Synthesis and Characterization of Zero and First Generation Organometallic Nanorods

by

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Abstract

There is substantial interest in new materials exhibiting one, two, and three-dimensional structures that are patterned on the nanoscale. Such organometallic materials have potential use in electronics, photonics, and nonlinear optical applications. The complexes discussed in this thesis were designed to have thermally and chemically stable repeating units such as [*trans*-$Mo(Ph_2PCH_2CH_2PPh_2)_2(\mu\text{-CN-1,4-}C_6H_4\text{-NC})$]. Isonitrile-bridged species have valuable features such that there is substantial conjugation down the oligomer backbone and because they form strong complexes with rationally tunable bonding characteristics. The aromatic isonitriles were prepared by reacting the aromatic amines with formic acid and then dehydrating the resulting formamides with trichloromethylchloroformate. The phosphine ancillary ligands were prepared by Grignard reactions and allow the nanorod's steric and electronic properties to be varied independently of one another. The phosphine ligands were reacted in the presence of $MoCl_5$ to form the desired dinitrogen complexes. The monomers and oligomers were prepared by condensation reactions between the un-complexed bifunctional isonitriles and $Mo(PR_3)_4(N_2)_2$ moieties. After synthesizing the nanorods of the desired length, they were capped on each end using the terminal organometallic groups such as, $Cr(CO)_5$ and $CpFe(CO)_2^+$.

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List of Abbreviations

a	Length of unit cell (as in X-ray diffraction)
Å	Angstrom
Ar	Substituted aryl group
b	Length of unit cell (as in X-ray diffraction)
β	Beta angle (as in X-ray diffraction)
c	Length of unit cell (as in X-ray diffraction)
°C	Degrees Celsius
C_6D_6	Benzene
$CDCl_3$	Chloroform
CH_2Cl_2	Dichloromethane
cm^{-1}	Reciprocal centimeters, wavenumbers
CO	Carbonyl ligand
"CN"	Coordination number
CNR	Isocyanide ligand
Cp	Cyclopentadienyl
d	Doublet (as in NMR spectroscopy)
δ	Chemical shift (as in NMR spectroscopy)
Δ	Heat (thermal reaction)
dd	Doublet of doublet (as in NMR spectroscopy)
dppe	1,2-bis(diphenylphosphino)ethane
Dx	Density (as in X-ray diffraction)

eq	Equivalents
Et	Ethyl
F	Structure factor refinement (as in X-ray diffraction)
Fc	Ferrocene
Fc	Calculated structure factor (as in X-ray diffraction)
Fo	Observed structure factor (as in X-ray diffraction)
FTIR	Fourier transform infrared
FW	Formula weight
g	Grams
h	Hour, Miller indices (as in X-ray diffraction)
Hz	Hertz
HOMO	Highest occupied MO
IR	Infrared (as in spectroscopy)
J	Coupling constant (as in NMR spectroscopy)
k	Miller indices (as in X-ray diffraction)
l	Miller indices (as in X-ray diffraction)
L	Ligand
LUMO	Lowest unoccupied MO
μ	Mu
M	Metal atom
m	Multiplet (as in NMR spectroscopy)
Me	Methyl
MHz	Megahertz

mL	Milliliters
mmol	Millimoles
Mn	Molecular weight
MO	Molecular orbital
Mr	Molecular weight
Mo Kα	Molybdenum K alpha (as in X-ray diffraction)
mol	Mole
MP	Melting point
η	Eta
NEt_3	Triethylamine
NLO	Nonlinear optical properties
NMR	Nuclear magnetic resonance
OMe	Methoxy
π	Bonding pi orbital
π*	Anti-bonding pi orbital
p	*Para*
ph	Phenyl
ppm	Parts per million
PR_3	Phosphine or Phosphite
R	Alkyl or aryl group
R	Discrepancy index (as in X-ray diffraction)
rt	Room temperature
σ	Bonding sigma orbital

S	Goodness of fit (as in X-ray diffraction)
s	Singlet (as in NMR spectroscopy)
T	Temperature
T*min*	Minimum transmission (as in X-ray diffraction)
T*max*	Maximum transmission (as in X-ray diffraction)
ω	Omega (*e.g.*, measurement angle used in X-ray diffraction)
θ	Theta (*e.g.*, angle between the incident and the diffracted beams as in X-ray diffraction)
θ_{max}	Theta (*e.g.*, maximum Bragg angle as in X-ray diffraction)
t	Triplet (as in NMR spectroscopy)
THF	Tetrahydrofuran
V	Cell volume (as in X-ray diffraction)
ν	Stretching frequency (as in IR spectroscopy)
ν_{as}	Asymmetric stretching frequency (as in IR spectroscopy)
ν_{sy}	Symmetric stretching frequency (as in IR spectroscopy)
in vacuo	High vacuum manifold
wR	Weighted discrepancy index (as in X-ray diffraction)
X	Alkyl or aryl group
Z	Number of molecules in unit cell (as in X-ray diffraction)

Chapter One - Introduction

Section One

1. Organometallic Structure and Bonding

Organometallic chemistry combines features of inorganic and organic chemistry. About fifty years ago, research in this area went through a renaissance driven by breakthroughs in both synthetic methods and bonding theories and began its current growth phase. Much of the interest in organometallic compounds has been due to their efficiency as catalysts for organic and polymer syntheses.[1] In turn, this efficacy stems from the seemingly infinite number of derivatives, which can be obtained by varying the ligands and metals of organometallic complexes. A transition metal organometallic compound is composed of one or more metal centers surrounded by a set of ligands. In the most basic terms, the ligands may be thought of as Lewis bases that donate pairs of electrons to the central metal atom(s), which acts as a Lewis acid(s).

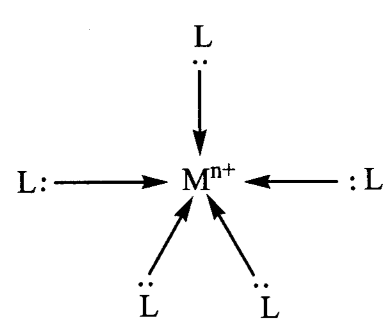


Figure 1.1.1 Metal "acting" as a Lewis acid

The relative stability of each complex is related to the valence electron count of the metal. Thus, the 18-electron rule predicts that a complex will be relatively stable if it has eighteen valence electrons associated with each metal center (*i.e.*, in the non-bonding orbitals of the metal and in the metal-ligand bonds). There are some exceptions to the rule, but metals in the middle of the transition series in low formal oxidation states generally obey the rule, (*e.g.*, the complexes that will be discussed in this thesis which contain chromium and molybdenum).[1,2]

Organometallic ligands may vary in the manner in which their valence electrons interact with the metal. For π-complexes in which unsaturated organic ligands are bonded "side on" to the metal (*e.g.*, olefins and aromatics), one or more π-bonds on the ligand may donate electrons to one or more metal atoms. The hapticity of the ligand (*i.e.*, its η^n number) is defined as the number of atoms that are within bonding distance of the metal atom. The total number and the nature of the ligands that are coordinated to a metal center determine its coordination number, CN. The number of coordination positions that a ligand occupies typically is equal to the number of electron pairs donated to the metal. While metal oxidation states and formal charges assigned to ligands do not accurately reflect the net electron charges in the complexes, they are useful bookkeeping tools and so are still widely used. Different ligands may vary in formal charge, the number of electrons that may be donated to the metal atom, and the number of coordination positions around the metal as shown in **Table 1.1.1**.[2]

Table 1.1.1 Structure and bonding properties of some commonly encountered ligands

Ligand	**Formal Charge(s)**	**Electrons Donated**	**Coordination Positions**
acyl	-1	2	1
η^2-alkene	0	2	1
alkyl	-1	2	1
alkylidene	-2	4	1
alkylidyne	-3	6	1
η^1-allyl	-1	2	1
η^3-allyl	-1	4	2
η^2-alkyne	0	2 to 4	1
amine	0	2	1
η^2-arene	0	2	1
η^6-arene	0	6	3
carbene	0	2	1
carbyne	0	3	1
carbonyl	0	2	1
η^1-cyclopentadienyl	-1	2	1
η^3-cyclopentadienyl	-1	4	2
η^5-cyclopentadienyl	-1	6	3
dinitrogen	0	2	1
halide (*e.g.*, Cl^-)	-1	2	1
hydride	-1	2	1

Ligand	**Formal Charge(s)**	**Electrons Donated**	**Coordination Positions**
isocyanide (isonitrile)	0	2	1
nitrile	0	2	1
nitrosyl (linear)	+1	2	1
nitrosyl (bent)	-1	2	1
phosphite	0	2	1
phosphine	0	2	1
pyridine	0	2	1

The carbonyl ligand is perhaps the most common ligand in transition metal organometallic chemistry. Its bonding in the linear terminal geometry is typical of other linear π-acidic ligands such as N_2, NO^+, and CN-R. In linear carbonyl complexes, the carbonyl is attached to the metal *via* the carbon atom, and the metal-carbon-oxygen angle is approximately 180°. According to the Dewar-Chatt-Duncanson model, σ-bonding occurs when a lone pair is donated from a filled σ-symmetry orbital on carbon (*i.e.*, the approximately sp hybrid orbital) to an empty σ-symmetry orbital on the metal (*i.e.*, the approximately d^2sp^3 hybrid orbital in an octahedral complex). There are also two π-backbonding interactions, which are perpendicular to one another. In each of the two backbonds, there is a filled π-symmetry orbital on the metal (*e.g.*, the approximately d_{xy}, d_{xz}, or d_{yz} in an octahedral complex), which donates a pair of electrons into an empty π-symmetry orbital on carbon monoxide (*i.e.*, the approximately CO π^*-antibonding orbital).

These σ-bonding and π-backbonding components are synergic and the overall metal-

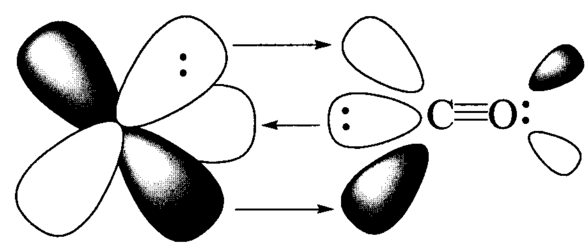
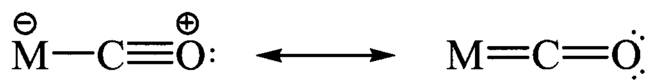


Figure 1.1.2 A Dewar-Chatt-Duncanson representation of the bonding of the carbonyl ligand to a transition metal.[3]

carbonyl bond is thus stronger than a linear sum of the two components. The electron transfer back to the ligand *via* the π-backbonding effectively neutralizes the electron transfer of the σ-bonding interaction to the metal. Thus, the overall metal-carbonyl bond is not polarized very much and there is only a small net electron transfer to the carbonyl ligand.

An alternate and complementary explanation for the bonding of metal carbonyls is provided by Valence Bond Theory. Valence Bond Theory represents the bonding as contributions from two resonance forms. The first resonance form has metal-carbon single and carbon-oxygen triple bonds, a formal charge of +1 on oxygen, and has oxygen sp hybridized. The second resonance form has both metal-carbon and carbon-oxygen interactions as double bonds, has no formal charges on carbon monoxide, and has oxygen sp^2 hybridized. In this interpretation, increased backbonding to the carbonyl is reflected in an increased contribution from the second "metalla ketone" resonance form.



"metal carbonyl" "metalla ketone"

Figure 1.1.3 Valence Bond Theory representation of the bonding of the carbonyl ligand.

Spectroscopy and X-ray diffraction may be used to provide experimental evidence of the nature and extent of the metal-carbonyl interaction. Infrared spectroscopy may be used to measure the amount of backbonding of the metal to the ligand. The IR stretching frequencies of carbonyls decrease from 2120 cm^{-1} to below 1850 cm^{-1} as the metal becomes more electron rich and, consequently, as the amount of backbonding increases. In turn, as the amount of backbonding increases, the CO bond order decreases and the carbon-metal bond order increases. Various studies have shown carbonyl ligands are poor σ-donors and strong π-acceptors. Thus, carbonyls act as net electron withdrawing ligands. Nuclear magnetic resonance spectroscopy may also be used to examine the electron richness of the complex. As the amount of backbonding increases, the chemical shift of the carbonyl carbon correlates with the electron richness of the complex (*i.e.*, shifting either downfield or up-field for a series of related complexes). X-ray diffraction may be used to examine metal-ligand interactions. Thus, as the bond order of the carbon-metal bond increases the corresponding bond length decreases and as the carbon-oxygen bond order decreases its bond length increases.[4]

Isonitrile ligands are isoelectronic with carbonyl ligands and their bonding is therefore closely related. However, isonitriles are less electronegative than carbon monoxide and the lobes of the π*-antibonding orbitals on C≡N are less polarized towards carbon. Thus, isonitriles are generally better net electron donors than are carbonyls. In terms of the Dewar-Chatt-Duncanson model, there is σ-donation from the lone pair of electrons on the carbon (*i.e.*, the approximately sp hybrid orbital) to an empty σ-symmetry orbital of the metal (*i.e.*, approximately d^2sp^3 in octahedral complexes). There is also π-backdonation from a pair of filled orbitals of π-symmetry on the metal (*i.e.*, the approximately d_{xy}, d_{xz}, or d_{yz} orbitals in octahedral metals) to a pair of empty π-symmetry orbitals on the isocyanide ligand (*i.e.*, the approximately π*-orbitals localized on C≡N).[3,4]

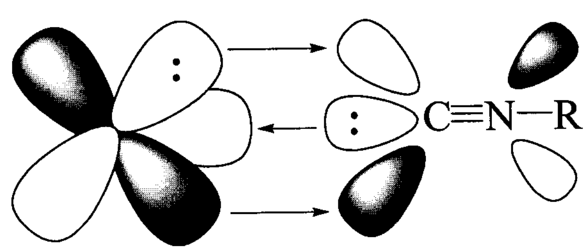


Figure 1.1.4 A Dewar-Chatt-Duncanson model representation of the bonding of an isocyanide ligand to a transition metal.

Valence Bond Theory provides an alternative and complementary explanation of the bonding that occurs during the coordination of an isonitrile to a transition metal. In Valence Bond terms, the coordination is explained *via* resonance. Thus, greater backbonding results in an increased contribution from the second resonance form and hence a decreased CN-R bond angle due to the sp^2 hybridization of the nitrogen atom on

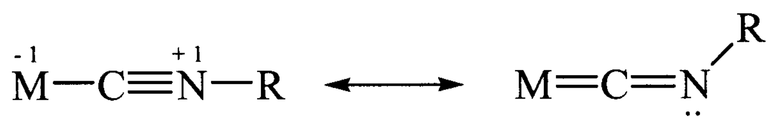


Figure 1.1.5 Valence Bond Theory model for the isocyanide ligand.

the latter.[5]

Both the Dewar-Chatt-Duncanson and Valence Bond Theory explanation can be used to rationalize the same experimental observations. The electron richness of the metal center affects the bond orders for the metal-carbon and carbon-nitrogen bonds as well as the CN-R angles. If the electron richness of the metal is increased, there is more backbonding and the second resonance form is favored. The metal-carbon bond order therefore increases and the carbon-nitrogen bond order decreases while the CN-R angle decreases. As with carbonyls, the electron richness of isonitrile complexes may be measured through infrared spectroscopy. The C≡N stretching frequency for isonitrile complexes is 250-350 wavenumbers lower than the stretching frequency for the free isonitrile reflecting both the weakening of the net C≡N σ- and π-bonds upon coordination.[3,4]

Olefins and related unsaturated organics are also common ligands. In the Dewar-Chatt-Duncanson model, the bonding of olefins involves a forward donation of π-electron density from the occupied π-bonding orbitals of the alkene (*i.e.*, σ-symmetry with respect to the metal) to empty σ-symmetry valence orbitals on the metal atom (*e.g.*, approximately d^2sp^3 on an octahedral complex). Backdonation occurs from filled π-symmetry orbitals on the metal (*e.g.*, approximately d_{xz}, d_{yz}, and d_{xy} on an octahedral metal center) into an empty π*-molecular orbital on the ligand, (*i.e.*, which have π-symmetry with respect to the metal).

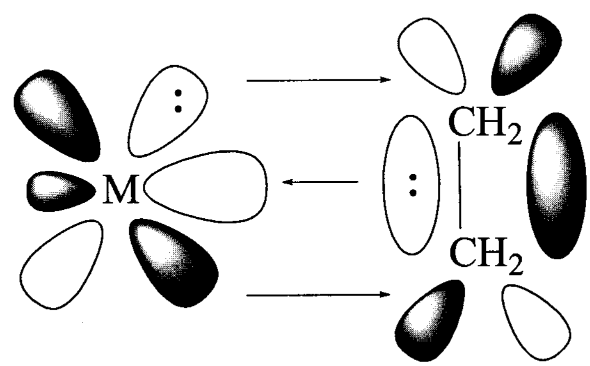


Figure 1.1.6 A Dewar-Chatt-Duncanson model representation for the bonding of an alkene ligand to a transition metal.

In Valence Bond terms, the two resonance forms of olefins are referred to as the metal-olefin and metallacyclopropane forms, which differ in both their metal-carbon and carbon-carbon bond orders and in the hybridizations of the carbon atoms. Thus, increased backbonding increases the contribution of the second resonance form, which increases the metal-carbon bond order, decreases the carbon-carbon bond order, and changes the carbon hybridization from sp^2 towards sp^3.

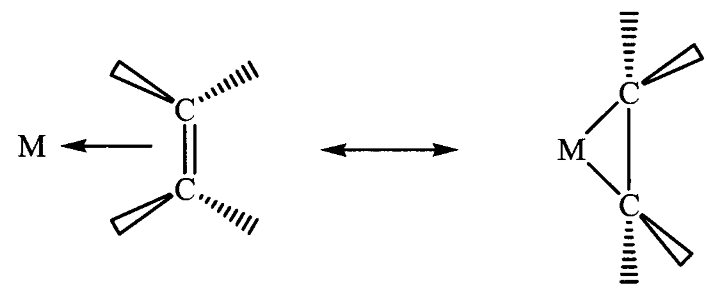


Figure 1.1.7 Valence Bond Theory representation of the bonding of a metal-olefin and metallocyclopropane.

As with carbon monoxide and CN-R, the electron richness of the metal containing olefin and related complexes may be measured through spectroscopy and X-ray diffraction. Increasing the electron richness on the metal produces increased backbonding and, therefore, the net bond order of the carbon-carbon bond decreases. X-ray diffraction has shown that increased electron richness on the metal and the subsequent backbonding decreases the metal to ligand bond distance, increases the carbon-carbon bond length, and decreases the H-C-H bond angles from 120° towards 109°. The π-bonded hydrocarbons such as olefins and η^6-arenes generally increase the net electron density on the metal in contrast to π-acidic ligands such as carbonyls and isocyanates, which typically decrease the net electron density on the metal.

The PR_3 ligand is widely used in metal coordination chemistry because it is a soft ligand and can be incorporated into metal complexes having central atoms in low oxidation states. The stability of complexes with PR_3 ligands results from the soft acceptor nature of the metal in low oxidation states and the stability of soft-donor/soft-acceptor combinations.[6] It is generally accepted that the bonding of phosphines to metals is almost entirely σ-donor in nature for alkyl phosphines. However, for aryl phosphines, phosphites, and fluorinated phosphines π-backbonding into phosphorus orbitals that have phosphorus-carbon σ*-orbital character become increasingly important in the order given. The 1,2-bis-diphenylphosphinoethane ligand (dppe) is typically a bidentate ligand in most complexes meaning that both phosphorus atoms coordinate to the metal. Each phosphorus atom has a lone pair of electrons from an sp^3 hybrid orbital that is donated to an empty σ-symmetry orbital on the metal (*e.g.*, approximately d^2sp^3 orbital on an octahedral metal center). For phosphine ligands such as those used in this thesis, backbonding plays little or no role because the aryl substituents are relatively electron rich.[7]

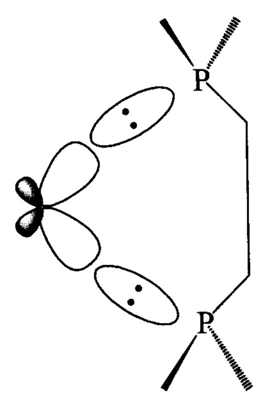


Figure 1.1.8 A Dewar-Chatt-Duncanson representation for the bonding of the bidentate dppe ligand to a transition metal.

The dinitrogen ligand usually is a linear monodentate ligand because only one pair of electrons from the dinitrogen molecule coordinates to the metal. As with carbon monoxide and CN-R, [2,7] one can describe $M\text{-}N_2$ bonding in both Dewar-Chatt-Duncanson (*i.e.*, σ-donation and π-backdonation) and Valence Bond (*i.e.*, two resonance contributions) terms. Free dinitrogen is IR inactive due to its lack of a dipole moment, but it is Raman active. The polarization that results from its synergic bonding to metal atoms leads to the observation of a N-N stretching vibration between 1920-2150 cm^{-1} and to chemical activation of the dinitrogen ligand.

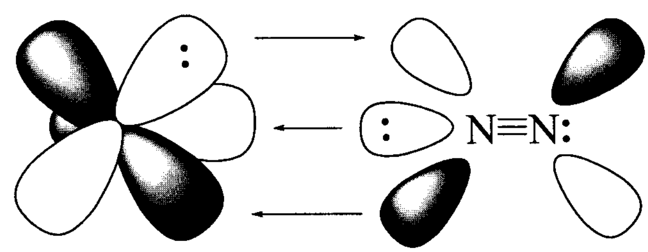


Figure 1.1.9 A Dewar-Chatt-Duncanson model representation for the bonding of a dinitrogen ligand to a transition metal.

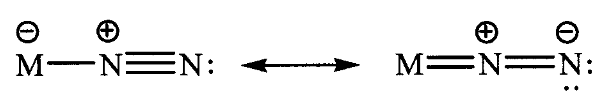
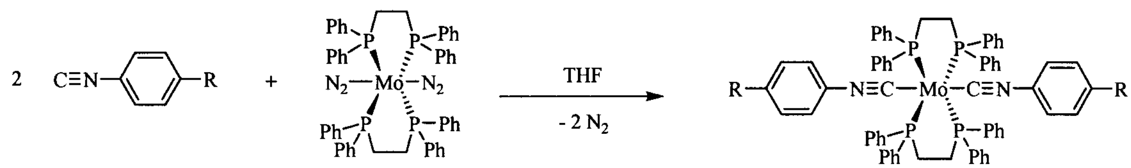


Figure 1.1.10 Valence Bond Theory representation of the bonding of a dinitrogen ligand to a transition metal.

However, for the terminal N_2 ligand net σ- and π-interactions are weaker than for other π-acid ligands such as carbonyls and isocyanides. Therefore, dinitrogen ligands often may be readily displaced from the complex by them, (*e.g.*, as in **Equation 1.1.1**).[8]



Equation 1.1.1

Section Two

Organometallic Polymers and Dendrimers

Metal-ligand complexes may be incorporated into polymers to produce new classes of organometallic polymers that are at least formally related to conventional organic and/or inorganic polymers. Most transition elements have a higher coordination number than carbon. This allows inorganic atoms incorporated into polymers to have more sidegroups. In addition, metal-ligand bonds are typically longer than conventional organic bonds (*e.g.*, carbon-carbon, carbon-nitrogen, and carbon-oxygen bonds). These differences in bonding and valences between carbon and metals produce different bond angles, internuclear distances, and backbone rigidities.[7] Because of their variable bonding characteristics, organometallic polymers may also possess intriguing electrical, conductivity, magnetic, optical, liquid crystalline, and redox properties. Polymers with inorganic fragments in their repeating unit have many actual and/or potential advantages compared to conventional organic polymers. In particular, inorganic elements are expected to induce properties in polymers that cannot easily be induced using conventional organic fragments.[9,10] Organometallic polymers of most relevance to this thesis are polymers having transition elements that possess M-C σ or π bonds in the backbone. Polyphosphazenes, polysiloxanes, and polysilanes are some inorganic polymers that have been produced commercially because of their novel properties.[7]

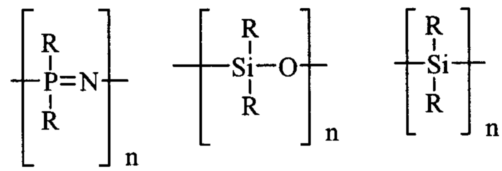


Figure 1.2.1 Structures of a polyphosphazene, polysiloxane, and polysilane.

To facilitate practical applications, a main goal of organometallic polymer researchers is to synthesize organometallic polymers with favorable materials processing characteristics (*e.g.*, melting point, solubility, and high or controllable molecular weights (Mn > 10,000)). Since the early 1950s, many organometallic polymers have been synthesized; however, these polymers typically had low molecular weights. They were also often insoluble or could not be melted without decomposing. In order to overcome these obstacles, researchers have attempted various synthetic approaches. Step growth polycondensation reactions involving the reaction of bisfunctional monomers were used because addition polymerization reactions could not usually be employed for main-chain organometallic polymers.[11] There are two approaches for preparing polymers using step growth polymerization (*e.g.*, as in **Equations 1.2.1 and 1.2.2**).[12]

$$n\ A{-}R{-}B \longrightarrow \left[R{-}X \right]_n$$

$$n\ A{-}R{-}A + n\,B{-}R'{-}B \longrightarrow \left[R{-}X{-}R'{-}X \right]_n$$

Equations 1.2.1 and 1.2.2

The first method uses a molecule that has two functional groups and the second method uses two different difunctional monomers.

The first soluble, well-characterized transition metal based polymers of appreciable molecular weight were ferrocene-containing materials with organosiloxane spacers, which were reported in 1974 by Pittman and co-workers.[13]

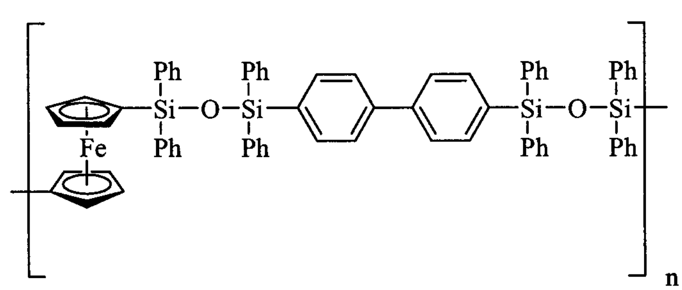


Figure 1.2.2 Transition metal based polymers containing ferrocene with organosiloxane spacers.

In 1977, the first high molecular weight rigid-rod metal polyyne materials were described by Hagihara et al.[14]

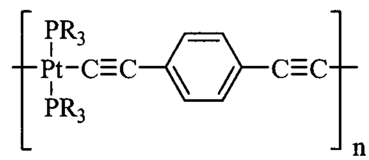


Figure 1.2.3 Example of a rigid-rod metal polyyne.

These are prototypical examples of main-chain organometallic polymers: Poly(metallocenes) and rigid-rod acetylide polymers.

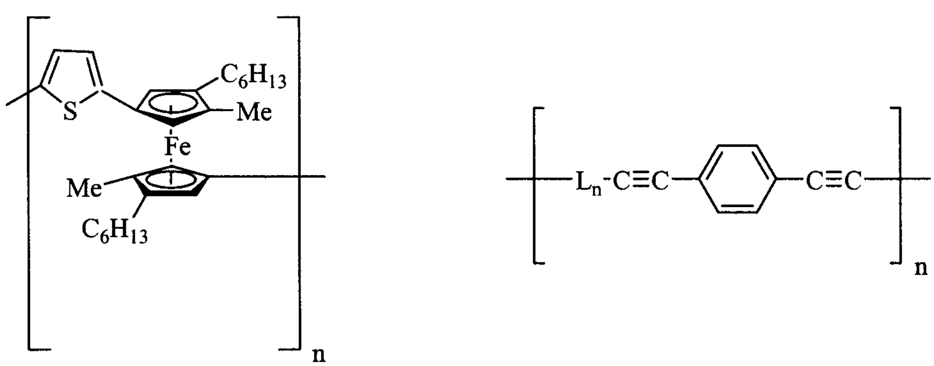


Figure 1.2.4 Some examples of main-chain organometallic polymers.

Many of the polymers shown in **Figure 1.2.4** are soluble in common organic solvents such as benzene, toluene, tetrahydrofuran, and dichloromethane. They also have good electrical, optical, and nonlinear optical (NLO) properties.[9]

Another type of organometallic compounds of interest are dendrimers (Greek: *dendron* = tree). Dendrimers are hyper-branched nanoscale materials that have potential applications as sequestration agents, microcatalyst chambers, viscosity modifiers, analogues of proteins and enzymes, etc. Dendrimers are also being used in analytical and NLO applications. The generation number of a dendrimer is essentially the number of branching points along each arm.

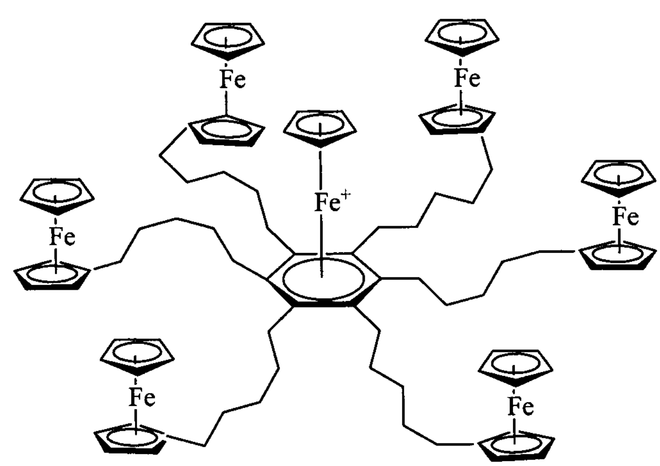


Figure 1.2.5 A first generation organometallic dendrimer

As the size of a dendrimer increases, steric crowding increases in the outermost layers. Thus, a typical high generation number dendrimer is sterically crowded on its surface layers, but has significant free space near its central core. This crowding gradient sets the maximum dendrimer generation number at about seven and is responsible for many of their useful properties.[15, 16]

Many rigid-rod organometallic main-chain oligomers and polymers are 0.5 to 1.0 nanometers in diameter and several hundreds of nanometers in length and are thus classified as nanomaterials. These materials may have potential uses for their electronic and nonlinear optical properties.[17] Nonlinear optical properties arise from interactions of the electromagnetic fields of light with those of matter. Materials possessing nonlinear optical properties are able to change the nature of light as it propagates through them and also to change their electronic and other properties as a function of the incident light. This allows different frequencies, amplitudes, polarization, or propagation characteristics to be produced and may also produce coupled changes in electrical and optical properties. Materials with NLO properties are of technological importance in areas that use optical devices such as optical data storage, optical communication, optical switching, image processing, and optical computing.[12,18]

Section Three

Organometallic Nanomaterials

1.3.1. Introduction

Aromatic isocyanides are of interest in the synthesis of organometallic nanomaterials because they are relatively stable, non-toxic, and non-volatile and because they form strong complexes with rationally tunable bonding characteristics.

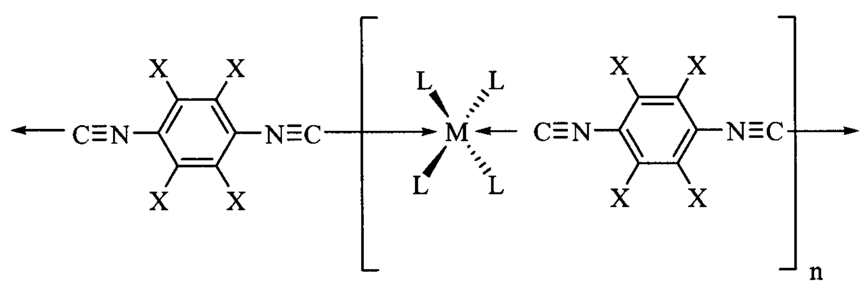


Figure 1.3.1 Organometallic polymer containing aromatic isocyanides.

In addition, free aromatic diisocyanide ligands are also of interest because they are effective molecular-level conductors.[19] These ligands are capable of bridging transition metal centers while mediating communication between the centers through a conjugated dπ-pπ-dπ network.[20] Thus, aromatic diisocyanide ligands could be deposited on a gold surface (**Figure 1.3.2**) and thus enhance the surface's electrochemical properties.

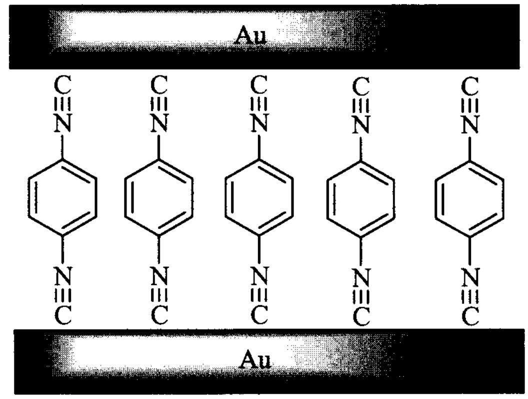


Figure 1.3.2 Free isonitriles bridging molecular wire junctions.[19]

If one uses metal phosphine centers, the steric and electronic properties of the resultant nanomaterials should also be tunable by varying the metal and PR_3 groups. There is a wide variety of structural data available from previous work on monometallic metal isonitriles and metal phosphines that should enable the prediction of the metal geometries of these complexes.

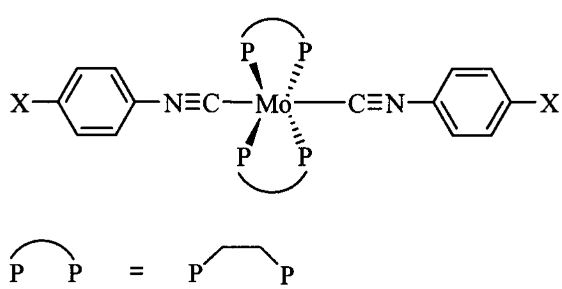


Figure 1.3.3 Metal phosphine center bridging aromatic isonitriles.

Inorganic materials having from three to seven ligands bound to a central metal atom or ion are expected to have star like shapes:

- Two coordinate: Au^{+}
- Three coordinate: Ag^{+}
- Four coordinate: Ni^{0}, Ag^{+}, Cu^{+}, Rh^{+}, Ni^{+2}, Pd^{+2}, Co^{+2}, etc.
- Five coordinate: Fe^{0}, Re^{0}, Co^{+}, Co^{+2}, etc.
- Six coordinate: Cr^{0}, Mo^{0}, W^{0}, Cr^{+}, Mn^{+}, Cr^{+2}, Fe^{+2}, etc.
- Seven coordinate: Mo^{+2}, W^{+2}, W^{+3}, etc.

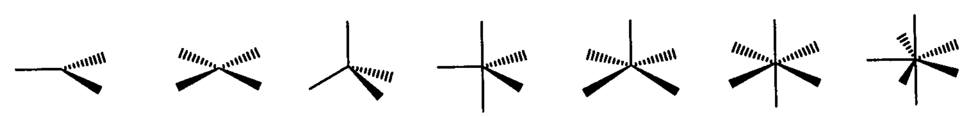


Figure 1.3.4 Possible geometries of homoleptic metal complexes.

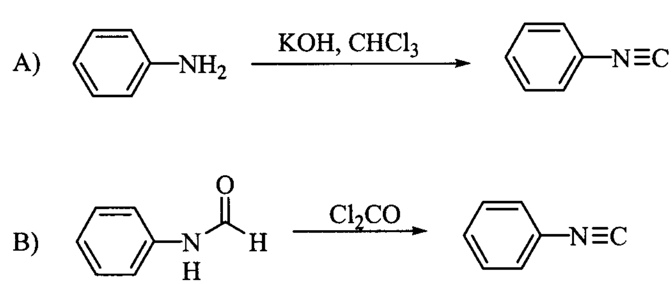
Whether they are fluxional or rigid, many homoleptic complexes have such geometries about their metal centers. By using linear organometallic chains instead of simple ligands such as carbon monoxide with these centers, analogous organometallic nanostars having isocyanide-bridged arms should result.

1.3.2. Requisite Organic and Organometallic Reagents

The organometallic nanomaterials described in this thesis contain bifunctional isonitrile ligands of the type 1,4-$C_6H_4(NC)_2$ and 1,4-$C_6Me_4(NC)_2$, and monofunctional isonitriles such as MeO-C_6H_4-NC. The chelating phosphines, (1,4-

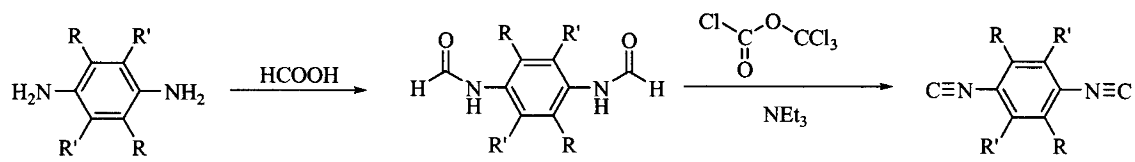
$C_6H_4Y)_2PCH_2CH_2P(1,4\text{-}C_6H_4Y)_2$ and $(1,4\text{-}C_6H_4Y)_2PC_6H_4P(1,4\text{-}C_6H_4Y)_2$ (where Y = OMe, Me, and Et) have been chosen because it is thought that these phosphines will improve the solubilities of the complexes compared to the parent phenyl species. In turn, the phosphines will be used to synthesize the dinitrogen starting materials $Mo(R_2PC_nH_mPR_2)_2(N_2)_2$. Based on molecular orbital arguments, it is expected that more electron rich metal centers (*e.g.*, Y = Me or Et) and electron poor bridges (*e.g.*, $C{\equiv}N\text{-}C_6F_4\text{-}N{\equiv}C$) will give increased electronic communication down the oligomer backbones.

Aromatic isonitriles have been prepared by a variety of methods. The two most common are treatment of aromatic amines with hydroxide in chloroform (A) and the dehydration of formamides with phosgene (B) or its precursors.[21]



Equations 1.3.1 and 1.3.2

For the synthesis of diisocyanides, method A gives typically poor results so method B is used. As an alternative to hazardous phosgene gas, the safer "diphosgene" (trichloromethylchloroformate) or "triphosgene" (bis(trichloromethyl)carbonate) liquid and solid may be used as the dehydrating agent.[22]



Equation 1.3.3

Phosphines will be used as ancillary ligands because they will allow us to tune the solubilities and electron richness of the products. To improve the solubilities of these species over the relatively insoluble dppe complexes, substituted dppe derivatives (*i.e.*, dppe' = $(1,4\text{-}C_6H_4Y)_2PCH_2CH_2P(1,4\text{-}C_6H_4Y)_2$ and $(1,2\text{-}C_6H_4Y)_2PC_6H_4P(1,4\text{-}C_6H_4Y)_2$ where Y = OMe, Me, Et, etc.) will be used to systematically change the electron richness at Mo and the materials' steric bulk.

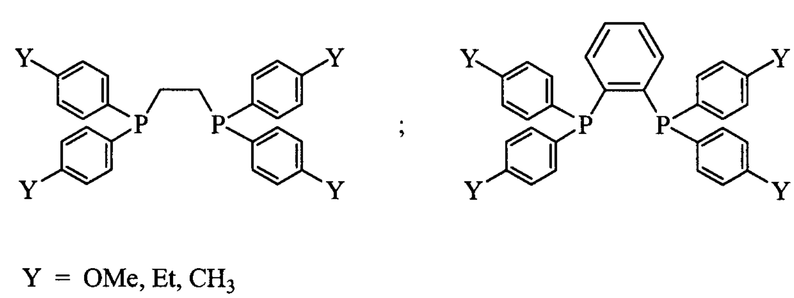
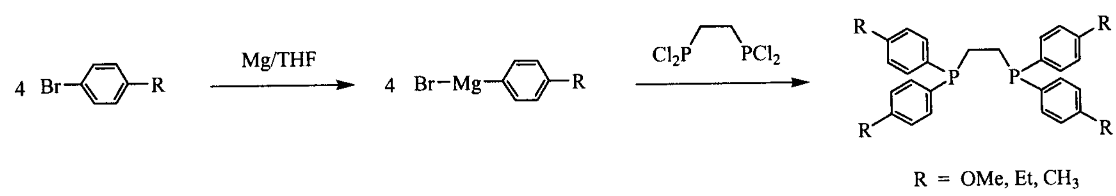


Figure 1.3.5 Examples of some chelating phosphines.

The typical synthetic route for preparing the phosphines is shown below.[23]



Equation 1.3.4

In this reaction, commercially available 1,2-bis(dichlorophosphino)ethane is used as the starting material. Reaction of this compound with a Grignard or organolithium reagent in THF generally produces the desired dppe derivatives.

The precursors used for the synthesis of our organometallic materials are molybdenum and tungsten dinitrogen complexes of the type $M(N_2)_2(PR_3)_4$. They are generally well known compounds for the phenyl derivatives and have been extensively investigated as possible catalysts for chemical low-pressure nitrogen fixation.[24] In our new chemistry, the dinitrogen ligands will be exchanged with diisonitrile molecules to get the first generation-metal-diisonitrile building blocks. Bis-isonitrile complexes of the molybdenum phosphine complex (*e.g.*, $Mo(PR_3)_4(C{\equiv}N\text{-}C_6H_5)_2)$) have previously been prepared by displacement of a weak ligand such as N_2 from the phosphine center. These starting materials (*e.g.*, $Mo(PR_3)_4(N_2)_2$ and $Mo(PR_3)_4(N_2)(NCMe)$) can be made by several routes, most commonly by the reduction of a molybdenum halide under an atmosphere of dinitrogen using a variety of reducing agents, or by analogous multistep procedures involving the isolation of intermediate products of this process, *e.g.*,[25]

$$MoCl_5 + 2\ dppe + exc.\ Mg \xrightarrow{THF/N_2} Mo(dppe)_2(N_2)_2$$

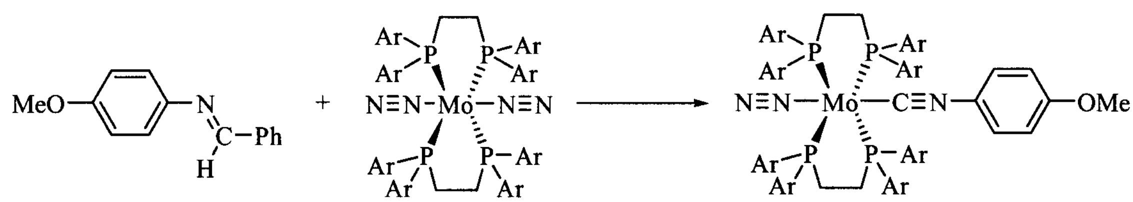
Equation 1.3.5

In the next step, the first new nanorod building blocks will be synthesized. To avoid the uncontrollable formation of polymers, an excess of the isonitrile ligand will be used:

$$2\ \ CN\text{-}C_6H_4\text{-}NC + Mo(dppe)_2(N_2)_2 \longrightarrow Mo(dppe)_2(CN\text{-}C_6H_4\text{-}NC)_2$$

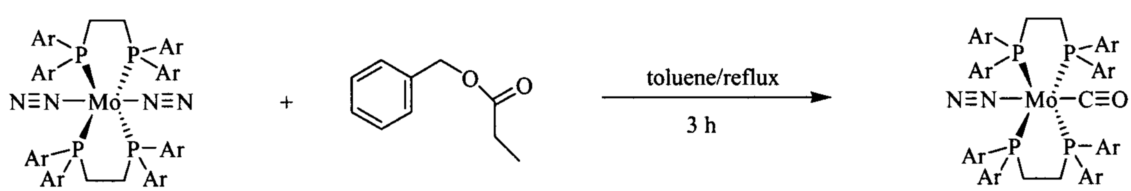
Equation 1.3.6

Similar monometallic complexes with only one isonitrile ligand per molybdeum center have been reported using a slightly different approach starting with Shiff-bases instead of diisonitriles.[26]



Equation 1.3.7

Longer oligomers will then be synthesized by combining the dinitrogen terminated first generation nanorods, the isonitrile terminated first generation nanorods, the bifunctional isonitriles, and/or the bis-dinitrogen complexes in appropriate proportions. When oligomers of the final desired chain length are made, they will be capped with terminal organometallic groups, including: $M(CO)_5$ (M = Cr, Mo, W), $CpFe(CO)_2^+$, $CpMn(CO)_2$, Mo(dppe')$_2$CO, or Mo(dppe')$_2$(CN-R). The organometallic 'caps' will be prepared *via* published routes (**Equation 1.3.8**).[27]



Equation 1.3.8

However, the syntheses will require careful exploration of the reaction conditions to optimize conditions and prevent mixtures of non-capped, mono-capped, and di-capped species from forming. When more electron poor caps such as $Mo(CO)_5$ are used, we expect that they will tend to polarize the organometallic isocyanide backbone and will also influence the degree of conjugation between the backbones and the caps. The most electron rich caps are expected to display the best conjugation. These 'capped' complexes will then be used to form organometallic nanostars.

Many metal-isocyanide complexes of the transition metals are known. They are typically prepared in excellent yields, either by reacting isocyanides with a metal salt or reducing the metal salt in the presence of isocyanides.[25]

$$MCl_x(\text{solvent})_k + z\ \text{CN-arene-X} \longrightarrow M(\text{CN-arene-X})_z^{x+}$$

$$MCl_x(\text{solvent})_k + \text{reducing agent} + z\ \text{CN-arene-X} \longrightarrow M(\text{CN-arene-X})_z$$

Equations 1.3.9 and 1.3.10

Each nanostar will be prepared by using the specific reaction conditions used for the metal and conventional aryl isocyanides. It is expected that high yields will be obtained, but a major synthetic challenge will be the purification of the nanostars. Possible methods for purification are fractional crystallization and chromatography. Fractional crystallization works remarkably well if the synthesis is designed so that any byproducts are different from the desired material. Chromatography is very effective at removing byproducts that have different end-groups. However, column chromatography is quite tedious and often unsuccessful if there is a mixture of oligomers varying only in the number of repeating units.

The proposed organometallic nanostars are expected to have varying degrees of electronic conjugation down their arms and across their central vertices. They are likely to have fascinating electrical, conductive/semiconductive (*i.e.*, when doped/partially oxidized), and NLO behavior when attached to surfaces. In molecular orbital terms, the maximum degree of electronic communication of the nanostars is expected when the metal fragment's highest occupied molecular orbitals, HOMOs (of predominately metal "d" character), are of relatively high energy and the isonitrile's lowest unoccupied molecular orbitals, LUMOs (of π^*-character), are of relatively low energy. It is also expected that increasing the electron richness at the molybdenum centers and decreasing it at the isonitriles should result in increased HOMO-LUMO overlap and hence conjugation.

1.3.3. Characterization of the Organometallic Building Blocks

It is expected that the new organometallic materials will be relatively air and thermally stable. Elemental analysis, IR, and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy will be used to characterize the physical and spectroscopic properties and for information on purity and identity. X-ray diffraction will be used to determine the solid-state crystal structures of these building blocks. This will provide detailed structural information including: the degree of linearity down their oligomer backbones, the three dimensional geometries at the central metal cores, and the extent of steric interactions. Intermetallic interactions can be quantitatively evaluated by cyclic voltammetric studies and qualitatively inferred from IR spectroscopy.

Section Four

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Chapter Two

Experimental

2.1. Reagents and reaction conditions

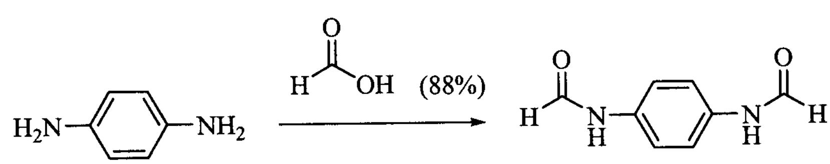
Reagent grade chemicals were purchased from the Aldrich, Fisher, Strem, and Acros Chemical companies or were prepared by literature methods. The dinitrogen gas was 99.999% pure and supplied by Praxair. All solvents were degassed and dried under nitrogen using conventional methods[1] as follows. Tetrahydrofuran and ether were dried over potassium/sodium alloy and benzophenone. Toluene was dried over sodium and benzophenone. Hexane was dried over potassium/sodium alloy. Dichloromethane was dried over calcium hydride. After drying and distillation, all solvents were degassed by bubbling nitrogen through them for 15 minutes. Liquid starting materials other than solvents were degassed by the freeze-pump-thaw method. All glassware was dried in an oven at 115°C before use. All reactions (except for the formamide syntheses) were carried out under a dinitrogen atmosphere on a vacuum line using standard Schlenk techniques.[2] The ^{1}H, ^{13}C, and ^{31}P NMR spectra were determined using a 400MHz Varian Gemini-2000 instrument. All solvents for NMR spectral analyses were dried with molecular sieves and degassed by the freeze-pump-thaw method. IR Spectra were recorded using a Perkin Elmer 1600 FTIR instrument. Single-crystal X-ray diffraction analyses data were recorded using a Bruker AXS SMART APEX CCD diffractometer. Melting points were determined using a 200V Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., of Knoxville, TN.

The following compounds were kindly provided by coworkers as follows: 1,4-bis(N-formylamino)-2,3,5,6-tetramethylbenzene and 1,4-bisisocyano-2,3,5,6-tetramethylbenzene by Cynthia L. Perrine, bis(1,4-diisocyanobenzene)bis(1,2-bis(di(*p*-ethylphenyl)phosphinobenzene)molybdenum(0) by James B. Updegraff III, and 1-isocyano-4-methoxybenzene, cyclooctene chromiumpentacarbonyl, and sodium amalgam by Dr. Matthias Zeller.

2.2 Syntheses

1. Synthesis of the formamides[2]

1a. Preparation of 1,4-bis(N-formylamino)benzene



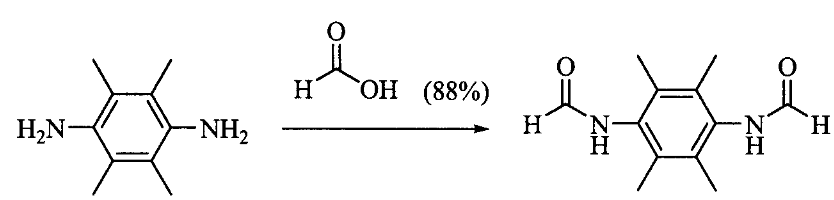
Equation 2.1.1a

Solid *p*-phenylenediamine (125.0g, 1.16mol) was added to 88% formic acid (130mL) in a 1000mL 3-necked round-bottomed flask. The mixture was magnetically stirred and heated to reflux (~100°C) using an oil bath and the heating was continued until the solid had totally dissolved. After removal of the oil bath, cold deionized water (500mL) was then added to the hot solution. The resulting mixture was cooled in an ice bath for one hour, by which time a brown precipitate had formed. This solid was collected on a sintered glass fritt in air and washed with cold deionized water (~500mL) until the pH of the filtrate became neutral (*i.e.*, as determined using pH paper). The beige colored product was then dried *in vacuo* for 24 hours and a brown powder was obtained in nearly quantitative yield (190.0g, 1.16mol, 99.7%). This product is stable towards air and moisture and is not soluble in any common organic solvents (*e.g.*, chloroform, toluene, and tetrahydrofuran). Therefore, no NMR, IR, or mass spectrometry data were collected.

FW: 164.2g/mol

MP: 208°C, dec

1b. Preparation of 1,4-bis(N-formylamino)-2,3,5,6-tetramethylbenzene



Equation 2.1.1b

2,3,5,6-Tetramethyl-1,4-phenylenediamine (90.0g, 548mmol) was placed in a 1L round-bottomed flask. Formic acid 88% (500mL) was added to the flask. The mixture was magnetically stirred and heated to reflux (~100°C) using an oil bath for two hours. After two hours, the solid had dissolved and the flask was removed from the oil bath. Cold deionized water (500mL) was then added to dilute the solution. The flask was then placed in an ice bath to cool for one hour, which caused a brown precipitate to form.

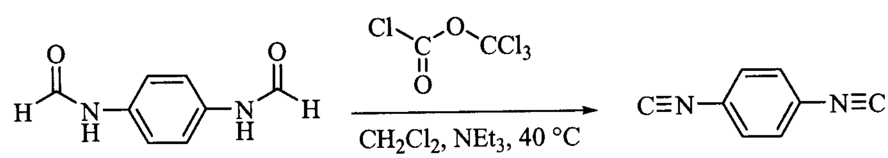
This solid was collected on a sintered glass fritt and washed with methanol (~500mL). The brown solid was dried *in vacuo* using a hot water bath (~100°C). The yield is quantitative (121.7g, 552mmol, 100%). The formamide product is not soluble in organic solvents such as toluene, tetrahydrofuran, hexane, or ether. The formamide is slightly soluble in dichloromethane and chloroform.

FW: 220.4g/mol

MP: 333°C, dec

2. Synthesis of the isonitriles[3]

2a. Preparation of 1,4-diisocyanobenzene



Equation 2.2.2a

Trichloromethylchloroformate **(Caution: Use in a fume hood; lachrymator)** (22.0mL, 36.1g, 183mmol) dissolved in dry dichloromethane (135mL) was added dropwise over a two-hour period into a boiling, stirred suspension of 1,4-bis(N-formylamino)benzene (30.4g, 185mmol), triethylamine (135mL), and dichloromethane (480mL). The solution was refluxed for two to three hours until all of the starting material dissolved. A clear, dark solution was obtained and was then allowed to cool to room temperature. After cooling, the solution was washed twice with aqueous 10% sodium bicarbonate (500mL) and once with deionized water (~100mL) using a separatory funnel. The organic layer was dried over anhydrous magnesium sulfate for one hour. The drying agent was then removed using a Schlenk filter. The solvent was removed under vacuum to give a brown solid which was then purified by chromatography on a neutral aluminum oxide column, using dichloromethane/hexane (1:1 mixture) as the eluent, followed by sublimation under oil pump vacuum at 100°C. The isonitrile was obtained as large, white crystals (10.3g , 80.4mmol, 44.0%).

FW: 128.1g/mol

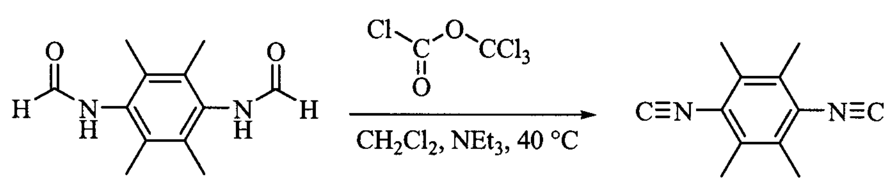
MP: 156°C, dec

^{1}H NMR (399.905 MHz, $CDCl_3$, rt): $\delta = 7.45$ (s, 4H).

^{13}C NMR (100.565 MHz, $CDCl_3$, rt): $\delta = 167.12$ (s, br, CN); 127.54 (s, C_{arom}); 126.70 (t, br, $J(^{13}C,^{14}N) = 15.0$ Hz, C_{arom}).

IR (toluene, CaF_2): 2122 cm^{-1} (s, νC≡N); 1496 cm^{-1} (vs, νC=C).

2b. Preparation of 1,4-bisisocyano-2,3,5,6-tetramethylbenzene



Equation 2.2.2b

Trichloromethylchloroformate (17.1mL, 28.1g, 142.1mmol) and dry dichloromethane (100mL) was added dropwise over a two-hour duration into a 1000mL 3-necked round-bottomed flask consisting of a stirred, boiling suspension of 1,4-bis(N-formylamino)-2,3,5,6-tetramethylbenzene (31.32g, 142.1mmol), dichloromethane (600mL), and triethylamine (100mL). The solution was refluxed until all the starting material dissolved (~5hr). A clear, dark solution was obtained and cooled to room temperature. After cooling, the solution was washed twice with 10% sodium bicarbonate (500mL) and deionized water (1000mL) using a separatory funnel. The organic layer was dried over anhydrous magnesium sulfate for two hours. The magnesium sulfate was removed using a Schlenk filter and the solvent was removed under *vacuo* to leave a brown precipitate. The brown solid was dried under vacuum for several hours in a hot oil bath to remove the triethylamine. The isonitrile was purified by sublimation and 5.97g (32.4mmol, 23.0%) of the isonitrile were isolated as white crystals.

FW: 184.2g/mol

MP: 164°C, dec

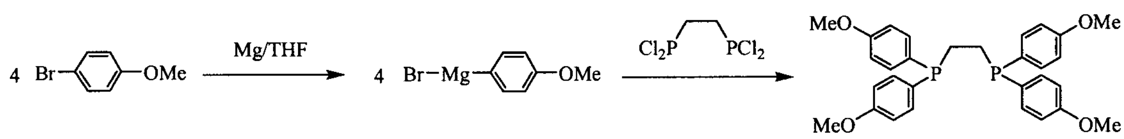
^{1}H NMR (399.905 MHz, $CDCl_3$, rt): $\delta = 2.36$ (s, 12H).

^{13}C NMR (100.565 MHz, $CDCl_3$, rt): $\delta = 168.87$ (s, CN); 131.55 (s, C_{arom}); 126.72 (t, $J(^{13}C^{14}N) = 12.5$ Hz, C_{arom}); 16.37 (s, CH_3).

IR (toluene, CaF_2): 2115 cm^{-1} (m, $\nu C\equiv N$); 1496 cm^{-1} (vs, $\nu C=C$).

3. Synthesis of the chelating phosphines[4]

3a. Preparation of 1,2-bis(di-*p*-anisylphosphino)ethane



Equation 2.3.3a

Magnesium turnings (8eq, 5.82g, 239.7mmol) and THF (50mL) were placed in a 500mL 3-necked round-bottomed flask equipped with a stir bar, nitrogen adapter, reflux condenser, and dropping funnel. A few iodine crystals were added to the magnesium turnings and the mixture was gently warmed with a heat gun until the color of the iodine disappeared, thus activating the magnesium. Then, *p*-bromoanisole (4.8eq, 26.89g, 18.0mL, 143.80mmol) and THF (50mL) was placed in the dropping funnel. The bromide solution was slowly added to the flask and a heat gun was used to initiate the reaction. Once the bromide solution was added, the resulting mixture was heated to reflux for an additional 30 minutes. A 1000mL 3-necked round-bottomed flask was then equipped with a stir bar, nitrogen adapter, and a 200mL inert gas sintered glass fritt. The Grignard compound was then filtered into the flask *via* the sintered glass fritt. In another flask, 1,2-bis(dichlorophosphino)ethane (1eq, 6.95g, 4.52mL, 30.0mmol) and THF (35mL) was mixed together and this mixture was then slowly added by syringe to the stirred Grignard solution. The resulting reaction warmed the mixture and an ice bath was therefore used for cooling. After approximately one hour, the yellow solution was allowed to warm up to room temperature and was then hydrolyzed and then washed with saturated aqueous ammonium chloride solution three times (150mL in total). The aqueous layer was removed by syringe and the organic layer was dried over anhydrous magnesium sulfate for two hours. The magnesium sulfate was removed using a Schlenk filter and all the solvent was removed under vacuum to leave a peach-colored oily residue. The residue was dissolved in a minimal amount of toluene (~20mL) and hexane (~40mL) was added to initiate crystallization of the product. The solution was stored at 4°C for approximately 24 hours, and 11.17g (21.5mmol, 69.0%) of the desired phosphine were isolated by filtration as a white powder.

FW: 518.5g/mol

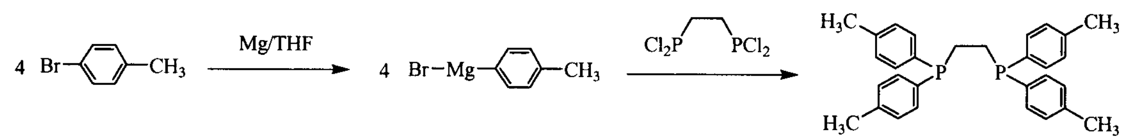
MP: 87°C

^{1}H NMR (399.905 MHz, $CDCl_3$, rt): $\delta = 7.27$ (dt, $J(^{1}H, ^{31}P) = 4.0$ Hz, $J(^{1}H,^{1}H) = 8.8$ Hz, 8H, H_{arom}); 6.85 (d, $J(^{1}H,^{1}H) = 8.8$ Hz, 8H, H_{arom}); 3.79 (s, 12H, CH_3); 2.02 (t, $J(^{1}H,^{31}P) = 7.2$ Hz, 4H, CH_3).

^{13}C NMR (100.565 MHz, $CDCl_3$, rt): $\delta = 159.99$ (s, C_{arom}); 133.9 (s, C_{arom}); 128.19 (s, C_{arom}); 114.02 (d, $J(^{13}C,^{31}P) = 18.3$ Hz, C_{arom}); 55.19 (m, CH_2); 24.14 (s, CH_3).

^{31}P NMR (161.884 MHz, $CDCl_3$, rt): $\delta = 32.862$ (s, P).

3b. Preparation of 1,2-bis(di-*p*-tolylphosphino)ethane



Equation 2.3.3b

Magnesium turnings (8eq, 11.5g, 472.0mmol) and THF (80mL) were placed in a 500mL 3-necked round-bottomed flask equipped with a stir-bar, nitrogen adapter, reflux condenser, and a dropping funnel. Then 4-bromotoluene (5.0eq, 48.3g, 35.7mL, 282.0mmol) and THF (90mL) was placed in the dropping funnel. The bromide solution was added dropwise to the flask and a heat-gun was used to initiate the Grignard reaction. During the addition the solution turns to a gray color. After addition, the mixture was heated to reflux for an additional half an hour with the help of a heat gun.

A 1000mL round-bottomed flask was then equipped with a stir-bar, nitrogen adapter, dropping funnel, and a 200mL Schlenk filter. The Grignard compound was filtered through the Schlenk filter to remove excess magnesium and washed with THF (20mL). After filtering the Grignard solution, a mixture of 1,2-bis(dichlorophosphino)ethane (1eq, 8.5mL, 13.1g, 56.3mmol) and THF (60mL) was added to the Grignard solution slowly *via* the dropping funnel. An ice bath was used when the mixture got too warm (*i.e.*, as indicated by reflux). After addition of the phosphino/THF solution, the mixture turned to a yellow color and a white precipitate formed. The yellow suspension was stirred for an additional half hour and was then hydrolyzed with degassed saturated aqueous ammonium chloride solution (200mL). After the addition, the solution turned clear and a white precipitate formed. Degassed deionized water (~100mL) was added to dissolve the white precipitate. The organic layer was collected and dried over anhydrous magnesium sulfate for two hours. The organic solution was filtered *via* a Schlenk filter and the solvent was removed *in vacuo* to leave a brown solid. The product was crystallized from a toluene (~30mL)/hexane (~50mL) mixture. After several days at 4°C, clear crystals formed. The solution was removed *via* syringe and the crystals were washed with hexane (40mL) and dried *in vacuo* to give 16.0g (36.2mmol, 62.5%) of the phosphine.

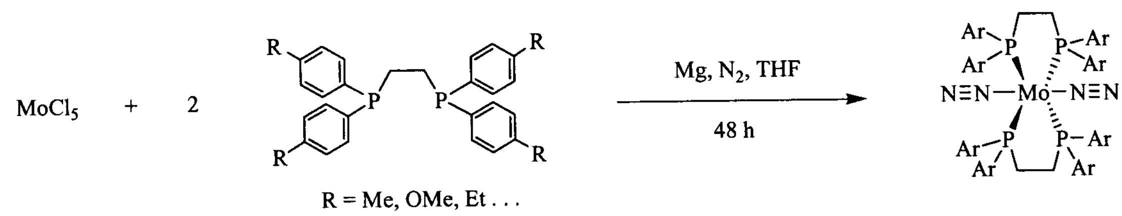
FW: 454.5g/mol

MP: 146°C

^{1}H NMR (399.905 MHz, $CDCl_3$, rt): $\delta = 7.24$ (m, 8H, H_{arom}); 7.12 (d, $J(^{1}H,^{1}H) = 7.6$ Hz, 8H, H_{arom}); 2.34 (s, 12H, CH_3); 2.06 (t, $J(^{1}H,^{31}P) = 4.4$ Hz, 4H, CH_2).

^{31}P NMR (161.884 MHz, $CDCl_3$, rt.): $\delta = 36.718$ (s, P).

4. Synthesis of the dinitrogen complexes[5]



Equation 2.4.4a

4a. Preparation of bis[1,2-bis(di-*p*-tolylphosphino)ethane]bis(dinitrogen) molybdenum(0)

Magnesium turnings (10.4g, 430.0mmol), THF (180mL), and 1,2-bis(di-*p*-tolylphosphino)ethane (2eq, 8.59g, 18.9mmol) were placed in a 1000mL round-bottomed Schlenk flask. Molybdenum pentachloride (1eq, 2.86g, 10.5mmol) was then added as a solid to the mixture. The mixture was stirred under dinitrogen for 48 hours. The solution turned to a dark red color and was filtered through celite. Degassed anhydrous methanol was then added to the THF solution to precipitate the dinitrogen complex. The dinitrogen complex precipitated as orange crystals and was collected by filtration. The complex was recrystallized using a THF (~20mL)/methanol (~40mL) mixture. The reaction produced the desired orange dinitrogen complex (2.94g, 2.76mmol, 26.4%).

FW: 1061.0g/mol

MP: 141°C, dec

^{1}H NMR (399.905 MHz, C_6D_6, rt): $\delta = 7.2$ (dd, br, $J(^{1}H,^{1}H) = 8.4$ Hz, $J(^{31}P,^{1}H) = 8.4$ Hz, 16H, H_{arom}); 6.85 (d, $J(^{1}H,^{1}H) = 8.4$ Hz, 16H, H_{arom}); 2.36 (t, $J(^{1}H,^{31}P) = 8.4$ Hz, 8H, CH_2); 2.03 (s, 24H, CH_3).

^{13}C NMR (100.565 MHz, C_6D_6, rt): $\delta = 138.39$ (s, C_{arom}); 137.00 (d, br, $J(^{13}C,^{31}P) = 10$ Hz, C_{arom}); 133.630 (s, C_{arom}); 129.46 (d, $J(^{13}C,^{31}P) = 12.2$ Hz, C_{arom}); 30.42 (m, CH_2); 22.08 (s, CH_3).

^{31}P NMR (161.884 MHz, C_6D_6, rt): $\delta = 63.12$ (s, P).

4b. Synthesis of bis[1,2-bis(di-*p*-anisylphosphino)ethane]bis(dinitrogen) molybdenum(0)

An alternate and less convenient route can be used to prepare the dinitrogen complexes. This route uses Na/Hg as the reducing agent;[6] 185.3g NaHg (2% Na, 3.71g Na, 161.2mmol Na), 14.2mL Hg, 1,2-bis(di-*p*-anisylphosphino)ethane (2eq, 9.54g, 18.4mmol), and THF (100mL) was added to a 1000mL round-bottomed Schlenk flask. Molybdenum pentachloride (1eq, 2.66g, 9.74mmol) was then added to the flask and the mixture was allowed to stir at room temperature for 24 hours under a dinitrogen atmosphere. The solution took on a brown color and was filtered *via* a Schlenk filter using celite and washed with toluene (50mL). The solvent volume was reduced and degassed methanol was added to precipitate the crude yellow product. The yellow solid was then crystallized from a toluene (~20mL)/methanol (~40mL) mixture at -19°C. The reaction produced the desired dinitrogen complex as yellow microcrystals (3.09g, 2.60mmol, 24.0%).

FW: 1189.0g/mol

MP: 130°C, dec

^{1}H NMR (399.905 MHz, C_6D_6, rt): δ = 7.28 (d, br, $J(^{1}H\ ^{1}H)$ = 8.8 Hz, 32H, H_{arom}); 6.69 (d, $J(^{1}H,^{1}H)$ = 8.8 Hz, 32H, H_{arom}); 3.23 (s, 24H, CH_3); 2.36 (t, $J(^{1}H,^{31}P)$ = 8.2 Hz, 8H, CH_2).

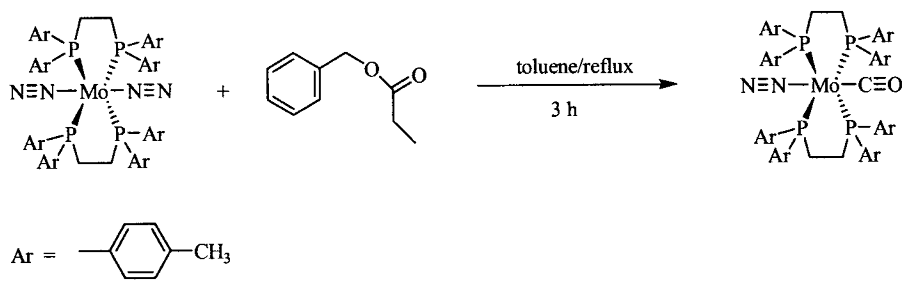
^{13}C NMR (100.565 MHz, C_6D_6, rt): δ = 160.52 (s, C_{arom}); 134.51 (d, $J(^{13}C,^{31}P)$ = 22.1 Hz, C_{arom}); 130.31 (d, $J(^{13}C,^{31}P)$ = 7.4 Hz, C_{arom}); 114.55 (s, C_{arom}); 54.79 (s, OCH_3); 25.79 (s, CH_2).

^{31}P NMR (161.884 MHz, C_6D_6, rt): δ = 62.212 (s, P).

IR (toluene, CaF_2): 1966 cm^{-1} (vs, ν N≡N).

5. Synthesis of the carbonyl "caps"[7]

5a. Synthesis of bis[1,2-bis(di-*p*-tolylphosphino)ethane]dinitrogencarbonyl molybdenum(0)



Equation 2.5.5a

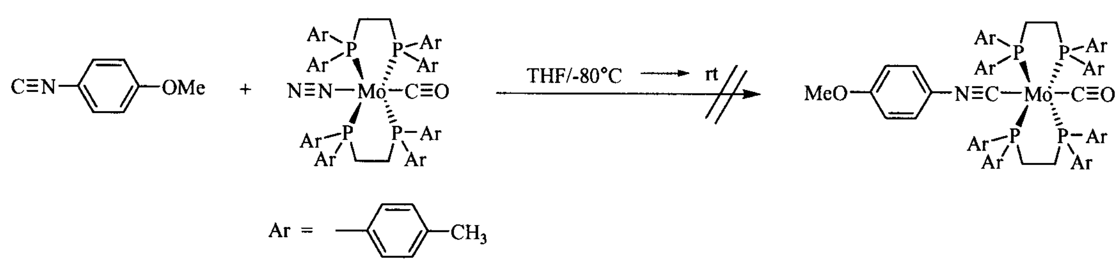
Bis[1,2-bis(di-*p*-tolylphosphino)ethane]bis(dinitrogen)molybdenum(0) (1eq, 0.62g, 0.58mmol) and toluene (35mL) was mixed together in a 250mL 3-necked round-bottomed flask. Benzyl propionate (10eq, 1.3mL) was added and the solution was heated to reflux for three hours upon which the solution became dark to nearly black. The solution was allowed to cool to room temperature under nitrogen, which resulted in some lightening of the color to golden brown. Hexane (15mL) was added and the product was crystallized by cooling the solution to 4°C and then to –19°C. The orange crystals were isolated and washed with hexanes (10mL). The yield is 0.307g (0.290mmol, 165%) and indicates that the product was impure.

FW: 1061.0g/mol

^{31}P NMR (161.884 MHz, C_6D_6, rt): $\delta = 64.03$ (s, P).

6. Synthesis of first generation nanorods containing monofunctional isonitriles

6a. Attempted preparation of 1-isocyano-4-methoxybenzene-bis-(1,2-bis(di-*p*-tolylphosphino)ethane)carbonylmolybdenum(0)



Equation 2.6.6a

The impure bis[1,2-bis(di-*p*-tolylphosphino)ethane]dinitrogen carbonylmolybdenum(0) from reaction 5a (1eq, 0.31g, 0.29mmol) was dissolved in THF (40mL). An isonitrile[3]/THF standard solution (0.088g/19.0mL) was prepared in a separate flask. Only 1eq (0.039g, 0.290mmol) of the isonitrile was needed for the reaction, so 8.5mL of the isonitrile/THF standard solution were placed in the dropping funnel. An additional 20mL of THF was then added to the dropping funnel. The receiving flask was cooled to -78°C using a dry ice/acetone bath. The isonitrile/THF mixture was slowly added *via* the dropping funnel. During the addition, the yellow solution turned orange, and upon complete addition the solution was allowed to warm to room temperature. The solution took on a red/orange color. The solid was crystallized from a THF (5mL)/hexanes (10mL) mixture as a mixture of yellow ((1,2-bis(di-*p*-tolylphosphino)ethane)$_2$MoH$_4$) and red ((1,2-bis(di-*p*-tolylphosphino)ethane)$_2$Mo(CNC$_6$H$_4$OMe)$_2$) crystals, which could not be completely separated.

Data for (1,2-bis(di-*p*-tolylphosphino)ethane)$_2$Mo(CNC$_6$H$_4$OMe)$_2$:

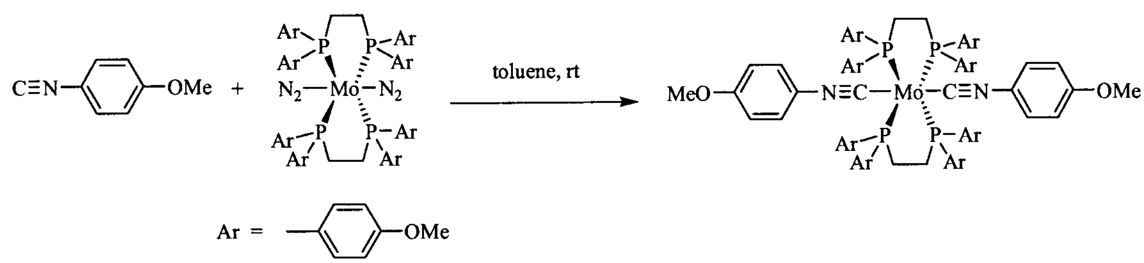
FW: 1166.2g/mol

^{1}H NMR (399.905 MHz, C$_6$D$_6$, rt): δ = 7.48 (d, $J(^1H,^1H)$ = 7.8 Hz, 32H, $H_{arom\ phosphine}$); 6.78 (d, $J(^1H,^1H)$ = 7.8 Hz, 32H, $H_{arom\ phosphine}$); 6.54 (d, $J(^1H,^1H)$ = 8.2 Hz, 4H, $H_{arom\ isonitrile}$); 6.33 (d, $J(^1H,^1H)$ = 8.2 Hz, 4H, $H_{arom\ isonitrile}$); 3.19 (s, 3H, OCH$_3$); 2.46 (br, 8H, CH$_2$); 2.03 (s, 24H, CH$_3$).

^{31}P NMR (161.884 MHz, C$_6$D$_6$, rt): δ = 71.34 (s, P).

7. Synthesis of zero generation nanorods containing monofunctional isonitriles[8]

7a. Preparation of bis(1-isocyano-4-methoxybenzene)bis[1,2-bis(di-*p*-anisylphosphino)ethane]molybdenum(0)



Equation 2.7.7a

The 1-isocyano-4-methoxybenzene (2.1eq, 0.064g, 0.48mmol) and bis[1,2-bis(di-*p*-anisylphosphino)ethane]bis(dinitrogen)molybdenum(0) (1eq, 0.218g 0.183mmol), and toluene (30mL) was placed in a 100 mL round-bottomed flask. The solution was stirred seven hours at room temperature and turned from a red/orange color to dark red. After stirring, some of the toluene was evaporated off and the solution was stored at 4°C overnight upon which red crystals formed. The solution was removed *via* syringe to leave red crystals, which were washed with 10mL of cold toluene (-80°C). The reaction produced (0.040g, 0.031mmol, 17.0%) of the desired complex.

FW: 1271.3g/mol

MP: 128°C, dec

^{1}H NMR (399.905 MHz, C_6D_6, rt): δ = 7.51 (d, br, $J(^1H,^1H)$ = 7.4 Hz, 32H, $H_{arom\ phosphine}$); 6.62 (d, $J(^1H,^1H)$ = 7.4 Hz, 32H, $H_{arom\ phosphine}$); 6.48 (d, $J(^1H,^1H)$ = 10 Hz, 4H,

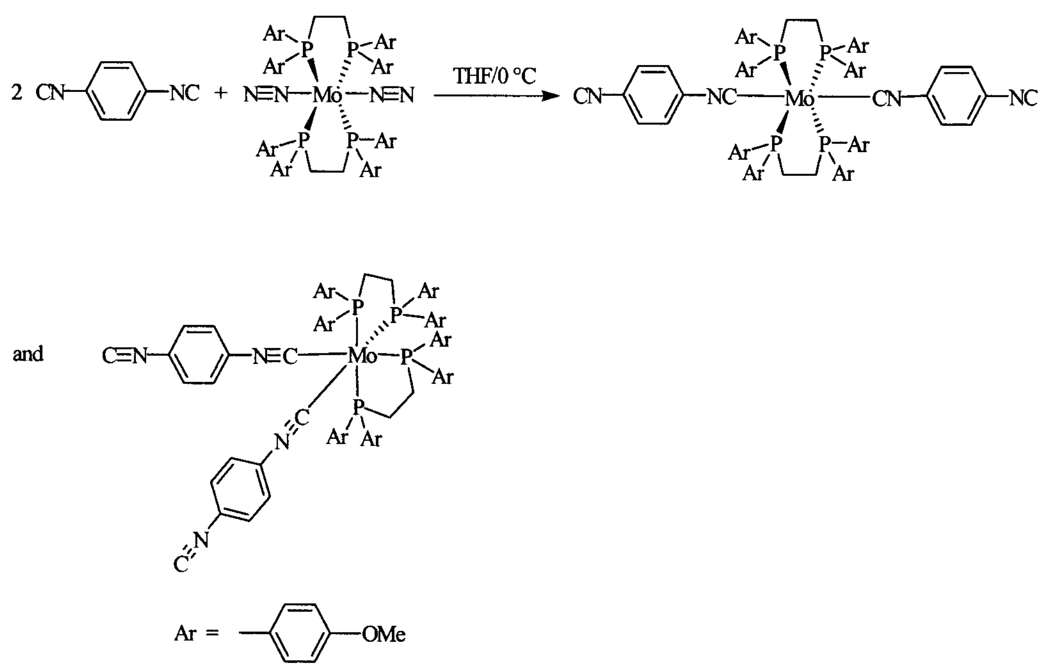
$H_{arom\ isonitrile}$); 6.40 (d, $J(^1H,^1H)$ = 10 Hz, 4H, $H_{arom\ isonitrile}$); 3.23 (s, 24H, CH_3); 3.166 (s, 6H, OCH_3); 2.47 (br, 8H, CH_2).

^{31}P NMR (161.884, C_6D_6, rt): $\delta = 70.53$ (s, P).

IR (toluene, CaF_2): 1878 cm^{-1} (s, ν C≡N); 1497 cm^{-1} (s, ν C=C).

8. Synthesis of zero generation nanorods containing bisfunctional isonitriles

8a. Preparation of bis(1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-anisylphosphino)ethane]molybdenum(0)



Equation 2.8.8a

1,4-Diisocyanobenzene (2.1eq, 0.0784g, 0.612mmol), bis[1,2-bis(di-*p*-anisylphosphino)ethane]bis(dinitrogen)molybdenum(0) (1eq, 0.3318g, 0.291mmol), and toluene (30mL) was placed in a 250mL round-bottomed Schlenk flask. The solution was stirred seven hours and turned yellow to green/yellow when mixing. Some of the toluene was evaporated off and hexane (5mL) was then added to the flask. Red powder-like crystals began to form at room temperature and the crystals were allowed to stand at room temperature for several hours. The crystals were collected on a Schlenk filter and washed with 10mL of cold ether (-80°C). The filtrate was reduced to dryness to give a brown viscous product. Ether (15mL) was added to dissolve the viscous product and the solution was then cooled to –19°C. Black micro-crystals formed and the solution was removed *via* syringe. The crystals were washed with toluene (-80°C) and dried *in vacuo*. Because of the small scale of the reaction an accurate yield could not be determined.

FW: 1390.3 g/mol

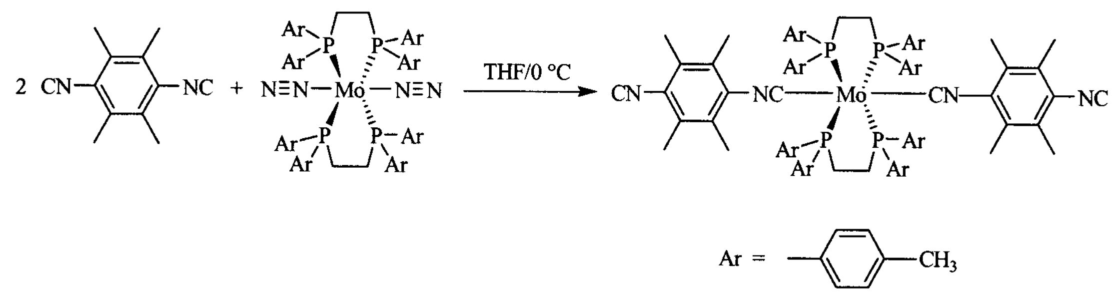
Melting Point: N/A

The ratio of *trans/cis* is approximately 1/2:

^{1}H NMR (399.905 MHz, C_6D_6, rt): **Signals for *cis*-complex:** δ = 7.87, 7.69, 7.47, 7.08, 6.97, 6.57, 6.45, 6.36 (all m, all 8H, all $H_{arom\ phosphine}$), 6.65, 6.49 (all m, all 8H, all $H_{arom\ isonitrile}$), 3.250, 3.149 (all s, all 12H, all H_{Me}). **Signals for *trans*-complex:** δ = 7.12 (m, 16H, $H_{arom\ phosphine}$), 6.55 (m, 16H, $H_{arom\ phosphine}$), 7.32, 7.02 (m, 4H, $H_{arom\ isonitrile}$), 3.16 (s, 24H, H_{Me}).

^{31}P NMR (161.884 MHz, C_6D_6, rt): **Signals for *cis*-complex:** δ = 19.351 (t, $J(^{31}P^{31}P)$ = 22.8 Hz, 2P), 40.592, (t, $J(^{31}P^{31}P)$ = 22.8 Hz, 2P). **Signals for *trans*-complex:** δ = 45.71 (s, 4P).

8b. Preparation of Bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-tolylphosphino)ethane]molybdenum(0)



Equation 2.8.8b

A 300mL 3-necked round-bottomed flask was equipped with a stir-bar, nitrogen adapter, and 100mL dropping funnel and then 1,4-bisisocyano-2,3,5,6-tetramethylbenzene (10eq, 0.751g, 4.08mmol) and THF (40mL) was placed in the flask. The bis[1,2-bis(di-*p*-tolylphosphino)ethane]bis(dinitrogen)molybdenum(0) (1eq, 0.433g, 0.408mmol) and THF (80mL) was placed in the dropping funnel. The flask was then placed in an ice bath and the dinitrogen complex/THF mixture was added dropwise to the flask. During the addition, the solution turned dark purple. After the addition was complete, the ice bath was removed and the solution was allowed to warm to room temperature. All of the solvent was removed under vacuum to leave a green solid. The green solid was washed three times with hexane (20mL) and collected using a Schlenk filter to remove any excess isonitrile. The solid, which was not soluble in hexane was dissolved using THF (50mL). Some of the THF was removed under vacuum and hexane (135mL) was added and the solution was cooled to -19°C to produce 0.168g, (0.123mmol, 30.0%) of brown micro-crystals.

FW: 1373.5g/mol

MP: 239°C, dec

^{1}H NMR (399.905 MHz, C_6D_6, rt): δ = 7.28 (d, $J(^{1}H,^{1}H)$ = 7.8 Hz, 32H, $H_{arom\ phosphine}$); 6.68 (d, $J(^{1}H,^{1}H)$ = 7.8 Hz, 32H, $H_{arom\ phosphine}$); 2.75 (d, br, 8H, CH_2); 1.92 (s, 24H, $CH_{3\text{-}phosphine}$); 1.90 (s, 24H, $CH_{3\ arom\ isonitrile}$); 1.28 (s, 24H, $CH_{3\ arom\ isonitrile}$).

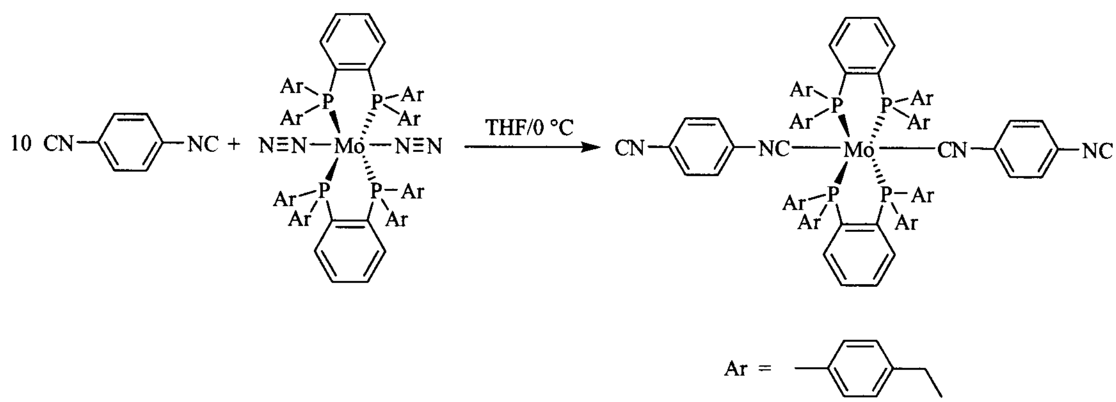
^{13}C NMR (100.565 MHz, C_6D_6, rt): δ = 170.71 (s, CN); 141.40 (s, br, $C_{arom\ phosphine}$); 137.97 (s, $C_{arom\ phosphine}$); 133.48 (s, $C_{arom\ phosphine}$); 132.70 (s, $C_{arom\ isonitrile}$); 131.11 (s, $C_{arom\ phosphine}$); 122.80 (s, $C_{arom\ isonitrile}$); 33.00 (s, br, CH_2); 21.91 (s, $CH_{3\ phosphine}$); 16.82 (s, $CH_{3\ isonitrile}$).

^{31}P NMR (161.884 MHz, C_6D_6, rt): δ = 66.27 (s, P).

IR (toluene, CaF_2): 1834 cm^{-1} (s, ν C≡N).

EA: Anal. Calc. for $C_{84}H_{88}P_4N_4Mo_1$: Carbon: 73.46%, Hydrogen: 6.46%, Nitrogen: 4.08%; Found: Carbon: 72.85%, Hydrogen: 6.62%, Nitrogen: 4.05%.

8c. Preparation of bis(1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-ethylphenylphosphino)benzene]molybdenum(0)



Equation 2.8.8c

1,4-Diisocyanobenzene (10eq, 0.31g, 2.43mmol) was placed in a 200mL 3-necked round-bottomed flask equipped with a stir-bar, nitrogen adapter, and 100mL dropping funnel. Bis[1,2-bis(di-*p*-ethylphenylphosphino)benzene]bis(dinitrogen)molybdenum(0) (1eq, 0.256g, 0.202mmol) was added to the dropping funnel. Tetrahydrofuran (40mL) was added to the flask and 80mL was added to the dropping funnel. The flask was placed in an ice bath and the dinitrogen complex/THF solution was slowly added to the flask. During the addition, the solution turned dark brown to black. After the addition was complete, the solution was allowed to warm to room temperature. The solvent was removed and the excess isonitrile was removed by sublimation to leave a brown solid. The solid was crystallized from a THF (5mL)/hexane (10mL) mixture at –19°C to produce brown microcrystals. Due to the small amount of product obtained, a percent yield could not be determined.

FW: 1469.6g/mol

MP: 241°C, dec

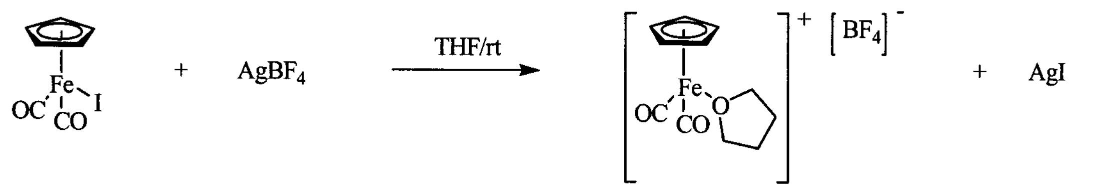
^{1}H NMR (399.905 MHz, C_6D_6, rt): δ = 7.70 (br, 8H, $H_{benzene\text{-}backbone}$); 7.17 (d, $J(^1H,^1H)$ = 9.4 Hz, 32H, $H_{arom\ phosphine}$); 7.00 (m, br, 8H, $H_{benzene\text{-}backbone}$); 6.80 (d, $J(^1H,^1H)$ = 9.4 Hz, 32H, $H_{arom\ phosphine}$); 6.46 (d, $J(^1H,^1H)$ = 8.6 Hz, 8H, $H_{arom\ isonitrile}$); 5.34 (d, $J(^1H,^1H)$ = 8.6 Hz, 8H, $H_{arom\ isonitrile}$); 2.37 (q, $J(^1H,^1H)$ = 7.6 Hz, 16H, CH_2); 1.04 (t, $J(^1H,^1H)$ = 7.6 Hz, 24H, CH_3).

^{31}P NMR (161.884 MHz, C_6D_6, rt): δ = 74.67 (s, P).

EA: Anal. Calc. for $C_{92}H_{88}P_4N_4Mo_1$: Carbon: 75.19%, Hydrogen: 6.04%, Nitrogen: 3.81%; Found: Carbon: 71.08%, Hydrogen: 5.84%, Nitrogen: 3.60%.

9. Synthesis of the iron complexes

9a. Synthesis of (dicarbonyl)(η^5-cyclopentadienyl)(tetrahydrofuran)iron(II) tetrafluoroborate[9]



Equation 2.9.9a

A 500mL Schlenk round-bottomed flask was wrapped in aluminum foil. A mixture of (η^5-C_5H_5)$Fe(CO)_2I$[10] (15.0g, 49.4mmol), $AgBF_4$ (9.79, 50.3mmol), and THF (250mL) was placed in the flask and stirred at room temperature for 24 hours. While stirring, the solution turned red and silver iodide formed as a white precipitate. After stirring, all the THF was removed under vacuum and the solid was filtered using celite and extracted with dichloromethane. The solvent was reduced to 125mL and ether (150mL) was added to precipitate red crystals out of solution. The flask was stored on ice for one hour upon which more red crystals formed. The crystals were filtered and washed with ether (50mL). The product was recrystallized from dichloromethane (100mL)/ether (150mL) containing a few drops of THF and was stored at 4°C. The reaction produced bright red and black crystals (11.2g, 33.3mmol, 67.5%).

FW: 335.9g/mol

MP: 99°C, dec

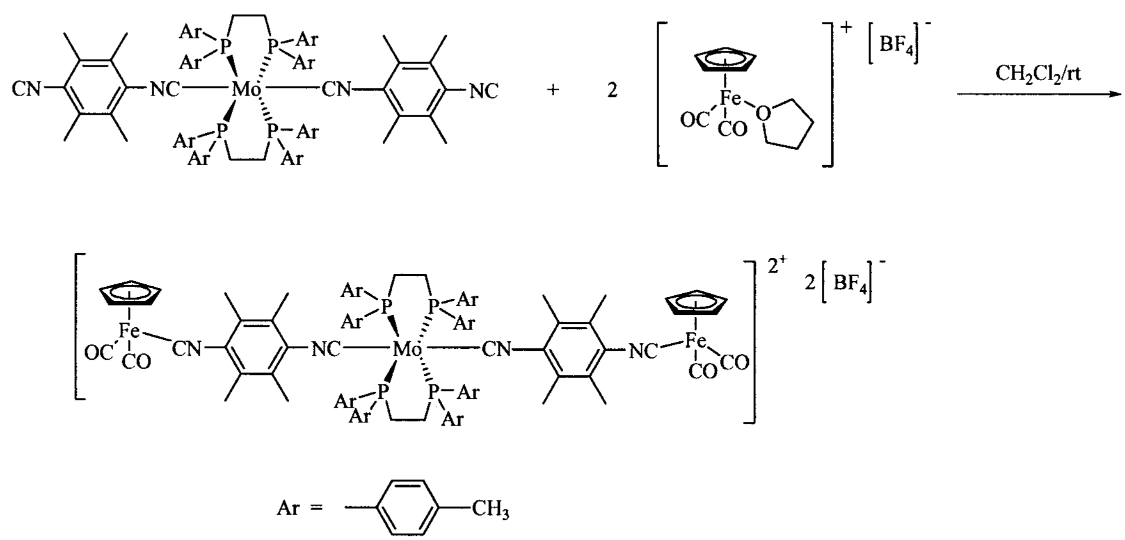
^{1}H NMR (399.905 MHz, acetone-d^6, rt): $\delta = 5.71$ (s, 5H, Cp-ring); 3.62 (m, 2H, thf); 1.82 (m, 2H, thf).

The NMR data are in agreement with the reported values.[9]

IR (CH_2Cl_2, CaF_2): 2070 cm^{-1} (vs, ν C≡O); 2023 cm^{-1} (vs, ν C≡O); 1262 cm^{-1} (vs, ν C=C).

10. Synthesis of first generation nanorods containing bisfunctional isonitriles

10a. Attempted preparation of μ-{bis[tetramethyl-1,4-(diisocyano)benzene]bis[1,2-bis(di-*p*-tolylphosphino)ethane]molybdenum(0)} bis[(dicarbonyl)(η^5-cyclopentadienyl)iron(II)]



Equation 2.10.10a

A stock solution was made containing (dicarbonyl)(η^5-cyclopentadienyl)(tetrahydrofuran)iron(II)tetrafluoroborate (0.498g) in dichloromethane (50mL). Bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-tolylphosphino)ethane]molybdenum(0) 0.202g (1eq, 1.147mmol) was placed in the flask. The stock solution (10mL) containing 0.202g (2eq, 0.147mmol) of the salt was then added to the flask. The solution turned pink quickly and dichloromethane (15mL) was added to the flask to increase the volume of solvent. The solution was stirred for 5 hours, layered with hexane (100mL), and stored at -19°C. Small red-brown microcrystals formed and the solvent was removed *via* syringe. The crystals were washed with hexane and dried under vacuum. The reaction produced 0.09g of product. The NMR spectra exhibited very broad lines and could not be interpreted. The other spectral and analytical data are only partially in agreement with the expected values and the identity of the product could not be determined.

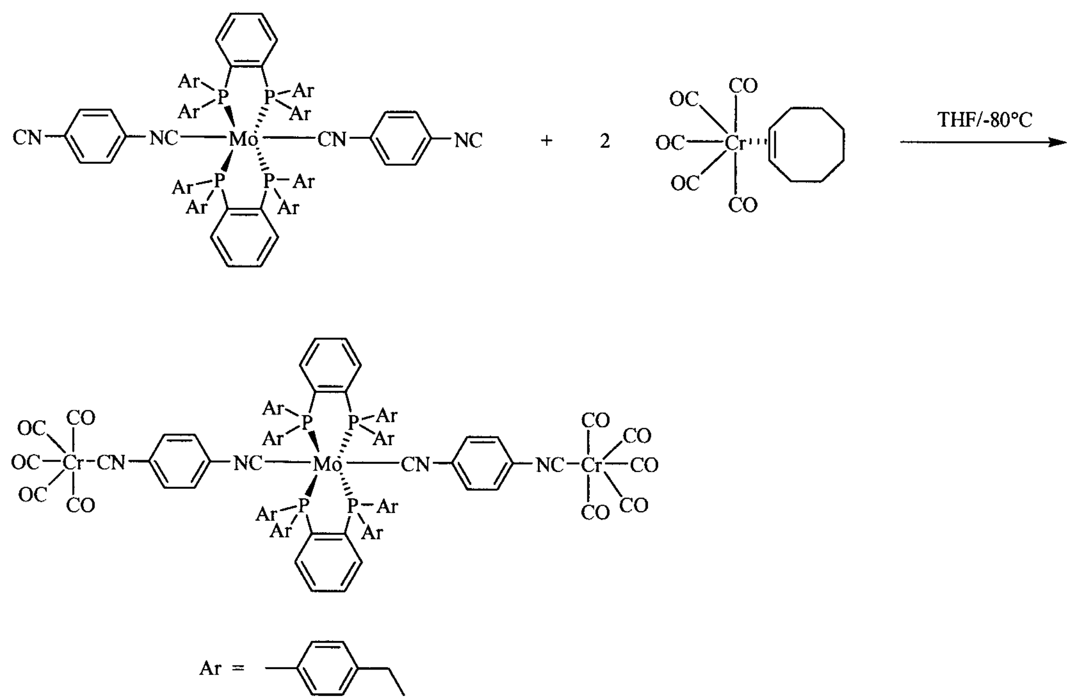
FW: 1901.0g/mol

MP: 305°C, dec

IR (CH_2Cl_2, CaF_2): 1921 cm^{-1} (m, ν C≡O); 1421 cm^{-1} (m, ν C≡N); 1261 cm^{-1} (vs, ν C=C).

EA: Anal. Calc. for $C_{98}H_{98}N_4O_4P_4Fe_2Mo_1$: Carbon: 61.92%, Hydrogen: 5.20%, Nitrogen: 2.94%; Found: Carbon: (1) 59.08%, (2) 59.23%, Hydrogen: (1) 5.11%, (2) 5.28%, Nitrogen: (1) 2.74%, (2) 2.74%

10b. Preparation of μ-{bis(1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-ethylphenylphosphino)benzene]molybdenum(0)}bis[(chromium pentacarbonyl)]



Equation 2.10.10b

Bis(1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-ethylphenyl)phosphino)benzene] molybdenum(0) (1eq, 0.0871g, 0.053mmol) and THF (20mL) was placed in a 100mL Schlenk round-bottomed flask. Cyclooctene chromiumpentacarbonyl[11] (2.1eq, 0.038g, 0.126mmol) was then added to the flask. The flask was placed in a dry ice/ethanol bath and the solution was stirred approximately five hours. While stirring the solution turned dark green. The flask was allowed to warm up to room temperature and all the solvent was removed under vacuum to leave a black solid. The black solid was dissolved in ether

(15mL) and the solution was cooled to -19°C. Black crystals formed at this temperature and were washed with 4 × 5mL hexane. Because of the small scale of the product, an accurate percent yield could not be determined.

FW: 1853.7g/mol

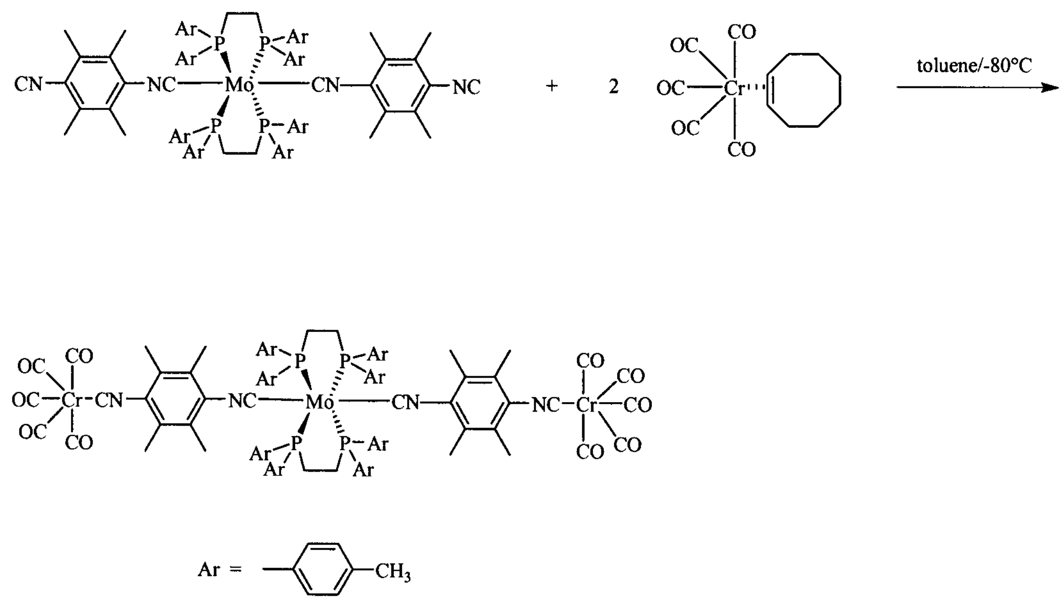
Melting Point: N/A

^{1}H NMR (399.905 MHz, CD_2Cl_2, rt): δ = 7.40 (br, 4H, $H_{benzene\text{-}backbone}$); 7.10 (s, br, 4H, $H_{benzene\text{-}backbone}$); 6.53 (dd, $J(^{1}H,^{31}P)$ = 22.0 Hz, 32H, $H_{arom\ phosphine}$); 6.51 (dd, $J(^{1}H,^{1}H)$ = 22.4 Hz, 32H, $H_{arom\ phosphine}$); 5.19 (d, $J(^{1}H,^{1}H)$ = 4.0 Hz, 8H, $H_{arom\ isonitrile}$); 2.29 (dd, $J(^{1}H,^{1}H)$ = 16 Hz, 16H, CH_2); 2.27 (dd, $J(^{1}H,^{1}H)$ = 16 Hz, 16H, CH_2); 0.90 (t, $J(^{1}H,^{1}H)$ = 7.6 Hz, 24H, CH_3).

^{13}C NMR (100.565 MHz, CD_2Cl_2, rt): δ = 246.40 (s, CO); 243.95 (s, CO); 162.18 (s, $C_{arom\ phosphine}$); 156.20 (s, $C_{arom\ phosphine}$); 58.08 (s, CH_2); 45.18 (s, CH_3).

IR (toluene, CaF_2): 2056 cm^{-1} (m, ν C≡O); 1956 cm^{-1} (vs, ν C≡O); 1844 cm^{-1} (w, ν C≡N).

10c. Preparation of μ-{bis[2,3,5,6-tetramethyl-1,4-(diisocyano)benzene]bis[1,2-bis(di-*p*-tolylphosphino)ethane]molybdenum(0)}bis[(chromium pentacarbonyl)]



Equation 2.10.10c

The complex bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-tolylphosphino)ethane]molybdenum(0) (1eq, 0.13g, 0.093mmol) and toluene (35mL) was placed in a 100mL round-bottomed Schlenk flask. The flask was placed in a dry ice/ethanol bath and cooled to -78°C. Cyclooctene chromiumpentacarbonyl (2.1eq, 0.063g, 0.208mmol) was then added to the flask, and the mixture was slowly warmed to room temperature. The solution turned purple to dark blue and was stirred for five hours. The toluene was removed under vacuum to leave a brown solid. The solid was then dissolved in a minimum amount of toluene and hexane (100mL) was added to crystallize the desired complex. The flask was stored at -19°C and small dark purple crystals formed after several days. The solvent was removed *via* syringe and the crystals were washed with a cold toluene/hexane mixture (1:3) at -78°C. Because of the small amount of the product, no accurate percent yield or elemental analysis could be determined.

FW: 1757.6g/mol

MP: 280°C

^{1}H NMR (399.905 MHz, CD_2Cl_2, rt): δ = 7.02 (br, 24H, $H_{arom\ phosphine}$); 6.68 (br, 24H, $H_{arom\ phosphine}$); 2.55 (br, 8H, CH_2); 2.15 (s, 24H, $CH_{3\ phosphine}$); 2.071 (s, 24H, $H_{arom\ isonitrile}$); 1.04 (s, 24H, $CH_{3\ isonitrile}$).

IR (CH_2Cl_2, CaF_2): 2056 cm^{-1} (w, νC≡O); 1954 cm^{-1} (m, νC≡O); 1833 (w, νC≡N).

EA: Anal Calc. for $C_{94}H_{88}N_4O_{10}P_4Cr_2Mo_1$: Carbon: 64.24%, Hydrogen: 5.05%, Nitrogen: 3.19%; Found: Carbon: 58.69%, Hydrogen: 4.59%, Nitrogen: 2.87.

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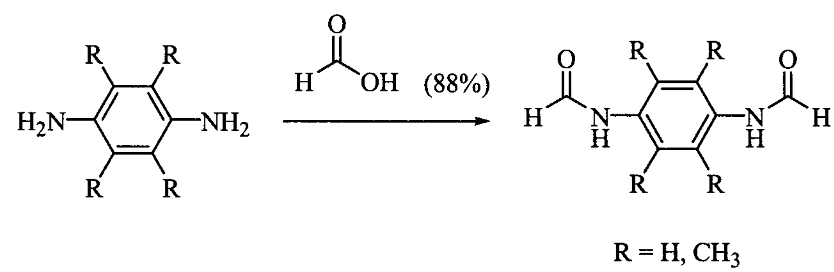
Chapter Three

Results and Discussion

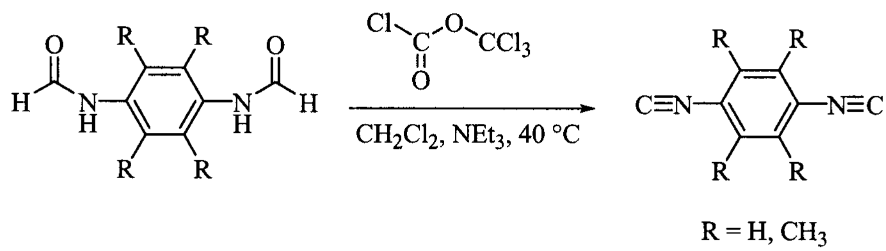
1. Formamide synthesis[1]



Equation 3.1

The formamides 1,4-bis(N-formylamino)benzene and 1,4-bis(N-formylamino)-2,3,5,6-tetramethylbenzene were prepared by previously reported methods.[1] Thus, the appropriate diamine was reacted with 88% formic acid to produce water and the desired formamide. The formamides are not soluble in any common organic solvents; therefore, no NMR, IR, or mass spectroscopy data were obtained. They were isolated as white or brown powders and their identities were confirmed by their transformations into the corresponding isonitriles. The formamides are stable towards air and moisture. The 1,4-bis(N-formylamino)benzene was isolated as a brown powder in nearly quantitative yield (190.0g, 1.16mol. 99.7%). The 1,4-bis(N-formylamino)-2,3,5,6-tetramethylbenzene was isolated as a white powder in quantitative yield (121.7g, 552mmol, 100%). The formamides have high melting points, which can be attributed to their hydrogen bonds.

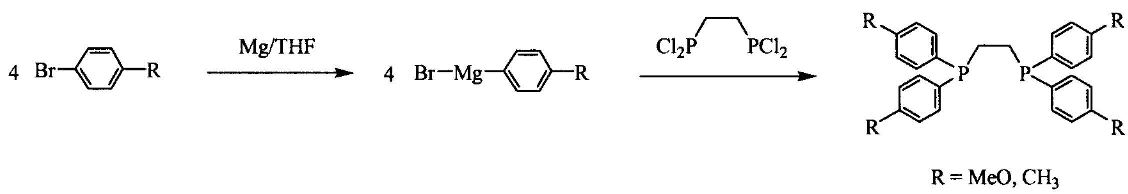
2. Isonitrile synthesis[2]



Equation 3.2

The isonitriles were also prepared by previously reported methods.[2] Trichloromethylchloroformate was used as the dehydrating agent to remove water and produce the desired isonitrile. When synthesizing 1,4-bisisocyano-2,3,5,6-tetramethylbenzene, the purification step using the neutral alumina column was omitted because it resulted in loss of product. Instead, the impure isonitrile was dried under vacuum for several hours in a hot oil bath to remove the excess triethylamine. Afterwards, the isonitrile was sublimed to obtain a pure product. The ^{1}H and ^{13}C NMR and IR data are consistent with literature values and show that the products are the desired isonitriles. The bifunctional isonitriles prepared in this thesis are stable towards air and moisture for a short time, but are stored under nitrogen because they decompose upon prolonged exposure to air and moisture. The white crystals slowly turn to a brown color upon decomposition. The isonitriles are decomposed by air more rapidly in solution and are therefore handled under a nitrogen atmosphere. The 1,4-diisocyanobenzene was isolated as large, white crystals (10.3g, 80.4mmol, 44.0%) while 1,4-bisisocyano-2,3,5,6-tetramethylbenzene was isolated as small white crystals (5.97g, 32.4mmol, 23.0%).

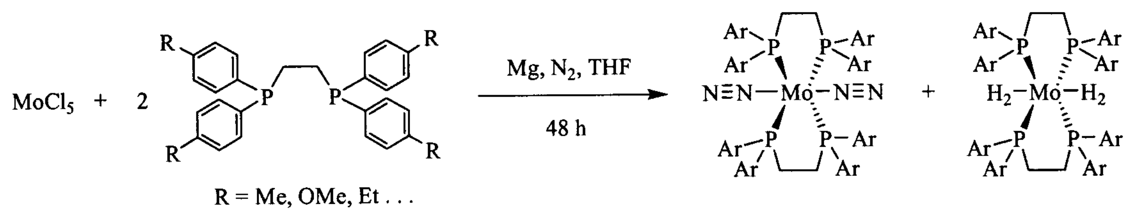
3. Chelating phosphines[3]



Equation 3.3

Using conventional methods,[3] the phosphines were successfully prepared using a Grignard route. Once the final Grignard solution is formed, 1,2-bis(dichlorophosphino)ethane is added to form the phosphine-backbone or "bridge". The reaction produces the phosphines as white crystalline powders, which are stable towards air and moisture in the solid state. However, the phosphines are air sensitive in solution and thus dissolved samples are handled under a nitrogen atmosphere. The ^1H, ^{13}C, and ^{31}P NMR data are consistent with the literature values and indicate that the desired phosphines were obtained. However, a ^{13}C NMR spectrum was not obtained for 1,2-bis(di-*p*-tolylphosphino)ethane because decoupler problems prevented the NMR spectrum from being analyzed. The 1,2-bis(di-*p*-anisylphosphino)ethane was isolated as a white powder (11.17g, 21.5mmol, 69.0%). The 1,2-bis(di-*p*-tolylphosphino)ethane was isolated as a clear crystalline powder (16.0g, 36.2mmol, 62.5%).

4. Dinitrogen complexes[4]

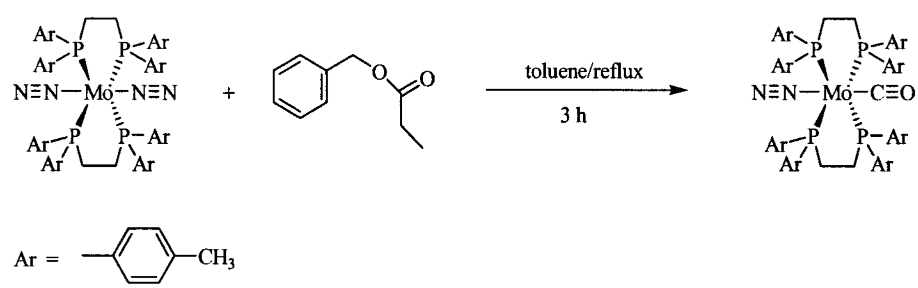


Equation 3.4

The dinitrogen complexes were prepared successfully under a nitrogen atmosphere by conventional methods.[4] When synthesizing the dinitrogen complexes, the tetrahydride is often formed as a byproduct and is isolated as yellow microcrystals. The tetrahydride is not easy to separate from the dinitrogen complex. Therefore, slow recrystallization from a THF/methanol mixture is required. When using sodium/amalgam as the reducing agent, less of the tetrahydride is present among the dinitrogen complex. However, the sodium amalgam route is less favored because of the hazards and disposal of mercury.

The dinitrogen complexes are stable towards air and moisture in the solid state. On the other hand, they are sensitive to air and moisture in solution and are handled under a nitrogen atmosphere. If exposed to air and moisture while in solution, the orange solution turns to a dark brown color within several minutes. The NMR and IR spectra indicate that clean dinitrogen complexes were obtained after recrystallization and these spectra are in accord with literature values. Bis[1,2-bis(di-*p*-tolylphosphino) ethane]bis(dinitrogen)molybdenum(0) was isolated as orange crystals (2.94g, 2.76mmol, 26.4%). Bis[1,2-bis(di-*p*-anisylphosphino)ethane]bis(dinitrogen)molybdenum(0) was isolated as yellow microcrystals (3.09g, 2.60mmol, 24.0%). The ^{1}H, ^{13}C, and ^{31}P NMR indicates that just the dinitrogen complex is present. The tetrahydride can be observed by ^{1}H NMR where one sees a double set of signals and a quintet at approximately -3.5 ppm. In ^{31}P NMR there is a coupling constant at approximately 30 Hz.

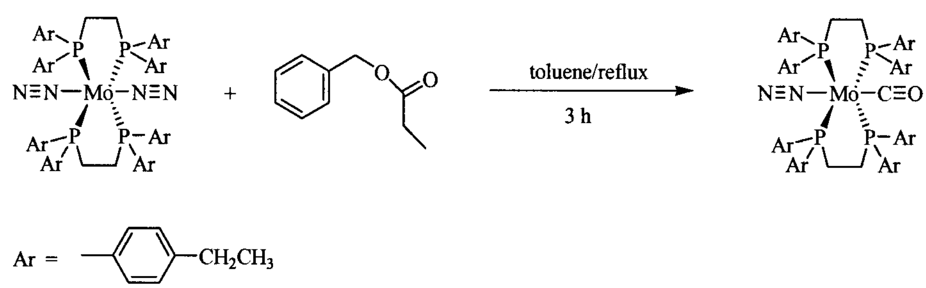
5. Carbonyl-capped complexes[5]



Equation 3.5a

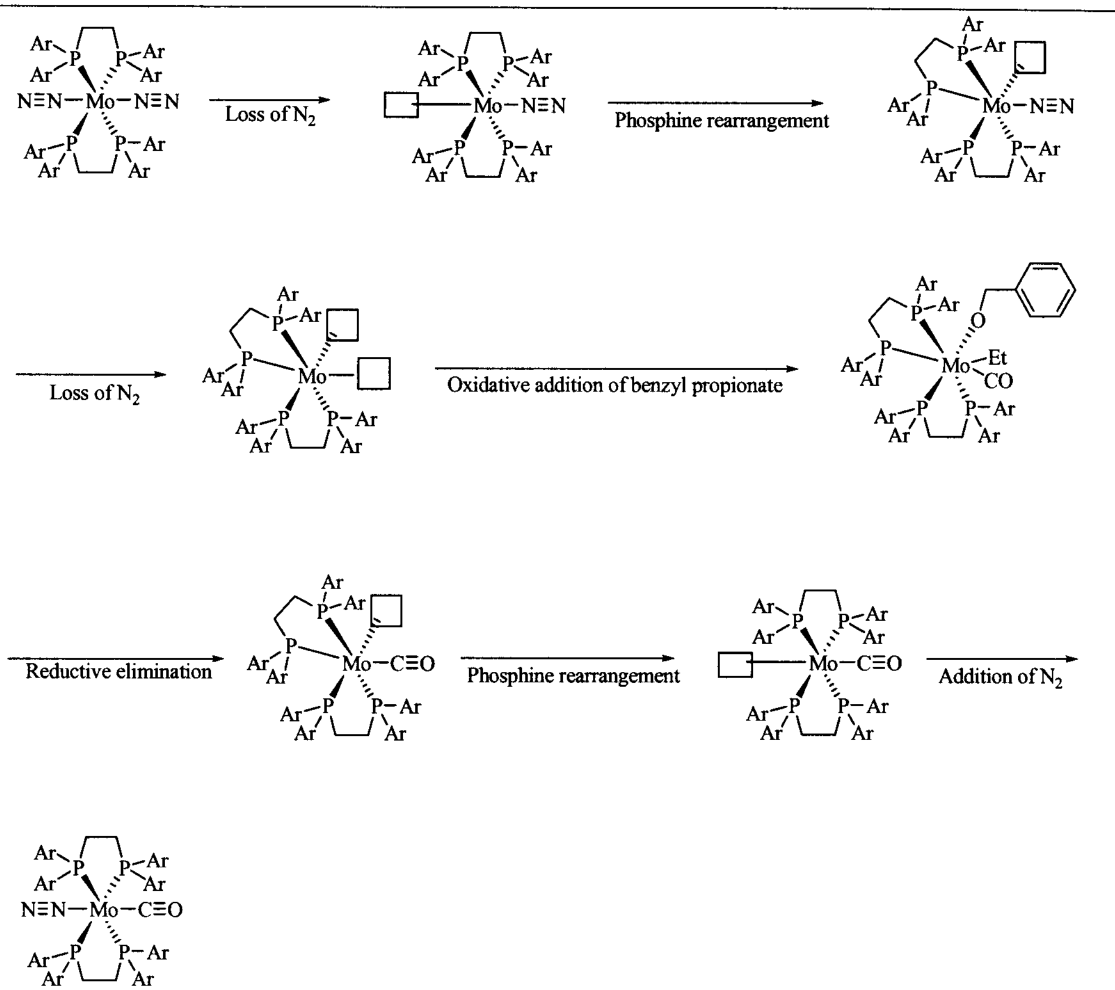
Bis[1,2-bis(di-*p*-tolylphosphino)ethane]dinitrogencarbonylmolybdenum(0) was synthesized according to literature methods.[5] However, the reaction did not proceed smoothly. The percent yield indicates that the product is impure even after several attempts at recrystallization. The ^{1}H and ^{31}P NMR indicates that there is starting material present in the product together with byproduct which could not be assigned. Other attempts have been tried to make the desired bis[1,2-bis(di-*p*-tolylphosphino)ethane]dinitrogencarbonylmolybdenum(0) complex, but the reaction could not be repeated for reasons, which are unknown. The impure product was isolated as orange powder-like crystals in 0.307g (2.290mmol, 165%). In order to determine if the desired CO-complex was produced, the reaction was monitored using both IR and nuclear magnetic resonance spectroscopy. Infrared spectroscopy will indicate if the dinitrogen complex has been completely converted to the CO-complex as indicated by a C≡O stretch at approximately 1818 cm^{-1}. Another alternative to benzyl propionate is the use of carbon monoxide gas to replace the dinitrogen ligand with the CO ligand.

Coworkers in the Hunter group tried to synthesize other carbonyl "caps" which could be used as analogues to bis[1,2-bis(di-*p*-tolylphosphino)ethane]dinitrogencarbonylmolybdenum(0). The carbonyl complex bis[1,2-bis(di-*p*-ethylphenylphosphino)ethane]dinitrogencarbonylmolybdenum(0) was successfully synthesized and characterized by Dr. Matthias Zeller (**Equation 3.5b**). The product was isolated as orange needles in a yield of 0.764g (0.65mmol, 30.6%).



Equation 3.5b

The mechanism for the reaction is quite complicated and is illustrated in the scheme below.

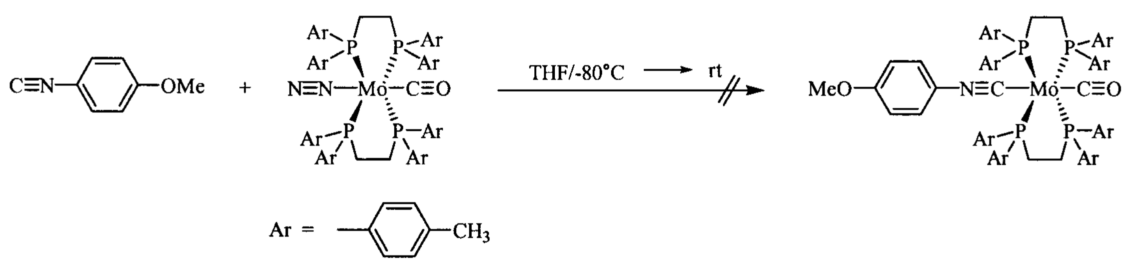


Scheme 3.1 Possible mechanistic scheme for the reaction of benzyl propionate with a dinitrogen complex.

This is an oxidative addition/reductive elimination reaction in which the metal is inserted into either the carbon-carbonyl carbon bond or the oxygen-carbonyl carbon bond. The mechanism for this reaction has not been established. However, it is known that this reaction occurs only when there are two empty and adjacent coordination sites present at the metal center. These two adjacent empty coordination sites may be obtained through a few steps as illustrated in **Scheme 3.1**. First, a dinitrogen ligand is lost. One phosphorus atom of a phosphine ligand migrates (perhaps *via* an intermediate dissociative step) and fills the site vacated by the dinitrogen ligand. The overall effect of this is that the empty coordination site is shifted next to the remaining dinitrogen ligand. The remaining dinitrogen ligand dissociates and the metal is inserted into one of the bonds of the benzyl propionate molecule. This is followed by a second oxidative addition-bond cleavage. The benzolate and alkyl groups are then reductively eliminated, leaving only the carbonyl attached to the metal. Migration of one of the phosphines and reattachment of a dinitrogen ligand *para* to the new carbonyl completes the reaction sequence. Multiple attempts of this reaction resulted in no product being isolated despite its success with dppe for both molybdenum and tungsten. A possible reason for this is due to the rigidity provided by the 1,2-phenylene backbone of the phosphine. Thus, this phenylene phosphine cannot readily dissociate and/or migrate and two adjacent empty coordination sites cannot be created. This observation is consistent with the great stability reported for many 1,2-$R_2PC_6H_4PR_2$ complexes.

6. First generation nanorods containing monofunctional isonitriles

6a. 1-isocyano-4-methoxybenzene-bis-(1,2-bis(di-*p*-tolylphosphino)ethane) carbonylmolybdenum(0)

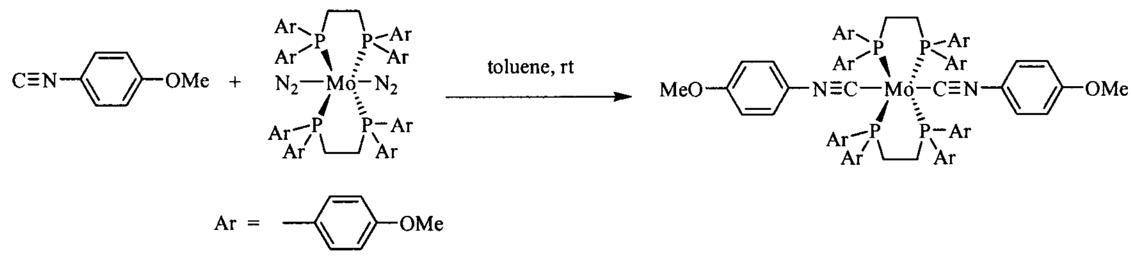


Equation 3.6

The reaction which used the impure starting material from above (bis[1,2-bis(di-*p*-tolylphosphino)ethane]dinitrogencarbonylmolybdenum(0)) produced a mixture of yellow and red crystals (1-isocyano-4-methoxybenzene-bis-(1,2-bis(di-*p*-tolylphosphino)ethane)carbonylmolybdenum(0)). The yellow crystals are a tetrahydride derivative as indicated by ^{1}H NMR and there are also two peaks at approximately 1.9 and 0.4 ppm, which could not be identified. Despite several attempts at recrystallization, the red and yellow crystals could not be separated; therefore a percent yield was not obtained. This is most likely due to similar solubilities for the two complexes. Further investigation needs to be considered on how to produce bis[1,2-bis(di-*p*-tolylphosphino)ethane]dinitrogencarbonylmolybdenum(0) in clean, quantitative yields. After achieving this, then the synthesis of the desired complex can be attempted.

7. Zero generation nanorods containing monofunctional isonitriles

7a. Bis(1-isocyano-4-methoxybenzene)bis[1,2-bis(di-*p*-anisylphosphino) ethane]molybdenum(0)[6]

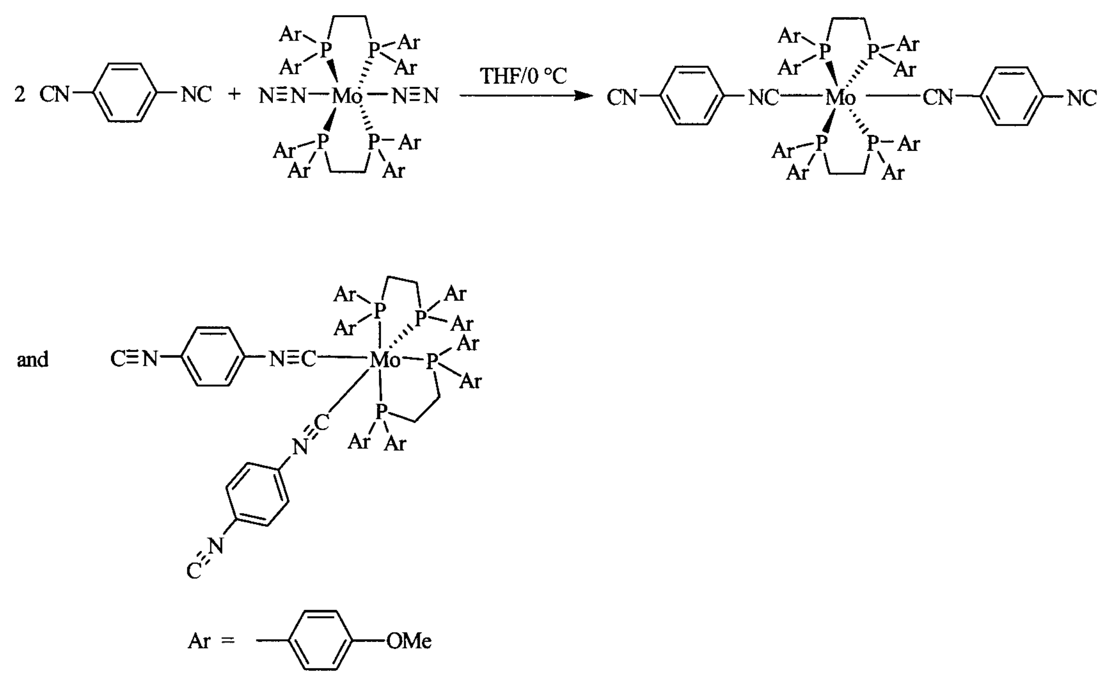


Equation 3.7

The complex was prepared successfully as indicated by NMR and IR. The ^{1}H and ^{31}P NMR spectra show that all of the required signals are present and that the complex exhibits the *trans*-conformation which is consistent with the literature values.[6] The *trans*-conformation is more stable than the *cis*-conformation because there is less steric hindrance among the phosphine ligands. IR spectroscopy also indicates the C≡N stretching frequency at 1878 cm^{-1}. The low isolated yield indicates that the reaction may not have gone to completion or that there was polymerization/decomposition of the isonitrile in solution. The monofunctional isonitrile is slightly sensitive in air and is volatile which may also have contributed to the low isolated yield (0.040g, 0.031mmol, 17.0%). Perhaps percent yield can be improved if the reaction mixture is stirred for a longer period of time while being monitored by IR. Infrared spectroscopy will indicate the absence of the dinitrogen ligands as they are replaced by each C≡N ligand of the monofunctional isonitrile.

8. Zero generation nanorods containing bisfunctional isonitriles

8a. Bis(1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-anisylphosphino)ethane] molybdenum(0)

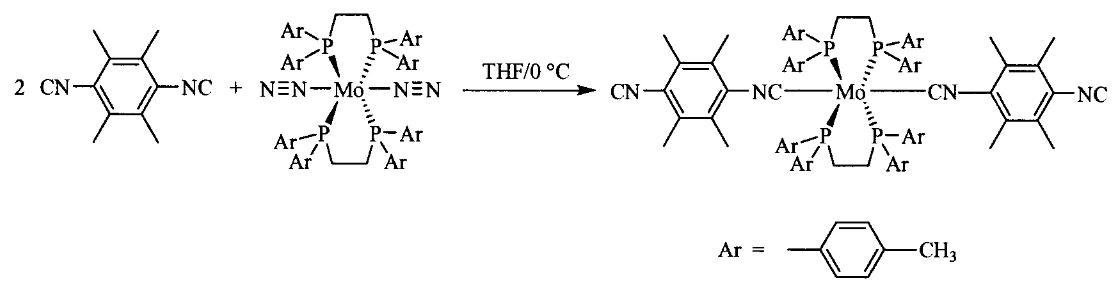


Equation 3.8a

When preparing this complex, the reaction did not proceed cleanly and could not be reproduced. It is thought that the dinitrogen complex containing the methoxy groups makes it much too soluble in solution to be separated from the byproducts by crystallization. Also, the 1,4-diisocyanobenzene decomposes more readily in solution as compared to other more electron rich isonitriles containing different substituents (*e.g.*, Me, Et, etc.). Only a few crystals could be isolated and a percent yield could not be determined. According to ^1H and ^{31}P NMR, the desired complex was synthesized, but is present in both the *cis*- and *trans*-conformations. In the aromatic region of the ^{1}H NMR spectrum, some of the signals are overlapping with each other and could not be fully analyzed. However, the remaining signals are well resolved, show the expected coupling patterns, and are in agreement with the postulated mixture of a *cis*- and *trans*-complex. When synthesizing the nanorods, the *trans*-symmetry is preferred because the conjugation between the metal centers will be maximized. A *cis*-conformation in the nanorods will most likely result in reduced conjugation between the metal centers because of the nature of the overlap of the two metal isonitriles. The *cis*-complex may be present because there is not as much steric hindrance between the hydrogens on the isonitriles and the *ortho*-substituents on the phosphine ligands.

When the *cis*-conformation is formed, the coordinated isocyanides exhibit surprisingly short metal-carbon bonds; therefore, there is substantial distortion of the ligand geometry resulting in strong electronic stabilization. This electronic stabilization results from the ability of the isocyanide ligand to polarize charge away from an electron-saturated metal center. In the *cis*-complex, the bulky bidentate phosphine ligands also create substantial steric constraints. When the complex exhibits the *trans*-conformation, these significant electronic effects are absent. In low-valent organometallic complexes, electronic stabilization usually depends on the ability of the ligands in the coordination sphere to polarize negative charge away from the electron-rich metal center, thus the isocyanide ligands behave as π-acceptors. In the *trans*-complex, the ligands behave as weak π-acceptors, while in the *cis*-conformation strong π-acids could create enough electronic stabilization while competing for π-electron density to overcome steric repulsions.[7]

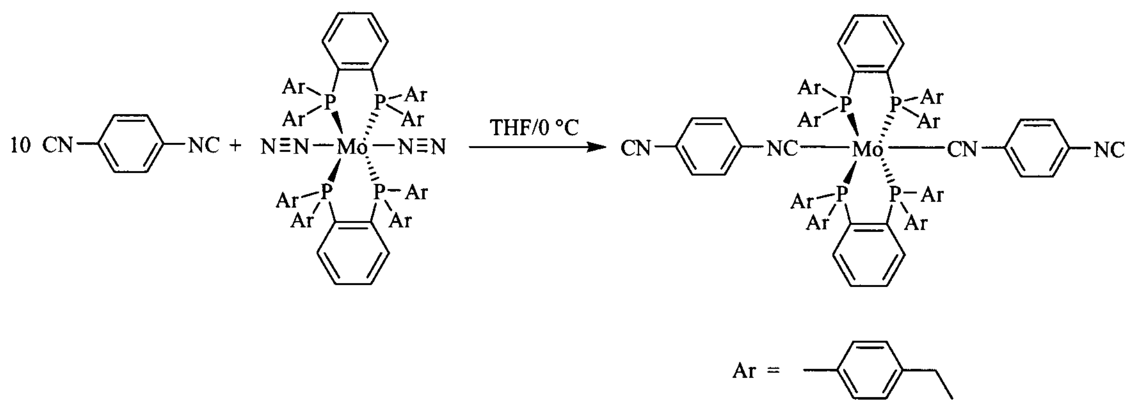
8b. Bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-tolyl phosphino)ethane]molybdenum(0)



Equation 3.8b

The bis(isonitrile) complex (**Equation 3.8b**) was synthesized because it was thought that the methyl groups on the isonitrile and the phosphine would enhance the solubility of the complex while allowing for less decomposition and easier crystallization. The complex was repeatedly produced in yields ranging from 17.0-30.0%. The relatively low yields are from an un-optimized isolation/recrystallization procedure. The identity of the complex was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Infrared spectroscopy and elemental analysis was also done to confirm the identity of the complex. Only the *trans*-complex is present because of adverse steric interactions in the *cis*-complex. This complex is more stable than bis(1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-anisylphosphino)ethane]molybdenum(0) because the isonitrile is more stable when it contains the methyl groups and the tolyl-phosphine ligand is less soluble than the anisole ligand which allows for easier recrystallization and purification. It is believed that the solubilities of various ligands are related to their rotational flexibility. The anisole ligands have lower barriers for rotation and are usually more soluble and harder to crystallize. The tolyl-phosphine ligands have high barriers for rotation; therefore making them less soluble and, thus easier to crystallize. According to elemental analysis, the amount of carbon was 72.85%, hydrogen 6.62%, and nitrogen 4.05% as compared to the theoretical values of carbon 73.46%, hydrogen 6.46%, and nitrogen 4.08%. The metallic-brown microcrystals obtained are soluble in toluene, tetrahydrofuran, methylene chloride, and benzene. When the complex is dissolved in the appropriate organic solvents, the solution turns dark purple in color. This change in color (from brown to purple) suggests there is a metal-to-ligand charge-transfer (MLCT) or ligand-to-metal charge-transfer transition (LMCT). It is most likely a MLCT because the metal acts as a donor species *via* its "d" orbitals. The isonitrile ligand acts as an acceptor and has a delocalized π-system of electrons, thus allowing a donated electron to be dispersed throughout the isonitrile ligand resulting in enhanced charge transfer. Metal-to-ligand charge-transfer transitions are most commonly observed in complexes with ligands that have low-lying π^*-orbitals, especially aromatic ligands such as the isonitrile ligands. The complex demonstrates solvatochromism, the variation of the transition frequency with changes in solvent permittivity and, as a result, there is a large shift in electron density as a result of the transition. The complex is relatively stable to air in the solid form, but is still stored under a nitrogen atmosphere. In the solution phase, the complex is air sensitive. If stored in air in the solution phase the solution changes from purple to red.

8c. Bis(1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-ethylphenylphosphino)benzene] molybdenum(0)

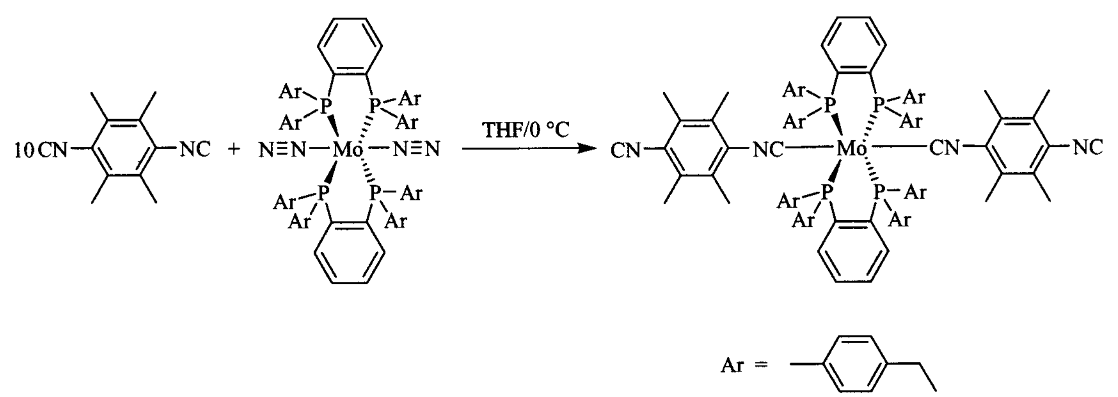


Equation 3.8c

The complex was successfully produced as indicated by ^{1}H and ^{31}P NMR spectroscopy, but a percent yield could not be determined because only a small amount of product was obtained. However, the ^{13}C NMR could not be successfully analyzed because of decoupling problems and broading of the peaks. Elemental analysis indicates that the amount of carbon was 71.08%, hydrogen 5.84%, and nitrogen 3.60% as compared to the theoretical values of carbon 75.19%, hydrogen 6.04%, and nitrogen 3.81%. The discrepancies in the elemental analyses indicate that the complex is probably impure and that byproducts could not be separated even after recrystallization and/or that there are solvent molecules in the crystal lattice. The complex is soluble in common organic solvents such as toluene, tetrahydrofuran, methylene chloride, and benzene. The complex is relatively stable to air, but is stored under a nitrogen atmosphere. The microcrystals are of brown color with a metallic shine and become dark blue when dissolved in the appropriate solvents, which also indicates there might be a MLCT taking place. The complex is sensitive to air in solution. This is indicated by a change in color of the solution as it turns from dark green to black when exposed to air.

8d. Bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis(di(*p*-ethylphenyl)phosphino)benzene]molybdenum(0)

Building on my work, James B. Updegraff III[8] synthesized the analogue bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-ethylphenylphosphino) benzene]molybdenum(0) to the complex in **Equation 3.8c** *via* a direct extension of my method.

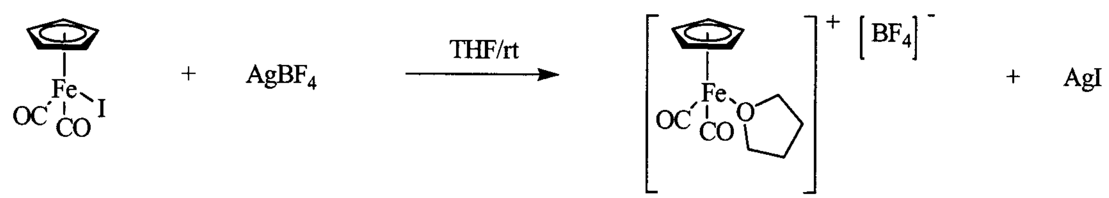


Equation 3.8d

The bis(diisonitrile) complex was isolated as dark green-to-blue microcrystals in 89.4% (1.89g, 1.20mmol) yield and was successfully characterized by ^{1}H and ^{31}P NMR spectroscopy and infrared spectroscopy. The reaction was allowed to stir for 24 hours and its completeness was monitored by infrared spectroscopy.

9. Synthesis of the iron complexes

9a. (Dicarbonyl)(η^5-cyclopentadienyl)(tetrahydrofuran)iron(II) tetrafluoroborate[9]

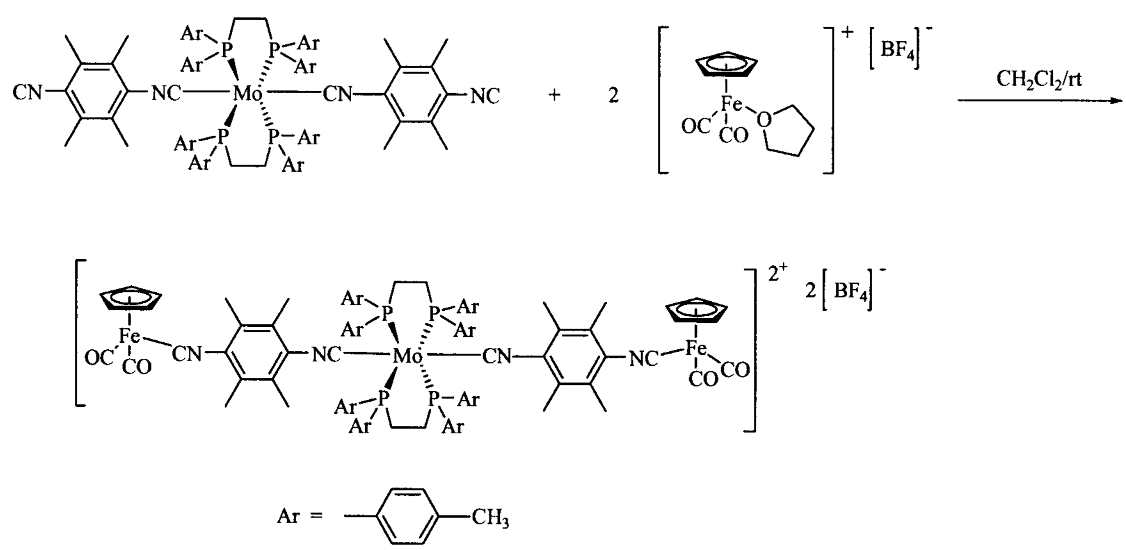


Equation 3.9

(Dicarbonyl)(η^5-cyclopentadienyl)(tetrahydrofuran)iron(II)tetrafluoroborate was synthesized according to the literature.[9] The product was isolated as bright red to black crystals (11.2g, 33.3mmol, 67.5%), identified by ^{1}H NMR and IR spectroscopy, and is stable towards air in the solid state. The product is soluble in methylene chloride and acetone and is relatively stable to air in solution. However, the product was handled under a dinitrogen atmosphere because it was used in the subsequent synthesis, which required a dinitrogen atmosphere.

10. Iron-capped first generation nanorods

10a. μ-{bis[tetramethyl-1,4-(diisocyano)benzene]bis[1,2-bis(di-*p*-tolylphosphino) ethane]molybdenum(0)}bis[(dicarbonyl)(η^5-cyclopentadienyl)iron(II)]



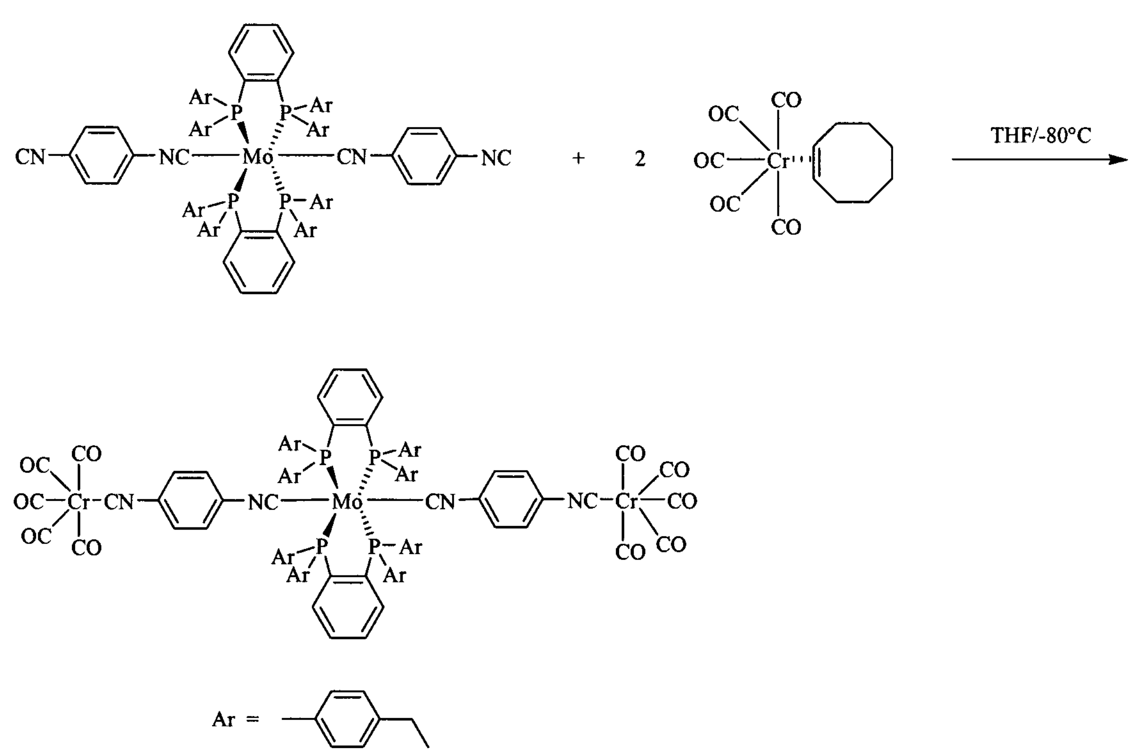
Equation 3.10

The isolated material could not be analyzed by NMR methods because of broading of the peaks. This is most likely due to a ferromagnetic impurity present in the sample. The plate-like crystals obtained are red in color and become bright pink when dissolved in solution. The material is soluble in methylene chloride and is sensitive to air in solution. However, the complex is relatively stable to air in the solid phase. According to infrared spectroscopy, the material is not the desired complex. The data indicate there is one CO stretching frequency at 1921 cm^{-1}; however there should be two CO stretching frequencies. Additionally, elemental analysis indicates that the sample is impure. Theoretical values for carbon, hydrogen, and nitrogen are 61.92%, 5.20%, and 2.94% respectively. However, values obtained for carbon, hydrogen, and nitrogen are (1)

59.08% (2) 59.23%; (1) 5.11% (2) 5.28%; (1) 2.74% (2) 2.74% respectively. The discrepancies in both the spectral properties as well as the elemental analyses results indicate that the sample is impure if the desired complex is present at all.

11. Chromium-capped first generation nanorods

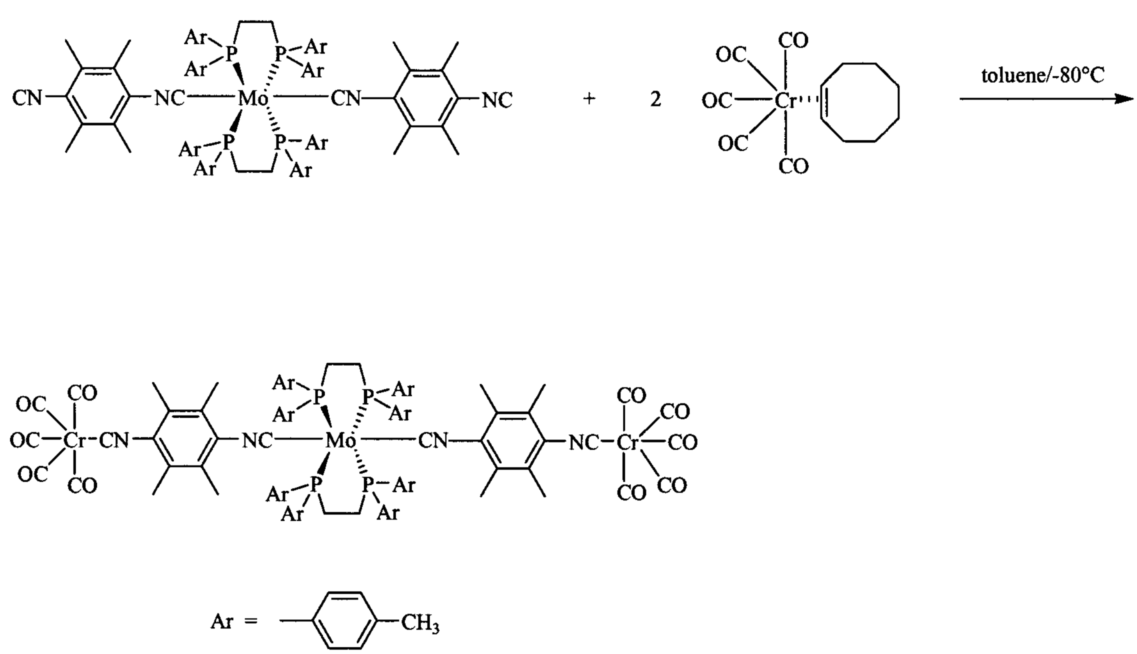
11a. μ-{bis(1,4-diisocyanobenzene)bis[1,2-bis(di-*p*-ethylphenylphosphino) benzene]molybdenum(0)}bis[(chromium pentacarbonyl)]



Equation 3.11a

According to NMR and IR spectroscopy, the chromium complex was successfully prepared. However a percent yield could not be determined because the amount of product obtained was too small. The complex is relatively stable to air, but is stored under a dinitrogen atmosphere. It is soluble in methylene chloride, ether, and tetrahydrofuran and was recrystallized as black plate-like microcrystals with a metallic shine. When dissolved in an appropriate solvent, the solution turns dark green, which indicates the possibility of a MLCT. The ^{1}H and ^{13}C NMR indicates that the required peaks are present. Infrared spectroscopy indicates there is a signal at 2056 cm^{-1} and 1956 cm^{-1} for the CO ligands, and 1844 cm^{-1} for the CN stretching frequencies respectively.

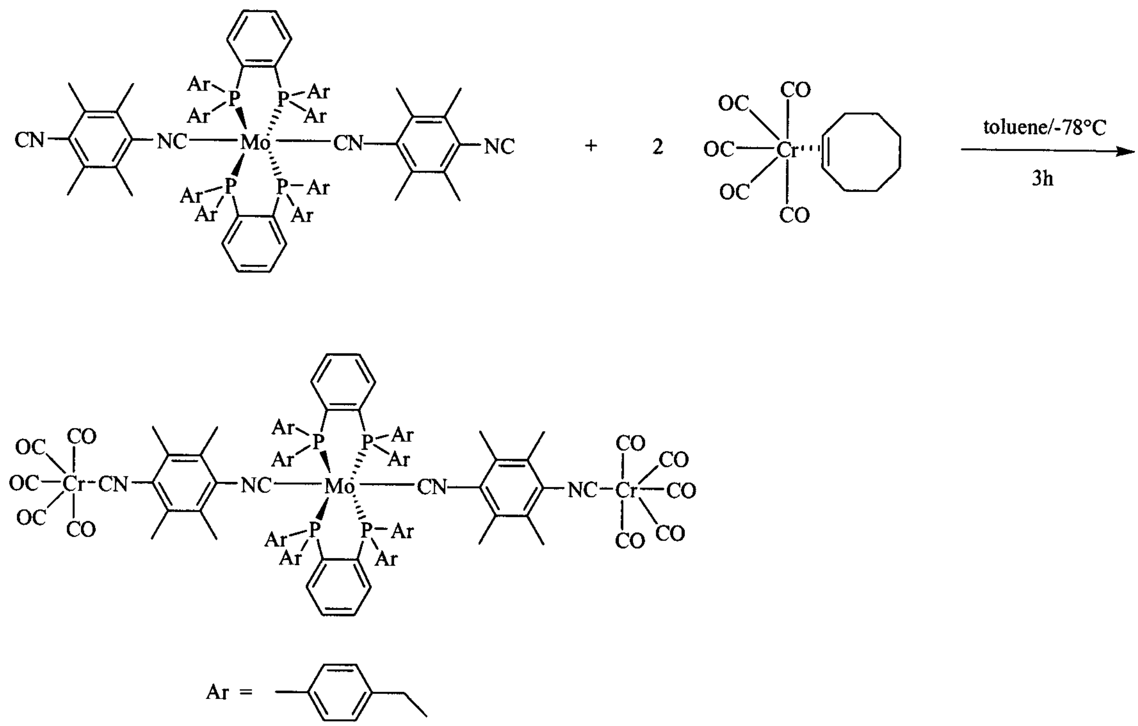
11b. μ-{bis[2,3,5,6-tetramethyl-1,4-(diisocyano)benzene]bis[1,2-bis(di-*p*-tolyl phosphino)ethane]molybdenum(0)}bis[(chromium pentacarbonyl)]



Equation 3.11b

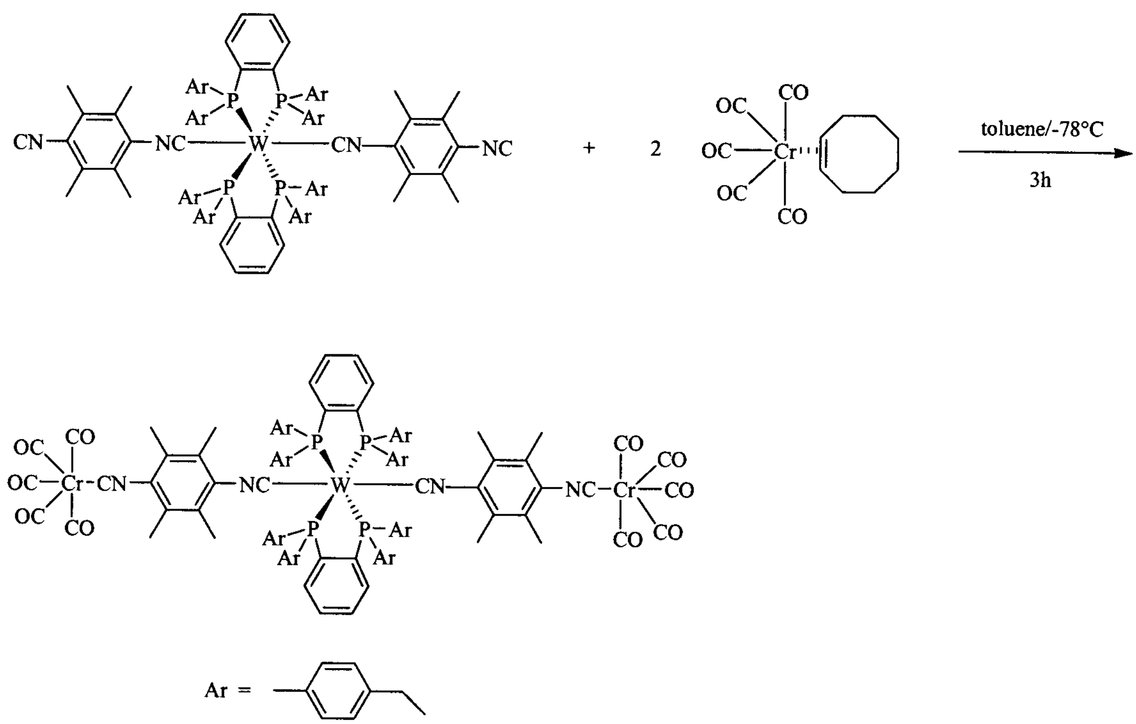
The material was isolated as tiny dark purple crystals; however, a percent yield was not determined because the amount of product obtained was much too small to get an accurate yield. The material is stable towards air in the solid phase, but is stored under a dinitrogen atmosphere. It is soluble in toluene and methylene chloride and is sensitive to air in the solution phase. Upon dissolving, the purple crystals turn to a dark blue color, which is indicative of a MLCT. ^{1}H NMR indicates that the required peaks are present, although the peaks are broadened. Infrared spectroscopy indicates the CO stretching frequencies to be at 2056 and 1954 cm^{-1} respectively and the CN stretching frequency at 1833 cm^{-1} respectively. However, elemental analysis indicates that the material is impure. It is found that carbon, hydrogen, and nitrogen are present at 58.69%, 4.59%, and 2.87% respectively. Theoretical calculations suggest that carbon, hydrogen, and nitrogen should be present at 64.24%, 5.05%, and 3.19% respectively. Even after several attempts at recrystallization, the material could not be totally purified.

Other attempts to synthesize analogue chromium-capped complexes were undertaken by two coworkers in the Hunter group (James B. Updegraff III and Dr. Matthias Zeller) by extensions of the above methods. The two trimetallic complexes, μ-C,C′-[bis(*p*-diisocyanotetramethylbenzene)bis[1,2-bis(di(*p*-ethylphenyl)phosphino) benzene]molybdenum(0)]bis(chromiumpentacarbonyl) **(Equation 3.11c)** and μ-C,C′-[bis[bis(*p*-diisocyanotetramethylbenzene)][bis[1,2-bis(di(*p*-ethylphenyl)phosphino) benzene]tungsten(0)]bis(chromiumpentacarbonyl) **(Equation 3.11d)** were synthesized and characterized by James B. Updegraff.[8] The complexes were synthesized *via* the routes below. The reactions were carried out at -78°C in order to minimize any side reactions that may occur.



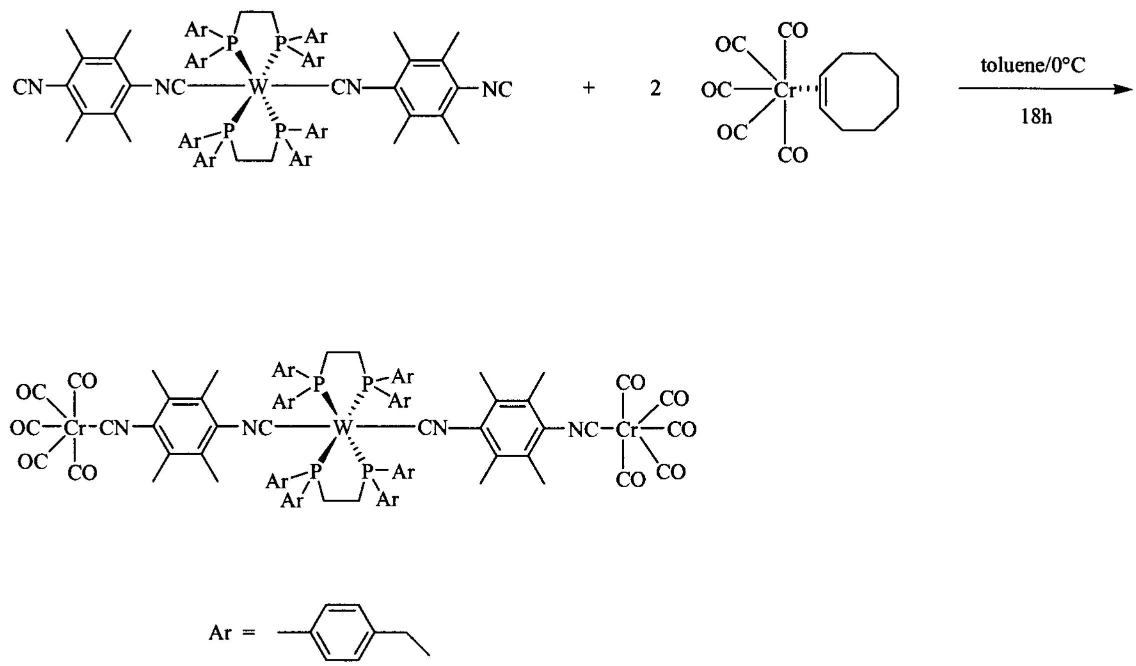
Equation 3.11c

The trimetallic complex in **Equation 3.11c** was isolated as black iridescent thin plates in a yield of 0.16g (0.0814mmol, 42.8%) and was successfully characterized IR and ^{1}H NMR. The product was only isolated as the *trans*-isomer as indicated by one set of signals in the ^{1}H NMR. Also, the tungsten complex in **Equation 3.11d** was synthesized by a route similar to the one used for its molybdenum analogue. The product was isolated in a yield of 0.06g (0.0292mmol, 48.8%) as black iridescent thin plates and was characterized by IR and ^{1}H NMR. Again, the ^{1}H NMR indicates that the complex is only present as the *trans*-isomer.



Equation 3.11d

The trimetallic complex μ-C,C′-[bis(1,4-bisisocyano-2,3,5,6-tetramethylbenzene)bis[1,2-bis(di(*p*-ethylphenyl)phosphino)ethane]tungsten(0) bis(chromiumpentacarbonyl)] (**Equation 3.11e**) was synthesized and characterized by Dr. Matthias Zeller. The complex was synthesized *via* the route below.



Equation 3.11e

The trimetallic complex in **Equation 3.11e** was synthesized and isolated as black crystallites to yield 50mg (0.0255mmol, 17.3%) and was characterized by ^{1}H and ^{31}P NMR as well as IR spectroscopy. Nuclear magnetic resonance indicates that the complex is present in both the *cis* and *trans* conformations.

Like the bis(diisonitrile) complexes, the chromium-containing trimetallic complexes are very promising candidates for future electrochemical studies. As solids the complexes have a metallic shine to them and range in color from dark brown to black. The colors of these complexes and the changes in color when dissolved indicate there are metal-to-ligand charge-transfer transitions occurring. Metal-to-ligand charge-transfer transitions indicate that these complexes are highly conjugated and thus should be capable of conducting electrons. The goal of synthesizing nanorods with tunable characteristics (*e.g.*, electrical and conductive properties) looks very promising owing to the synthesis and characterization of these trimetallic complexes.

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Chapter Four

Conclusion

When synthesizing the zero and first generation nanorods, 1,4-bisisocyano-2,3,5,6-tetramethylbenzene was used as the bridging isonitrile ligand because of its better stability and lower decomposition rate as compared to 1,4-diisocyanobenzene. The chelating phosphine ligands, 1,2-bis(di-*p*-tolylphosphino)ethane and 1,2-bis(di-*p*-ethylphenylphosphino)benzene were chosen for their higher barriers for rotation as compared to 1,2-bis(di-*p*-anisylphosphino)ethane. These characteristics in stability and rotation barriers are responsible for enhanced solubility, therefore allowing for easier purification and isolation. Synthesizing the "caps" for the nanorods proved to be challenging. The carbonyl-capped complex, bis[1,2-bis(di-*p*-tolylphosphino)ethane]dinitrogencarbonylmolybdenum(0) was isolated as an impure material; however, its analogue, bis[1,2-bis(di-*p*-ethylphenylphosphino)ethane]dinitrogencarbonylmolybdenum(0) was successfully isolated and characterized by spectroscopic methods. The iron-capped complex, μ-{bis[tetramethyl-1,4-(diisocyano)benzene]bis[1,2-bis(di-*p*-tolylphosphino)ethane] molybdenum(0)}bis[(dicarbonyl)(η^5-cyclopentadienyl)iron(II)] was not isolated as a pure material, probably owing to a ferromagnetic impurity in the sample. On the other hand, the chromium-capped complexes proved to be the most successful when synthesizing the first generation nanorods. The zero and first generation nanorods synthesized may exhibit desired conductive properties as indicated by their metallic shine and change in color when dissolved in the appropriate solvents.

Appendix 1: Crystallographic Data Tables for 1,2-Bis(ditolylphosphino)ethane

Table 1.1 Crystal data	**Table 1.2 Data collection**
$C_{30}H_{32}P_2$	Bruker AXS SMART APEX CCD diffractometer
$M_r = 454.50$	ω scans
Monoclinic, $P2_1/c$	Absorption correction: none
$a = 9.5469$ (5) Å	12864 measured reflections
$b = 11.8565$ (6) Å	3137 independent reflections
$c = 14.3645$ (7) Å	2920 reflections with $I > 2\sigma(I)$
$\beta = 128.731$ (1) °	$R_{\text{int}} = 0.046$
$V = 1268.40$ (11) Å ^{3}	$\theta_{\max} = 28.3°$
$Z = 2$	$h = -12 \rightarrow 12$
$D_x = 1.190$ Mg m^{-3}	$k = -15 \rightarrow 15$
Mo K_α radiation	$l = -19 \rightarrow 18$
Cell parameters from 9472 reflections	
$\theta = 2.2$-$28.3°$	
$\mu = 0.19$ mm^{-1}	
$T = 90$ (2) K	
Block, colorless	
0.62 × 0.52 × 0.25 mm	

Table 1.3 Refinement

Refinement on F^2
$R(F) = 0.044$
$wR(F^2) = 0.123$
$S = 1.02$
3137 reflections
147 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 0.6662P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Figure 1.1 ORTEP plot of title compound. Ellipsoids are at the 30% probability level.

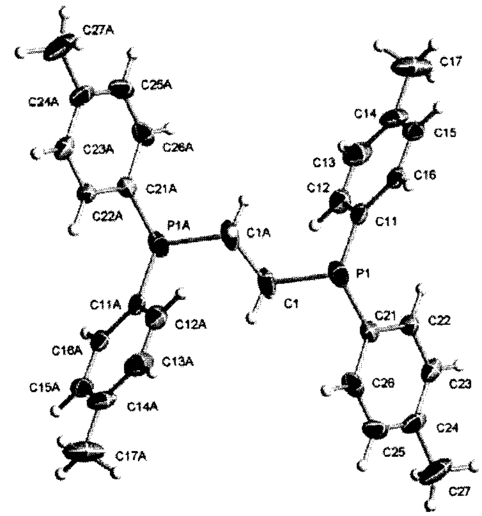

Table 1.4
Selected geometric parameters (Å, °).

P1–C11 1.8215 (15)	C12–C13 1.377 (3)
P1–C21 1.8247 (13)	C25–C26 1.381 (2)
P1–C1 1.8489 (15)	C25–C24 1.385 (3)
C11–C16 1.3911 (17)	C23–C24 1.384 (2)
C11–C12 1.392 (2)	C14–C15 1.385 (2)
C21–C26 1.3929 (18)	C14–C13 1.390 (2)
C21–C22 1.3933 (17)	C14–C17 1.503 (2)
C22–C23 1.3853 (18)	C1–C1^{i} 1.529 (3)
C16–C15 1.385 (2)	C24–C27 1.508 (2)
C11–P1–C21 102.99 (6)	C21–P1–C1 98.67 (6)
C11–P1–C1 101.86 (8)	C1^{i}–C1–P1 111.25 (13)

Appendix 2: Crystallographic Data Tables for η^5-Cyclopentadienyl-dicarbonyl-iodo-iron

Table 2.1 Crystal data	**Table 2.2 Data collection**
$C_7H_5FeIO_2$	Bruker AXS SMART APEX CCD
$M_r = 303.86$	diffractometer
Monoclinic, $P2_1/c$	ω scans
$a = 13.1442$ (7) Å	Absorption correction: multi-scan
$b = 10.2568$ (6) Å	(SADABS, BRUKER 1997) $T_{\min} = 0.2945$,
$c = 12.8680$ (7) Å	$T_{\max} = 0.4000$
β = 101.5020 (10) °	17192 measured reflections
$V = 1699.99$ (16) Å ^{3}	4207 independent reflections
$Z = 8$	4077 reflections with $I > 2\sigma(I)$
$D_x = 2.374$ Mg m^{-3}	$R_{\text{int}} = 0.0253$
Mo K_α radiation	$\theta_{\max} = 28.31°$
λ = 0.71073 Å	h = -17 → 17
Cell parameters from 6438 reflections	k = -13 → 13
$\theta = 2.5385\text{-}28.294°$	l = -17 → 17
$\mu = 5.350$ mm^{-1}	every ∞ reflections frequency : ∞ min
$T = 100$ (2) K	intensity decay : none
Block, red	
0.22 × 0.17 × 0.17 mm	

Table 2.3 Refinement

Refinement on F^2

$R(F) = 0.0256$

$wR(F^2) = 0.0589$

$S = 1.322$

4207 reflections

229 parameters

H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 0.6662P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.663$ e Å^{-3}

$\Delta\rho_{min} = -0.686$ e Å^{-3}

Extinction correction : none

Scattering factors from *International Tables for Crystallography* (Vol. C)

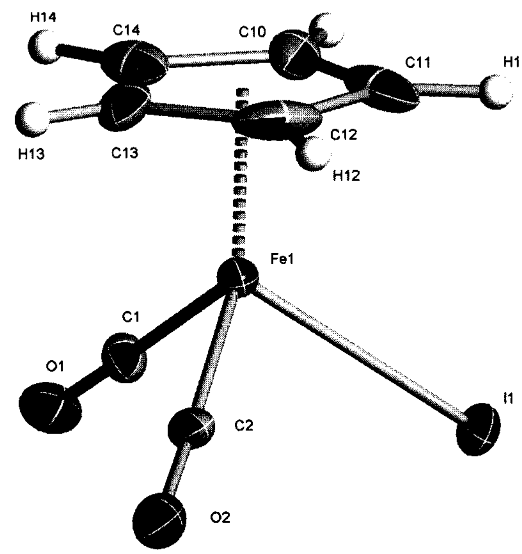

Figure 2.1 ORTEP plot of title compound. Ellipsoids are at the 30% probability level.

Table 2.4

Selected geometric parameters (Å, °).

C3–Fe2 1.777(3)	Fe1–C2 1.780 (3)
I2–Fe2 2.6082 (4)	Fe1–C1 1.783 (3)
I1–Fe1 2.6063 (4)	Fe2–C4 1.785 (3)
C2–Fe1–C1 93.95 (12)	C3–Fe2–C4 93.83 (12)
C2–Fe1–I1 91.41 (8)	C3–Fe2–I2 90.55 (9)
C1–Fe1–I1 89.41 (9)	C4–Fe2–I2 89.18 (8)