Synthesis and Characterization of Organometallic Compounds:
I. Cyano- and Isocyanoarene Iron(II) and Molybdenum(0) Complexes;
II. 1,3,5-Trimethylcalix[4]arene and Its Chromium and Molybdenum Derivatives

by

Xiaochun Wang

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

in the

Chemistry

Allen Hunter July 29/94

Advisor, Dr. Allen D. Hunter Date

Aug 8, 1994

Dean of the Graduate School Date

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THESIS

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ABSTRACT

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Master of Science
Youngstown State University, 1994

The synthesis and spectroscopic characterization of a series of mono- and bimetallic complexes containing $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ and $Mo(Ph_2PCH_2CH_2PPh_2)_2$ units and bridging or terminal isocyano and cyano arene ligands, a zerovalent organometallic polymer of molybdenum, and 1,3,5-trimethylcalix[4]arene and its chromium and molybdenum derivatives are reported. The mono-iron and di-iron complexes may be prepared via reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]Cl$ or $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with $p\text{-}CNC_6H_4X$ or $p\text{-}NCC_6H_4X$ (X= CN, NC, Cl) in the presence of silver(I) salts. The electron-rich molybdenum complexes are synthesized via replacement of dinitrogen in $Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$ by isocyanides (e.g., $p\text{-}CNC_6H_4NH_2$, $p\text{-}CNC_6H_4Cl$). The organometallic polymer, $[Mo(\mu\text{-}CNC_6H_4NC)(Ph_2PCH_2CH_2PPh_2)_2]_n$, is obtained by the reaction of $Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$ with p-diisocyanobenzene. The ^1H and ^{13}C NMR and IR spectroscopic data for each complex establishes its structure and suggests that the isocyano and cyano groups bind to the metal centers in the linear terminal coordination mode and that there forms an extended π- conjugation between the bridges and metal centers. The X-ray crystal structures of the complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(p\text{-}CNC_6H_4Cl)]PF_6$ ($C_{14}ClF_6FeH_9NO_2P$; a =7.0833(5) Å, b = 14.903(1) Å, c = 16.591(2) Å, β=98.674(7)°; V =

1731.4(3) Å^3; monoclinic; $P2_1/c$; Z = 4) and *trans*-[Mo(*p*-CNC$_6$H$_4$Cl)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (C$_{66}$Cl$_2$H$_{56}$MoP$_4$; *a* =29.182(2) Å, *b* = 12.324(1) Å, *c* = 19.205(2) Å, β=94.77(1)°; V = 6883(1) Å^3; monoclinic; C2/c; Z = 4) have been determined and comfirm that they have the expected structures including essentially linear isocyanide ligands. 1,3,5-trimethylcalix[4]arene was prepared by a tintetrachloride-catalyzed reaction of 2-chloromethyl-1,3,5-trimethylbenzene. The organometallic macromolecules 1,3,5-trimethylcalix[4]arenechromiumtricarbonyl and 1,3,5-trimethylcalix[4]arenemolybdenum-tricarbonyl are synthesized by the reaction of 1,3,5-trimethylcalix[4]arene with the appropriate metal hexacarbonyl in refluxing dioxane. They have been partially characterized by spectroscopic techniques and are shown to contain Cr- or Mo-arene π bonds.

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LIST OF ABBREVIATIONS

ABBREVIATION	**MINING**
DMSO	Dimethylsulfoxide, $(CH_3)_2SO$
DPPE	1,2-Bis(diphenylphosphion)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$
Fp	Cyclopentadienylirondicarbonyl, $(\eta^5\text{-}C_5H_5)Fe(CO_2)^+$
HOMO	Highest Occupied Molecular Orbital
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
Na-Hg	Sodium amalgam
NMR	Nuclear Magnetic Resonance
ppm	parts per million
THF	Tetrahydrofuran, $(CH_2)_4O$
TMS	Tetramethylsilane, $Si(CH_3)_4$
v	frequency.

PART ONE

Cyano- and Isocyanoarene Iron(II) and Molybdenum(0) Complexes

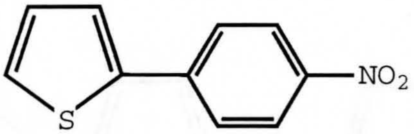
CHAPTER I

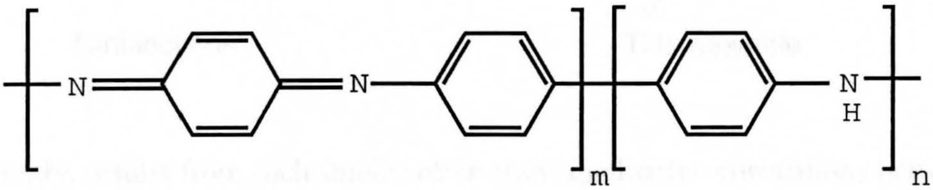
INTRODUCTION

Elecrically conducting polymers have been the subject of sporadic interest to chemists and physicists over the past 30 years.[1] The field was relatively dormant until the early 1970's when two significant events occured. First, a chemistry group led by Hideki Shirakawa reported the synthesis of continuous, free-standing films of polyacetylene. Secondly, this discovery came to the attention of an interdisciplinary team of chemists and physicists led by Alan MacDiarmid and Alan Heeger at the University of Pennsylvania. This term was already studying the inorganic polymer ploy(sulphurnitride), $(SN)_n$, and on turning their attention to Shirakawa's polyacetylene, they rapidly proved that conductivity in the metallic regime was possible for this organic polymer. These results stimulated interest in laboratories around the world. More recently this interest has extended to the study of polymeric materials which incorporate transition metal atoms in the polymer backbone.

1. Organic model compounds and polymers with delocalized backbones: Foreruners to organometallic polymers.

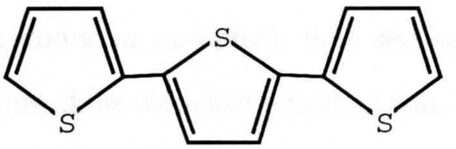
Organic polymers and oligomers whose backbones contain delocalized π-systems have been of increasing interest during the last decade. Examples of such delocalized π-systems include polyacetylenes, poly(*p*-phenylene) and poly(*p*-phenyleneamineimine), as illustrated below;



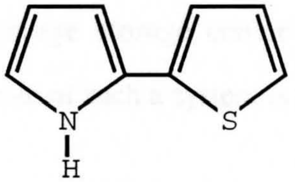


The π-electron delocalization in such species imparts several useful properties such as electrical conductivity and non-linear optical behaviour on these materials.[1] Such delocalized repeating units are increasingly being used as bridging ligands in organometallic complexes, the results of which are novel oligomers and polymers. These materials, whose structures can be thought of as extensions of those of the organic compounds, have been receiving considerable attention as a result of their potentially advantagous properties. Indeed, it has been noted[2] that, with the exception of a few instances, introduction of a metal group into an organic polymer in any of the forms mentioned in the next section results in an enhanced conductivity. This may arise from an additional conduction route which the metal provides by virtue of its own electronic properties.

A thorough understanding of the electronic properties of well-defined and more easily processible lower molecular weight species (oligomers) of these organic materials often provides the basis for determining such structural properties as conjugation length of the more complex polymeric species. Most importantly, such studies provide a key to the developement of a microscopic understanding of the electron transport properties of these materials. Recently reported examples of these studies include a study of the lowest energy singlet excited states of terthiophene and thienylpyrrole (see structures below) for a better understanding of the optical and vibrational spectra of polythiophene and polythienylpyrrole respectively,[1a] and the use of the redox properties (studied via cyclic voltammetry) of oligomeric *p*-phenylenes (i.e., H-(-1,4-C_6H_4-)$_n$H) to predict the charge storage mechanism of conducting poly(*p*-phenylene).[1c]



Terthiophene

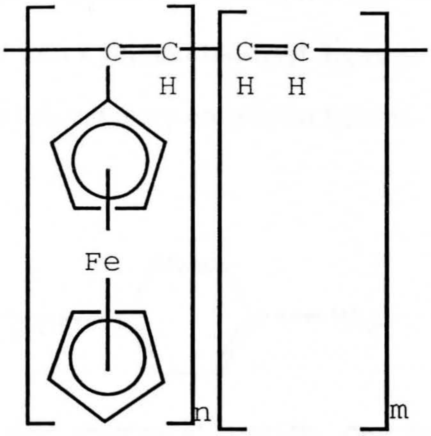


Thienylpyrrole

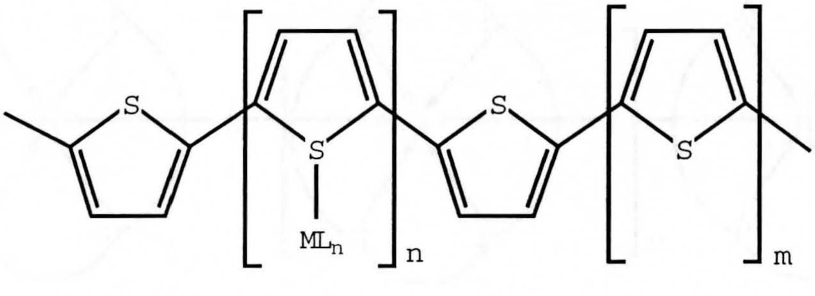
Gratifyingly, results from such studies often show qualitative correlations between the electronic behaviour of these model compounds and their higher molecular weight analogues.

2. Inorganic and organometallic polymers and model compounds containing delocalized π–systems.

A novel and growing area of organotransition metal chemistry is the study of organometallic polymers. Earlier materials going by this nomenclature were generally comprised of organic polymer backbones, with the organometallic fragments incorporated as appendages as illustrated below.

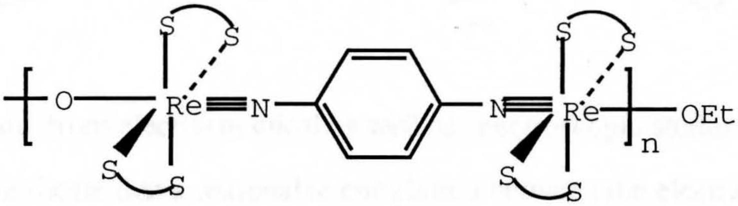


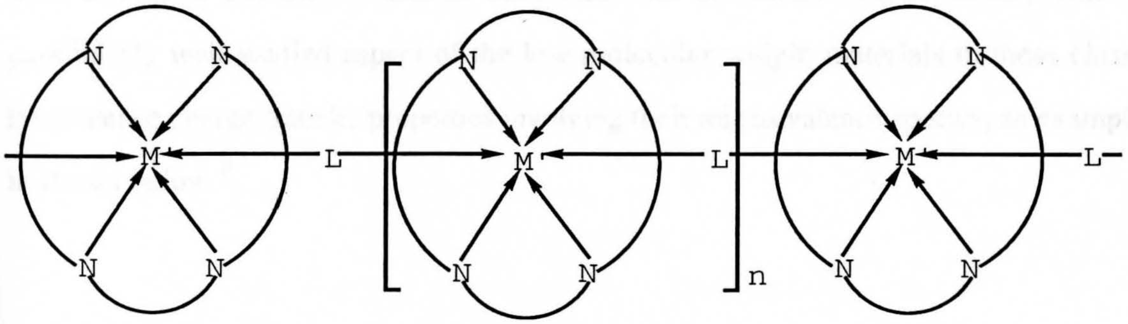
Interest in materials of this nature originally stemmed from the desire to use such species as catalysts.[3,4] More recently, the magnetic and electrical properties of such species have become of interest.[5] In these species, the organometallic fragment can be regarded as a dopant (acting as an electron donor or acceptor), thus serving as a charge storage center during charging and discharging of the particular repeating unit. An example of such a system is shown below.[5]



Polymers and model compounds in which the metal center is contained in the main polymer chain backbone are relatively few. Most materials in this category contain bifunctional bridging ligands such as the N-heterocyclics and *p*-phenylenediimido.[6] Generally in such species, the metal centers are bonded to the ligands through heteroatoms (eg. N, O, S, etc.) hence such species can be regarded as coordination compounds. More recently, several examples of lower molecular weight species in which other ligands bonded to the metal center that are traditional organometallic ligands such as carbonyl and cyclopentadienyl ligands have been reported.[6c-f] Illustrative examples of compounds in this category are shown below.

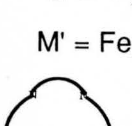
$ML_n = Ru(NH_3)_5^{2+}, Fe(CN)_5^{2-}, W(CO)_5, Cp(CO)_2Mn$, etc.





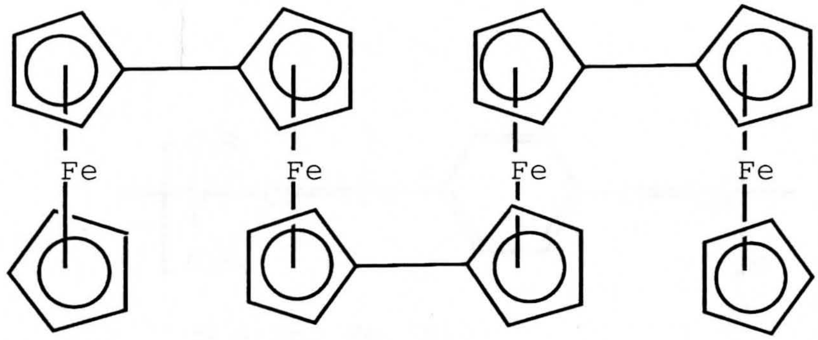
L = Pyrazine, bipyridine, pyrimidine etc.

M' = Fe, Ru, Os.

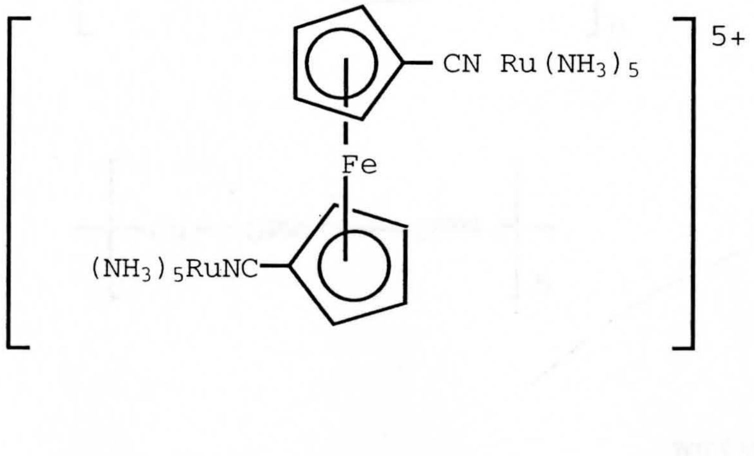


= Phthalocyanine

Another class of coordination polymers and model compounds in which the metal forms part of the main chain backbone are the metallocenyl complexes, an example of which is shown below.[7]

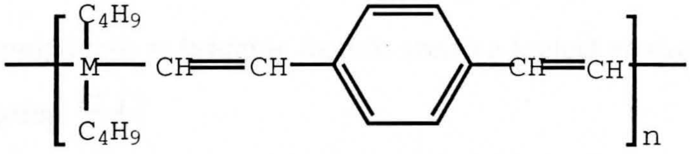


Results from electrochemical as well as spectroscopic studies on these last two classes of compounds indicate that a reasonable correlation between the electron transfer behaviours of the model compounds and the higher molecular weight species exists. Both classes of materials have been shown to exhibit reasonable bulk electrical conductivities, especially when doped. A particularly well studied aspect of the low molecular weight materials in these classes is their intervalence charge transfer properties involving their mixed valence species, an example of which is shown below.[8]



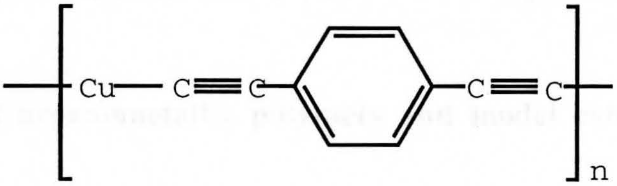
Such species can be considered as prototype fragments of semiconductors, with two equivalent electron localization sites at the ends, and a third central localization site which could either be a ligand or another metal center.

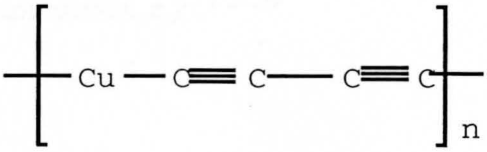
Polymers and oligomers in which the metals in the polymer backbone are linked to the chain carbon atoms through metal-carbon σ-bonds are few, even for the main group-metals.[2]



M = Sn, Ge, Si.

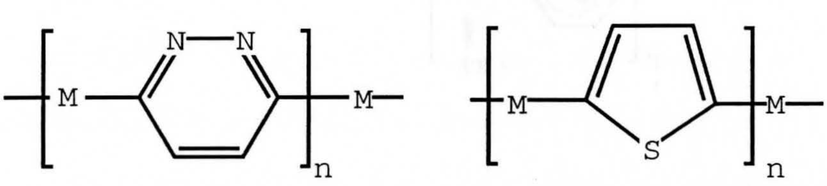
The introduction of such elements into the chain does not destroy the conjugative path because these elements contain d-orbitals which can act as π-acceptors, thus leading to pπ-dπ overlap. Unfortunately, these materials are very poor conductors.[2] The first examples of transition-metal organometallic polymers containing such linkages was reported by Korshak and coworkers in 1960.[2], These polymers contain acetylide and phenylacetylide bridging ligands.





Conductivity as well as ESR studies on these polymers show[2] that they are semiconducting and photoconducting, and that there is a high degree of delocalization in the conjugated chain. Furthermore, the metal group has also been shown to act as an electron donor.

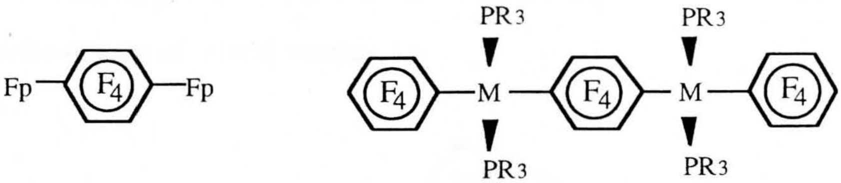
Several organic polymers and oligomers containing heteroaromatic rings either as part of the polymer backbone, (e.g. polypyrrole, polythiophene) or as substituents are known to exhibit useful properties as earlier mentioned. As an extension of the study of model organometallic complexes in which the metal center is directly attached to the ring carbon, the use of heteroaromatic compounds as bridging ligands seems a logical progression from the earlier work from Hunter's group.[12,13]



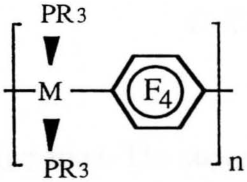
The formal introduction of a heteroatom to a benzene ring is known to have substantial effects on the spectro-electronic properties of the arene ring.[11] Such heteroaromatic compounds were studied as bridging ligands in the materials of interest.[12,13] Moreover, such complexes might also be useful in bioinorganic chemistry since such transition metal substituted complexes might mimic the organic molecules often encountered in living systems.

3. Arene bridged organometallic polymers and model compounds

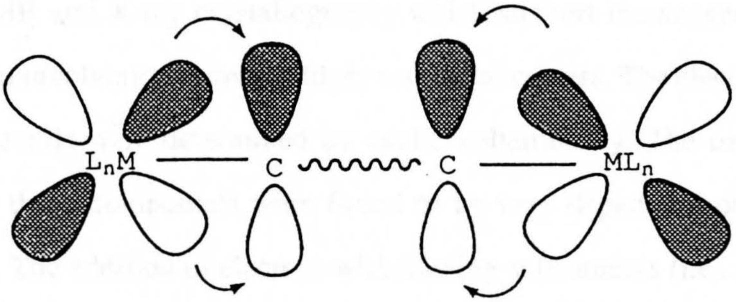
As the contribution to this area, Allen Hunter and coworkers have studied a series of arene-bridged organometallic complexes, e.g.,[14-19]



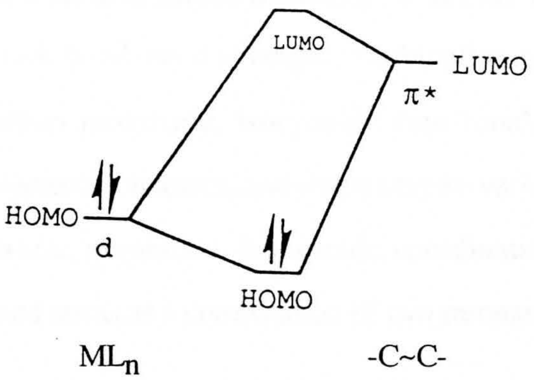
(where Fp = (η^5-C_5H_5)Fe(CO)$_2$ and M=Ni and Pd) which served as models for the analogous organometallic polymers which have been prepared, e.g.[11]



The electronic conjugation between the adjacent metal centers in such arene bridged materials occurs primarily by interactions of π symmetry between the highest occupied molecular orbitals, HOMO, on the metal centers with the empty π* orbitals on the bridging ligands, i.e.



Such linkages have the potentially useful feature that the degree of overlap of the frontier orbitals of the fragments (and hence intermetallic conjugation) is tunable by variation of the structures and energies of the ML_n HOMO and -C~C- LUMO fragments. Thus, increasing the electron richness on the metal (e.g., by replacing ligands by stronger σ-donor ligands or using lower oxidation state metals), which will raise the energy of the ML_n HOMO, and/or decreasing the electron richness of the aromatic bridging group, which will lower the energy of the -C~C- LUMO, would be expected to increase the degree of orbital overlap, i.e.



and thus the degree of intermetallic conjugation. The successful confirmation and quantification of such an effect of electron richness upon intermetallic conjugation would allow the rational design of new organometallic polymers of which the conjugation down their backbones was high and tunable. This, in turn, has the potential to give such materials useful properties such as tunable electrical conductivity.

The structures of arene bridged organometallic model compounds and oligomers have been confirmed by NMR and X-ray crystallography which support the suggestion of an extended π conjugated system involving the arene bridges and metal centers. The electrochemical behavior of the model compounds were determined by cyclic voltammetry. The oxidation potentials and reversibilities of these compounds were found to be very dependent on the structures of the aromatic ligands. The addition of electron-withdrawing substituents (i.e., fluorine) increase both the oxidation potentials and chemical reversibilities for the aryl complexes.[13]

4. Isocyanoarene bridged organometallic polymers and model compounds

We have resently become interested in a different class of organometallic material bridged by bifunctional organic ligands (e.g. dicyanobenzene and diisocyanobenzene) which are formally neutral in charge. The choice of these ligands for conjugated polymers was based on their low-formal oxidation states, on their strong metal-ligand bonds, and on the similarity between their coordination properties and those of carbon monoxide, which are well understood. The isocyanide ligands chosen for the task bond via a synergic combination of σ-donation and π*–acceptor interactions. Unlike carbon monoxide, isocyanide functionalities are part of large organic molecules, whose size, electron richnesses, and shape may be varied in order to introduce variation in thier steric and electronic properties. Isocyanide coordination to a transition metal can be represented in valence bond terms as a combination of two resonance forms

$$\overset{+}{\mathrm{M}}\text{-C}{\equiv}\overset{-}{\mathrm{N}}\text{-R} \quad \longleftrightarrow \quad \mathrm{M{=}C{=}}\ddot{\mathrm{N}}\text{-R}$$

I II

terminal ligand

An increased contribution from resonance form II results in an increased M-C bond order, decreased C-N bond order, and increased bending of the C-N-R bond. This would be expected to occur for more electron rich metal centers and for more electron withdrawing R groups.

Since CNR and CO are isoelectronic (i.e.,:C≡O: is formally isoelectronic with :C≡N-R) their molecular orbital descriptions are very similar. The M-CNR bond is composed of M<—C σ-donation from a σ-symmetry molecular orbital on CNR (i.e., the lonepair on C) and of M—>C back donation from filled d orbitals on the metal into the empty π* molecular orbitals on CNR. Because the electronegativity of an NR group is less than that of an oxygen atom, the donor and acceptor molecular orbitals of a CNR ligand are higher in energy than those of CO. This energy difference makes isocyanide ligands much better σ-donors and slightly poorer π–acceptors than CO. The strong σ-donation by isocyanides is reflected in their ability to form stable complexes with metals in higher oxidation states than is typical for the most closely related carbonyls. Thus homoleptic carbonyls are most commonly neutral or anionic (i.e., $M_n(CO)_m$ or $M_n(CO)_m{}^{x-}$)

while homoleptic isocyanides are most commonly neutral or cationic (i.e., $M_n(CNR)_m$ or $M_n(CNR)_m^{x+}$).

As might be expected, C-N stretching frequencies of isocyanide ligands provide useful information about M-CNR bonding. In free isocyanides, ν_{CN} values are about 2130 cm^{-1}. Complexation to positively charged metals or binary metal carbonyl moieties (both of which are relatively electron poor) shifts these frequencies by as much as 150 cm^{-1} to higher energy. Such shifts are consistent with strong M<—CNR σ-donation from the slightly C-N antibonding lone pair on CNR and essentially no M—>CNR back bonding. Complexation to electron-rich and low-valent metals may shift ν_{CN} to lower energy by 60-340 cm^{-1}, although the average shift is about 115 cm^{-1}. These shifts are explained by extensive dπ–pπ* M—>CNR back bonding, which reduces the C-N bond order considerably.

Although hundreds of metal isocyanide compounds have been prepared,[20] only a few aryl isocyanide bridged organometallic polymers were reported. The work reported in this part of my thesis is an extension of previous work on model compounds containing arene bridging ligands. The syntheses and characterization of both dicyanobenzene and diisocyanobenzene bridged and terminal complexes of iron and molybdenum are reported.

CHAPTER II

EXPERIMENTAL SECTION

Unless otherwise noted, all reactions and subsequent manipulations were performed by conventional techniques for the manipulation of air-sensitive compounds as described previously.[21] Thus, anaerobic and anhydrous conditions were maintained by using a prepurified dinitrogen atmosphere using vacuum-line and inert-atmosphere glovebox techniques.[22]

1. Reagents

The reagents used were purchased from commercial suppliers or were prepared according to the published procedures. The chemicals used were of reagent grade or comparable purity, and where necessary, they were purified before use. Thus, *p*-diisocyanobenzene, *p*-chlorophenyl isocyanide and *p*-aminoisocyanobenzene were prepared via either the dichlorocarbene reaction or the phosgene method.[23] The Fp_2 and FpCl (where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$) were prepared and purified by standard procedures.[24] The $Mo(N_2)_2(DPPE)_2$ (where DPPE = $Ph_2PCH_2CH_2PPh_2$) was prepared via reduction of $MoCl_4$ and DPPE using sodium amalgam in THF.[25] Solvents used were dried and deaerated by standard procedures and stored under purified N_2 or Ar.[26] Unless specified otherwise, the reactions and any subsequent manipulations described below were effected at ambient temperature (~23°C).

2. Apparatus

Infrared spectra were recorded on a Pye Unicam PU9522 infrared spectrophotometer calibrated with the 1601 cm^{-1} band of polystyrene. NMR spectra were recorded on a Bruker WH-300 spectrometers with reference to the deuterium signal of the solvent employed. The ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR chemical shifts are reported in parts per million downfield from external Me_4Si and 85% H_3PO_4, respectively. Analytical data was obtained from combustion analysis.

3. N,N'-diformyl-1,4-diaminobenzene

Solid p-phenylenediamine (25 g, 231 mmol) was added to 90% formic acid (26 ml) and heated to reflux for an hour. Cold water (100 ml) was added to dilute the hot solution. Cooling the solution in an ice-bath caused a white solid to precipitate. This was filtered, washed with cold water (300 ml) until the pH value of filtrate was neutral, and dried in vacuo to give white product N,N'-diformyl-1,4-diaminobenzene (35.9 g , 219 mmol, 94.6% yield).

4. *p*-isocyanoaniline

Solid *p*-phenylenediamine (30 g, 277 mmol), potassium hydroxide (200 g), water (800 ml), alcohol (120 ml), and chlorofrom (400 ml) were added in a 2L round-bottomed flask. The solution spontaneously boiled during the dissolution. After it had cooled down, the solution was heated to boiling and refluxed for 2 hours. The chloroform layer was separated and the aqueous layer was washed with chloroform (3 x 100 ml). The combined chloroform solutions were washed with water (50 ml) and dried over anhydrous $MgSO_4$. The solution was filtered and the filtrate was evaporated to give tarry residue. To this residue was added 400 ml of ligroin, and this mixture was shaken vigorously and filtered (repeated four times).The combined organic washings were reduced in volume to about 500 ml. They were then cooled to 0^oC, producing yellow crystals of *p*-aminophenyl isocyanide (8.64 g, 73 mmol, 26% yield).

5. *p*-diisocyanobenzene

5.1. prepared by the phosgene method

Triphosgene (20 g, 67 mmol) dissolved in dry dichloromethane (70 ml) was added dropwise, over 2-hour duration, into a white boiling suspension consisting of N,N'-diformyl-1,4-diaminobenzene (15 g, 92 mmol), triethylamine (70 ml), and dichloromethane (250 ml). After an additional 5 hours of reflux, the reaction mixture was allowed to cool to ambient temperature. It was then washed with an aqueous 10% Na_2CO_3 solution (3 x 100 ml). The organic layer was dried over anhydrous $MgSO_4$ and then to dryness in vacuo to afford a crude brown product. The product was purified by chromatography on a neutral alumina oxide column using chloroform as eluent. Removal of solvent in vacuo gave a white product *p*-diisocyanobenzene (4.2 g, 33 mmol, 36% yield).

5.2. prepared by the dichlorocarbene reaction

Solid *p*-aminophenyl isocyanide (2.0 g, 17 mmol) was dissolved in a mixed solvent of methanol (8ml) and chloroform (10ml). When sodium hydroxide powder (6.5g) was added to it, the solution was boiled. The mixture was cooled with an ice bath to prevent its frothing into the condenser. After ten minutes, the ice-bath was removed and the mixture was stirred over night. It was diluted with 100ml of ether and filtered. The filtrate was washed with water (3 x 100 ml), 10% sulphuric acid solution (2 x 100 ml), and water (3 x 100 ml) and dried over anhydrous $MgSO_4$. Removal of solvent in vacuo left the product *p*-diisocyanobenzene (0.6 g, 4.7 mmol, 28%).

6. *p*-isocyanochlorobenzene

Solid 98% p-chloroaniline (18 g, 138 mmol), potassium hydroxide (100 g), water (400 ml), ethanol alcohol (60 ml), and chloroform (200 ml) were added in a 1L round-bottomed flask. The solution boiled spontaneously during the dissolution. After it had cooled, the solution was heated to boiling and refluxed for 2 hours. The chloroform layer was separated and the aqueous layer was washed with chloroform (3 x 50 ml). The combined chloroform solutions were washed with water (100 ml) and dried over anhydrous $MgSO_4$. The solution was filtered and filtrate was evaporated to give tarry residue. Sublimation of the residue under vacuo at 50°C gave a white crystalline product *p*-isocyanochlorobenzene (3.5 g, 25 mmol, 18%).

7. $Mo(N_2)_2(DPPE)_2$

1,2-bis(diphenylphosphion)ethane, DPPE (8.8 g, 22 mmol) was dissolved in a dried THF (210 ml) in a 3-necked round-bottomed flask. $MoCl_5$ (2.73 g, 10 mmol) was added to produce a brown suspension and then 2% Na/Hg (220 g, 191 mmol) was added. After 28 hours of stirring, the THF slurry was decanted, filtered throungh celite, and washed with dried benzene (200ml). The solvent was removed by rotary evaporator. The orange-brown residue was dissolved in benzene (150 ml), followed again by celite filtration and benzene wash (100 ml). The product was precipitated by the addition of methanol (400ml). The orange crystalline product $Mo(N_2)_2(DPPE)_2$ (5.0 g, 5 mmol, 50% yield) was filtered, washed with methanol (50ml), and dried under a nitrogen steam at ambient temperature. $^{31}P\{^1H\}$ NMR data for the complex is 65.13 ppm (in CD_2Cl_2).

8. $[Fp(OCMe_2)][PF_6]$

A solution of $[CpFe(CO)_2]_2$ (1.4 g, 4 mmol) in 50 ml of oxygen-free acetone was treated with $AgPF_6$ (2.0 g, 9.4 mmol). After stirring for one day, the mixture was filtered and the solid residue was washed with acetone (20 ml). The filtrate was concentrated to 20 ml in vacuo, then 100 ml of dried ether was carefully injected along the wall of the flask to make two layers. Deep red cubic crystals of $[Fp(OCMe_2)][PF_6]$ (1.0 g, 2.6 mmol, 33% yield) were obtained after filtration and drying in vacuo.

9. $[Fp(NCC_6H_4Cl)][PF_6]$

p-cyanochlorobenzene (0.22 g, 1.6 mmol) was added to a stirred solution of $[Fp(OCMe_2)][PF_6]$ (0.60 g, 1.6 mmol) in dichloromethane (20 ml) warmed to 50°C. After 10 hours, the reaction mixture was filtered and the red filtrate was concentrated in vacuo to ~10 ml. Dried diethyl ether (20 ml) was carefully added along the wall and two layers formed. Yellow crystals of the product $[Fp(NCC_6H_4Cl)][PF_6]$ (0.40 g, 0.87 mmol) were obtained after filtration and air drying in 55% yield.

Analytical and spectroscopic data for this and the other new organometallic compounds below are presented in Tables I and II.

TABLE 1. Yields, Analytical, Mass-Spectral and Infrared Data for Cyanide and Isocyanide Complexes

complex [a]		anal. data						FAB mass spectral	infrared data
		C		H		N			ν_{CO} and ν_{CN}
	yield (%)	calcd	found	calcd	found	calcd	found	data P^+, *m/z*	(KBr disks, cm^{-1}) [b]
$[Fp(p\text{-}NCC_6H_4Cl)](PF_6)$ [c]	55.1	36.60	36.40	1.97	1.89	3.05	2.96	314	2034 (s), 2084 (s), d
$[Fp(p\text{-}CNC_6H_4Cl)](PF_6)$	38.7	36.60	36.13	1.97	2.44	3.05	3.17	314	2039 (s), 2083 (s), 2201 (s)[e]
$[Fp(p\text{-}NCC_6H_4CN)](BF_4)$	49.0	45.92	45.72	2.31	2.11	7.14	8.71		2030 (s), 2077 (s), 2233 (s)[e]
$[Fp(p\text{-}NCC_6H_4CN)Fp](PF_6)_2$	82.4	34.23	33.53	1.83	1.80	3.63	3.45	627	2041 (s), 2084 (s), d
$[Fp(p\text{-}CNC_6H_4NC)Fp](PF_6)_2$	59.6	34.23	34.57	1.83	2.28	3.63	3.81	626	2046 (s), 2085 (s), 2185 (s)[e]
$Mo(p\text{-}CNC_6H_4Cl)_2(DPPE)_2$ [f]	85.5	71.06	70.40	5.37	5.28	2.07	2.15		1863 (s)[e]
$Mo(p\text{-}CNC_6H_4NH_2)_2(DPPE)_2$	68.0	70.21	69.70	5.36	5.53	4.96	4.44		1894 (s)[e]
$[Mo(\mu\text{-}CNC_6H_4NH_2)(DPPE)_2]_n$	62.2	70.59	71.08	5.13	5.55	2.74	3.88		1817 (s)[b]

[a] Where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ and DPPE = $Ph_2PCH_2CH_2PPh_2$.

[b] Abbreviations w (weak), m (medium), s (strong), sh (shoulder), v (very), br (broad).

[c] Cl %: calc. 7.72, found 7.70.

[d] the ν_{CO} and ν_{CN} peaks overlap.

[e] The ν_{CN} modes.

[f] Cl %: calc. 5.24, found 5.42.

TABLE 2. ^{1}H and ^{13}C NMR Data for Iron Complexes (δ in ppm)

	^{1}H NMR (Hz)		^{13}C NMR[a] (Hz)		
COMPLEX[a]	Cp[b]	*p*-XC_6H_4X'	Cp	C_6H_4	CO
[Fp(*p*-NCC_6H_4Cl)](PF_6)	5.46 (s, 5H)	7.51 (1H)	87.11		207.74
		7.54 (1H)			
		7.71 (1H)			
		7.76 (1H)			
[Fp(*p*-CNC_6H_4Cl)](PF_6)	5.58 (s, 5H)	7.47 (1H)	88.33	128.07	205.77
		7.50 (1H)		128.72	
		7.54 (1H)		130.48	
		7.56 (1H)		137.60	
[Fp(*p*-NCC_6H_4CN)](BF_4)	5.52 (s, 5H)	7.80 (1H)	87.43	133.20	207.72
		7.82 [1H)		134.00	
		7.97 (1H)		134.29	
		8.00 (1H)		134.59	
[Fp(*p*-NCC_6H_4CN)Fp](PF_6)$_2$	5.79 (s, 5H)	8.15 (m, 4H)			
[Fp(*p*-CNC_6H_4NC)Fp](PF_6)$_2$	5.90 (s, 5H)	7.94 (m, 4H)	88.61	127.69	206.40
				128.18	
				128.37	
				127.59	

a. where Fp = η^5-$C_5H_5Fe(CO)_2^+$.

b. where Cp = η^5-C_5H_5.

10. [Fp(CNC_6H_4Cl)][PF_6]

The synthesis of this compound was carried out by a procedure analogous to that described in the literature.[27] Thus, to a solution of of FpCl (196 mg, 0.945 mmol) in dichloromethane (30 mL) was added $AgPF_6$ (210 mg, 0.982 mmol) and the solution was stirred for about 2 hours. The mixture was filtered into a second flask containing a solution of *p*-chloroioscyanobenzene (130 mg, 0.945mmol) in dichloromethane (2 ml). After 24 hours, the solution was filtered and the filtrate was then taken to dryness in vacuo. The resulting golden needles were recrystallized from CH_2Cl_2/hexane (1:2 v/v) to give a 39% yield (168 mg, 0.366 mmol) of [FpCNC_6H_4Cl][PF_6].

11. [Fp(NCC_6H_4CN)][BF_4]

A solution of Fp_2 (708 mg, 2.00 mmol) and an excess of *p*-dicyanobenzene (750 mg, 5.85 mmol) in dried and oxygen-free acetone (25 ml) was treated with $AgBF_4$ (930 mg, 4.80 mmol). After 15 hr. the reaction mixture was filtered and the filtrate was reduced in vacuo to about 10 ml. Diethyl ether (20 ml) was added to this solution to produce a yellow precipitate. This yellow product was collected by filtration and washed with 10 ml of diethyl ether and dried in vacuo to give [Fp(NCC_6H_4CN)][BF_4] in 49% yield (680mg, 1.73 mmol).

12. [Fp(NCC_6H_4CN)Fp][PF_6]$_2$

Solid *p*-dicyanobenzene (88 mg, 0.67 mmol) was added to a stirred solution of [Fp($OCMe_2$)](PF_6) (500 mg, 1.32 mmol) in dichloromethane (30 ml). The solution was warmed to 50°C for 30 minutes. The resulting yellow crystals were collected by filtration, washed with dichloromethane (3 X 5 ml), and dried in vacuo giving [Fp(NCC_6H_4CN)Fp][PF_6]$_2$ in 82% yield (420 mg, 0.544 mmol).

13. [Fp(CNC_6H_4NC)Fp][PF_6]$_2$

A *p*-diisocyanobenzene (128 mg, 1.00 mmol) was added to a stirred solution of [Fp($OCMe_2$)](PF_6) (385 mg, 1.01 mmol) in dichloromethane (20 ml). The solution was warmed to 50°C for 15 minutes. The resulting yellow crystals were collected by filtration, washed with dichloromethane (3 X 5 ml), and dried in vacuo giving [Fp(CNC_6H_4 NC)Fp][PF_6]$_2$, in 60% yield (230mg, 0.590 mmol).

14. *trans*-[Mo(*p*-CNC_6H_4Cl)$_2$(DPPE)$_2$]

Solid *p*-isocyanochlorobenzene(174 mg, 1.26 mmol) was sublimed before use and then dissolved in THF (5 ml) in a 100 ml, 3-necked round-bottomed-flask. An orange solution of *trans*-Mo(N_2)$_2$(DPPE)$_2$ (600 mg, 0.63 mmol) in THF (40 ml) was filtered into this flask and the resulting solution was stirred for 30 minutes at ambient temperature and was then heated to reflux for 12 hours. The resulting red solution was allowed to cool and was then filtered. Removing solvent from the filtrate in vacuo, washing the deep-red solid with hexane (100 ml), and drying it under a dinitrogen steam and then under vacuo produced *trans*-[Mo(p-CNC_6H_4Cl)$_2$(DPPE)$_2$] in 86% yield (700 mg, 0.5 mmol). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) 72.47 ppm.[28]

15. *trans*-[Mo(*p*-$CNC_6H_4NH_2$)$_2$(DPPE)$_2$]

Solid *p*-isocyanoaniline (0.30 g, 2.54 mmol) was dissolved in THF (5 ml) in a 200 ml, 3-necked round-bottomed-flask. A solution of *trans*-Mo(N_2)$_2$(DPPE)$_2$ (1.21 g, 1.28 mmol) in THF (50 ml) was filtered into this flask and the resulting solution was stirred for 30 min. at ambient temperature and was then heated to reflux for 12 h. The solution was allowed to cool and was filtered to remove traces of a yellow-white solid. Removing solvent from the filtrate in vacuo, washing the resulting brick-red solid with hexane, and drying it under a dinitrogen steam and then vacuum produced *trans*-[Mo(p-$CNC_6H_4NH_2$)$_2$(DPPE)$_2$] in 68% yield (1.0g, 0.89 mmol). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) 73.38 ppm.

16. $[Mo(\mu\text{-}CNC_6H_4NC)(DPPE)_2]_n$

Solid *p*-diisocyanobenzene (0.080 g, 0.63 mmol) was sublimed before use and then dissolved in THF (5 ml) in a 100 ml, 3-necked round-bottomed-flask. A solution of $Mo(N_2)_2(DPPE)_2$ (0.60 g, 0.63 mmol) in THF (35 ml) was filtered into this flask and the resulting solution was stirred for 30 minutes at ambient temperature and then was heated to reflux for 26 hours. The solution was allowed to cool and was filtered. Washing the resulting black precipitate with benzene(5 ml), and drying it under a dinitrogen steam and then vacuo produced the polymer $[Mo(\mu\text{-}CNC_6H_4NC)(DPPE)_2]_n$ in 62% yield (0.40g, 0.39 mmol).

17. X-ray crystal structure determinations for complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(p\text{-}CNC_6H_4Cl)]PF_6$

Crystals of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(p\text{-}CNC_6H_4Cl)]PF_6$ have been obtained by dissolving the solid product in dry dichloromethane/hexane (1:2 v/v) and allowing solvent to slowly evaporate under dinitrogen. A single golden needle shaped crystal with dimensions 0.08 x 0.12 x 0.72 mm was mounted in a glass capillary. Unit-cell dimensions (a =7.0833(5) Å, b = 14.903(1) Å, c = 16.591(2) Å, β=98.674(7)^o; V = 1731.4(3) Å^3; monoclinic; $P2_1/c$; Z = 4) were determined by least-squares refinement of the setting angles of 25 reflections with $2\theta > 30^o$. Room-temperature data were collected on a Enraf-Nonius CAD4 diffractometer with the $\theta/2\theta$ scan technique and graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71073Å). Three standard reflections monitored throughout the data collection showed less than 1% change in intensity. A total of 2429 reflections with $2^o < 2\theta < 46^o$ were measured and averaged to give 2297 unique reflections, and the internal agreement factor $R(F)$= 0.016. Data were corrected for Lorentz and polarization effects and for absorption via empirical scans. The transmission factors ranged from 0.83 to 1.09. The structure was solved based on space group $P\ 2_1/c$. Upon examination of the refined atomic parameters in the $P\ 2_1/c$ space group the centrosymmetric nature of the structure was evident. The presence of a center of symmetry was supported by the intensity statistics. A total of 2230 unique reflections with $I > 6\sigma(I)$ were used in the final full-matrix refinement with anisotropic thermal parameters for all but the C atoms of the benzene ring, and isotropic thermal parameters were used for the C atoms of the benzene ring. The positions of H atoms were calculated at idealized position using a C-H distance of 0.95 Å and included in the structure-factor calculation. A total of 200 variables were refined, minimizing the function $\Sigma[w(|F\text{obs}| - k|F\text{cal}|)^2]$, where $w=1/\sigma^2(F)$; $\sigma(F)=\sigma(F^2)/2F$; $\sigma(F^2)=[\sigma^2\text{counting} + (0.02|F|^2)^2]^{1/2}$. Parameter shifts in the final least-squares cycle were smaller than 0.016σ. For 2230 reflections, $R(F)=0.0555$, $wR(F)=0.0539$. Final fractional atomic coordinates and equivalent isotropic thermal parameters, selected bond lenths and angles are given in Table 3 and 4 respectively.

18. X-ray crystal structure determinations for *trans*-[Mo(*p*-CNC$_6$H$_4$Cl)$_2$(DPPE)$_2$]·2CH$_3$C$_6$H$_5$

Crystals of *trans*-[Mo(*p*-CNC$_6$H$_4$Cl)$_2$(DPPE)$_2$] have been prepared by dissolving solid product in dry toluene and allowing solvent to slowly evaporate under dinitrogen flow. A single crystal of the brown purple complex with dimensions 0.24 x 0.26 x 0.32 mm, was mounted on a glass fiber. Unit-cell dimensions (a =29.182(2) Å, b = 12.324(1) Å, c = 19.205(2) Å, β=94.77(1)°; V = 6883(1) Å^3; monoclinic; C2/c; Z = 4) were determined by least-squares refinement of the setting angles of 25 reflections with $2\theta > 30^\circ$. Room-temperature data were collected on a Enraf-Nonius CAD4 diffractometer with the $\theta/2\theta$ scan technique and graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71073Å). Three standard reflections monitored throughout the data collection showed less than 1% change in intensity. A total of 3555 reflections with $2^\circ < 2\theta < 40^\circ$ were measured and averaged to give 3497 unique reflections, and it was found that the internal agreement factor $R(F)$= 0.02. Data were corrected for Lorentz and polarization effects and for absorption via empirical scans. The transmission factors ranged from 0.87 to 1.15. The structure was solved based on space group C 2/c. Upon examination of the refined atomic parameters in the C 2/c space group, the centrosymmetric nature of the structure was evident. The presence of a center of symmetry was supported by the intensity statistics. 3497 unique reflections with $I > 6\sigma(I)$ were used in the final full-matrix refinement with anisotropic thermal parameters for Mo, P, and Cl atoms, and isotropic thermal parameters for the rest of the non-H atoms. The positions of the H atoms were calculated using a C-H distance of 0.95 Å and included in the structure-factor calculation. A total of 197 variables were refined, minimizing the function $\Sigma[w(|F\text{obs}| - k|F\text{cal}|)^2]$, where $w=1/\sigma^2(F)$; $\sigma(F)=\sigma(F^2)/2F$; $\sigma(F^2)=[\sigma^2\text{counting} + (0.02|F|^2)^2]^{1/2}$. Parameter shifts in the final least-squares cycle were smaller than 0.02σ. For 3497 reflections, $R(F)=0.0566$, $wR(F)=0.0632$. Final fractional atomic coordinates and equivalent isotropic thermal parameters, selected bond lenths and angles are given in Table 5 and 6 respectively.

Table 3. Positional and Equivalent Isotropic Gaussian (Å^2) Parameters for Complex [(η^5-C_5H_5)Fe$(CO)_2$(*p*-CNC_6H_4Cl)]PF_6.^{a,b}

Atom	x	y	z	Ueq
Fe	0.1360(1)	0.13450(9)	0.38306(8)	3.97(2)
Cl	0.2921(4)	0.7041(2)	0.5236(2)	7.25(8)
O1	-0.0141(8)	0.1027(5)	0.5349(4)	6.8(2)
O2	0.5338(8)	0.0871(5)	0.4408(5)	7.1(2)
N	0.2003(8)	0.3287(5)	0.4259(5)	4.7(2)
C1	0.0478(9)	0.1152(6)	0.4772(6)	4.6(2)
C2	0.378(1)	0.1060(7)	0.4200(6)	5.1(2)
C3	0.178(1)	0.2539(6)	0.4080(6)	4.1(2)*
C4	0.2265(9)	0.4176(6)	0.4484(5)	3.9(2)*
C5	0.235(1)	0.4402(7)	0.5290(6)	4.8(2)*
C6	0.258(1)	0.5287(7)	0.5523(6)	4.7(2)*
C7	0.267(1)	0.5928(6)	0.4943(6)	4.4(2)*
C8	0.258(1)	0.5701(7)	0.4147(6)	4.4(2)*
C9	0.238(1)	0.4819(7)	0.3906(6)	4.6(2)*
C11	0.087(1)	0.0256(7)	0.3039(7)	5.4(2)
C12	-0.087(1)	0.0558(7)	0.3227(6)	5.0(2)
C13	-0.113(1)	0.1455(8)	0.2994(6)	5.5(2)
C14	0.045(1)	0.1695(8)	0.2622(7)	6.3(3)
C15	0.167(1)	0.0973(9)	0.2658(6)	6.6(3)
P	0.4701(3)	0.1669(2)	0.6930(2)	4.89(6)
F1	0.2579((7)	0.1502(5)	0.7070(5)	8.8(2)
F2	0.6777(8)	0.1817(6)	0.6805(6)	12.8(3)
F3	0.441(1)	0.1067(8)	0.6193(6)	15.5(3)
F4	0.409(1)	0.2497(7)	0.6482(7)	20.5(3)
F5	0.528(1)	0.0819(8)	0.7410(7)	16.6(3)
F6	0.486(1)	0.2259(8)	0.7685(7)	18.4(3)

[a] Starred atoms were refined isotropically.

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a2*B(1,1)+b2*B(2,2)+c2*B(3,3)+ab(cos gamma)*B(1,2)+ ac(cos beta) *B(1,3)+bc(cos alpha)*B(2,3)]

Table 4. Selected Bond Lengths (Å) and Angles (°) for Complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(p\text{-}CNC_6H_4Cl)]PF_6$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom3	Angle
Fe	C1	1.79(1)	C1	Fe	C2	96.0(4)
Fe	C2	1.780(7)	C1	Fe	C3	91.4(4)
Fe	C3	1.842(9)	C2	Fe	C3	92.3(4)
Fe	C11	2.08(1)	Fe	C1	O1	177.5(6)
Fe	C12	2.094(9)	Fe	C2	O2	178(1)
Fe	C13	2.077(8)	Fe	C3	N	177.7(8)
Fe	C14	2.08(1)	C3	N	C4	179.1(9)
Fe	C15	2.07(1)	N	C4	C5	118.8(8)
O1	C1	1.13(1)	N	C4	C9	120.2(8)
O2	C2	1.13(9)	C4	C5	C6	119.6(9)
N	C3	1.16(1)	C5	C6	C7	119.3(9)
N	C4	1.38(1)	C7	C8	C9	120.7(9)
C4	C5	1.37(1)	C4	C9	C8	118.7(9)
C4	C9	1.37(1)	Cl	C7	C6	119.2(7)
C5	C6	1.38(1)	Cl	C7	C8	120.0(7)
C6	C7	1.36(1)	C11	C12	C13	109.5(8)
C7	C8	1.35(1)	C12	C13	C14	106.5(9)
C8	C9	1.38(1)	C13	C14	C15	109.(1)
C11	C12	1.39(1)	C11	C15	C14	108.6(9)
C11	C15	1.41(2)	C3	Fe	C11	154.3(4)
C12	C13	1.40(2)	C3	Fe	C12	137.1(3)
C13	C14	1.40(1)	C3	Fe	C14	89.4(4)
C14	C15	1.38(2)	C1	Fe	C14	141.6(4)
Cl	C7	1.73(1)	C1	Fe	C14	122.3(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

Table 5. Positional and Equivalent Isotropic Gaussian (Å^2) Parameters for Complex *trans*-[Mo(p-CNC$_6$H$_4$Cl)$_2$(DPPE)$_2$]·2CH$_3$C$_6$H$_5$.[a,b]

Atom	x	y	z	Ueq
Mo	0.000	0.3507(1)	0.250	3.04(3)
Cl	0.2924(1)	0.3916(4)	0.4378(3)	9.2(1)
P1	0.0138(1)	0.4807(3)	0.1581(2)	3.66(8)
P2	0.0182(1)	0.2253(3)	0.1579(2)	3.79(8)
N31	0.1064(3)	0.3367(9)	0.3013(5)	5.6(2)*
C1	0.0190(4)	0.406(1)	0.0739(6)	4.5(3)*
C2	0.0483(4)	0.3030(9)	0.0914(6)	4.3(3)*
C31	0.0659(4)	0.344(1)	0.2825(5)	4.3(2)*
C32	0.1506(4)	0.346(1)	0.3332(6)	4.7(3)*
C33	0.1593(5)	0.328(1)	0.4022(7)	6.1(3)*
C34	0.2033(4)	0.342(1)	0.4349(6)	6.2(3)*
C35	0.2375(4)	0.373(1)	0.3965(6)	5.4(3)*
C36	0.2304(5)	0.389(1)	0.3288(7)	6.7(4)*
C37	0.1871(5)	0.374(1)	0.2945(7)	6.8(4)*

[a] Starred atoms were refined isotropically.

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a2*B(1,1)+b2*B(2,2)+c2*B(3,3)+ab(cos gamma)*B(1,2)+ac(cos beta) *B(1,3)+bc(cos alpha)*B(2,3)]

Table 6. Selected Bond Lengths (Å) and Angles $(^{o})$ for Complexe *trans*-$[Mo(p\text{-}CNC_6H_4Cl)_2(DPPE)_2]\cdot 2CH_3C_6H_5$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom3	Angle
Mo	P1	2.441(3)	P1	Mo	P2	80.4(1)
Mo	P2	2.441(3)	P1	Mo	C31	92.3(3)
Mo	C31	1.97(1(1)	Mo	P1	C1	109.2(4)
P1	C1	1.88(1)	Mo	P2	C2	108.2(4)
P2	C2	1.87(1)	Mo	C31	N31	178.(1)
N31	C31	1.21(1)	N31	C32	C33	121.(1)
N31	C32	1.38(1)	N31	C32	C37	121.(1)
C1	C2	1.55(2)	C33	C32	C37	118.(1)
C32	C33	1.35(2)	C32	C33	C34	121.(1)
C32	C37	1.39(2)	C33	C34	C35	119.(1)
C33	C34	1.39(2)	C1	C35	C34	119.0(9)
C34	C35	1.35(2)	C1	C35	C36	120.(1)
C35	C36	1.31(2)	C34	C35	C36	121.(1)
C36	C37	1.39(2)	C35	C36	C37	121.(1)
			C31	N31	C32	167.(1)
			P1	C1	C2	107.3(7)
			P2	C2	C1	106.4(8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

CHAPTER IV

RESULTS AND DISCUSSION

1.Syntheses of the iron complexes

Addition of a silver salt AgY (Y= PF_6^- or BF_4^-) to an acetone solution of Fp_2 or FpCl yields the red complex $[Fp(Me_2CO)]Y$

$$\text{Fp-Fp} + 2\,\text{AgY} + 2\,(CH_3)_2CO \longrightarrow 2\,[Fp((CH_3)_2CO)]Y + Ag \qquad (1)$$

$$\text{FpCl} + \text{AgY} + (CH_3)_2CO \longrightarrow [Fp((CH_3)_2CO)]Y + AgCl \qquad (2)$$

In reaction 1, the silver salt acts as an oxidant to cleave the Fe-Fe bond while in reaction 2 it acts as a metathesis reagent to replace the chloride anion. Since the silver salts $AgPF_6$ and $AgBF_4$ are not very soluble in acetone, the reactions have been carried out using a well-stirred suspension of finely ground AgY. The species $[Fp(Me_2CO)]Y$ dissolves in acetone and they are thus easily separated from the precipitated Ag or AgCl. The $[Fp(Me_2CO)]PF_6$ may be either isolated or prepared and used *in situ*..

The cyanide and isocyanide ligands readily displace the labile acetone ligand from the species $[Fp(Me_2CO)]$, generally in 15 - 30 minutes,

$$[Fp((CH_3)_2CO)](PF_6) + CNC_6H_5Cl \longrightarrow [Fp(CNC_6H_5X)](PF_6) + (CH_3)_2CO \qquad (3)$$

$$[Fp((CH_3)_2CO)](PF_6) + NCC_6H_5Cl \longrightarrow [Fp(NCC_6H_5X)](PF_6) + (CH_3)_2CO \qquad (4).$$

The monometallic products are soluble in acetone or dichloromethane, while the dimetallic complexes precipitate from solution. The dimetallic complexes are insoluble in most common solvents, but dissolve in DMSO. The complexes are air-stable in the solid state.

Dicyanobenzene reacts with $[Fp(Me_2CO)](PF_6)$ to produce mono- or dimetal complexes depanding on the ratio of the reactants.

$$[Fp((CH_3)_2CO)](PF_6) + \mathbf{NCC_6H_5CN} \longrightarrow [Fp(\mathbf{NCC_6H_5CN})](PF_6) + (CH_3)_2CO \quad (5)$$

$$2\ [Fp((CH_3)_2CO)](PF_6) + \mathbf{NCC_6H_5CN} \longrightarrow [Fp(\mathbf{NCC_6H_5CN})Fp](PF_6)_2 + 2\ (CH_3)_2CO \quad (6)$$

However, diisocyanobenzene reacts with $[Fp(Me_2CO)]Y$ to give only dimetallic complexes even when two equivalents of ligand per equivalent iron are used.

$$2\ [Fp((CH_3)_2CO)](PF_6) + \mathbf{CNC_6H_5NC} \longrightarrow [Fp(\mathbf{CNC_6H_5NC})Fp](PF_6)_2 + 2\ (CH_3)_2CO \quad (7)$$

Thus, the diisocyanide more readily forms bridges in these complexes than does the dicyanide. Our efforts to prepare bridged oligmers and polymers were therefore directed towards the isocyanides.

2.Syntheses of the molybdenum complexes

A wide varity of dinitrogen complexes of molybdenum have been prepared since the initial report of $Mo(N_2)_2(PPh_3)_2.C_6H_5CH_3$.[29] These complexes were obtained by the reduction of an appropriate molybdenum complex in the +2 to +5 oxidation state. In this work, the dinitrogen complex $Mo(N_2)_2(DPPE)_2$ was prepared by the reduction of molybdenum(V) chloride with sodium amalgam in THF under a dinitrogen atmosphere,

$$MoCl_5 + 2\ DPPE \xrightarrow{\text{Na-Hg, THF, } N_2} \textit{trans-}Mo(N_2)_2(DPPE)_2 + 5\ NaCl \quad (8)$$

Dinitrogen was bubbled slowly through the THF solution. The reaction was judged to be complete by solution infrared spectrum (ν_{N_2} at 1970 cm^{-1}). Solid $Mo(N_2)_2(DPPE)_2$ can be stored in a desiccator for several months without decomposition, but in solution the complex is air sensitive. It is soluble in benzene and dichloromethane but is insoluble in methanol and petroleum ether. The complex is stable in acetonitrile for a day but is unstable in chloroform and carbon tetrachloride, since evolution of dinitrogen occurs. Also, it loses dinitrogen rapidly upon heating in solution.

trans-$Mo(N_2)_2(DPPE)_2$ has two weakly coordinated dinitrogen which are easily replaced by isocyanides in THF:

$$trans\text{-}Mo(N_2)_2(DPPE)_2 + 2\ CNC_6H_4X \longrightarrow trans\text{-}Mo(CNC_6H_4X)_2(DPPE)_2 + 2N_2 \qquad (9)$$

where X= Cl and NH_2. Reaction (9) was carried out in THF and proceeds smoothly to completion (judged by IR when a ν_{N_2} at 1970 cm^{-1} disappears and a ν_{CN} at 1810-1890 cm^{-1} appears). No mono(dinitrogen) complexes of substituted isocyanobenzene were observed in these reactions:

$$trans\text{-}Mo(N_2)_2(DPPE)_2 + 2\ CNC_6H_4NC \cancel{\longrightarrow} trans\text{-}Mo(N_2)(CNC_6H_4NC)(DPPE)_2 + N_2. \qquad (10)$$

Attempts were made to prepare a bis(*p*-diisocyanobenzene) molybdenum complex by the above route. However, they give only black solid polymer:

$$rans\text{-}Mo(N_2)_2(DPPE)_2 + 2\ CNC_6H_4NC \cancel{\longrightarrow} trans\text{-}Mo(CNC_6H_4NC)_2(DPPE)_2 + 2N_2 \qquad (11)$$

$$n\ trans\text{-}Mo(N_2)_2(DPPE)_2 + n\ CNC_6H_4NC \longrightarrow [Mo(\mu\text{-}CNC_6H_4NC)(DPPE)_2]_n + 2n\ N_2. \qquad (12)$$

The black solid does not dissolve in any organic solvent. Its element analysis and solid-state infrared spectrum (Table 1) are consistant with a polymeric structure. The ploymer is stable in air for a few minuts and changes color to dark brown after being exposed in air for several hours.

Considering the existance of two terminal functional groups in *trans*-$Mo(CNC_6H_4NH_2)_2(DPPE)_2$, the related organometallic polymers are expected to be formable by polycondensation reactions, e.g.

$$n\ trans\text{-}Mo(CNC_6H_4NH_2)_2(DPPE)_2 + n\ \mathbf{OCN\text{-}Ar\text{-}NCO} \longrightarrow [\text{-}Mo(DPPE)_2CNC_6H_4NH\text{-}\mathbf{CONH\text{-}Ar\text{-}NHCO}\text{-}NHC_6H_4NC\text{-}]_n \quad (12)$$

These polymerizations involving organometallic oligomers are under investigation.

3. Spectroscopic characterization of the iron complexes

The IR spectra in the carbonyl region of the five iron complexes, shown in Table I, are similar to those that have been reported for other cyanide or isocyanide derivatives of Fp^+.[30,31] Thus, stretching frequencies attributable to the carbonyl ligands were observed in the expected regions (i.e. a symmetric band between 2077 and 2085 cm^{-1} and an asymmetric band between 2030 and 2046 cm^{-1}). The values of the carbonyl absorptions are very close for the cyanide or isocyanide complexes (Figure 1). The IR spectra also show absorptions characteristic of the cyanide or isocyanide ligands. The stretching frequency of the cynano groups shift to low frequency relative to their positions in the free ligands, this indicates that a decrease in C-N bond order has occurred. In the spectra of the isocyanide complexes, on the other hand, the stretching frequency of the isocynano groups shift to a higher frequency. This indicates an increase in the C-N bond order on the ligand.

In the NMR spectra of the five iron complexes, shown in Table II, the proton resonances of the cyanide and isocyanide are all shifted downfield relative to their positions in the free ligands and establish the coordination geometries of the ligand (Figure 2).

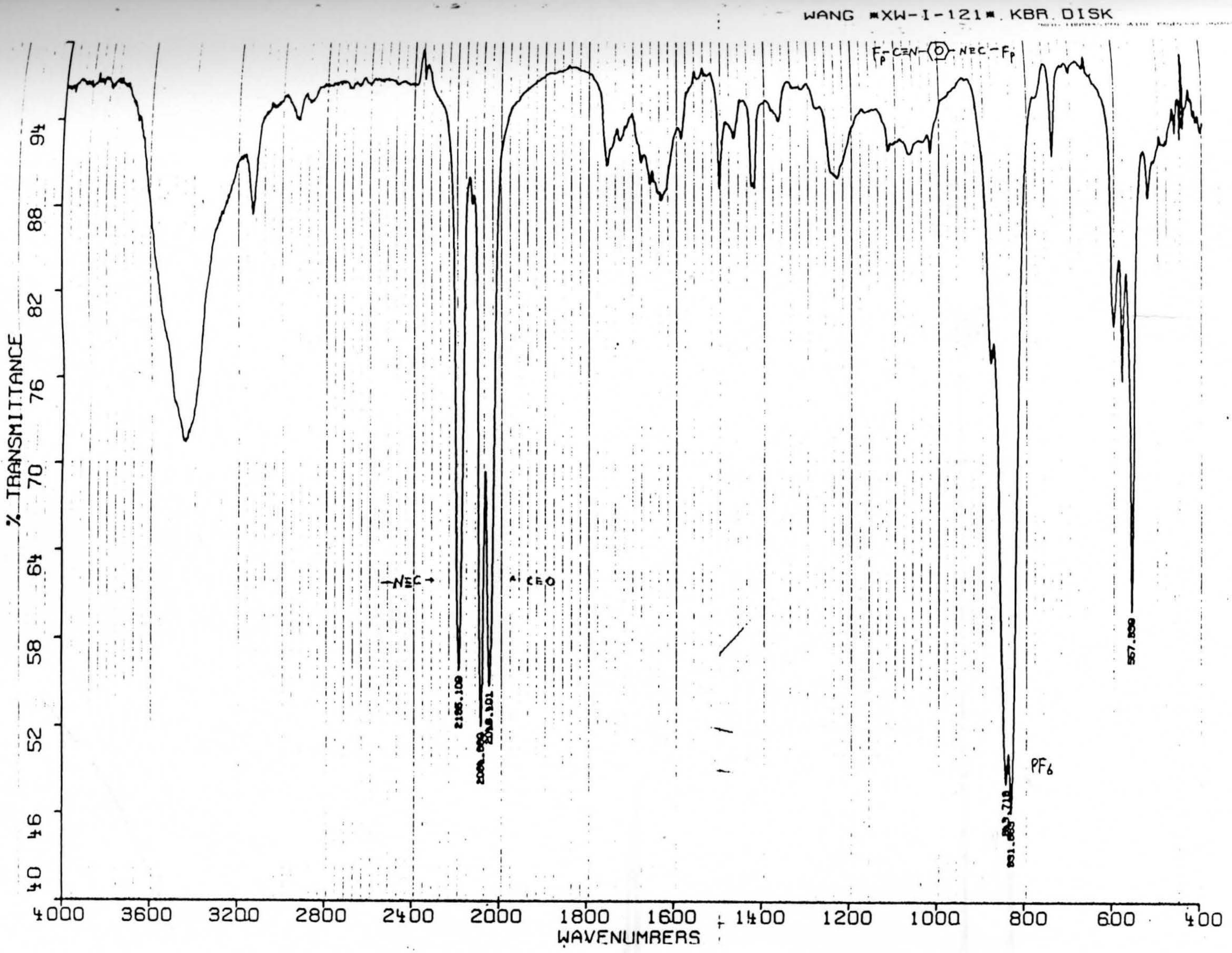


FIGURE 1 Infared spectrum of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4(p\text{-}CNC_6H_4NC)](PF_6)_2$

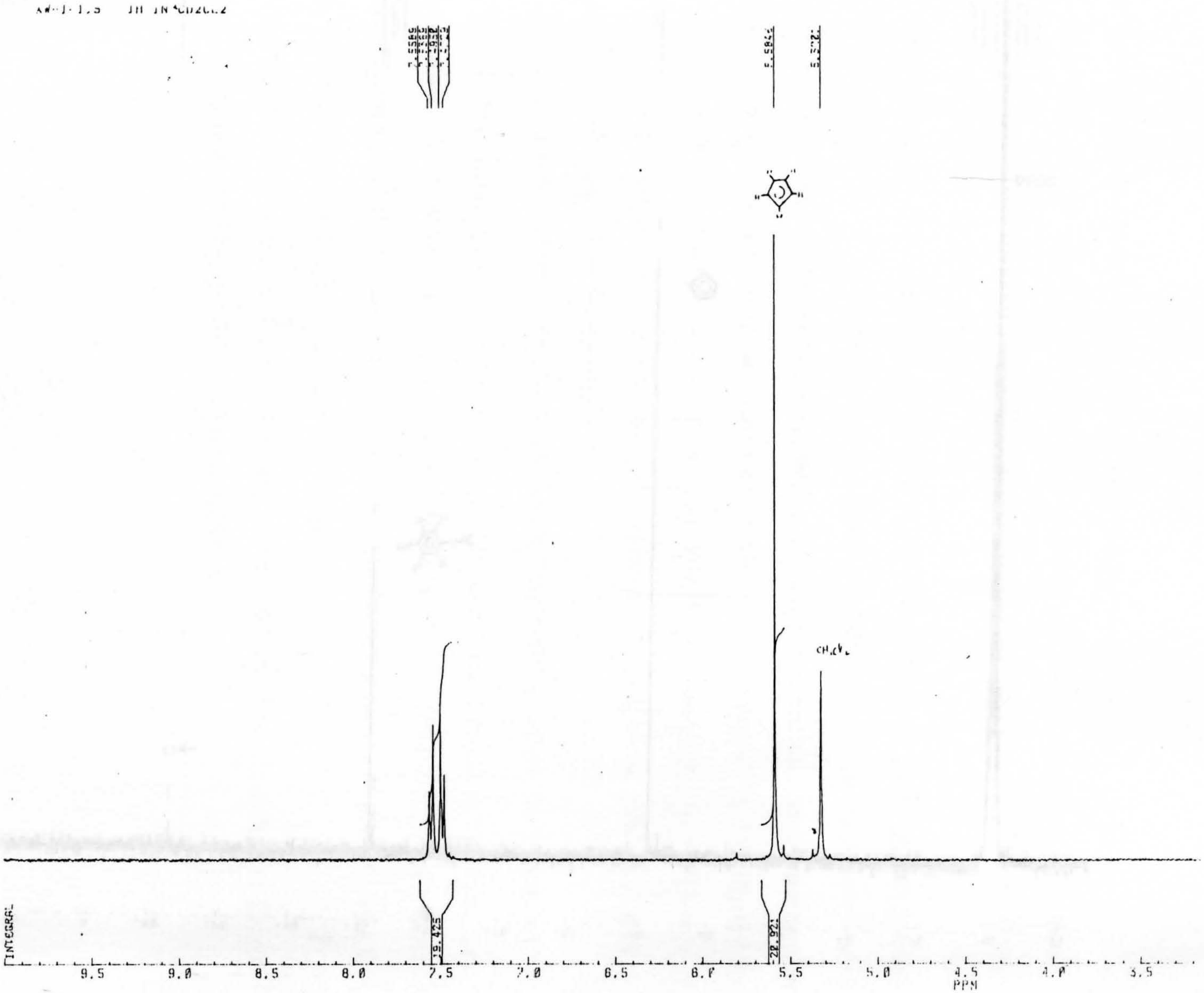


FIGURE 2 ^{1}HNMR spectrum of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(p\text{-}CNC_6H_4Cl)](PF_6)$

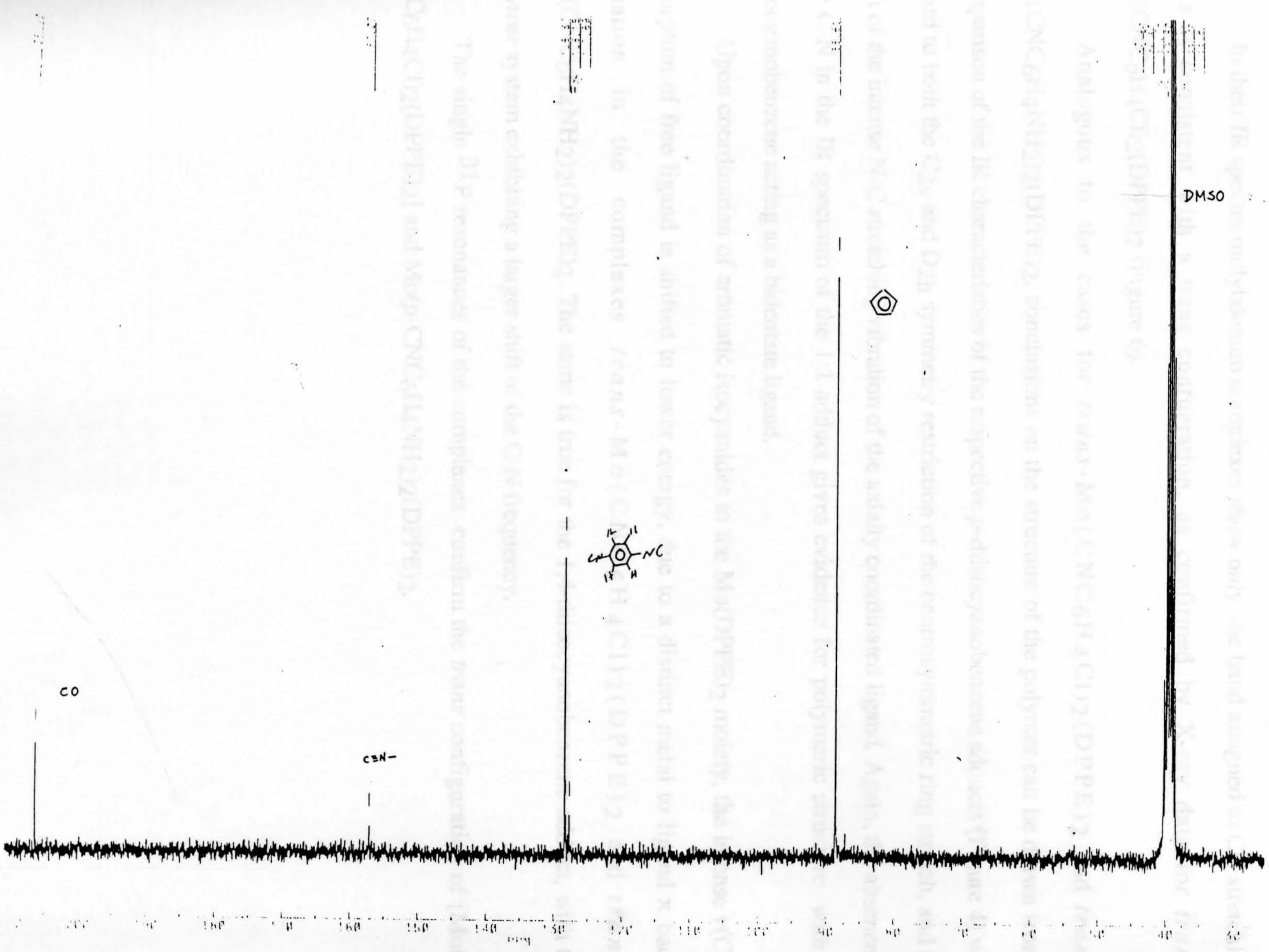


FIGURE 3 ^{13}CNMR spectrum of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4(p\text{-}CNC_6H_4NC)](PF_6)_2$

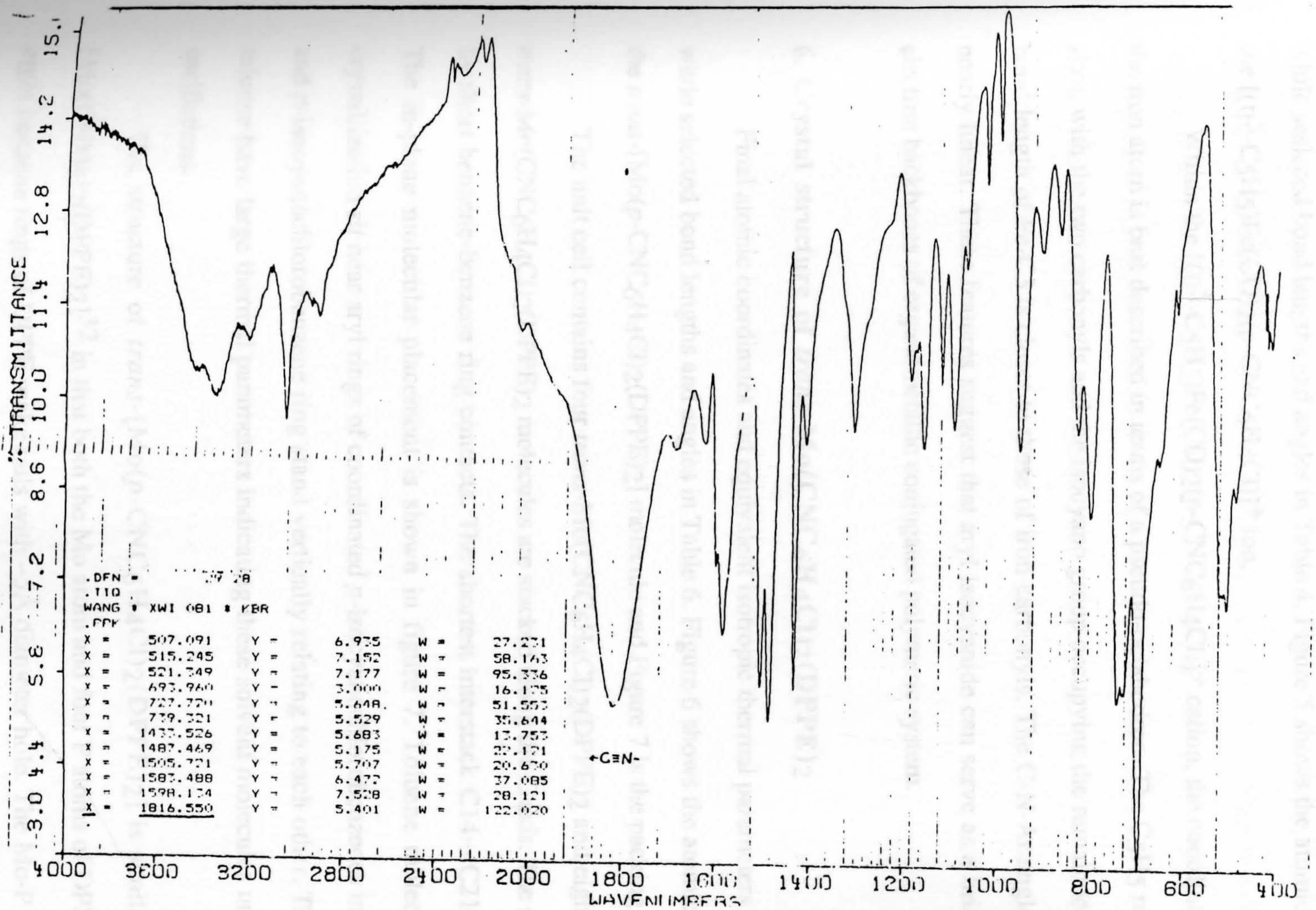
4. Spectroscopic characterization of the molybdenum complexes

In their IR spectra molybdenum complexes show only one band assigned to CN stretching. This is consistent with a trans confugration, as confirmed by X-ray data for *trans*-$Mo(CNC_6H_4Cl)_2(DPPE)_2$ (Figure 6).

Analogous to the cases for *trans*-$Mo(CNC_6H_4Cl)_2(DPPE)_2$ and *trans*-$Mo(CNC_6H_4NH_2)_2(DPPE)_2$, conclusions on the structure of the polymer can be drawn from a comparison of the IR characteristics of the respective *p*-diisocyanobenzene adducts (Figure 4) with regard to both the C_{2v} and D_{2h} symmetry restriction of the centrosymmetric ring stretch, and the shift of the intense N-C stretching vibration of the axially coordinated ligand. Again, the absence of free C-N in the IR spectrum of the 1:1 adduct gives evidence for polymeric structure with *p*-diisocyanobenzene acting as a bidentate ligand.

Upon coordination of aromatic isocyanides to the $Mo(DPPE)_2$ moiety, the intense *ν*(CN) absorption of free ligand is shifted to lower energy, due to a distinct metal to ligand π back-donation in the complexes *trans*-$Mo(CNC_6H_4Cl)_2(DPPE)_2$ and *trans*-$Mo(CNC_6H_4NH_2)_2(DPPE)_2$. The same is true for the 1,4-diisocyanobenzene adduct, with the polymer system exhibiting a larger shift of the C-N frequency.

The single ^{31}P resonances of the complexes confirm the *trans* configuration of [Mo(*p*-$CNC_6H_4Cl)_2(DPPE)_2$] and Mo(*p*-$CNC_6H_4NH_2)_2(DPPE)_2$.



```
.DFN = [illegible]
.TIQ
WANG * XWI 081 * KBR
.PPK
X =    507.091    Y =    6.935    W =    27.231
X =    515.245    Y =    7.152    W =    58.163
X =    521.349    Y =    7.177    W =    95.336
X =    693.960    Y =    3.000    W =    16.175
X =    727.770    Y =    5.648.   W =    51.553
X =    739.321    Y =    5.529    W =    35.644
X =   1433.526    Y =    5.683    W =    13.753
X =   1487.469    Y =    5.175    W =    22.171
X =   1505.721    Y =    5.707    W =    20.630
X =   1583.488    Y =    6.472    W =    37.085
X =   1598.134    Y =    7.528    W =    28.121
X =   1816.550    Y =    5.401    W =   122.020
```

FIGURE 4 Infared spectrum of $[Mo(p\text{-}CNC_6H_4NC)(DPPE)_2]_n$

5. Crystal structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(p\text{-}CNC_6H_4Cl)]PF_6$.

Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 3, while sesleced bond lengths and angles in Table 4. Figure 5 shows the atomic labeling scheme for the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(p\text{-}CNC_6H_4Cl)]^+$ ion.

Within the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(p\text{-}CNC_6H_4Cl)]^+$ cation, the coordination geometry about the iron atom is best described in terms of a pseudo-octahedron. The C_5H_5 moiety occupies three sites, with the two carbonyls and the isocyano group occupying the remainder. The Fe-isocyanide bond length of Fe-C3 is closer to those of iron-carbonyls. The C-N-Ar angle is $179.1(9)^o$ and is nearly linear. These features suggest that aryl isocyanide can serve as a bridge to form large π-electron backbones of organometallic conjugated polymeric system.

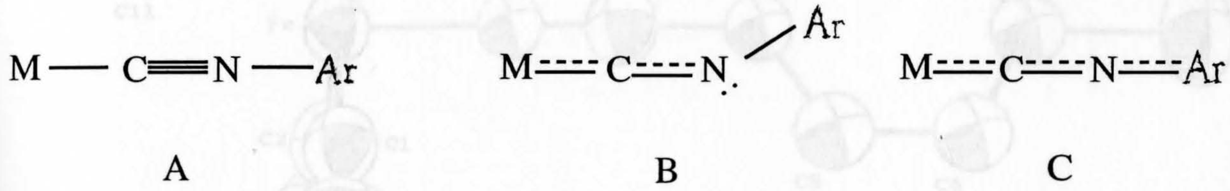
6. Crystal structure of *trans*-$Mo(CNC_6H_4Cl)_2(DPPE)_2$

Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 5, while selected bond lengths and angles in Table 6. Figure 6 shows the atomic labeling scheme for the *trans*-$[Mo(p\text{-}CNC_6H_4Cl)_2(DPPE)_2]$ molecule and Figure 7 is the packing diagram.

The unit cell contains four *trans*-$Mo(CNC_6H_4Cl)_2(DPPE)_2$ and eight toluene molecules. *trans*-$Mo(CNC_6H_4Cl)_2(DPPE)_2$ molecules are stacked along the C axis. The stacks are interlinked by short benzene-benzene ring contacts. The shortest interstack C14····C214 distance is 3.53Å. The in-plane molecular placement is shown in figure 7. Toluene molecules as solvents of crystallization sit near aryl rings of coordinated *p*-isocyanochlorobenzenes in a 1:1 ratio. Toluene and *p*-isocyanochlorobenzene ring stand vertically relating to each other. The seven C atoms in toluene have large thermal parameters indicating these solvent molecules undergo large thermal oscillations.

The structure of *trans*-$[Mo(p\text{-}CNC_6H_4Cl)_2(DPPE)_2]$ is similar to that of *trans*-$[Mo(CNMe)_2(DPPE)_2]$[32] in that both the Mo atom and four P atoms of DPPE share a plane and eight benzene rings of DPPE make rails with ~5Å diameter hole. The Mo-P bond lengths are the same, 2.441Å in both complexes, while the Mo-C bond length (1.97(1)Å) of *trans*-[Mo(*p*-$CNC_6H_4Cl)_2(DPPE)_2$] is shorter than in *trans*-[Mo$(CNMe)_2(DPPE)_2$] (2.101(7)Å) or Mo$(CO)_6$ (2.06Å), and nearly the same as in *trans*-[Mo(CO)$(N_2)(DPPE)_2$][33] (1.97(2)Å) suggesting that *p*-isocyanochlorobenzene is as strong a π-acceptor in this compound as is carbon monoxide. Thus, the electron-rich Mo$(DPPE)_2$ site releases electron density into the π–antibonding orbitals of isocyanides so strongly that they attain a 'carbene-like' character, resulting in a particularly low C-N frequency and a fairly short Mo-C distance.

An interesting feature of the structure is that the C-N-Arene angle is 167.(1)^{o}, smaller than the ideal 180^{o} angle expected for sp hybidized carbon, but larger than the angle observed in *trans*-[Mo$(CNMe)_2(DPPE)_2$] (156(1)^{o}). In valence bond theory the canonical forms involved in metal isocyanide bonds are[34]



The bend of isocyanide ligands in complexes means that a substantial contribution to the electronic structure is made by the bent canonical form B. However the contribution of form B in this complex is relatively smaller due to conjugation of CN group and aryl ring (form C).

In both structures of [(η^5-C_5H_5)Fe$(CO)_2$(p-CNC_6H_4Cl)]PF_6 and *trans*-[Mo(*p*-$CNC_6H_4Cl)_2(DPPE)_2$], the anisotropic thermal parameter of the Cl atom shows that its movement on the arene plane is larger than along the perpendicular direction. It seems that the Cl atom is confined on a plane by the π conjugation of arene and Cl atom.

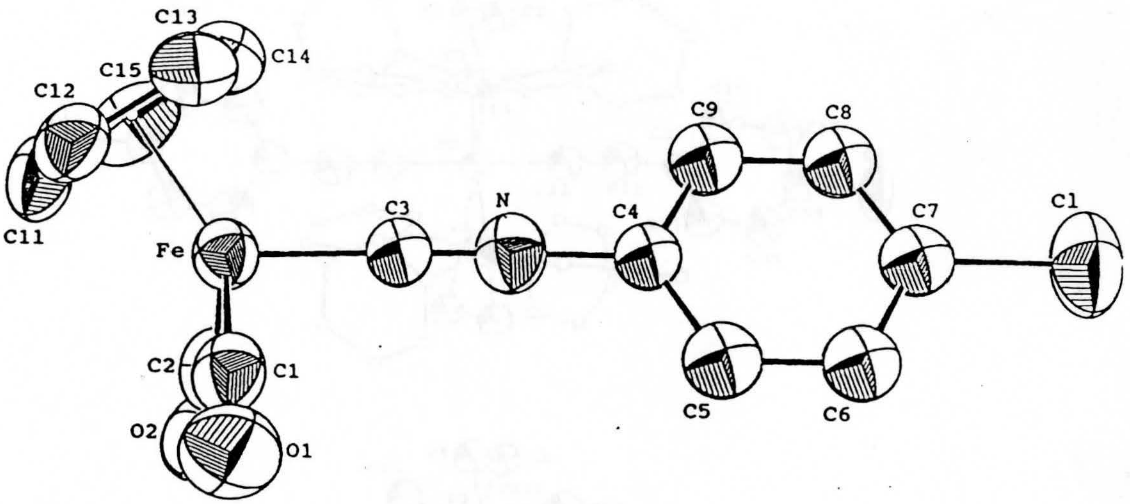


FIGURE 6. ORTEP plot for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(p\text{-}CNC_6H_4Cl)]^+$

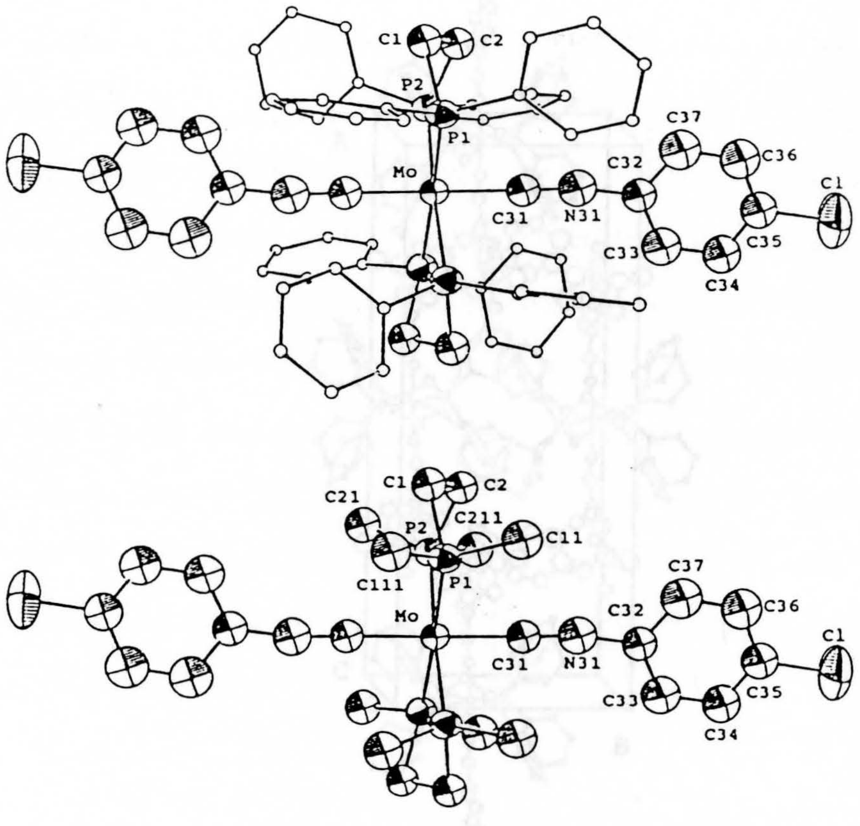


FIGURE 7. The molecular structure and atom-numbering system of *trans*-[Mo(*p*-$CNC_6H_4Cl)_2$(DPPE$)_2$]

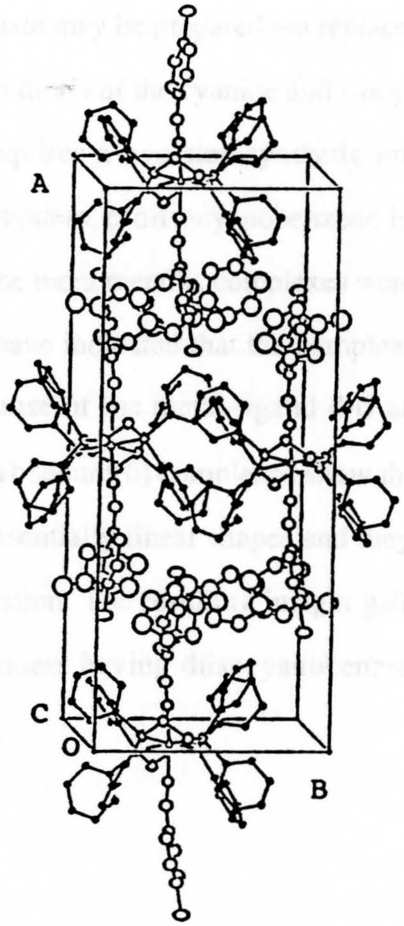


FIGURE 8. Molecular packing for trans-[Mo(p-CNC$_6$H$_4$Cl)$_2$(DPPE)$_2$]·2CH$_3$C$_6$H$_5$

CHAPTER IV

CONCLUSIONS

In this study, we have prepared a series of mono-and bimetallic compounds containing cyano- and isocyanoarene ligands. Both molybdenum complexes with zero oxidation state and iron complexes having a +2 oxidation state may be prepared via replacement of the weakly coordinated neutral ligands. Specifically, the synthesis of the cyanide and isocyanide compounds having a high oxidation state metal generally requires a two-step synthetic procedure involving the solvent-coordinated intermediates. In this system, *p*-diisocyanobenzene is such a strongly bidente ligand that no terminal *p*-diisocyanobenzene monometallic complexes were obtained.

The spectroscopic studies have indicated that the complexes are well conjugated with the aryl rings on the isocyanides because of the metal-ligand d-σ and d-π interactions. The X-ray structures of both iron(II) and molybdenum(0) complexes show that isocyanide groups terminally coordinate to metal centers with essentially linear shapes and they have short M-C distances and long C-N bonds due to the conjugation. The resulting insight gained in this study will allow the synthesis of organometallic polymers having diisocyanobenzene bridges as one-dimentional conductors and semiconductors.

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PART TWO

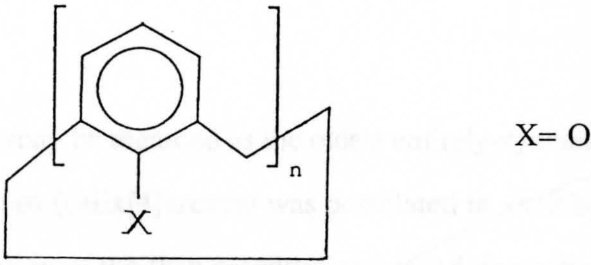
1,3,5-Trimethylcalix[4]arene and Its Chromium and Molybdenum Dirivatives

CHAPTER I

INTRODUCTION

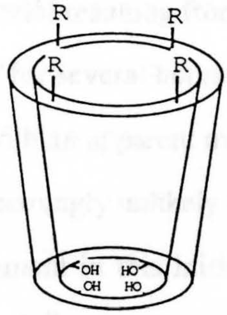
In recent years, scientists in the field of macrocyclic chemistry have produced novel compounds that show remarkably selective chemical behavior. Macrocycles provide especially good bases for the development of reagents having selectivity for ions and molecules and for reagents that can modify the chemical properties of the complexed species. These macrocycles are of particular interest to the scientists involved in molecular design because they provide one with both ions and molecules with enzyme-like properties. An excellent example of these macrocycles is calixarenes.

The calixarenes are defined to include all molecules containing a $[1_n]$ metacyclophane framework, as depicted by structure **1**.



Structure 1. $[1_n]$ metacyclophane

They are generally formed by the condensation of phenols with formaldehyde at elevated temperatures. By changing the reaction conditions and workup procedures, calixarenes may be readily isolated on a kg scale. Calixarenes have very complicated stereochemical behavior with a number of conformers existing in solution in rapid equilibrium. The tetrameric species, i.e. calix[4]arenes, have the most rigid and conformationally stable structures. Their overall shape is cup like with the bottom of the cup being closed by a tight network of hydroxyl hydrogen bonds or substituted groups, i.e.



A wide variety of small molecules interact strongly with cailix[4]arenes to give new materials. The resulting host-guest complexes often display high stabilities and may exhibit significant changes in structures and properties compared to those of the uncomplexed molecules. The geometries of these complexes are determined by both the steric requirements of the combining fragments and the electronic requirements of the host-guest interactions. Such steric and electronic interactions give the guest molecules in such complexes unusual physical, structural, and chemical features.

1. History

Phenol-formaldehyde resins may be regarded as the oldest entirely-synthetic polymers. The existence of [1,1,1,1]metacyclophanes (calix[4]arenes) was postulated in 1912 by Raschig,[1] who speculated on the possible composition of the then recently introduced commercial plastic called Bakelite. This hard, resinous solid, obtained by the reaction of formaldehyde with phenyl under fairly strenuous conditions, was discovered and exploited by Leo Baekeland.[2] Raschig suggested that the approximately 1:1 ratio of methylene and phenol moieties in Bakelite could be explained in terms of a tetracyclic structure . There is now no doubt that macrocycles can be obtained from the condensation of certain *p*-substituted phenols and formaldehyde.

The formation of macrocycles was first demonstrated by Zinke and Ziegler[3] in 1941 during their investigation of the 'curing' phase of the bakelite process, viz., the step in which the initially formed phenol-formaldehyde condensate is heated to produce the final resin. They treated *p-tert*-butylphenol with aqueous formaldehyde and sodium hydroxide, first at 50-55°C and then 110-120°C for 2 hours. The friable material resulting from this treatment was finely ground, suspended in linseed oil, and heated at 200°C for several hours to produce a substance melting above 340°C and yielding an acetyl derivative with an apparent molecular weight of 1725. Presumably because this high value would require the seemingly unlikely presence of eight aromatic moietes, Zinke and Ziegler made no structural assignment in this initial publication. Instead, they subjected other phenols to the same procedure,[4-8] including *p*-cresol, *p-tert*-amyl phenol, *p*-(1,1,3,3-tetramethylbutyl)-phenol, *p*-cyclohexylphenol, *p*-benzylphenol, and *p*-phenylphenol and in all cases obtained very refractory, high melting materials. Disregarding the earlier molecular weight determination on the acetyl derivative of the product from *p-tert*-butylphenol and instead using the molecular weight value of 873 obtained for the acetyl derivative of the product from p-tert-octylphenol, Zinke assigned cyclic tetrameric structures to all of these materials and tacitly assumed them to be pure entities. Only subsequently, as a result of the work of Cornforth and coworkers[9] and the more recent work of Gutsche and coworkers[10-13] has it been realized that the Zinke reaction yields a mixture of products and that the size of the macrocycle that is formed is a function of the reaction conditions that are employed.

The nonplanar character of the cyclic tetramers that were thought to be produced by the Zinke reaction was pointed out by Megson,[14] Ott and Zinke,[15] and Cornforth and coworkers[9] in the early 1950's. In the late 1970's, Gutsche and Muthukrishnan[16] perceived a similarity between the shape of a Greek vase called a Calix Crater and a space-filling model of the nonplanar form of the Zinke cyclic tetramer in which all of the aryl moieties are oriented in the same direction. They assigned the name calixarene to these complexes (calix, Greek for "vase'; arene, specifying the incorporation of aryl residues in the macrocylic shape). Although this name quite accurately portrays the shape of the cyclic tetramers and pentamers, it becomes less descriptive for the large macrocyclic rings. The cyclic octamer, for example, assumes an almost planar shape in the solid state. In spite of its pictorial limitations, however, the term calixarene has become widely accepted.

2. Synthesis and chemical modifications

Phenol derived calixarenes are usually prepared by the condensation of phenols and formaldehyde either as an aqueous solution or as paraformaldehyde under alkaline conditions in polar solutions.

$$R\text{-}C_6H_4\text{-}OH + CH_2O \xrightarrow{\text{NaOH or KOH}} \text{-}[R\text{-}C_6H_2CH_2]\text{-}_n \qquad n=4,6,8$$

The cyclic tetra-, hexa-, or octamer can be obtained depending on variation in the reaction conditions such as the amount of catalyst, reaction time and temperature. Calixarenes with an odd number of t-butylphenol units (n=5 or 7) have also been prepared by direct condensation but with low yields.

The determination of the reaction pathways that are involved in the transformation of p-substituted phenols into calixarenes provides a formidable puzzle that has been only partially solved. It is quite certain that the first events in the overall reaction involve the condensation of the phenolate anion with formaldehyde to form a hydroxymethylphenol (as shown in figure 8). Subsequent condensation of hydroxymethylphenol with the starting phenol then ensues to form linear dimers, trimers, tetramers, and so on, and this occurs via a Michael-like reaction between phenolate anions and o-quinonemethide (as shown in figure 8). The linear oligomers then condense to the cyclic tetramer.

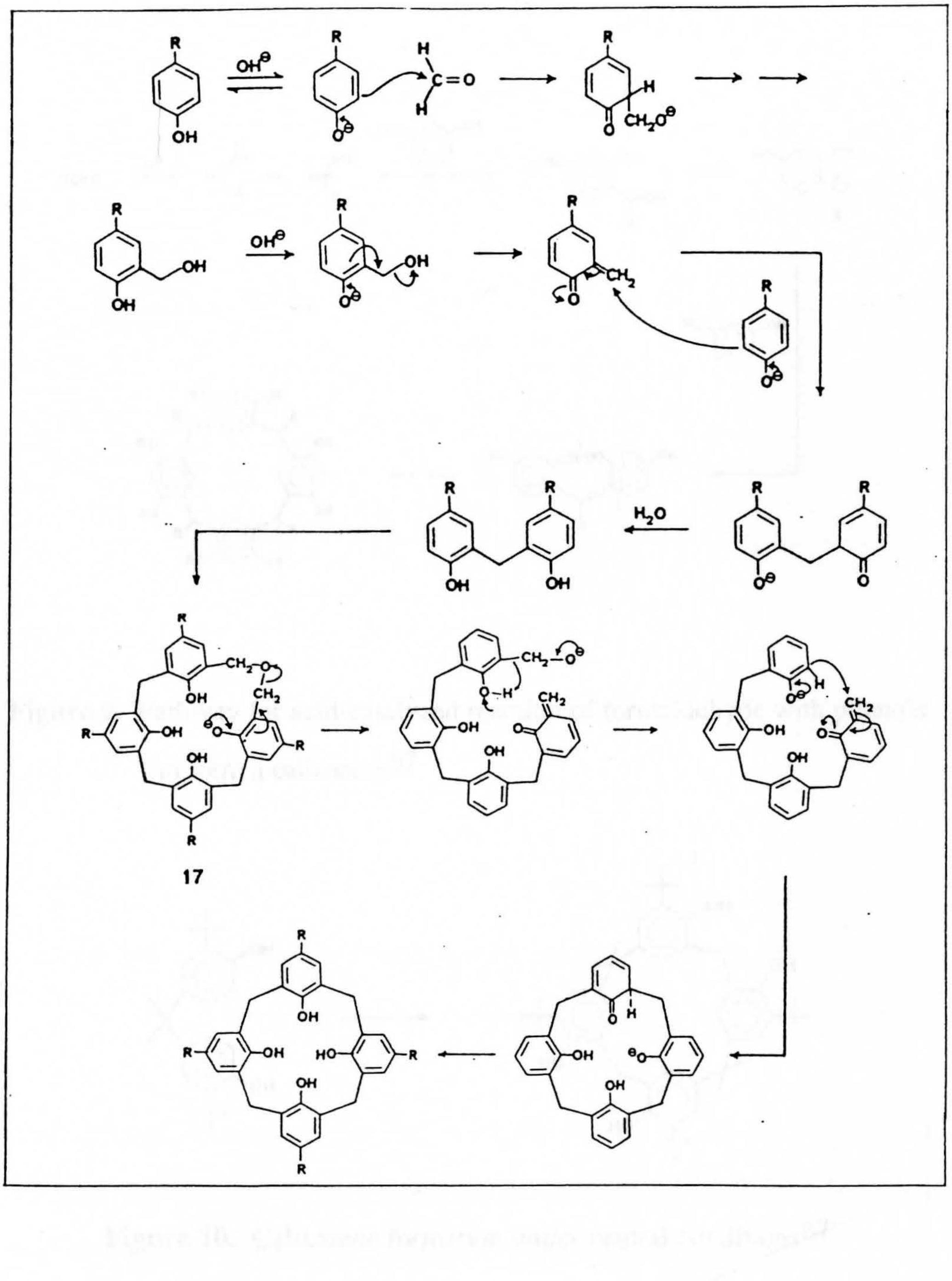


Figure 8. Base-catalyzed reaction of formaldehyde with p-substituted phenol to form a calixarene[67]

Calixarenes can also been synthesized via acid-catalyzed phenol-aldehyde condensation[17-21] or under neutral conditions.[22]

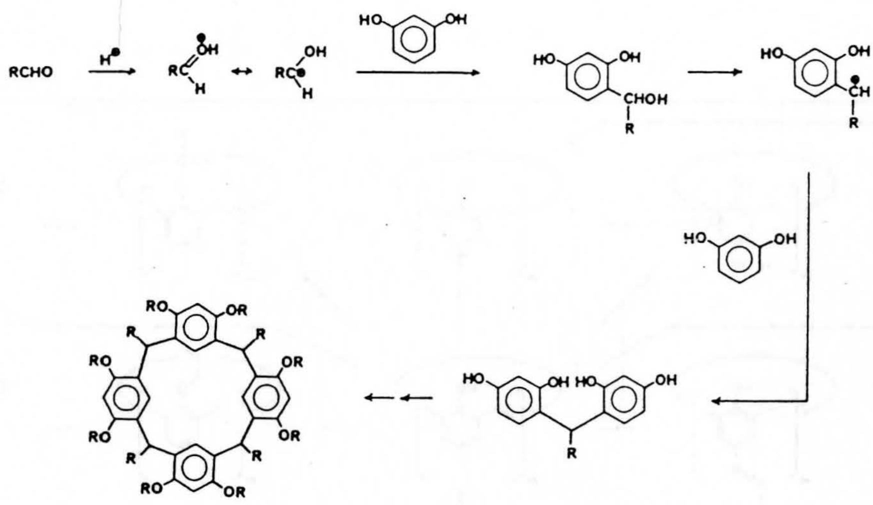


Figure 9. Pathway for acid-catalyzed reaction of formaldehyde with phenols to form a calixarene[67]

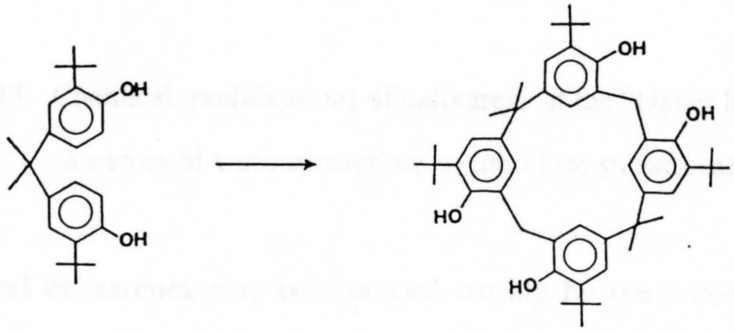


Figure 10. Calixarene formation under neutral conditions[67]

The ease of access to t-butylcalixarenes is beneficial, as the t-butyl group can be eliminated by transalkylation with AlCl3 in the presence of a suitable acceptor, e.g. toluene or phenol. This reaction plays a key role in calixarene chemistry giving nearly all types of electrophilic substituents or functional groups bind in para positions.

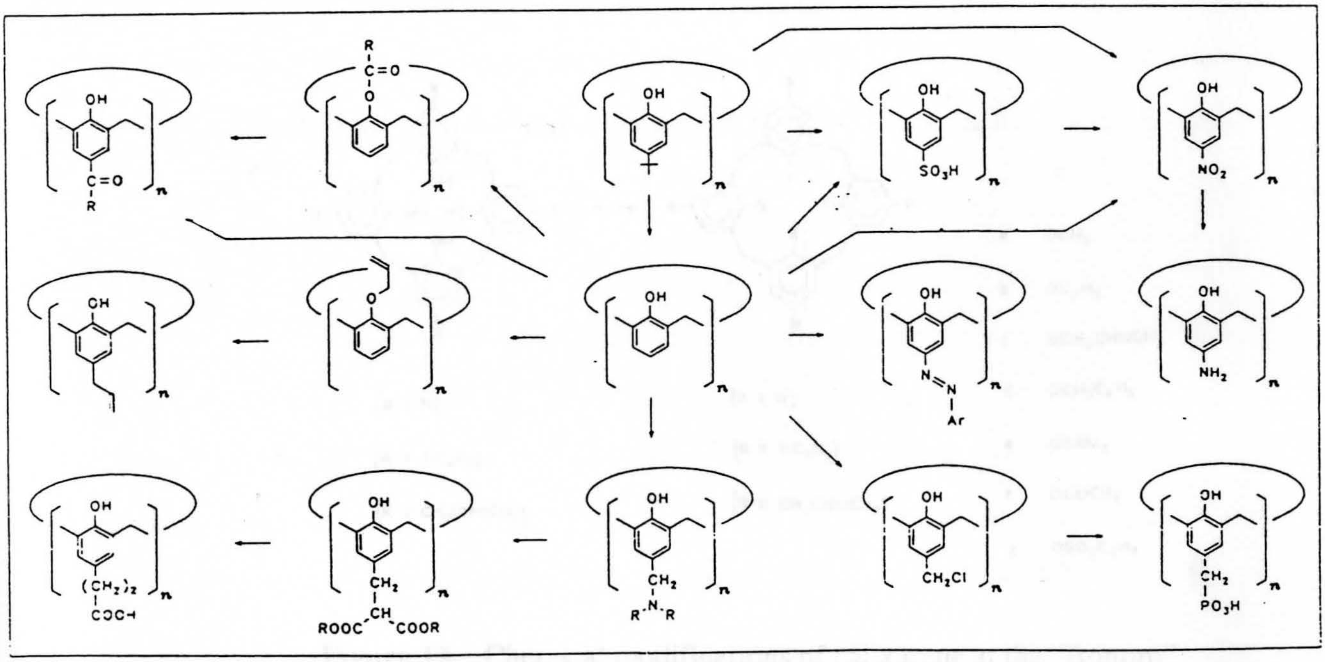


Figure 11. Chemical modifications of calixarene at the "Upper Rim"[66]
- a survey of various reactions to introduce substituents in the para position

Phenol-derived calixarenes may be modified mainly by the introduction of residues (functional groups) to the phenolic oxygens and by substitution at the para positions relative to the phenolic hydroxyl groups. This easy modification makes them superior to any other class of macrocycles, e.g. crown ethers or cyclodextrins (Figure 12). A useful method for introducing alkyl group on to the hydroxyl oxygens of the calixarenes involves treatment of the calixarene with an alkyl halide in THF/DMF solution in the presence of sodium hydride. Methyl, ethyl, allyl, and benzyl ethers have all been prepared in high yields by this method (Figure 12, structure a-d).[23] A series of polyalkyloxy ethers have been synthesized by treatment of the tosylate of the alkylating agent in the presence of potassium tert-butoxide.[24] Partial alkylation is observed when less reactive alkylation conditions have been employed.[23] When an excess of acylating agent is used, all of the hydroxyl groups are generally converted to ester groups.[25]

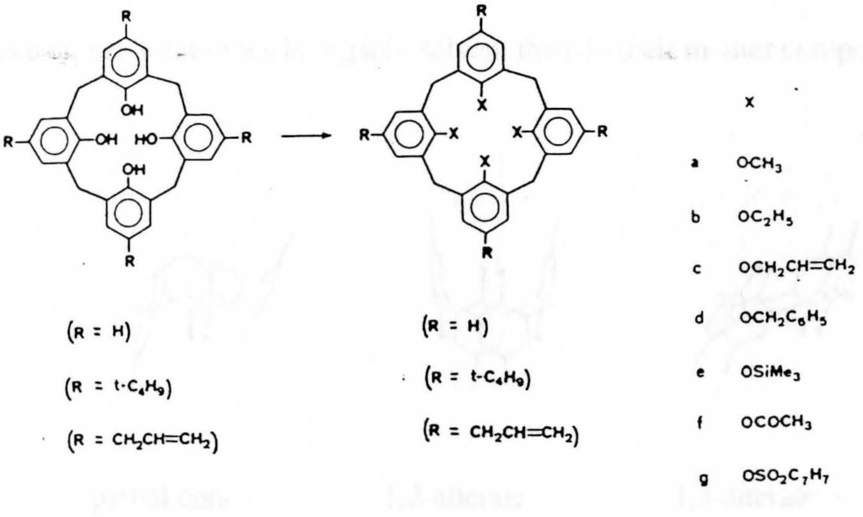


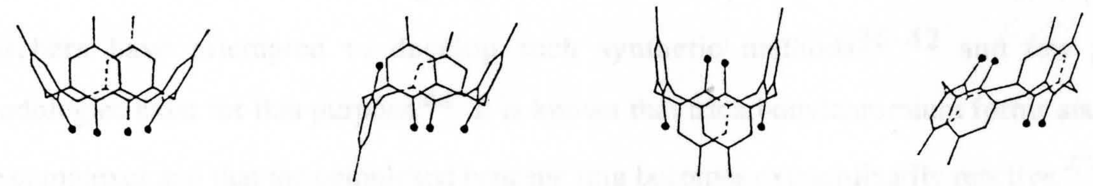
Figure 12. Chemical modifications of calixarene at the "Bottom" - introduction of substituents on hydroxyl groups

Further potentially important modifications of the calixarene skeleton include the oxidation of phenolic units to p-quinone[26] which can subsequently undergo addition reactions or reduction to hydroquinone, and the elimination of OH groups [27,28] or their replacement by NH_2 groups[29] or SH groups.[28,30]

3. Physical and conformational properties

A distinguishing feature of the calixarenes is their unusually high melting points. All calixarenes reported have melting points above 200°C. For instance, p-tert-butylcalix[4]arene melts at 345°C, p-tert-butylcalix[6]arene melts at 380°C, and p-tert-butylcalix[8]arene melts at 401°C. But calixarene esters and ethers have lower melting points. For example, tetramethyl ether of p-tert-butylcalix[4]arene melts at 227°C and tetrabenzyl ether of p-tert-butylcalix[4]arene melts at 230°C. Calixarenes are particularly stable compounds. The compounds *p*-tert-Butylcalix[4]arene and *p*-tert-butylcalix[8]arene are found to be negative for mutagenicity by toxicity test.[31]

Although calixarenes have low solubilities in organic solvents, most of them have sufficient solubility in chloroform, pyridine, or carbn disulfide to allow spectroscopic determination of their structures. Functionalization of calixarenes can alter solubilities. Thus, the esters and ethers of calixarenes generally have higher solubilities in organic solvent than do their mother compounds.



cone partial cone 1,2-alterate 1,3-alterate

Figure 13. The four basic conformations of calix[4]arenes[66]

One of the most appealing features of calixarenes is their three-dimensional structure. Molecular models show that the smaller rings cannot be planar. By rotation of the phenolic units around the Ar-CH$_2$-Ar bonds, four principal conformations can be distinguished for a calix[4]arene (Figure 13). It is well established that calix[4]arenes normally assume the 'cone' conformation. All hydroxyl groups are at the same side of the molecule. This has been shown in the crystalline state by single crystal X-ray analysis for numerous examples.[32]

In solution, the cone conformation follows unambiguously from the ^{1}HNMR spectrum, which shows, for t-butylcalix[4]arene, one singlet for OH, Ar-H and t-butyl protons. At low temperature, the Ar-CH_2-Ar protons appear as a pair of doublets (geminal coupling), indicating that all four methylene groups are equivalent, but the two protons of each methylene groups are different (diastereotopic). With increasing temperature, these signals broaden, then coalesce and finally become a sharp singlet, as a rapid interconversion of opposite cone conformation on the NMR timescale.

As calix[4]arenes have a cavity-shaped architecture, they are useful as building-blocks to design host-guest-type catalysts through appropriate modification of the rind edges.[33-35]

4. Organotransition metal calixarenes

To design functionalized calixarenes, it is essential to develop methods for the selective introduction of desired functional groups on the desired benzene unit. In fact, only a few researchers have attempted to develop such synthetic methods[36-42] and few general methodologies exist for this purpose.[44] It is known that tricarbonylchromium forms stable η^6-arene complexes and that the complexed benzene ring becomes extraordinarily reactive.[43-46] It is expected that the functional group would be selectively introduced onto the benzene unit which was activated through complexation with $Cr(CO)_3$ or $Mo(CO)_3$.

Organometallic compounds exhibit extensive reactivity toward a large variety of reagents. Many molecules become more susceptible to nucleophilic attack upon coordination to a metal atom. The $Cr(CO)_3$ metal moiety withdraws considerable π-electron density from the arene molecule. For this reason, (η^6-arene)$Cr(CO)_3$ complexes undergo facile nucleophilic attack. Coordinated arenes are very susceptible to nucleophilic attack by a wide variety of nucleophiles. Thus, a variety of arene derivatives can be obtained by nucleophilic reaction.

The η^6-chlorobenzene complex is converted to an η^6-anisole complex when treated with methoxide ion as shown below

$$(C_6H_5Cl)Cr(CO)_3 \xrightarrow{NaOMe/MeOH} (C_6H_5Me)Cr(CO)_3$$

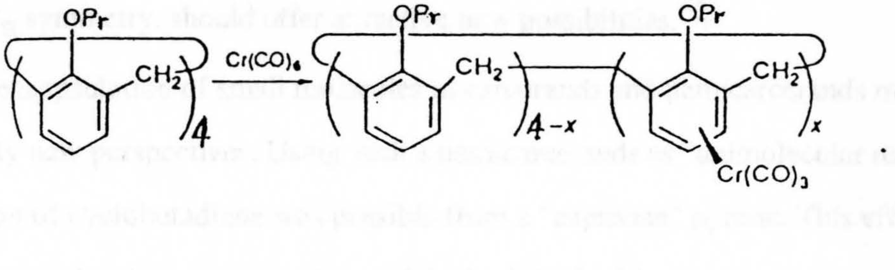
The rate of this substitution reaction is comparable to that for chloride displacement from uncomplexed p-nitrochlorobenzene. When a more reactive carbonion, like n-butyllithium, is used, a metallation reaction is observed. Oxidation of the metallation product by I_2 affords iodobenzene.

$$(C_6H_6)Cr(CO)_3 + \text{n-butylLi} \longrightarrow (C_6H_5Li)Cr(CO)_3 + \text{butane}$$

$$(C_6H_5Li)Cr(CO)_3 + I_2 \longrightarrow C_6H_5I + LiI$$

The $Cr(CO)_3$ group also has the effect of making the ring and benzylic protons more acidic than in the free arene. The ring protons are more acidic due to inductive stabilisation of the aryl anion by the $Cr(CO)_3$ group whereas the benzylic protons are more acidic due to resonance stablisation of the benzyl anion. The acidity of the ring protons is increased more than the acidity of the benzylic protons. The direct metallation of (benzene)$Cr(CO)_3$ proceeds in low yield unless the conditions are carfully controlled.[48]

Iki and coworkers have reported their work on the synthesis of calix[4]arene-chromiumtricarbonyl for the first time.[49,50] They synthesized the 1:1, 1:2, 1:3, and 1:4 arenechromiumtricarbonyl complexes by increasing the ratio of $Cr(CO)_6$ against tetrapropoxycalix[4]arene:



5. Applications

Ion-sensitive electrodes and ion-sensitive field-effect transistors for Na^+, K^+, and Cs^+ have been described,[51,32] and the incorporation of heteroatom donor groups (containing S or N functions) has led to sensors for heavy and transition metals (Ag^+, Cu^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}).[52] Various chromogenic,[53] fluorogenic,[54] and 'light-switchable'[55] ionophores will open further possibilities. Resorcinol-based calixarenes show strong and specific interactions via hydrogen bonding with certain sugars. This interaction may lead to specific sensors.[56]

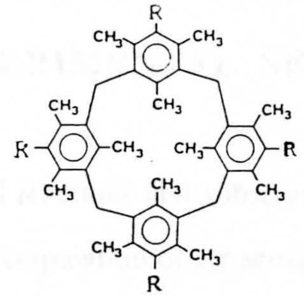
Strong and specific complexation reactions can be used to extract Uranium ($UO_2{}^{2+}$) from seawater,[32] to remove $CHCl_3$ from drinking water, or to form stable complexes for diagnostic or other medical application.[57]

New liquid crystalline materials have been obtained from tungsten-capped calix[4]arene.[58] The p-nitro derivatives of calixarene ethers show nonlinear optical properties useful for frequency doubling of laser light.[59] They may be ordered within polymer matrices by strong electric fields or by the Langmuir-Blodgett method.[60] The latter technique has also been used to produce "perforated" monolayers leading to membranes with permeabilities defined on the molecular level ("molecular sieving").[61]

The nonplanar structure of calixarene enables the construction of various new host-molecules with inherent chirality, a field still in its infancy. Dissymmetric molecules, especially those with C_n symmetry, should offer attractive new possibilities.[62]

The encapsulation of small molecules in carcerands and hemicarcerands mentioned above opens entirely new perspectives. Using such a hemicarcerands as "unimolecular reaction vessels", the generation of cyclobutadiene was possible from a "captivate" pyrone. This effective isolation prevented intermolecular reactions (dimerization) of this highly reactive species and permitted its controlled reaction with oxygen to give maleic dildehyde.[63]

Although phenol derived calixarenes have been extensively studied in recent years, few methylcalixarene were reported.[64]



These type of calixarenes may be obtained only by Lewis acid mediated oligimerization. In this work we study the synthesis of 1,3,5-trimethylcalix[4]arene and its chromium and molybdenum derivatives in order to obtain a new class of substituted calixarene by introducing functional groups on arene rings.

CHAPTER III

EXPERIMENTAL SECTION

Unless otherwise noted, all reactions and subsequent manipulations were performed by conventional techniques for the manipulation of air-sensitive compounds as in Part One. Thus, anaerobic and anhydrous conditions were maintained by using vacuum-line and inert-atmosphere techniques.[65]

1. Reagents

The reagents used were purchased from commercial suppliers. The chemicals used were of reagent grade or comparable purity, and were not purified before use. Solvents used were dried and deaerated by standard procedures and stored under purified N_2. Thus Bu_2O and CH_2Cl_2 were distilled over CaH_2 and THF and dioxane were distilled over Na. Unless specified otherwise, the reactions and any subsequent manipulations described below were carried out under a nitrogen atmosphere.

2. Apparatus

Infrared spectra were recorded on a Perkin Elmer Model 1600 infrared spectrophotometer calibrated with the 1601 cm^{-1} band of polystyrene. ^{1}H NMR (60 MHz) spectra were recorded on a Varian EM-360 spectrometer. The chemical shifts are reported in parts per million downfield from internal Me_4Si.

3. 1,3,5-Trimethylcalix[4]arene

Solid 98% α^2-chloroisodurene (1.7 g, 10 mmol) was placed in a 3-necked round-bottom flask (100 ml), the flask was evacuated, and then purified nitrogen was added. Dried dichloromethane (20 ml) was added to give a clear solution. Tintetachloride (1.2 ml, 10 mmol) was added dropwise using a syringe. The white-pink mixture was stirred at room temperature (~23^{o}C) for 10 minutes and then it was heated to reflux for another 2 hours while the mixture turned white. After it had cooled to room temperature, the white product, 1,3,5-trimethylcalix[4]arene (1.0 g, 0.77 mmol, 77%), was collected by suction filtration, washed by cold dichloromethane (50 ml), and dried under vacuo for two days. m.p.>410^{o}C. ^{1}HNMR (CD_3Cl) 1.18 (s, 3H), 2.36(s, 6H), 3.90(s, 2H), 6.85(s, 1H).

4. (η^{6}-1,3,5-Trimethylcalix[4]arene)chromiumtricarbonyl

1,3,5-Trimethylcalix[4]arene (0.14 g, 0.26 mmol) was dissolved in hot p-dioxane (40 ml, ~50^{o}C) and chromiumhexacarbonyl (0.11 g, 0.50 mmol) was added. The solution was heated to reflux (~98^{o}C) for 5 hours. The yellow-green solution was filtered and the solvent was removed by rotary evaporation. The solid products were dried in vacuo for 2 days yielding 0.09 g of a green-yellow solid product, (η^{6}-1,3,5-Trimethylcalix[4]arene)chromiumtricarbonyl (0.09 g, 0.14 mmol, 54%). ^{1}HMNR (CD_3Cl) 1.16 (s, CH_3), 2.36(s, 2CH_3), 3.73(s,CH_2), 3.90(s, CH_2), 5.06(b, ArH), 6.80(s, ArH). IR (KBr) ν_{CO} 1869(s), 1950(s) cm^{-1}.

5. (η^{6}-1,3,5-Trimethylcalix[4]arene)molybdenumtribarbonyl

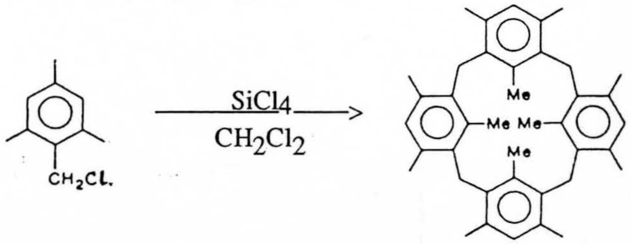
1,3,5-Trimethylcalix[4]arene (0.26 g, 0.49 mmol) was dissolved in a hot p-dioxane (~50^{o}C) and molybdenumhexacarbonyl (0.26 g, 0.98 mmol) was added. The solution was heated to reflux (50 ml) for 5 hours. The dark-yellow solution was filtered and the solvent was removed by rotary evaporation. The yellow solid products were dried in vacuo for 2 days yielding a yellow solid product (η^{6}-1,3,5-Trimethylcalix[4]arene)molybdenumtribarbonyl (0.18 g, 0.25 mmol, 51%). ^{1}HMNR (CD_3Cl) 1.18 (s, CH_3), 2.36(s, 2CH_3), 3.70(s,CH_2), 3.90(s, CH_2), 5.03(b, ArH), 6.70(s, ArH). IR (KBr) ν_{CO} 1884(s), 1961(s) cm^{-1}.

CHAPTER IV

RESULTS AND DISCUSSIONS

1.Synthesis of the compounds

1,3,5-Trimethylcalix[4]arene may be prepared by an aluminum chloride-catalyzed reaction. For my work, tintetrachloride was used as an alternate Lewis acid catalyst.



As soon as tintetrachloride was added to chloroisodurene solution, the solution turned red because of the complexation of tintetrachloride and chloroisodurene. A white-pink precipitate formed in a few minutes and finally it turned to white indicating the end of the reaction. Since both of starting materials are soluble and the product is insoluble in dichloromethane, the separation was easy.

A variety of (η^6-arene)M(CO)$_3$ complexes have been synthesized and studied. The complexation reaction must be carried out under appropriate conditions. The reaction temperature should be high to complete the reaction, on the other hand, it should be kept as low as possible to avoid decomposition of the complex. Thus, it is important to select a solvent or mixture of solvents which have an appropriate boiling point. In the preparation of (η^6-1,3,5-trimethylcalix[4]arene)chromiumtricarbonyl and (η^6-1,3,5-trimethylcalix[4]arene)molybdeniumtricarbonyl, we found that *p*-dioxane is a suitable solvent. It boils around 98^{o}C and dissolves 1,3,5-trimethylcalix[4]arene. A commonly used mixed solvent, Bu$_2$O/THF, 9:1 v/v, was tried in these preparations and gave long reaction times and low yields due to insolubility of the calixarene and decomposition of the product, respectively. Comparing the reactions of the calixarene with both Cr(CO)$_6$ and Mo(CO)$_6$, the latter is faster. When Mo(CO)$_6$

was added to calixarene solution, the solution turned yellow in a few minutes, while for addition of $Cr(CO)_6$, it took one hour for a color chang.

2.Spectroscopic characterization of the compounds

^{1}H NMR spectrum of 1,3,5-trimethylcalix[4]arene shows four singlets for the aryl hydrogens, the methyl hydrogens, and methylene hydrogens (Figure 14). The chemical shifts are assigned as 1.18 for "bottom" methyl hydrogens, 2.36 for "upper rim" methyl hydrogens, 3.90 for methylene hydrogens, and 6.85 aryl hydrogens.

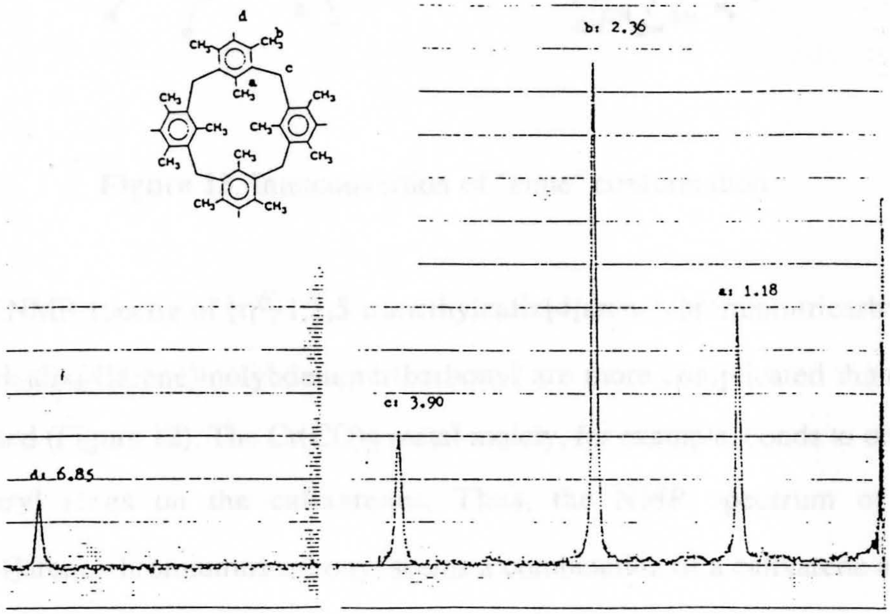


Figure 14. ^{1}H NMR spectrum of 1,3,5-Trimethylcalix[4]arene

As mentioned in Chapter I, the calix[4]arenes have four possible conformations, i.e. cone, partial cone, 1,2-alternate, and 1,3-alternate. The spectrum can be best interpreted in terms of a "cone" conformation. For methylene hydrogens in a "cone" conformation there are two kinds of hydrogens. These resonances are different and should give rise to two doublets. However, the spectum shows only one resonance at 3.90 ppm. This can be interpreted in terms of "cone" conformation that is interconverting rapidly on the NMR time scale at room temperature (Figure 15). It also shows that the product is a cyclic compound and no linear polymer forms.

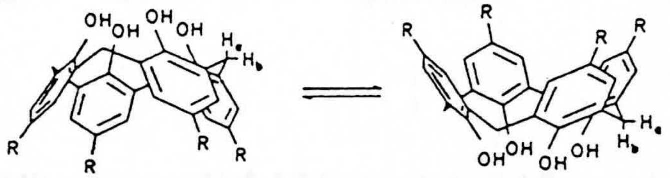


Figure 15. Interconvertion of "cone" conformation

The ^{1}H NMR spectra of (η^6-1,3,5-trimethylcalix[4]arene)chromiumtricarbonyl and (η^6-1,3,5-Trimethylcalix[4]arene)molybdenumtribarbonyl are more complicated than that of their mother compound (Figure 12). The $Cr(CO)_3$ metal moiety, for example, bonds to only one or two of the four aryl rings on the calixarenes. Thus, the NMR spectrum of (η^6-1,3,5-trimethylcalix[4]arene)chromiumtricarbonyl seems a combination of a calixarene and chromium derivative. The four resonances, i.e. at 1.18, 2.36, 3.90, 6.85 ppm, remain and two new peaks appear at 3.73 and 5.06 ppm positions. These two peaks can be assigned as the shifts of methylene hydrogens and aryl hydrogens due to the $Cr(CO)_3$ complexation. It seems consistant with the expected effects of the $Cr(CO)_3$ unit on the ring and benzylic protons. The acidity of the ring protons is increased more than the acidity of the benzylic protons by the $M(CO)_3$ complexation. The chemical shifts of the ring hydrogens and benzylic (methylene) hydrogens are

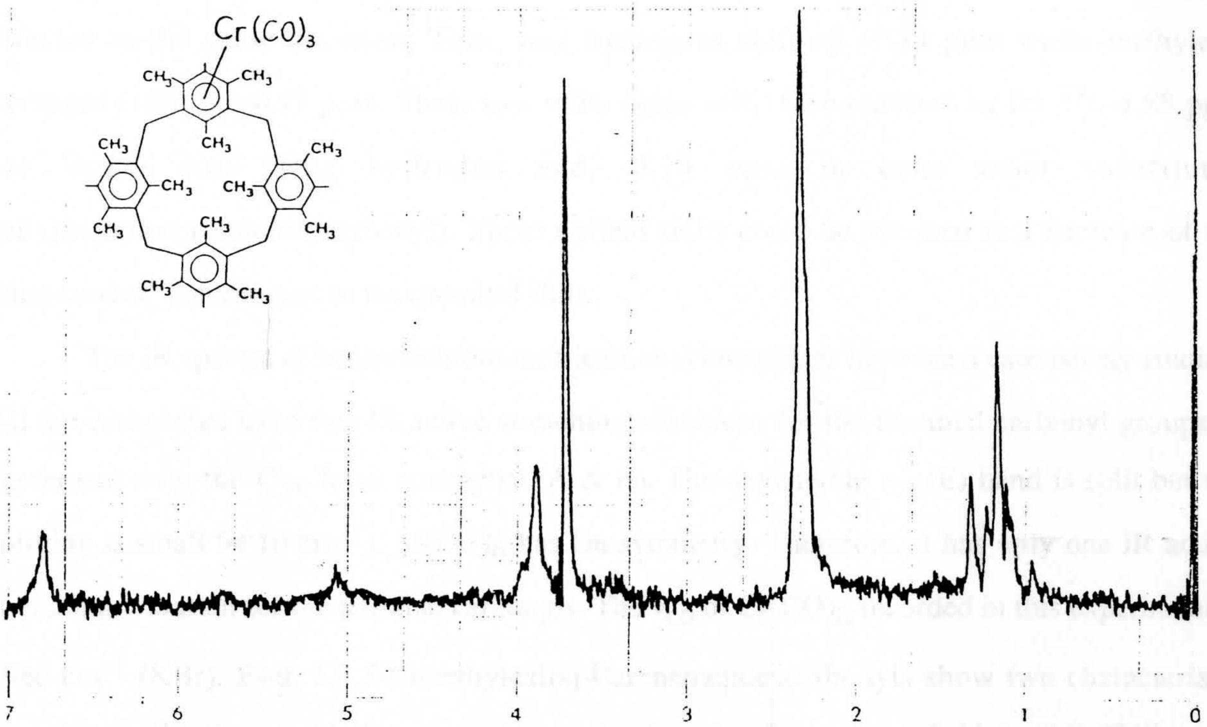


Figure 16. ^{1}HNMR spectrum of (η^6-1,3,5-trimethylcalix[4]arene)chromiumtricarbonyl

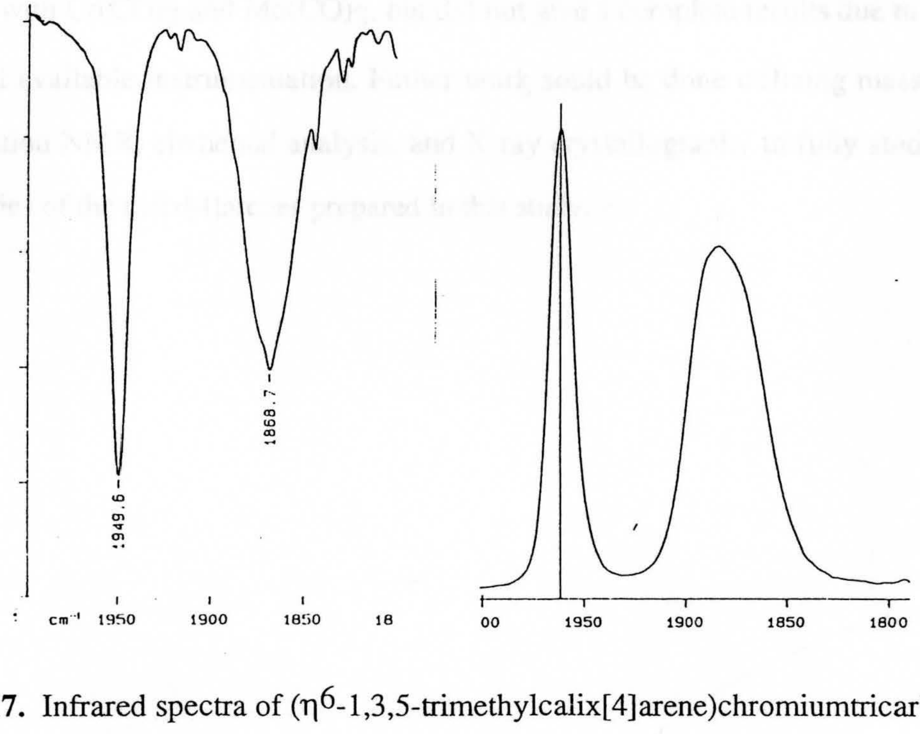


Figure 17. Infrared spectra of (η^6-1,3,5-trimethylcalix[4]arene)chromiumtricarbonyl and (η^6-1,3,5-Trimethylcalix[4]arene)molybdenumtricarbonyl

effected in the same direction. Thus, ring hydrogens shift by -1.74 ppm while methylene hydrogens shift by -0.17 ppm. These two shifts agree with those reported by Iki [37](-1.88 ppm for 'upper rim" ring hydrogen and -0.14 ppm in cone ether substituted calix[4]arenechromiumtricarbonyl). These upfield shifts could be ascribed to a decrease of the "ring current" contribution to the chemical shift.

The IR spectra of benzenechromiumtricarbonyl complexes have been extensively studied. All the complexes have two IR active stretching vibrations for the terminal carbonyl groups in agreement with the C_{3v} local symmetry (A & E). The degenerate $\nu_{CO}(E)$ band is split but the splitting is small (< 10 cm^{-1}). $M(CO)_6$ has Oh symmetry. Therefore, it has only one IR active stretching vibration for the terminal carbonyls. The ν_{CO} of $Cr(CO)_6$ recorded in this experiment is 1980 cm^{-1} (KBr). Both 1,3,5-trimethylcalix[4]arenemetaltricarbonyls show two characteristic stretching vibrations with low energies indicating the formation of (Arene)$Cr(CO)_3$ and (Arene)$Mo(CO)_3$ complexes (Figure 17).

The present work partialy demonstrats that 1,3,5-trimethylcalix[4]arenes can form stable complexes with $Cr(CO)_3$ and $Mo(CO)_3$, but did not give a complete results due to the limitations of time and available instrumentation. Futher work sould be done utilizing mass spectroscopy, high resolution NMR, elemental analysis, and X-ray crystallography to fully study the structure and properties of the calix[4]arenes prepared in this study.

CHAPTER V

CONCLUSIONS

1,3,5-Trimethylcalix[4]arene may be prepared by a tintetrachloride-catalyzed reaction of 2-chloromethyl-1,3,5-trimethylbenzene. This simple reaction proceeds in high yield. (η^6-1,3,5-trimethylcalix[4]arene)chromiumtricarbonyl and (η^6-1,3,5-trimethylcalix[4]arene)molybdenumtribarbonyl are synthesized by the reaction of 1,3,5-trimethylcalix[4]arene with the appropriate metal hexacarbonyl in refluxing dioxane. They have been partialy characterized by spectroscopic techniques and are shown to contain Cr- or Mo-arene π bonds. The yields need to be improved and more spectroscopic work must be done to confirm the proposed structures.

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