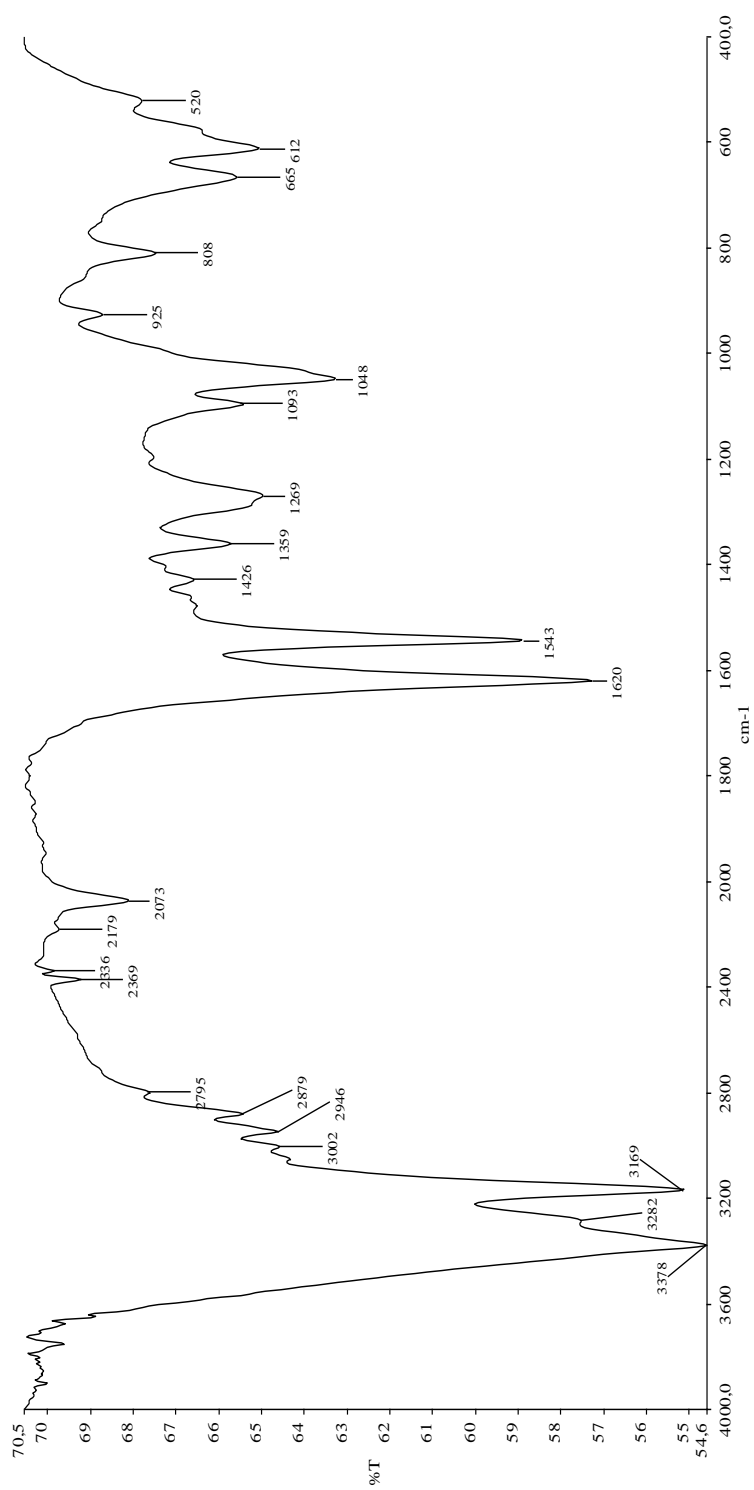
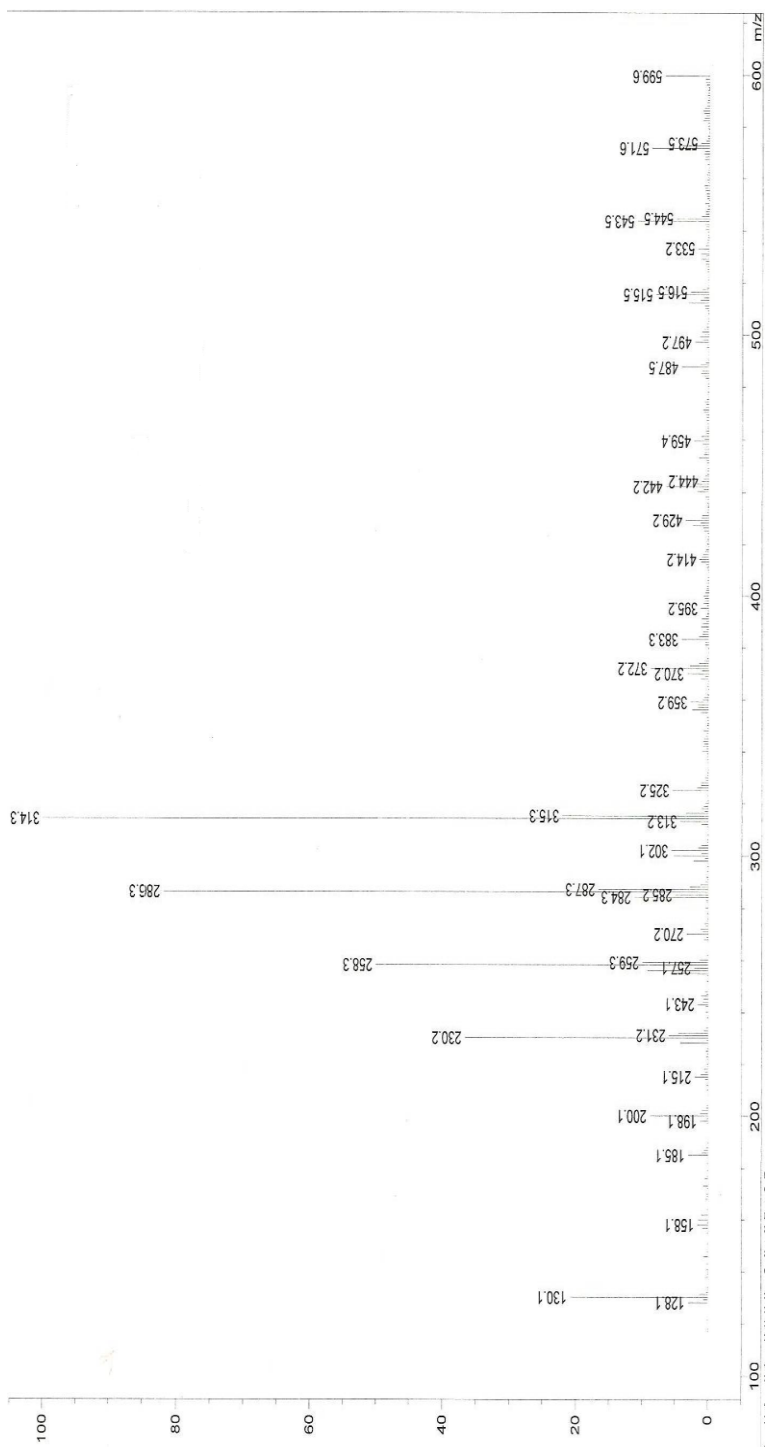


Figure 3.13 Characteristic FTIR bands (cm^{-1}) of $[(\eta^5\text{-Cp})\text{Mn}(\text{CO})(\eta^2\text{-N,N-TSC})]$

Figure 3.14 Mass spectroscopy data for $[(\eta^5\text{-Cp})\text{Mn}(\text{CO})(\eta^2\text{-N,N-TSC})]$

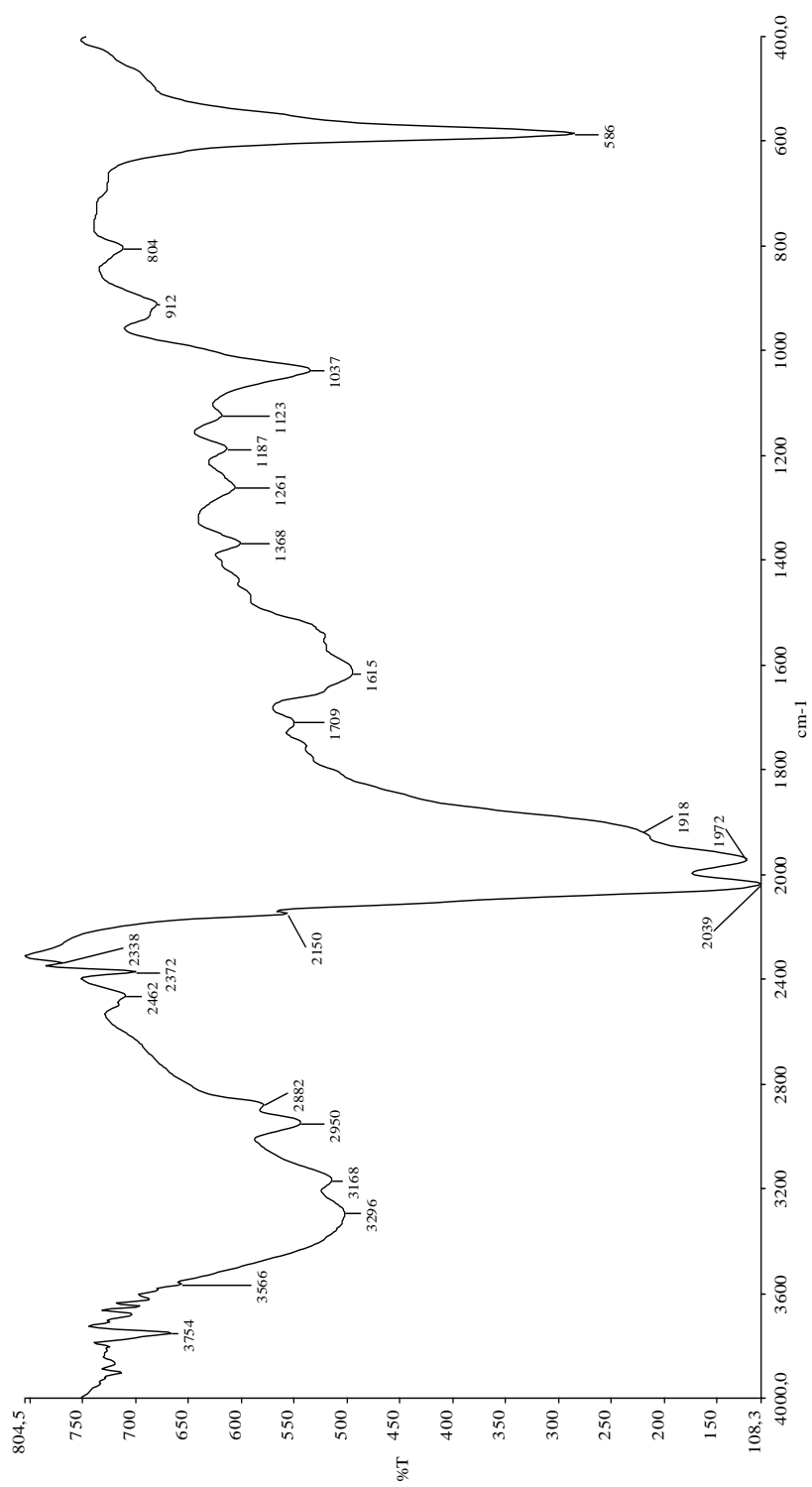


Figure 3.15 Characteristic FTIR bands (cm⁻¹) of *fac*-[ReBr(CO)₃(η²-N,N-TSC)]

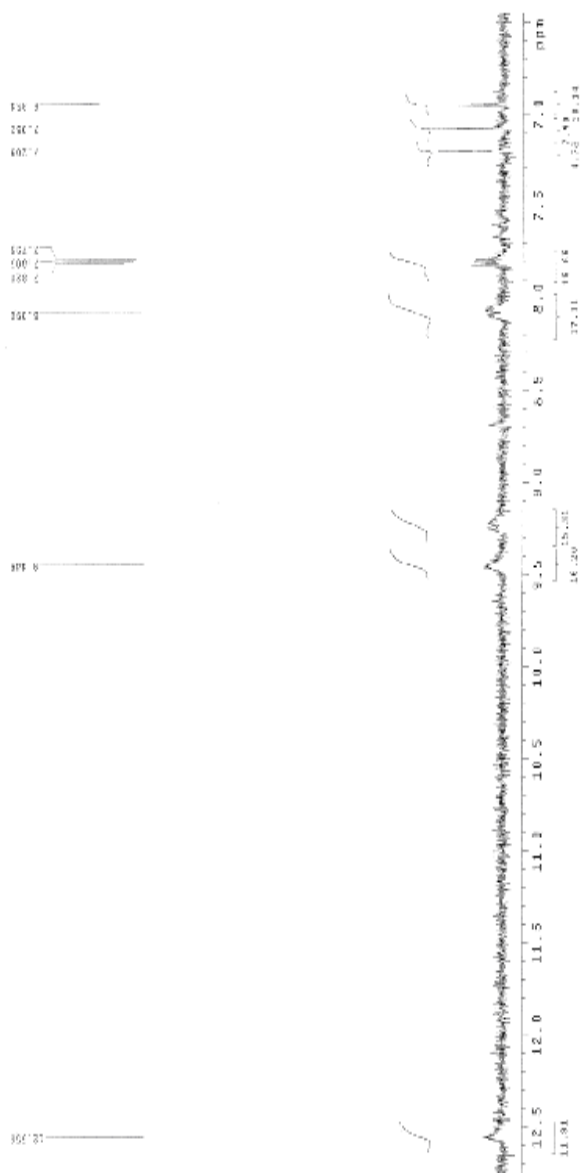


Figure 3.16 ^1H NMR data for $\text{fac-}[\text{ReBr}(\text{CO})_3(\eta^2\text{-N,N-TSC})]$ in DMSO-d_6 solution

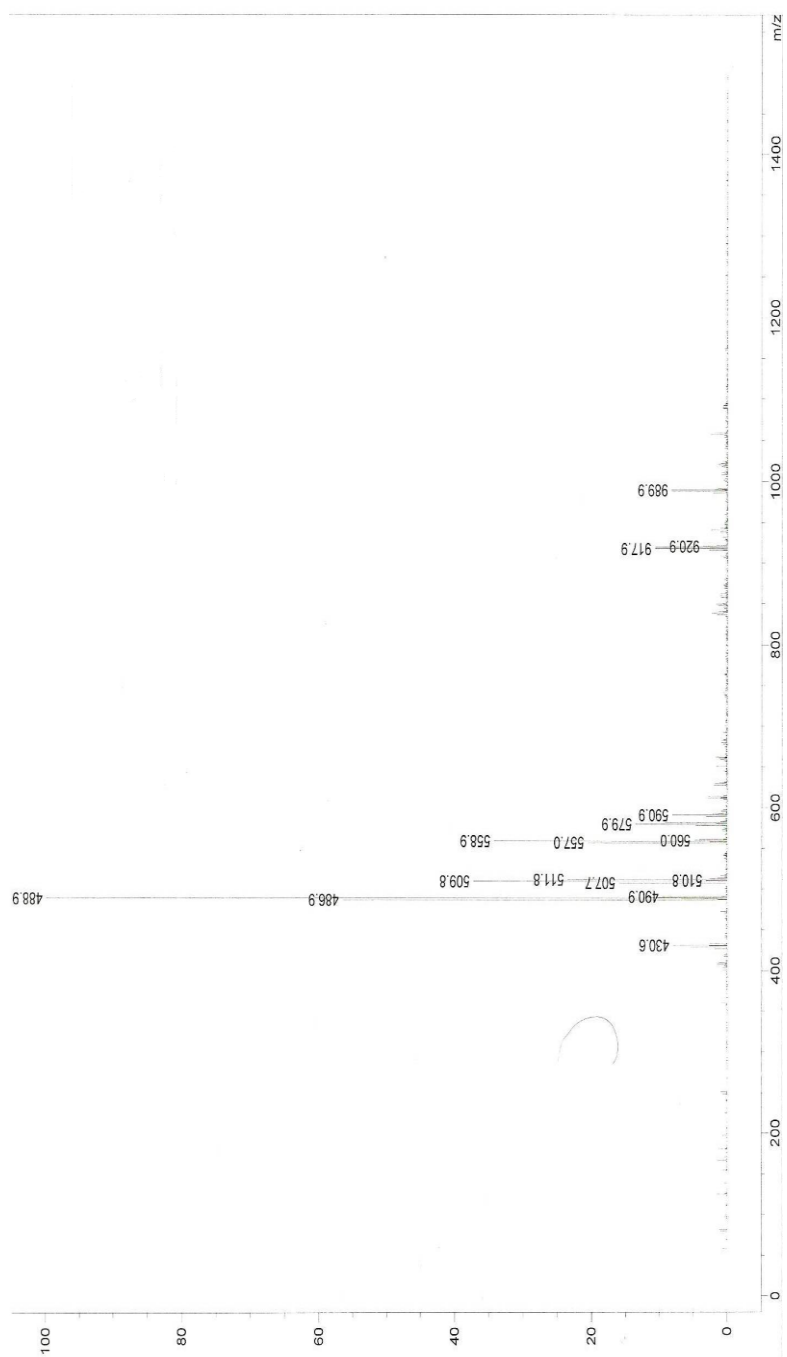


Figure 3.17 Mass spectroscopy data for $\text{fac-}[\text{ReBr}(\text{CO})_3(\eta^2\text{-N,N-TSC})]$

CHAPTER-FOUR

4.1. Results and Discussion

Photogeneration of $M(\text{CO})_5$ from $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) has been extensively studied. These 16-electron containing $M(\text{CO})_5$ fragments react avidly with any available donor to form $M(\text{CO})_5\text{L}$ species, and where L is a chelating bidentate ligand, rapid continuation to afford the $M(\text{CO})_4\text{L}$ product can occur. (Cotton, 1988) The photochemical reactions of $M(\text{CO})_5\text{THF}$ ($M = \text{Cr}, \text{Mo}, \text{W}$), $[\text{Re}(\text{CO})_5\text{Br}]$ and $[(\eta^5\text{-Cp})\text{Mn}(\text{CO})_3]$ with TSC proceed in this expected manner to yield the hitherto unknown series of complexes **1-5** as shown in Figure 1.

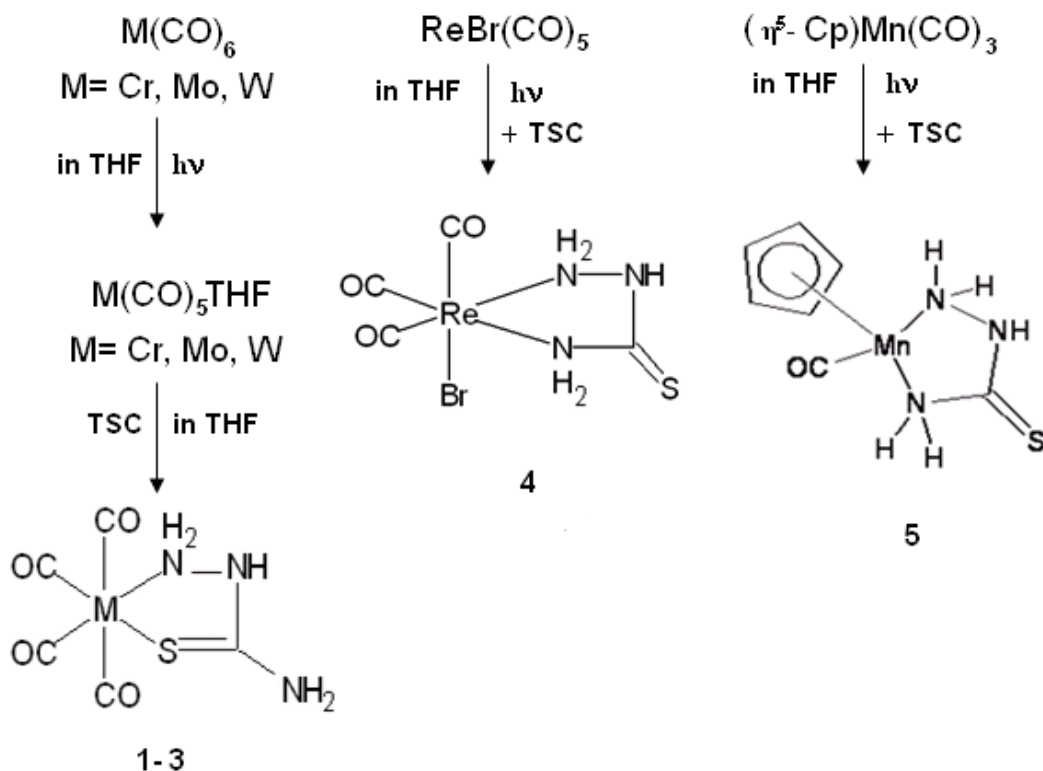


Figure 4.1 Photogeneration of *cis*- $[\text{M}(\text{CO})_4(\eta^2\text{-}N,S\text{-TSC})]$, [$M = \text{Cr}$; **1**, Mo ; **2**, W ; **3**]; *fac*- $[\text{ReBr}(\text{CO})_3(\eta^2\text{-}N,N\text{-TSC})]$, **4** and *cis*- $[(\eta^5\text{-Cp})\text{Mn}(\text{CO})(\eta^2\text{-}N,N\text{-TSC})]$, **5**.

The complexes were synthesized by reacting thiosemicarbazide with the metal carbonyls in 2:1 (M:L) ratio in THF. The analytical data and spectral analysis agree well with the proposed composition of the complexes **1-5**. The analytical data for novel complexes are summarized in Table 1. The stoichiometry of the ligands and their complexes were confirmed by their elemental analyses.

Table 4. 1 Elemental analysis results and physical properties for the complexes.

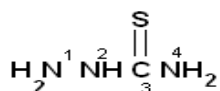
Complex	Yield (%)	Colour	Found (Calcd.) (%)		
			C	H	N
1	60	light brown	23.78 (23.53)	2.14(1.96)	16.74(16.47)
2	65	light brown	20.45 (20.07)	1.88(1.67)	14.54(14.05)
3	70	dark yellow	15.89 (15.5)	1.43(1.29)	10.99(10.85)
4	73	light brown	11.05(10.91)	1.32(1.14)	9.85(9.55)
5	67	dark brown	35.32 (35.15)	4.37(4.18)	17.83(17.57)

The assignments of the significant IR spectral bands of **TSC** and its metal carbonyl complexes are presented in Table 2. An insight about the mode of chelation for each ligand is gathered by comparing the FT-IR spectra of the **TSC** ligand with its complex and by considering the previous work on similar compounds.

Table 4.2 Characteristic FTIR bands (cm^{-1}) of **TSC** and the complexes

Complex	$\nu(\text{CO})$	$\nu(\text{N}^1\text{H})$	$\nu(\text{N}^4\text{H})$	$\nu(\text{N}^2\text{H})$	$\delta(\text{NH}_2)$	$\nu(\text{N-N})$	$\nu(\text{C=S})$
Cr(CO)₆	1999s	-	-	-	-	-	-
Mo(CO)₆	2001s	-	-	-	-	-	-
W(CO)₆	1996s	-	-	-	-	-	-
ReBr(CO)₅	1991s, 2047vs, 2158s	-	-	-	-	-	-
CpMn(CO)₃	1939, 2025	-	-	-	-	-	-
TSC^a	-	3345	3266	3165	1640	1000	799
1	2061, 1972, 1930, 1890	3434	3264	3170	1697	1048	872, 822
2	2061, 1986, 1932, 1888	3434	3266	3170	1697	1046	872, 822
3	2067, 1990, 1922, 1890	3422	3272	3170	-	1034	875, 819
4	2032, 1972, 1921	3293	3167	3170	1654	1037	800
5	2073	3379	3292	3170	1620	1049	802

a



The IR spectra of **TSC** ligand showed characteristic bands due to the functional groups N-H, C=S and N-N bonds. The IR spectra of all complexes displayed the ligand characteristic bands with appropriate shifts due to complex formation. The bands at 3365 cm^{-1} and 3266 cm^{-1} in **TSC** due to $\nu_{\text{as}}(\text{NH}_2)$ and $\nu_{\text{s}}(\text{NH}_2)$ is shifted to higher frequencies in the complexes (**1-5**). **TSC** has two bands at 1640 and 1619 cm^{-1} . The former is the deformation mode, $\delta(\text{NH}_2)$, of the amine in the hydrazine residue, and the latter is the amide (II) band of primary amine. These bands shift towards higher frequencies due to the involvement of one of the (NH_2) group in coordination. Strong evidence is the appearance of the $430\text{-}459\text{ cm}^{-1}$ band due to $\nu(\text{M-N})$. The $\nu(\text{N-N})$ of **TSC** is found at 1000 cm^{-1} . The increase in the frequency of this band in the spectra of the complexes, due to the increase in the bond strength, again confirms the coordination via terminal amino nitrogen of **TSC** in each complex. Although strong band at 800 cm^{-1} assigned to C=S stretching vibration shifts to higher frequencies and splits into two peaks in the complexes, indicating the involvement of thioketo sulfur in complex formation in (**1-3**), the $\nu(\text{C=S})$ bands

remain unaffected in the spectra of complexes (4-5). TSC ligand coordinates to the central metal ion through terminal hydrazine nitrogen and sulfur donor atoms in (1-3), whereas TSC coordinates to the central metal ion through both terminal hydrazine and thioamide nitrogens in (4-5). Thus, it is concluded that the ligand acts as a bidentate chelating agent in all of the complexes (1-5).

The number of carbonyl bands provides important clues to the environment of the centres. The IR spectra of complexes (1-3) exhibit four prominent bands between 2067cm^{-1} and 1888cm^{-1} in the CO stretching vibrational region. These four bands belong to terminal CO groups. These modes shift to lower wave numbers when compared with $\text{M}(\text{CO})_6$ (M: Cr, Mo and W). The presence of four CO bands in the IR spectra suggested that TSC bound to the metal in *cis* positions. (Sabry et al., 2003) The $\nu(\text{CO})$ pattern indicates that the local C_{2v} symmetry of $\text{M}(\text{CO})_4$ unit in (1-3). (Nakamoto, 1986)

Facial geometry around the rhenium atom is suggested by the three strong $\nu(\text{CO})$ bands in the range $2030\text{-}1900\text{cm}^{-1}$ in the spectrum of *fac*- $[\text{ReBr}(\text{CO})_3(\eta^2\text{-N,N-TSC})]$, **4** (the lowest-energy vibration is a shoulder). The FT-IR spectrum is consistent with a structure in which the rhenium atom is octahedrally co-ordinated to three carbonyl carbon atoms in *fac* arrangement, a bromine atom, and two nitrogen atoms of TSC ligand, with which the metal forms a five-membered chelate ring. The FT-IR spectra of the complexes contain three strong carbonyl bands allowing an unequivocal assignment of the compound as the *fac*-isomer of C_s symmetry. (Mazzi et al., 1977; Reiman and Singleton, 1973)

As expected, only one band arising from $\nu(\text{CO})$ vibration is seen for the complex, $[(\eta^5\text{-Cp})\text{Mn}(\text{CO})(\eta^2\text{-N,N-TSC})]$, **5** which presumably have the local C_{4v} (A_1) symmetry of the $\text{M}(\text{CO})$ unit. (Mazzi et al., 1977; Reiman and Singleton, 1973)

The $\nu(\text{CO})$ mode of the complex move to lower wave numbers compared with the starting $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ molecule, as weakening of the CO bond on complexation would result in a shift to lower wave number. (Burzlaff et al., 2001)

^1H NMR data in DMSO-d_6 solutions of the complexes are collected in Table 3.

Table 4.3 ^1H NMR data for TSC and metal complexes in DMSO- d_6 solution^a

Complex	N^2H (1H,br,s)	N^4H_2 (2H,br,s)	N^1H_2 (2H,br,m)
TSC	11.01	7.90	7.43-7.40
2	11.02	7.91	7.70-7.50
3	11.02	7.91	7.70-7.45
4	12.55	9.45	7.82-7.79

^a δ in ppm

The ^1H NMR spectra of the chromium and manganese complexes of **TSC** could not be obtained since the former was not sufficiently soluble in DMSO- d_6 and the latter was paramagnetic. **TSC** ligand shows three prominent signals belong to NH, (S=C-NH₂) and NH₂ (hydrazine residue) functional group protons at 11.01; 7.90 and 7.43 ppm respectively. In ^1H NMR spectra of the complexes **2**, **3** and **4**, primer

amine NH₂ (hydrazine residue) proton signals have been observed in lower field than those of free ligand. Except that the chemical shift of NH₂ (hydrazine residue) proton value, all of the other chemical shifts of the coordinated TSC ligand of the compounds **2** and **3** have almost similar values to those of the free ligand. However, (S=C-NH₂) and NH₂ (hydrazine residue) proton signals alteration have been found for rhenium complex, **4**. This situation supports the coordination of ligand to the metal center as a bidentate ligand via its nitrogen and sulfur donor atoms in **2** and **3**, and via both nitrogen donor atoms in **4**.

Data for mass spectra of **1-5** are given in Table 4 and show fragmentation *via* successive loss of CO groups and TSC ligand.

Table 4.4 Mass spectroscopy data for (1-5)

Complex	M.W.	Relative intensities of the ions m/z ^a
1	255	255(5.0), [CrC ₅ H ₅ N ₃ O ₄ S]; 230(36), [CrC ₄ H ₅ N ₃ O ₃ S-(CO)]; 199 (8.8), [CrC ₃ H ₅ N ₃ O ₂ S-(CO)]; 183 (3), [CrC ₃ H ₃ N ₂ O ₂ S – (NH ₂)] 155(1.6), [CrC ₂ H ₃ N ₂ OS-(CO)];127(2.1) , [CrCH ₃ N ₂ S-(CO)]
2	299	299 (15) [MoC ₅ H ₅ N ₃ O ₄ S]; 283 (73), [MoC ₅ H ₃ N ₂ O ₄ S -(NH ₂)]; 258 (30), [MoC ₄ H ₃ N ₂ O ₃ S -(CO)];230(22) [MoC ₃ H ₃ N ₂ O ₂ S-(CO)] 216 (1.8), [MoC ₃ H ₂ NO ₂ S-(NH)]; 199 (2.2), [MoC ₃ O ₂ S -(NH ₂)];168(4.2), [MoC ₂ OS-(CO)]; 140(1.7)[MoCS]
3	387	387 (1.0), [WC ₅ H ₅ N ₃ O ₄ S]; 371(17), [WC ₅ H ₃ N ₂ O ₄ S]-(NH ₂); 315(15)[WC ₃ H ₃ N ₂ O ₂ S-(CO)-(CO)] 287 (12),[WC ₂ H ₃ N ₂ OS-(CO)]; 259 (3.0), [WCH ₃ N ₂ S-(CO)]
4	440	440 (3.0), [ReC ₄ H ₅ N ₃ O ₃ SBr]; 412 (1.9),[ReC ₃ H ₅ N ₃ O ₂ SBr-(CO)] 384(2), [ReC ₂ H ₅ N ₃ OSBr] -(CO)]; 356 (1.1), [ReCH ₅ N ₃ SBr- (CO)]
5	239	239 (1.1), [MnC ₇ H ₁₀ N ₃ OS]; 211(1.4) [MnC ₆ H ₁₀ N ₃ S -(CO)]; 195(4.5) [MnC ₇ H ₈ N ₂ OS-(NH ₂)]

^aRelative intensities are given in parentheses and assignments in square brackets

CHAPTER FIVE

CONCLUSION

In summary, the spectral data suggest the involvement of sulfur and terminal amino nitrogen of **TSC** in coordination to the central metal ion for **VI B** metal carbonyl complexes *cis*-[M(CO)₄(η²-*N,S*-TSC)], [M= Cr; **1**, Mo; **2**, W; **3**] whereas both of the terminal amine and thioamide nitrogens of **TSC** in coordination to the central metal ion for **VII B** metal carbonyl complexes, *fac*-[ReBr(CO)₃(η²-*N,N*-TSC)], **4** and *cis*-[(η⁵-Cp)Mn(CO)(η²-*N,N*-TSC)], **5**. On the basis of spectral studies, an octahedral geometry has been assigned for all of the complexes. IR spectra of the complexes and observation of carbonyl bands in the CO stretching region are consistent with the formulation of the complexes **1–5**. ¹H NMR data exhibited expected integrals and shifts. Mass spectra fragmentation patterns are in line with the proposed structures of **1–5**.

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