# The Synthesis of Organometallic Nanorods from Molybdenum and Tungsten Diisonitrile Complexes and a New Method to Synthesize Air-Stable Sodium Cyclopentadienide (NaCp)

By

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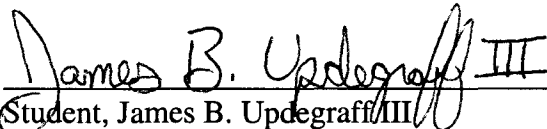Chemistry

Program

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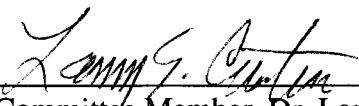
by

James B. Updegraff III

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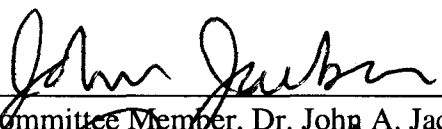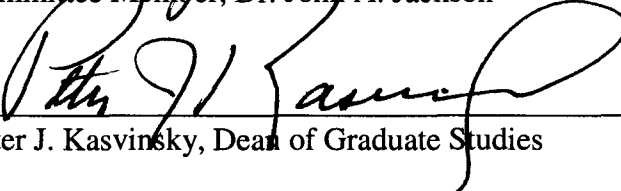
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# Abstract

Bis(diisonitrile) complexes were synthesized, characterized and are reported. The precursor to the bis(diisonitrile) complex, the bis(dinitrogen) complex, was synthesized by reducing the appropriate metal halide, $MoCl_5$ or $WCl_6$, with magnesium metal in the presence of two equivalents of a bidentate phosphine under an inert nitrogen atmosphere in THF. The bis(diisonitrile) complex was then synthesized by reacting the appropriate dintrogen metal complex with ten equivalents of 1,4-diisocyanobenzene or a derivative thereof. The solubility of these complexes was tuned *via* alkyl substituents on both the phosphine and the bis(diisonitrile) ligands although substitution on the phosphine had the greatest effect. The trimetallic isonitrile bridged complexes were then synthesized by combining the bis(diisonitrile) complex with two equivalents of *cis*-(cyclooctene)pentacarbonylchromium(0). The trimetallic complexes exhibited an iridescent color denoting the presence of a highly conjugated π-system. The presence of this highly conjugated system implies that these complexes may posses electrical conductivity properties.

A new, one-pot synthesis, of sodium cyclopentadienide, NaCp, is also reported. In this new method, dicyclopentadiene was cracked in a high-boiling, inert, non-polar solvent while sodium metal was being melted and finely divided in the same flask. The resulting CpH monomer then reacted with the finely divided sodium metal to produce NaCp, with precipitates out of the non-polar solvent. The NaCp that was produced shows remarkable stability towards air, is not pyrophoric like that produced by conventional

methods, and does in fact have Cp ring-transfer capabilities as shown by the successful synthesis of ferrocene using the NaCp produced by this new one-pot method.

Service crystallography of samples provided by Dr. Guy Crundwell of Central Connecticut State University is also reported.

# Acknowledgements

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Last, but certainly not least, I owe my undying gratitude to not only God, but to my family as well. Without the love and support of my parents, Jim and Cheryl, and my brother and sister, Shaun and Holly, nothing that I have done would have ever been possible.

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# List of Abbreviations

| | |
|---|---|
| $a$ | Length of unit cell axis (as in X-ray diffraction) |
| $\alpha$ | Alpha angle (as in X-ray diffraction) between $a$ and $b$ axis |
| Å | Angstrom |
| Ar | Substituted aryl group |
| as | Asymmetric stretch (as in Infrared spectroscopy) |
| $b$ | Length of unit cell axis (as in X-ray diffraction) |
| $\beta$ | Beta angle (as in X-ray diffraction) between $a$ and $c$ axis |
| $t$-Bu | *tert*-Butyl |
| $c$ | Length of unit cell axis (as in X-ray diffraction) |
| $CDCl_3$ | Deuterochloroform |
| $CH_2Cl_2$ | Dichloromethane |
| $cm^{-1}$ | Reciprocal centimeters, wave numbers |
| CO | Carbonyl ligand |
| "CN" | Coordination number |
| CNR | Isocyanide ligand |
| Cp | Cyclopentadienyl ($\eta^5$- $C_5H_5$) |
| CV | Cyclic voltammogram |
| d | Doublet (as in NMR spectroscopy) |
| $\delta$ | Chemical shift (as in NMR spectroscopy) |
| $\Delta$ | Heat (thermal reaction) |
| dd | Doublet of doublet (as in NMR spectroscopy) |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| DMF | Dimethylformamide |
| Dx | Density (as in X-ray diffraction) |
| Eq | Equivalents |
| Et | Ethyl |
| EtOH | Ethanol |
| $F$ | Structure factor (as in X-ray diffraction) |
| $Fc$ | Calculated structure factor (as in X-ray diffraction) |

| | |
|---|---|
| *Fo* | Observed structure factor (as in X-ray diffraction) |
| FTIR | Fourier transform infrared |
| g | Grams |
| $\gamma$ | Gamma angle (as in X-ray diffraction) between *b* and *c* axis |
| h | Hour, Miller indices (as in X-ray diffraction) |
| Hz | Hertz |
| HOMO | Highest occupied molecular orbital |
| IR | Infrared (as in spectroscopy) |
| *J* | Coupling constant (as in NMR spectroscopy) in Hz |
| k | Miller indices (as in X-ray diffraction) |
| l | Miller indices (as in X-ray diffraction) |
| L | Ligand; liter |
| LAH | Lithium aluminum hydride |
| LUMO | Lowest unoccupied molecular orbital |
| $\mu$ | Mu |
| m | multiplet (as in NMR) |
| Me | Methyl |
| MHz | Megahertz |
| mL | Milliliters |
| mm | Millimeters |
| Mo $K_{\alpha}$ | Molybdenum K alpha (as in X-ray diffraction) |
| mol | Mole |
| mmol | Millimole |
| MO | Molecular Orbital |
| Mr | Molecular weight (as in X-ray diffraction) |
| $M_w$ | Molecular weight |
| $\eta$ | Eta |
| N | Normality |
| NLO | Nonlinear optical |
| NMR | Nuclear Magnetic Resonance |
| *o* | *Ortho* |

| | |
|---|---|
| OMe | Methoxy |
| $\pi$ | Bonding pi orbital |
| $\pi^*$ | Anti-bonding pi orbital |
| *p* | *Para* |
| pd | pseudo-doublet (as in NMR spectroscopy) |
| Ph- | Phenyl |
| ppm | Parts per million (as in NMR) |
| $PR_3$ | Phosphine or Phosphite |
| R | Alkyl or aryl group |
| *R* | Discrepancy index (as in X-ray diffraction) |
| $\sigma$ | Bonding sigma orbital |
| S | Goodness of fit (as in X-ray diffraction) |
| s | Singlet (as in NMR spectroscopy); strong (as in IR spectroscopy) |
| sy | Symmetric stretch (as in Infrared spectroscopy) |
| T | Temperature |
| T*min* | Minimum transmission (as in X-ray diffraction) |
| T*max* | Maximum transmission ( as in X-ray diffraction) |
| $\omega$ | Omega (*e.g*, measurement angle used in X-ray diffraction) |
| $\theta$ | Theta (*e.g.*, Angle between the incident and the diffracted beams, as in X-ray diffraction) |
| $\theta_{max}$ | Theta (*e.g.*, maximum Bragg angle as in X-ray diffraction) |
| t | Triplet (as in NMR spectroscopy) |
| THF | Tetrahydrofuran |
| UV-Vis | Ultraviolet visible (as in spectroscopy) |
| V | Cell volume (as in X-ray diffraction) |
| $\nu$ | Stretching frequency (as in IR spectroscopy) |
| *in vacuo* | High vacuum manifold |
| *wR* | Weighted discrepancy index (as in X-ray diffraction) |
| w | weak (as in Infrared spectroscopy) |
| X | Cl, Br, or I ligand |
| 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. Roughly fifty years ago, research in this area went through a renaissance driven by breakthroughs in both synthetic methods and bonding theories thus beginning 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).
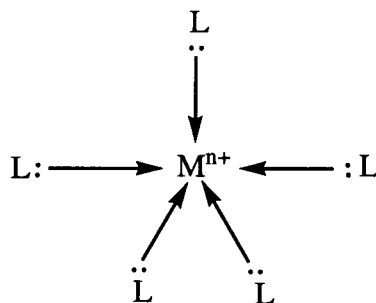


**Figure 1.1.1**                    Metal "acting" as a Lewis acid

The relative stability of each complex is related to the valence electron count of the metal. 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, molybdenum and tungsten).[1,2]

Organometallic ligands may vary in the manner in which their valence electrons interact with the metal. For $\pi$-complexes in which unsaturated organic ligands are bonded "side on" to the metal (*e.g.*, olefins and aromatics), one or more $\pi$-bonds on the ligand may donate electrons to one or more metal atoms. The hapticity of the ligand (*i.e.*, its $\eta^n$ 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.[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 |
| $\eta^2$-alkene | 0 | 2 | 1 |
| Alkyl | -1 | 2 | 1 |
| Alkylidene | -2 | 4 | 1 |
| Alkylidyne | -3 | 6 | 1 |
| $\eta^1$-allyl | -1 | 2 | 1 |
| $\eta^3$-allyl | -1 | 4 | 2 |
| $\eta^2$-alkyne | 0 | 2 to 4 | 1 |
| Amine | 0 | 2 | 1 |
| $\eta^2$-arene | 0 | 2 | 1 |
| $\eta^6$-arene | 0 | 6 | 3 |
| Carbene | 0 | 2 | 1 |
| Carbine | 0 | 3 | 1 |
| Carbonyl | 0 | 2 | 1 |
| $\eta^1$-cyclopentadienyl | -1 | 2 | 1 |
| $\eta^3$-cyclopentadienyl | -1 | 4 | 2 |
| $\eta^5$-cyclopentadienyl | -1 | 6 | 3 |
| Dinitrogen | 0 | 2 | 1 |
| Halide (*e.g.*, Cl⁻) | -1 | 2 | 1 |
| Hydride | -1 | 2 | 1 |
| Isonitrile | 0 | 2 | 1 |

| Ligand | Formal Charge(s) | Electrons Donated | Coordination Positions |
|---|---|---|---|
| Nitrile | 0 | 2 | 1 |
| Nitrosyl (linear) | +1 | 2 | 1 |
| Nitrosyl (bent) | -1 | 2 | 1 |
| Phosphate | 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 $\pi$-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 bond angle is approximately 180°. According to the Dewar-Chatt-Duncanson model,[2] $\sigma$-bonding occurs when a lone pair is donated from a filled $\sigma$-symmetry orbital on carbon (*i.e.*, the approximately sp hybrid orbital) to an empty $\sigma$-symmetry orbital on the metal (*i.e.*, the approximately $d^2sp^3$ hybrid orbital in an octahedral complex). There are also two $\pi$-back-bonding interactions, which are perpendicular to one another. In each of the two back bonds, there is a filled $\pi$-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 $\pi$-symmetry orbital on carbon monoxide (*i.e.*, the approximately CO $\pi^*$-antibonding orbital).

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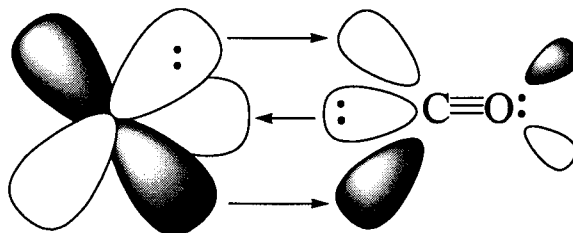


**Figure 1.1.2**  A "Dewar-Chatt-Duncanson" representation of the bonding of a carbonyl ligand to a transition metal.[3]

carbonyl bond is thus stronger than a linear sum of the two components. The electron

transfer back to the ligand *via* π-back-bonding 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



"metal carbonyl"                    "metalla ketone"
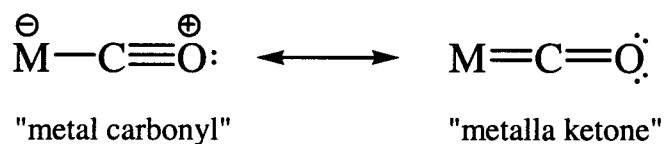
**Figure 1.1.3**  Valence Bond Theory representation of the bonding of a carbonyl ligand.

is provided by Valence Bond Theory.[2] 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, with a formal charge of +1 on an sp hybridized oxygen. 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 back-bonding to the carbonyl is reflected in an increased contribution from the second "metallo-ketone" resonance form.

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 back-bonding 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 back-bonding increases. In turn, as the amount of back-bonding 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 back-bonding 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 also 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 $\pi^*$-antibonding orbitals on the carbon atom are less polarized. Thus, isonitriles are generally better net electron donors than are carbonyls. In terms of the Dewar-Chatt-Duncanson model, there is $\sigma$-donation from the lone pair of electrons on the carbon (*i.e.*, the approximately sp hybrid orbital) to an empty $\sigma$-symmetry orbital of the metal (*i.e.*, approximately $d^2sp^3$ in octahedral complexes). There is also $\pi$-back donation from a pair of filled orbitals of $\pi$-symmetry on the metal (*i.e.*, the approximately $d_{xy}$, $d_{xz}$, or $d_{yz}$ orbitals in octahedral metals) to a pair of empty $\pi$-symmetry orbitals on the isocyanide ligand (*i.e.*, the approximately $\pi^*$-orbitals localized on C≡N).[3,4]
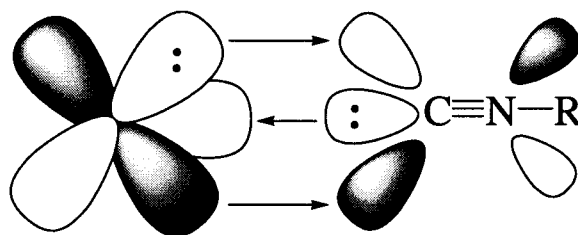


**Figure 1.1.4**   A Dewar-Chatt-Duncanson model representation of the bonding of an isocyanide ligand to a transition metal.

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 back-bonding 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 the

$$M{-}C{\equiv}N{-}R \longleftrightarrow M{=}C{=}N{\nearrow}R$$
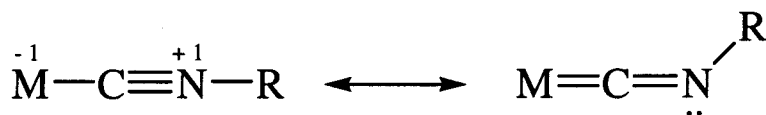
**Figure 1.1.5** Valence Bond Theory model for the isocyanide ligand.

latter.[5]

Both the Dewar-Chatt-Duncanson and Valence Bond Theory explanations 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 bond angles. If the electron richness of the metal is increased, there is more back-bonding 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). Back donation occurs from filled $\pi$-symmetry orbitals on the metal (*e.g.*, approximately $d_{xz}$, $d_{yz}$, and $d_{xy}$ on an octahedral metal center) into an empty $\pi^*$ molecular orbital on the ligand, (*i.e.*, which have $\pi$-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.
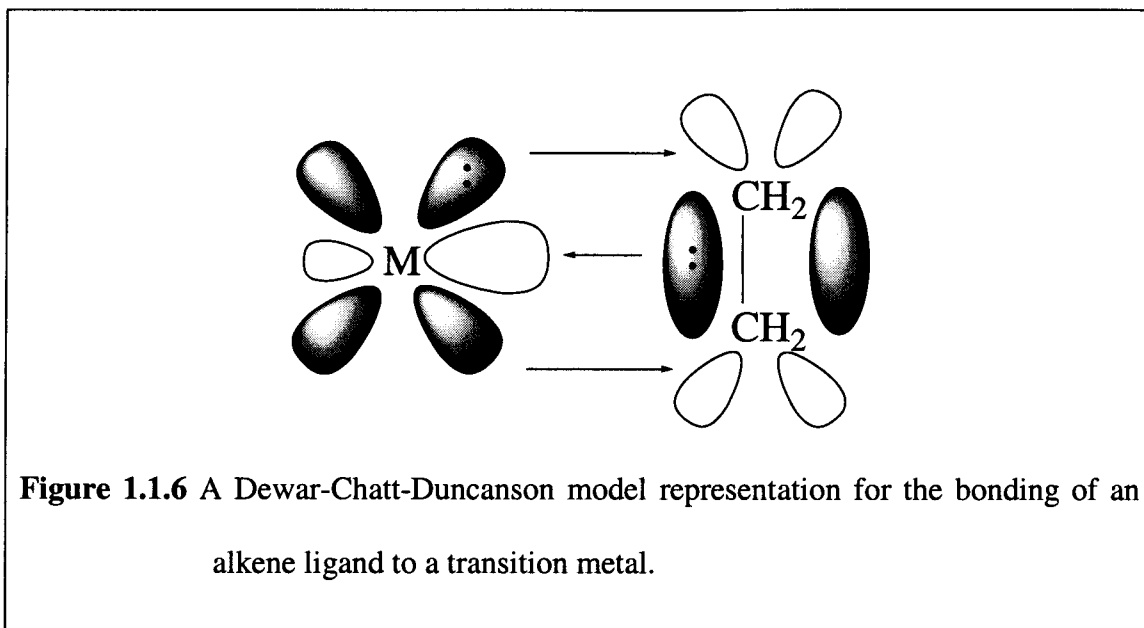
In Valence Bond terms, the two resonance forms of olefins are referred to as the metal-olefin and metallo-cyclopropane forms, which differ in both their metal-carbon and carbon-carbon bond orders and in the hybridizations of the carbon atoms. Thus, increased back-bonding increases the contribution of 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.
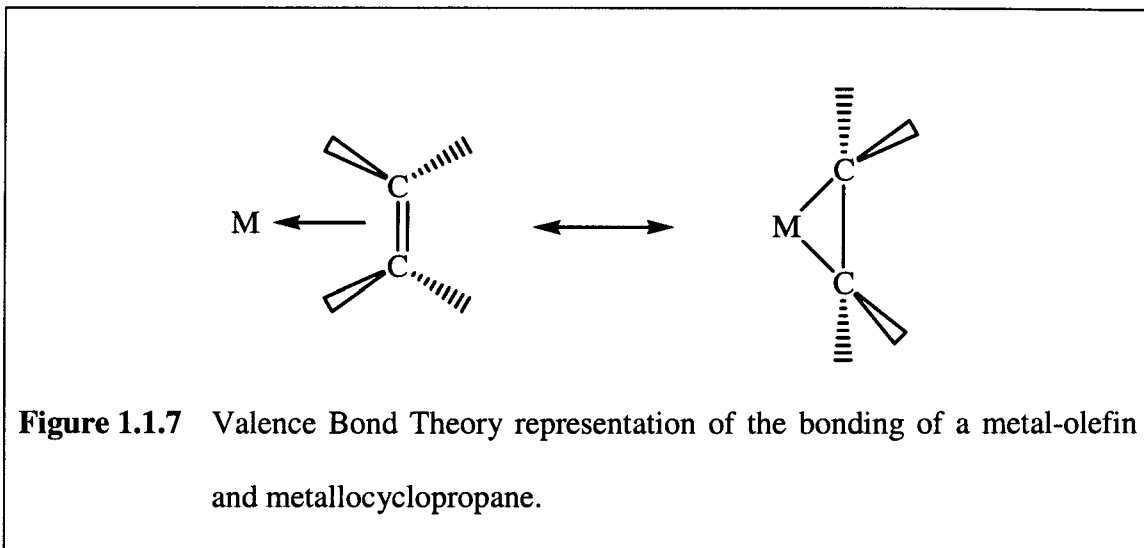
As with carbon monoxide and CN-R, the electron richness of the metal containing olefin and related complexes may be measured through spectroscopy and X-ray diffraction.  Increasing the electron richness on the metal produces increased back-bonding and, therefore, the net bond order of the carbon-carbon bond decreases.  X-ray diffraction has shown that increased electron richness on the metal and the subsequent back-bonding, 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 $\eta^6$-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-back-bonding into phosphorus orbitals that have phosphorus-carbon σ* orbital character become increasingly important in the order given. The 1,2-bis(diphenylphosphino)ethane 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 the phosphine ligands such as those used in this research, back-bonding plays little or no role because the aryl substituents are relatively electron rich.[7]
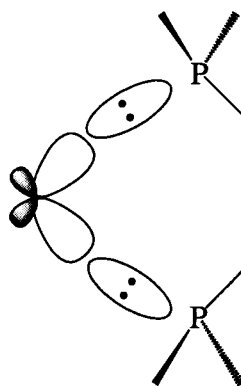


**Figure 1.1.8**   A Dewar-Chatt-Duncanson representation for the bonding of the

bidentate dppe ligand to a transition metal.

The dinitrogen ligand is usually 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-N$_2$ bonding in both Dewar-Chatt-Duncanson

(*i.e.*, σ-donation and π-back-donation) 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.
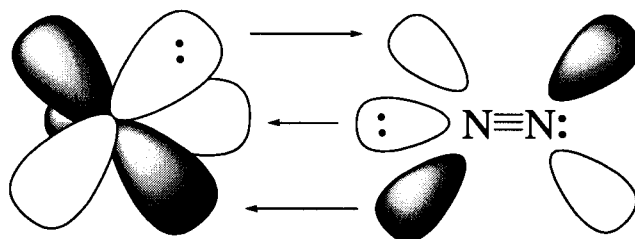


**Figure 1.1.9**  A Dewar-Chatt-Duncanson model representation for the bonding of a dinitrogen ligand to a transition metal.
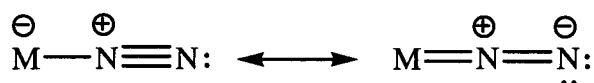


**Figure 1.1.10**  Valence Bond Theory representation of the bonding of a dinitrogen ligand to a transition metal.

However, for the terminal $N_2$ ligand net σ and π interactions are weaker than for other π-acidic ligands such as carbonyls and isocyanides. Therefore, dinitrogen ligands can be readily displaced by these π- acidic ligands, *e.g.*, as in equation 1.1.[8]

**Equation 1.1.1** General synthesis for a bis(diisonitrile) complex.
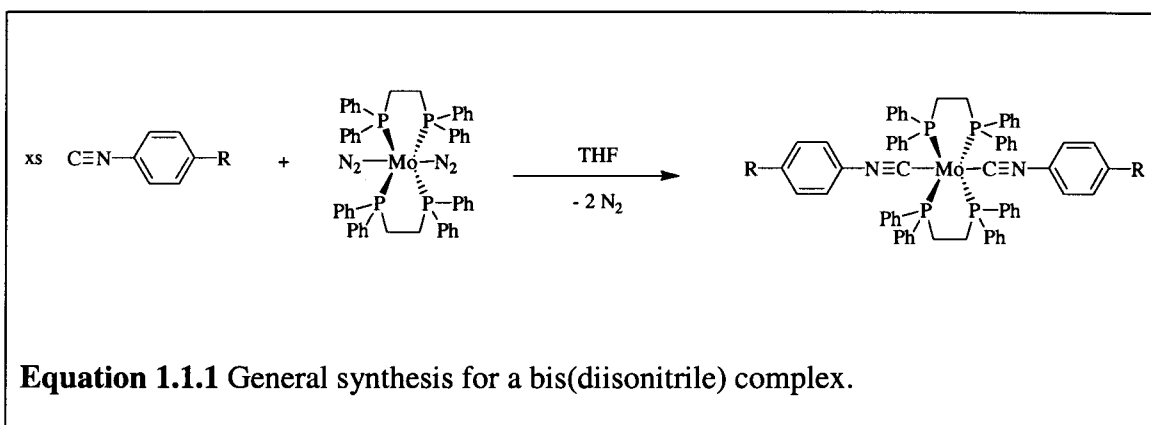
# Section Two

# 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 fragments incorporated into polymers to have more side groups. In addition, metal-ligand bonds are typically longer than conventional carbon bonds (*e.g.* carbon-carbon, carbon-nitrogen, and carbon-oxygen bonds). These differences in bonding and valences between carbon and transition metals produce different bond angles, internuclear distances, and backbone rigidities.[7] Due to their variable bonding characteristics, organometallic polymers may also possess intriguing electrical, conductivity, magnetic, optical, liquid crystalline, and redox properties. Polymers with organometallic fragments in their repeating unit have many actual and/or potential advantages compared to conventional organic polymers. In particular, organometallic fragments 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 research are polymers having transition elements that possess M-C $\sigma$ or $\pi$ bonds in the backbone. Polyphosphazenes, polysiloxanes, and polysilanes are some inorganic polymers that have been produced commercially because of their novel properties.[7]

$$\begin{bmatrix} R \\ | \\ -P{=}N- \\ | \\ R \end{bmatrix}_n \qquad \begin{bmatrix} R \\ | \\ -Si{-}O- \\ | \\ R \end{bmatrix}_n \qquad \begin{bmatrix} R \\ | \\ -Si- \\ | \\ R \end{bmatrix}_n$$
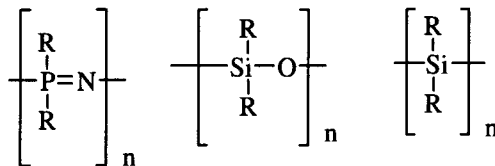
**Figure 1.2.1** Structures of a polyphosphazene, polysiloxane, and polysilane.

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 1950's, 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 bifunctional 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.[12]

$$n \; A-R-B \; \longrightarrow \; -\!\!\left[R-X\right]_{\overline{n}}$$

$$n \; A-R-A \; + \; n \, B-R'-B \; \longrightarrow \; \left[R-X-R'-X\right]_n$$
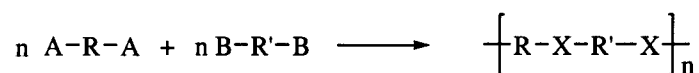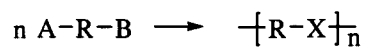
**Equations 1.2.1 and 1.2.2** Methods to prepare polymers by step growth polymerization.

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]
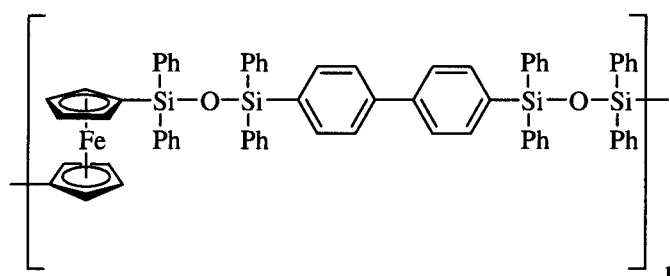


**Figure 1.2.2** Transition metal based polymers containing ferrocene with organosiloxane spacers.

In 1977, the first high molecular weight rigid-rod metal polyyne materials were described

by Hagihara *et al.*[14]
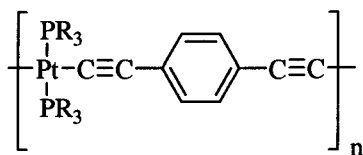


**Figure 1.2.3**   Example of a rigid-rod metal polyyne.

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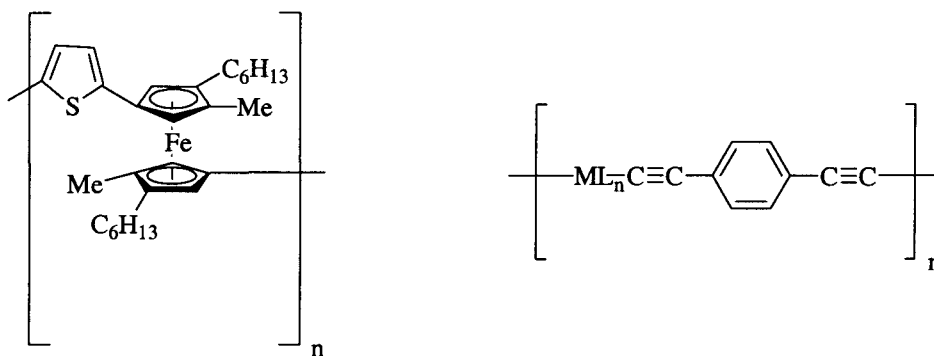


**Figure 1.2.4**   Some examples of main-chain organometallic polymers.

Many of the polymers shown in Figure 2.4 are soluble in common organic solvents such as benzene, toluene, tetrahydrofuran, and dichloromethane. They also have good electrical, optical, and nonlinear optical 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, micro-catalyst 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
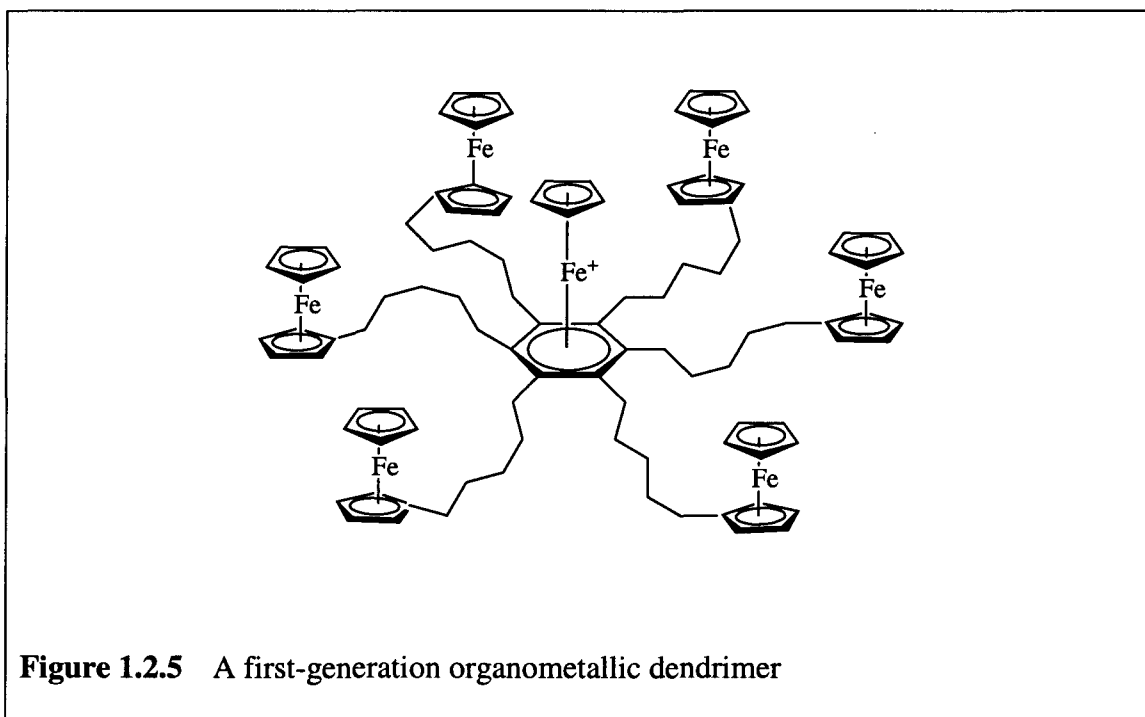
As the size of a dendrimer increases, steric crowding increases in the outermost layers. Thus, a typical high generation number dendrimer is sterically crowded on its surface layers, but has significant free space near its central core. This crowding gradient sets the

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 nm 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 (NLO) properties.[17] Non-linear optical properties arise from interactions of the electromagnetic fields of light with those of matter. Materials possessing nonlinear optical, NLO, 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. Introduction

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

**Figure 1.3.1** Organometallic polymer containing aromatic isocyanides.
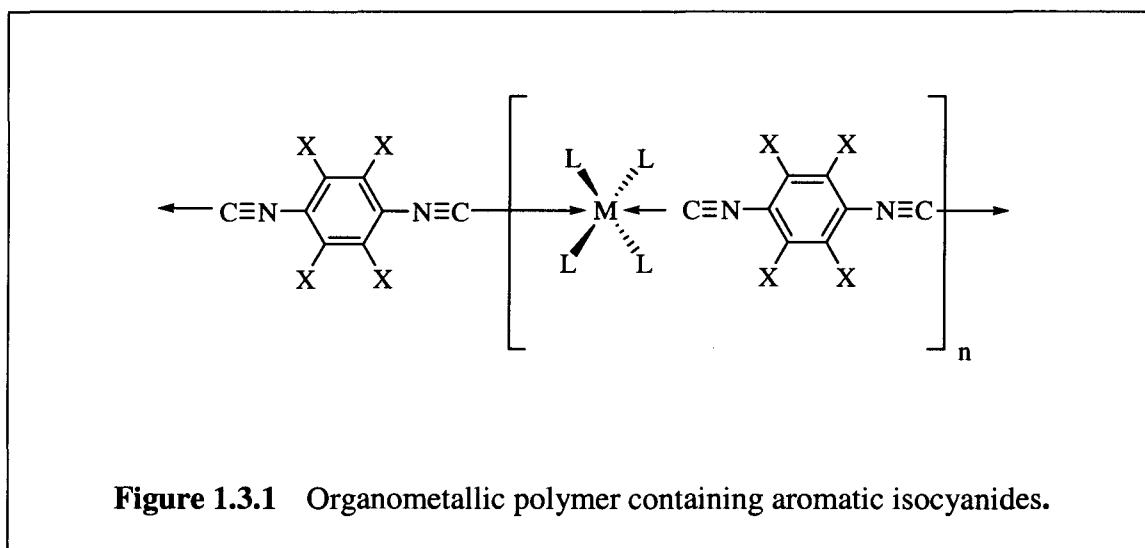
In addition, free aromatic diisocyanide ligands are also of interest because they are effective molecular-level conductors.[19] These ligands are capable of bridging transition metal centers while mediating communication between the centers through a conjugated $d\pi$-$p\pi$-$d\pi$ network.[20] Thus, aromatic diisocyanide ligands could be deposited on a gold surface (**Figure 1.3.2**) to enhance the surface's electrochemical properties.
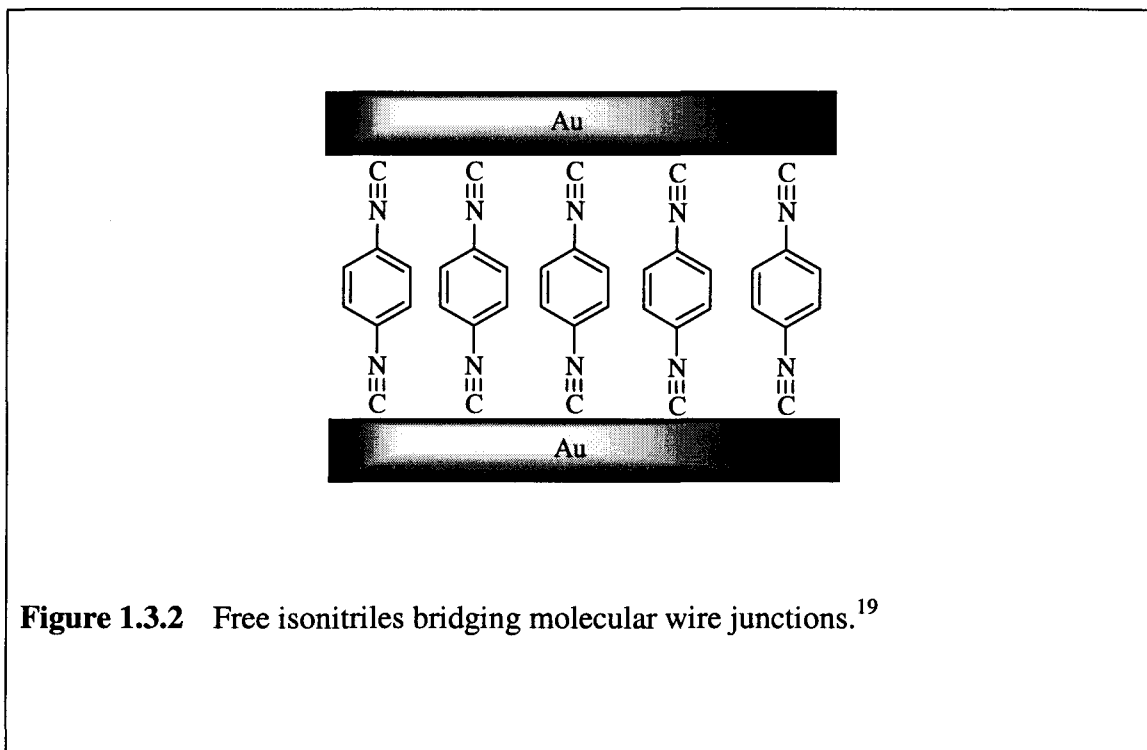
**Figure 1.3.2**  Free isonitriles bridging molecular wire junctions.[19]

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 geometries of these complexes.
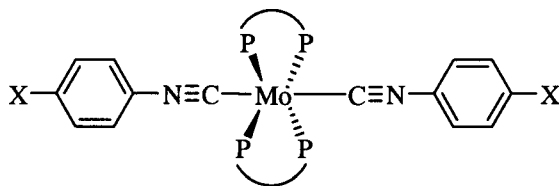
**Figure 1.3.3**  Metal phosphine center bridging aromatic isonitriles.

Some inorganic materials having from three to seven ligands bound to a central metal atom or ion are expected to have a star like shapes due to the geometryof the bonding orbitals. Examples of these types of systems are:

- Two coordinate: $Au^+$

- Three coordinate: $Ag^+$

- Some four coordinate systems: $Ni^0$, $Ag^+$, $Cu^+$, $Rh^+$, $Ni^{+2}$, $Pd^{+2}$, $Co^{+2}$.

- Some five coordinate systems: $Fe^0$, $Re^0$, $Co^+$, $Co^{+2}$.

- Some six coordinate systems: $Cr^0$, $Mo^0$, $W^0$, $Cr^+$, $Mn^+$, $Cr^{+2}$, $Fe^{+2}$.

- Some seven coordinate systems: $Mo^{+2}$, $W^{+2}$, $W^{+3}$.
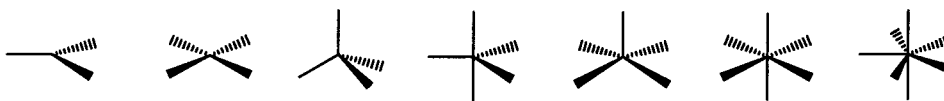


**Figure 1.3.4**  Possible geometries of homoleptic metal complexes.

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.

## 2. Requisite Organic and Organometallic Reagents

The organometallic nanomaterials described in this thesis contain bifunctional isonitrile ligands of the type $1,4\text{-}C_6H_4(NC)_2$ and $1,4\text{-}C_6Me_4(NC)_2$, and monofunctional isonitriles such as $MeO\text{-}C_6H_4\text{-}NC$. The chelating phosphines, $(1,4\text{-}C_6H_4Y)_2PCH_2CH_2P(1,4\text{-}C_6H_4Y)_2$ 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]

A) $\text{C}_6\text{H}_5-\text{NH}_2 \xrightarrow{\text{KOH, CHCl}_3} \text{C}_6\text{H}_5-\text{N}{\equiv}\text{C}$

B) $\text{C}_6\text{H}_5-\underset{\text{H}}{\text{N}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{H} \xrightarrow{\text{Cl}_2\text{CO}} \text{C}_6\text{H}_5-\text{N}{\equiv}\text{C}$
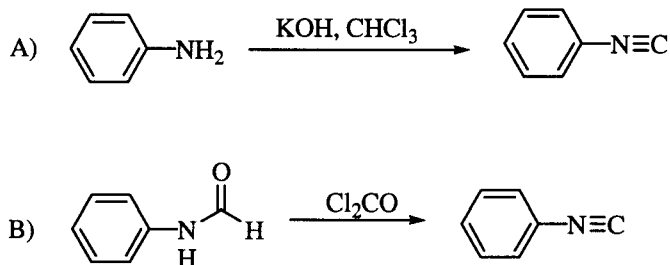
**Equations 1.3.1 and 1.3.2** Synthetic methods for preparing isonitriles.

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

$$\underset{\text{R}'\ \ \ \ \text{R}}{\overset{\text{R}\ \ \ \ \text{R}'}{\text{H}_2\text{N}-\text{C}_6-\text{NH}_2}} \xrightarrow{\text{HCOOH}} \underset{\text{R}'\ \ \ \ \text{R}}{\overset{\text{R}\ \ \ \ \text{R}'}{\text{H}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\underset{\text{H}}{\text{N}}-\text{C}_6-\underset{\text{H}}{\text{N}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{H}}} \xrightarrow[\text{NEt}_3]{\text{Cl}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-\text{CCl}_3} \underset{\text{R}'\ \ \ \ \text{R}}{\overset{\text{R}\ \ \ \ \text{R}'}{\text{C}{\equiv}\text{N}-\text{C}_6-\text{N}{\equiv}\text{C}}}$$
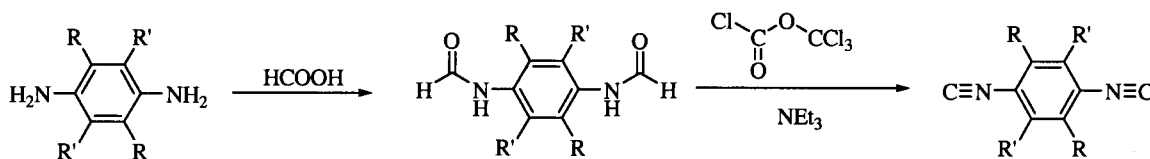
**Equation 1.3.3** General synthesis for bis(isonitriles).

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' = $(1,4-C_6H_4Y)_2PCH_2CH_2P(1,4-C_6H_4Y)_2$ and $(1,2-C_6H_4Y)_2PC_6H_4P(1,4-C_6H_4Y)_2$

where Y = OMe, Me, Et, etc.) will be used to systematically change the electron richness at Mo and the materials' steric bulk.



Y = OMe, Et, CH$_3$

**Figure 1.3.5** Examples of some chelating phosphines.
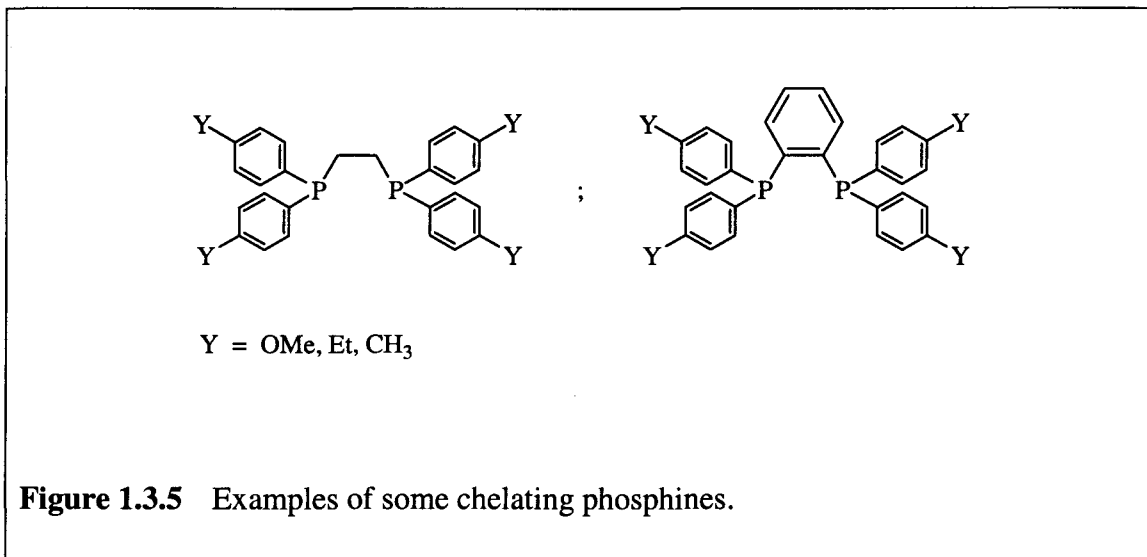
The typical synthetic route for preparing phosphines that are derivatives of dppe is shown below.[23]



R = OMe, Et, CH$_3$

**Equation 1.3.4** Synthetic route for the preparation of phosphines derived from dppe.
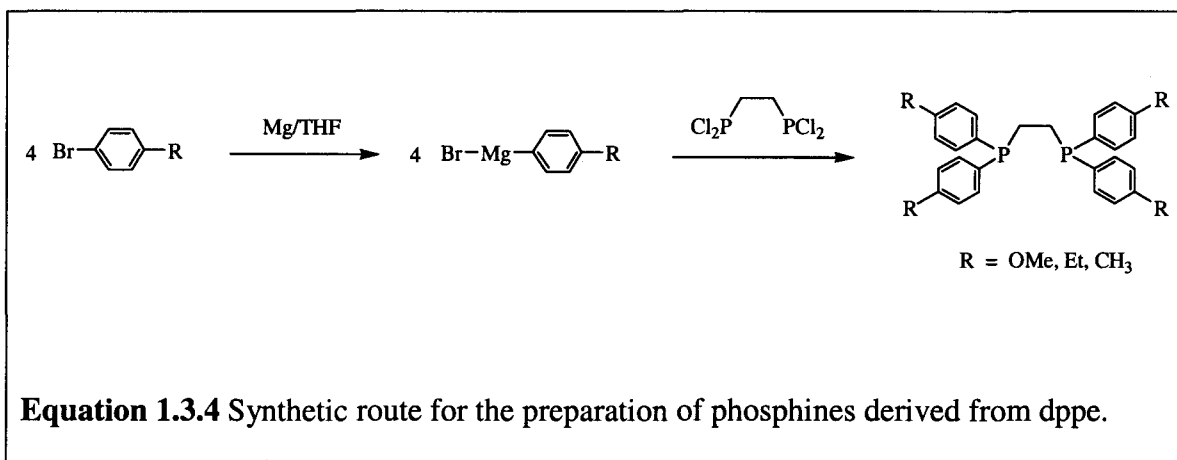
In this reaction, commercially available bis(dichlorophosphino)ethane is used as the starting material. Reaction of this compound with a Grignard or organolithium reagent in THF generally produces the desired dppe derivatives.

In addition to the phosphines derived from dppe, 1,2-bis(phosphino)benzene derivative will also be used. Instead of possessing an ethyl bridge between the phosphorus atoms, there is a benzene bridge (this type of phosphine is shown on the right in **Fig. 1.3.5**). The addition of the benzene backbone is expected to provide the polymer with a greater amount of stability since there is less rotational freedom present in a benzene ring than there is with an alkanediyl bridge.

The synthetic route to preparing the "benzene backbone" phosphines and its derivatives is similar to the route shown in **Equation 1.3.4**. Thus, the aryl Grignard reagent is first prepared and is then combined with 1,2-bis(dichlorophosphino)benzene. Unlike 1,2-bis(dichlorophosphino)ethane, which is commercially available, the starting material for the dppe derivative phosphines, 1,2-bis(dichlorophosphino)benzene, must be synthesized. A useful synthetic route to 1,2-bis(phosphino)benzene has been reported by Kyba et. al.[24] and is detailed below.



**Equation 1.3.5**      Synthetic route to 1,2-bis(phosphino)benzene
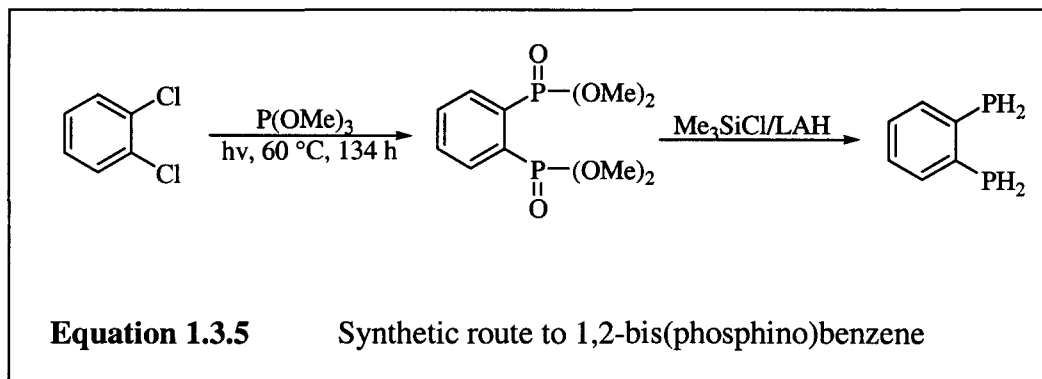
The chlorination reaction is carried out by a method similar to the method reported by

Dahlenburg *et. al.*[25]



**Equation 1.3.6** Chlorination reaction of 1,2-bis(phosphino)benzene
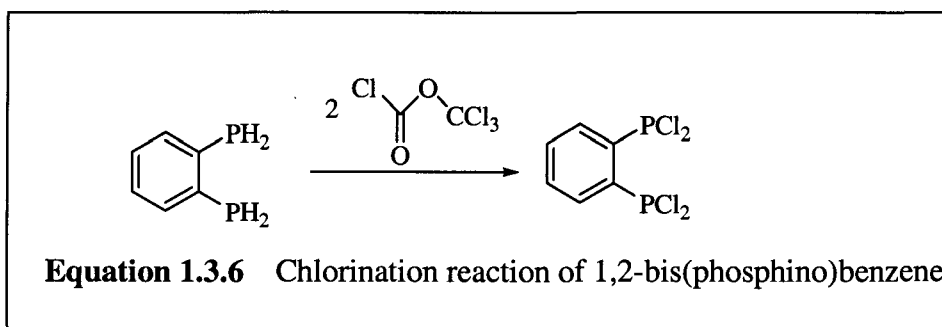
The precursors used for the synthesis of our organometallic materials are

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 models and/or catalysts for chemical low-pressure nitrogen

fixation.[26] In our new chemistry, the dinitrogen ligands will be exchanged with

diisonitrile molecules to give the first generation metal-diisonitrile building blocks. Bis-

isonitrile complexes of the molybdenum phosphine complex (*e.g.*, $Mo(PR_3)_4(C\equiv N-$

$C_6H_5)_2$) have previously been prepared by displacement of a weak ligand such as $N_2$ from

the metal center. These starting materials (*e.g.*, $Mo(PR_3)_4(N_2)_2$ and

$Mo(PR_3)_4(N_2)(CNMe)$) 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.[27]

$$\text{MoCl}_5 \; + \; 2 \, \text{dppe} \; + \; \text{exc. Mg} \quad \xrightarrow{\text{THF/N}_2} \quad \text{Mo(dppe)}_2(\text{N}_2)_2$$
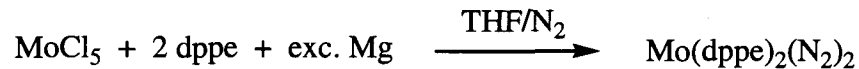
**Equation 1.3.7** Synthetic route for the preparation of dintrogen complexes.

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:

$$\text{xs} \quad \text{CN-C}_6\text{H}_4\text{-NC} \; + \; \text{Mo(dppe)}_2(\text{N}_2)_2 \quad \longrightarrow \quad \text{Mo(dppe)}_2(\text{CN-C}_6\text{H}_4\text{-NC})_2$$
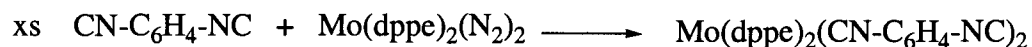
**Equation 1.3.8** Synthetic route for the preparation of bis(diisonitrile) complexes.

Similar monoisonitrile complexes with only one isonitrile ligand per molybdenum center have been reported using a slightly different approach starting with imines instead of diisonitriles.[28]

**Equation 1.3.9** Synthetic route for the preparation of a terminal metal complex.
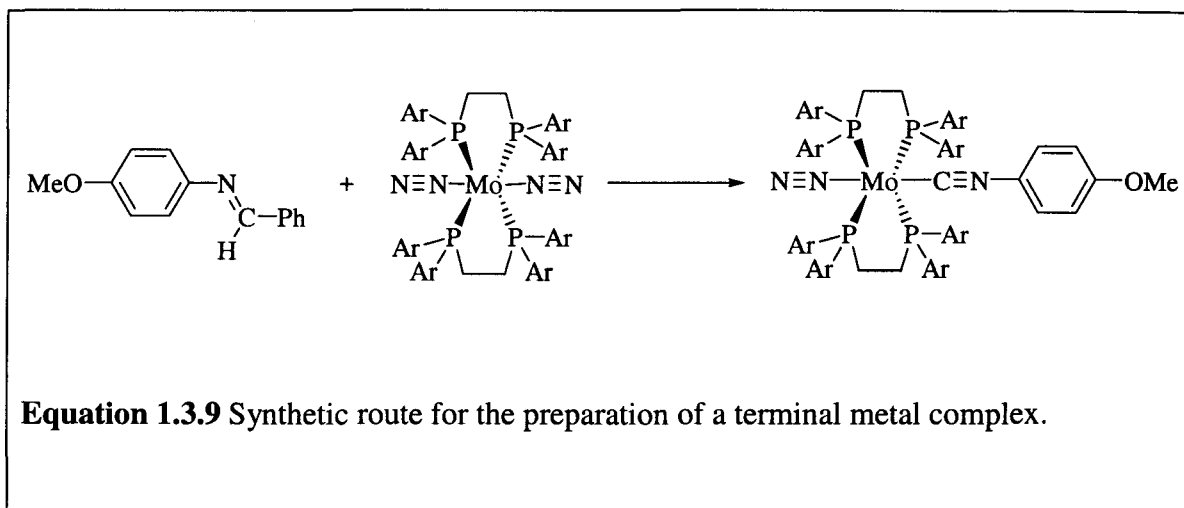
Longer oligomers will then be synthesized by combining the dinitrogen terminated first generation nanorods, the isonitrile terminated first generation nanorods, the bifunctional isonitriles, and/or the bis-dinitrogen complexes in appropriate proportions. When oligomers of the final desired chain length are made, they will be capped with terminal organometallic groups, including: $M(CO)_5$ (M = Cr, Mo, W), $CpFe(CO)_2^+$, $CpMn(CO)_2$, $Mo(dppe')_2CO$, or $Mo(dppe')_2(CN-R)$. The organometallic 'caps' will be prepared *via* published routes (equation 3.8).[29]



**Equation 1.3.10** Synthetic pathway for the preparation of a carbonyl-terminated metal complex.
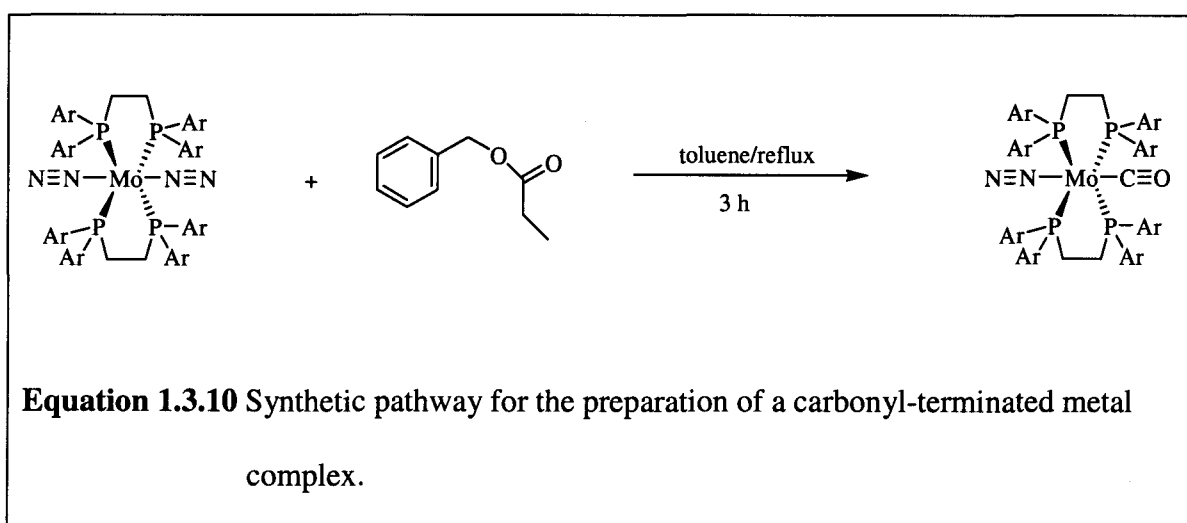
However, the syntheses will require careful exploration of the reaction conditions to optimize conditions and prevent mixtures of non-capped, mono-capped, and di-capped species from forming. When electron poor caps such as $Mo(CO)_5$ are used, it is expected that they will tend to polarize the organometallic 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.[27]

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

$$MCl_x(solvent)_k + reducing\ agent + z\ CN\text{-arene-}X \longrightarrow M(CN\text{-arene-}X)_z$$
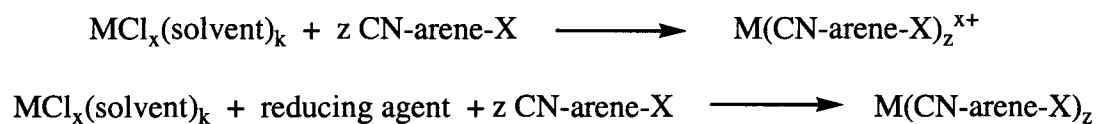
**Equation 1.3.11 and 1.3.12** General patways for the preparation of metal-isonitrile complexes.

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 have different solubility than that of 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 possibly may 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 $\pi^*$ 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.

### 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 of the complexes 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

# References

1.      P. R. Jenkins. *Organometallic Reagents in Synthesis*; Oxford University Press: New York, **1992**.

2.      (a) B. Douglas, D. McDaniel, J. Alexander. *Concepts and Models of Inorganic Chemistry*; John Wiley and Sons Inc.: New York, **1994**. (b) J. J. Eisch. *The Chemistry of Organometallic Compounds: The Main Group Elements*; The Macmillan Company; New York, **1967**. (c) J. E. Huheey. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper Collins Publishers Inc.: New York, **1983**.

3.      R. F. Heck. *Organotransition Metal Chemistry: A Mechanistic Approach*; Academic Press: New York, **1974**.

4.      C. M. Lukehart. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishing Company: Monterey, California, **1985**.

5.      (a) H. K. Hall Jr. *J. Amer. Chem. Soc.*, **1956**, *78*, 2717 (1956). (b) E. L. Wittbecker, P. W. Morgan. *J. Polymer Sci.*, **1959**, *40*, 289. (c) H. F. Mark, S. M. Atlas, N. Ogata. *J. Polymer Sci.* **1962**, *61*, S49.

6.      D. F. Shriver, P. W. Atkins. *Inorganic Chemistry:* 3$^{rd}$ ed; Oxford University Press: Oxford, **1999**; p 278.

7.      J. E. Mark, H. E. Allcock, R. West. *Inorganic Polymers*; Prentice-Hall Inc.: Englewood Cliffs, New Jersey, **1992**.

8.      T. A. George, C. D. Seibold, *Inorg. Chem.* **1973**, *12*, 2544-2547.

9.      P. Nguyen, P. Gomez-Elipe, I. Manners. *Chem. Rev.* **1999**, *99*, 1515-1548.

10.     J. E. Keaton. *Organic Semiconducting Polymers* **1968,** p240, Marcel Dekker: New York.

11.     I. Manners. *Agnew. Chem., Int. Ed. Engl.* **1996,** *35*, 1602.

12.     M. P. Stevens. *Polymer Chemistry: An Introduction;* 3rd ed; Oxford University Press: New York, 1999; p 12, 120.

13.     C. U. Pittman Jr., O. E. Ayers, B. Suryanarayanan, S. P. McManus, J. E. Sheats. *Makromol. Chem.* **1974,** *175*, 1427.

14.     (a) Y. Fujikura, K. Sonogashira, N. Hagihara. *Chem. Lett.* **1975,** 1067. (b) K. Sonogashira, S. Takahashi, N. Hagihara. *Macromolecules* **1977,** *10*, 879.

15.     A. W. Bosman, H. M. Janssen, E. W. Meijer. *Chem. Rev.,* **1999,** *99*, 1665-1668.

16.     C. E. Carraher Jr. *Polymer Chemistry*; 5th ed; Marcel Dekker, Inc.: New York, 2000; p 380.

17.     A. M. McDonagh, N. T. Lucas, M. P. Cifuentes, M. G. Humphrey, S. Houbrechts, A. Persoons. *J. Organomet. Chem.* **2000,** *605*, 184-192.

18.     I. R.Whittall, A. M. McDonagh, M. G. Humphrey. *Adv. Organomet. Chem.* **1998,** *42*, 291-362.

19.     J. Chen, L. C. Clavet, M. A. Reed, D. W. Carr, D. S. Grubisha, D. W. Bennett. *Chem. Phys. Lett.* **1999,** *313*, 741-748.

20.     N. L. Wagner, F. E. Laib, D. W. Bennett. *Inorg. Chem. Comm.* **2000,** *3*, 87-90.

21.     I. Ugi, U. Fetzner, U. Ebholzer, H. Knupfer, K. Offermann. *Agnew. Chem., Int. Ed. Engl.* **1965,** *4*, 472.

22. A. Efraty, I. Feinstein, L. Wackerle, A. Goldman. *J. Org. Chem.* **1980,** *45*, 4059-4061.

23. J. Chatt, W. Hussain, G. J. Leigh, H. M. Ali, C. J. Pickett, K. A. Rankin. *J. Chem. Soc. Dalton. Trans.* **1985,** 1131-1136.

24. Adapted from E. P. Kyba, S-T Jui, R. L. Harris. *Organometallics* **1983**, *2*, 1877-1879 and E. P. Kyba, M. C. Kerby, S. P. Rines. *Organometallics* **1986**, *5*, 1189-1194.

25. Adapted from L. Dahenburg, A. Kaunert. *Eur. J. Inorg. Chem.* **1998**, 885-887

26. M. Hidai, K. Tominari, Y. Uchida, A. Misono. *Chem. Commun.* **1969,** 1392.

27. J. Chatt, J. R. Dilworth, R. L. Richards. *Chem. Rev.* **1978,** *78*, 589.

28. G. Nakamura, Y. Harada, C. Arita, H. Seino, Y. Mizobe, M. Hidai. *Organometallics* **1998,** *17*, 1010-1012.

29. M. Sato, T. Tatsumi, T. Dodama, M. Hidai, T. Uchida, Y. Uchida. *J. Am. Chem. Soc.* **1978,** *100*, 4447-52.

# Chapter II –Experimental

Unless otherwise stated, all reactions were carried out under a dry, inert atmosphere using standard Schlenk techniques for the handling of air-sensitive materials.

## 1. Reagents

All reagents used were either purchased commercially or were synthesized prior to use. The reagents that were purchased were of reagent grade or comparable purity and were not further purified prior to use. Samples were deareated by either bubbling ultra high purity nitrogen through the chemical or by the *freeze-pump-thaw* method (the reagent to be purified is frozen using liquid nitrogen, the air pumped off, then the reagent is allowed to thaw; the process is repeated at a minimum of three times). Solvents were dried and deareated using standard methods[1] and stored under nitrogen. Thus, THF, diethyl ether and toluene were distilled from benzophenone ketyl radical over Na-K amalgam for THF and diethyl ether and Na for toluene. Hexane was distilled over Na-K amalgam. Dichloromethane was distilled over calcium hydride.

## 2. Instrumentation

Infrared spectra were measured using a JASCO FT/IR-410 infrared spectraphotometer. NMR spectra were measured on a Varian Gemini 2000 400 MHz spectrometer with reference to the deuterium signal of the solvent used. The $^1$H, $^{13}$C, and

$^{31}$P NMR chemical shifts were measured in parts per million (ppm) downfield from external Me$_4$Si and 85% H$_3$PO$_4$, as appropriate.

### 3. 1,2-Bis(dimethoxyphosphoryl)benzene[2]
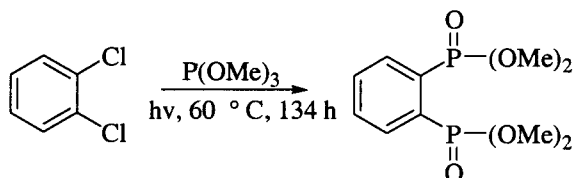


The photochemical reaction vessel used was purchased from Ace Glass, catalog number 7861-255 1000mL. The power supply has catalog number 7830-60, with a power rating of 450 watts. The lamp used was catalog number 7825-34 for a 450W UV immersion lamp with a 4.3" arc length. Trimethyl phosphite (Aldrich, 97%, 900 mL, 947 g, 8 mol) and 1,2-dichlorobenzene (Aldrich, 99%, 300 mL, 391.5 g, 2.66 mol) are photolyzed for 134 h at 60 °C under an atmosphere of nitrogen. The solution is then transferred to a 3 L flask and reduced in volume by half (i.e. to 600 mL). Acetone (approximately 200 mL) is added and the solution is placed in the freezer (-19 °C) to crystallize. Re-crystallization (when needed) can be done by dissolving the crystals in hot acetone and placing the mixture in the freezer (-19 °C) overnight giving 106.63 g (362.46 mmol, 13.6%) of 1,2-bis(dimethoxyphosphyl)benzene as clear, colorless crystals. The supernatant can then be recycled for use in this reaction as it contains a mixture primarily composed of the starting material, the monosubstitution product, and the desired product.

**Spectroscopic Data**

NMR data: ^{31}P NMR (161.884 MHz, $CDCl_3$): $\delta$ = –4.634(s); ^{1}H NMR (399.905 MHz, $CDCl_3$): $\delta$ = 7.895 (m, 2 H, $C_6\underline{H}_4$), 7.411 (m, 2 H, $C_6\underline{H}_4$), 3.580 (pd, 12 H, $C\underline{H}_3$)

## 4. 1,2-Bis(phosphino)benzene[1]
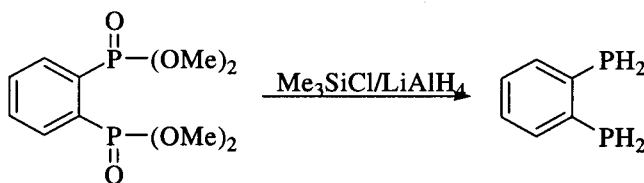


Lithium aluminum hydride (Aldrich, 95%, 15.6 g, 410 mmol) is added to a 1 L 3-neck flask fitted with a stopper, $N_2$ adaptor, and an over-sized bean-shaped stirring bar. The flask is evacuated and filled with nitrogen. THF (500 mL) is added and the flask is cooled to –78 °C using a dry ice-ethanol bath. Trimethylchlorosilane (Aldrich, 98%, 51.8 mL, 44.5g, 410 mmol) is then added drop-wise to the cold solution and the solution is stirred while warming to room temperature for 2 h. 1,2-Bis(dimethoxyphosphoryl)benzene (20.0 g, 68 mmol) is dissolved in THF (200 mL). This solution is then added drop-wise *via* syringe to the reducing mixture after it has cooled back down to –78 °C. This addition must be done slowly as gas and heat evolve from this reduction. The solution is stirred for 36 h. **Note**: the next step should be done **slowly**, as the excess LAH reacts **violently** with water. The reaction is quenched with water (100 mL), followed by 1M KOH (250 mL; both degassed prior to use). The organic layer is removed and the aqueous layer is extracted with diethyl ether (4 × 200 mL portions). The ether portions are then combined, concentrated to 30 mL, and dried over magnesium

sulfate overnight. After the magnesium sulfate is removed by filtration, the extracts are fractionally distilled *in vacuo* to give 6.27 g (44.13 mmol, 64%) of the desired product as a clear, colorless to slightly yellow liquid with a boiling point (in oil pump vacuum) of 60 °C.

**Spectroscopic Data**

^{1}H NMR (399.905 MHz, CDCl$_3$) δ 7.25 (m, 2H, C$_6$$\underline{H}_4$), 6.90 (m, 2H, C$_6$$\underline{H}_4$), 3.90 (pd, 4H, P$\underline{H}_2$). [31]P NMR (161.884 MHz, CDCl$_3$) δ -147.69

**5. 1,2-Bis(dichlorophosphino)benzene[3]**
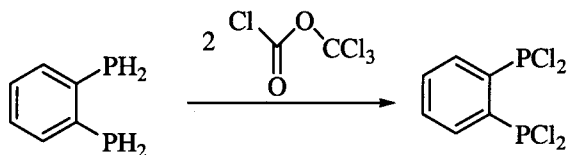


A 500 mL 3-neck flask is fitted with a stopper, N$_2$ adaptor, and a 50 mL addition funnel. It is then evacuated and filled with nitrogen. 1,2-Bis(phosphino)benzene (10.13 g, 71.3 mmol) and THF (200 mL) are added to the flask. Trichloromethyl chloroformate (Lancaster, 98%, 17.4 mL, 144.3 mmol) in THF (30 mL) are added *via* the addition funnel drop-wise to the solution of 1,2-bis(phosphino)benzene over 1 h. After addition is complete, the reaction mixture is allowed to stir for an additional 2 h. The solution is then concentrated to 50 mL and fractionally vacuum distilled, resulting in 7.35 g (26.27 mmol, 36.8%) of a yellow tinted liquid with a boiling point (under vacuum) of 85-90 °C for 1,2-

$C_6H_4(PCl_2)_2$. Due to its reactivity, this product was not further characterized except by its products.

### 6. Attempted synthesis of 1,2-bis(di(pentafluorobenzene)phosphino)benzene[4]
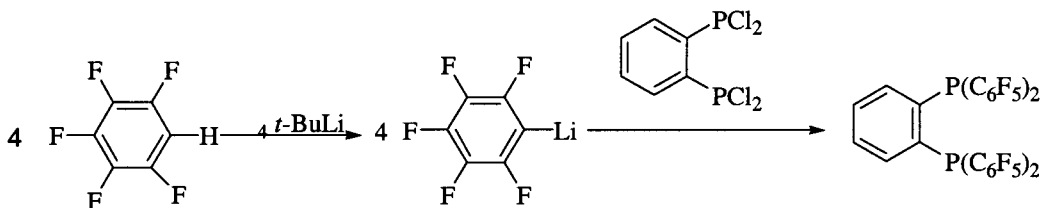


To a 250 mL 3-neck flask fitted with a nitrogen adapter, addition funnel, and a stopper, are added 30 mL diethyl ether and 3.3 mL (5 g, 29.8 mmol) 1,2,3,4,5-pentafluorobenzene (Aldrich, 99%) (The reaction vessel is evacuated and filled with nitrogen prior to the addition). The solution is then cooled to −55 °C using a dry ice/ethanol bath. The 17.5 mL (12.3 g, 29.8 mmol) of $t$-butyl lithium is added $via$ syringe and the solution is stirred for 1 h. 1,2-Bis(dichlorophosphino)benzene (1.60 g, 5.72 mmol) and 20 mL diethyl ether are then combined in the addition funnel and added to the mixture drop-wise over the course of 1 h. The resulting orange solution is stirred for an additional 2 h. The mixture is then placed in the freezer (-19 °C) to crystallize. No product was isolated.

## 7. 1,2-Bis({3,5-bis(trifluoromethyl)benzene}phosphino)benzene[3]
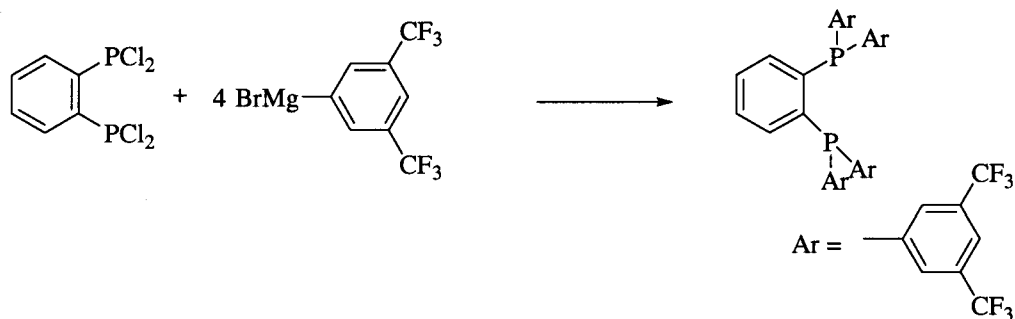


### Grignard Reagent Preparation

To a 500 mL 3-neck flask fitted with a nitrogen adapter, stopper, and a 50 mL addition funnel, are added 0.73 g (30 mmol) magnesium turnings (Aldrich, 99+%) and 150 mL THF. The addition funnel is then charged with 4.4 g (15 mmol, 2.6 mL) 3,5-bis(trifluoromethyl)bromobenzene (Aldrich, 99%) and 30 mL THF. This mixture is added drop-wise to the Mg/THF slurry over the course of 45 min. The resulting orange-brown solution is stirred for an additional hour.

### Phosphine Synthesis

To a 500 mL Schlenk flask fitted with a 250 mL Schlenk filter, are added 1.08 g (3.58 mmol) of 1,2-bis(dichlorophosphino)benzene and 250 mL toluene (Fisher, ACS grade, 99.9%). This solution is then cooled to 0 °C. The Schlenk filter is charged with the Grignard reagent in **A**, which is slowly filtered so that it is added drop-wise to the solution of 1,2-bis(dichlorophosphino)benzene over the course of 45 min at 0 °C. The reaction mixture is stirred for an additional 2 h. The solution is then concentrated *in vacuo* to approximately 50 mL and hexane (100 mL) is added. The resulting dark orange-

brown solution is then placed in the freezer (-19 °C) to crystallize. The resulting brown crystals are re-dissolved in toluene (20 mL) and filtered through Celite. 100 mL Toluene and 250 mL hexane are added and the solution is placed in the freezer and left to crystallize over the course of 5 days. The solution is decanted off from the resulting quartz-like crystals and they are slurried in hexane and filtered through Whatman 41 filter paper. The crystals are then allowed to dry on the filter paper to give 0.71 g ( 0.71 mmol, 18.5%) of the desired phosphine.

**Spectroscopic Data**

$^1$H NMR (399.886 MHz, CDCl$_3$) δ 7.88 (s), 7.57 (m, 2 H, Ph-H), 7.11 (m, 2 H, Ph-H)

### 8. 1,2-Bis(di($p$-anisole)phosphino)benzene[3]
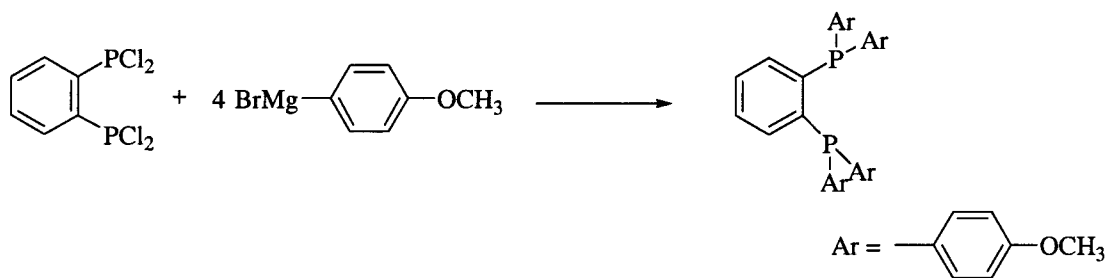


To a 500 mL 3 neck flask fitted with a nitrogen adapter, stopper, and 25 mL addition funnel, is added 2.06 g (84.76 mmol) magnesium turnings (Aldrich, 99+%) and 250 mL THF (Aldrich, HPLC grade, 99.9%). The addition funnel is charged with 6.5 mL (53.6 mmol) of 4-bromoanisole (Aldrich, 99%) and 15 mL of THF. The solution is then added drop-wise to the magnesium slurry over the course of 1 h. The solution is heated to reflux for an additional 10 min and is then stirred for an additional 2 h. To a 500 mL

Schlenk flask fitted with a 250 mL Schlenk filter, is added 100 mL THF and 3.0 g (10.72 mmol) 1,2-bis(dichlorophosphino)benzene. The filter frit is then charged with the anisole Grignard reagent described above. The Grignard reagent is added to the 1,2-bis(dichlorophosphino)benzene solution drop-wise *via* the filter frit over the course of 1h. This reaction mixture is then allowed to stir for an addition 2h. The excess Grignard reagent is hydrolyzed with a 10% solution of ammonium chloride (3 × 100 mL). The organic layer is removed and then stirred over anhydrous magnesium sulfate (Fisher, anhydrous) overnight. The yellow-green solution is filtered and the solvents are removed from the filtrate *in vacuo*. The resulting pale yellow residue is re-dissolved in diethyl ether (100 mL) and the solution is left to crystallize in the freezer (-19 °C) giving 0.71 g (1.25 mmol, 11.7%) of the white phosphine.

**Spectroscopic Data**

$^1$H NMR (399.886 MHz, CDCl$_3$): δ = 7.26 (m, 2 H, Ph-H), 7.09 (m, 2 H, Ph-H), 6.74 (d, $J$ ($^1$H$^1$H) = 8 Hz, 4 H Ph-H), 3.78 (s, 12 H, CH$_3$)

### 9. Bis(di(*p*-tolyl)phosphino)ethane[5]
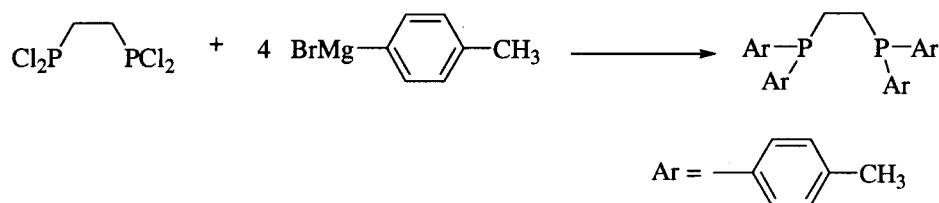
To a 500 mL 3 neck flask fitted with a nitrogen adapter, stopper, and 50 mL addition funnel, is added 11.47 g (472 mmol) of magnesium turnings (Aldrich, 99+ %) and 160 mL of THF (Aldrich, HPLC grade, 99.9 %). The addition funnel is charged with 37 mL (51 g, 298 mmol) of 4-bromotoluene (Aldrich, 99 %) and 10 mL of THF. This solution is then added drop-wise to the magnesium slurry over the course of 1 h and is stirred for an additional 1 h. To a 500 mL Schlenk flask fitted with a 250 mL Schlenk filter is added 100 mL of THF and 15.36 g (66.26 mmol, 10 mL) of 1,2-bis(dichlorophosphino)ethane. The sintered glass filter is then charged with the toluene Grignard reagent prepared previously. The Grignard reagent is then added to the 1,2-bis(dichlorophosphino)ethane solution drop-wise *via* the Schlenk filter over the course of 1 h. The reaction mixture is stirred for an additional 2 h. The excess Grignard reagent is then hydrolyzed with a 10% solution of ammonium chloride (3 × 100 mL). The organic layer is removed *via* a separatory funnel and stirred over anhydrous magnesium sulfate (Fisher, anhydrous) overnight. The yellow solution is filtered off and the solvents are removed from the filtrate *in vacuo*. The resulting pale yellow residue is re-dissolved in toluene (100 mL) and hexane (40 mL) is added. The solution is placed in the freezer (-19 °C), where it is left to crystallize. The solvent is removed using a syringe and the phosphine is re-crystallized from a 1:3 toluene/hexane mixture (the phosphine is first dissolved in toluene, and then layered with three times as much hexane (approximately 60 mL) giving 6.34 g (13.95 mmol, 21.1%) of the white crystalline phosphine.

**Spectroscopic Data**

$^1$H NMR (399.886 MHz, C$_6$D$_6$): δ = 7.36 (m), 6.89 (d, $J(^1$H $^1$H) = 8 Hz), 2.32 (t, $J(^1$H $^1$H)

= 4 Hz, 4 H, C$\underline{H}_2$), 2.03 (s, 12 H, C$\underline{H}_3$). $^{13}$C NMR (100.560 MHz, C$_6$D$_6$): δ = 139.00 (s,

$\underline{C}_6$H$_4$), 136.63 (s, $\underline{C}_6$H$_4$), 133.82 (s, $\underline{C}_6$H$_4$), 130.20 (s, $\underline{C}_6$H$_4$), 25.91 (s, $\underline{C}$H$_2$), 22.10 (s,

$\underline{C}$H$_3$).

## 10. Bis(dinitrogen)bis(diphenylphosphinoethane)tungsten (0)[6]
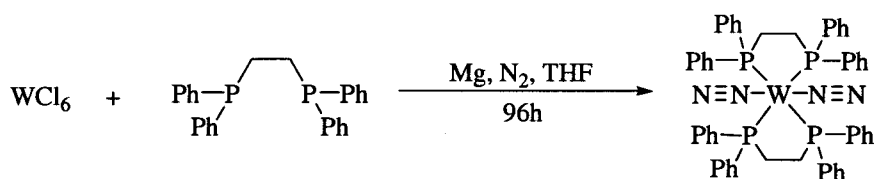


To a 1 L Schlenk flask equipped with a stir bar and stopper are added 24 g (1 mol)

of Mg turnings (Aldrich, 99.9+ %; note: it is important that the Mg turnings are as clean

as possible) and 25 g (62.75 mmol) of 1,2-bis(diphenylphosphino)ethane (Aldrich, 97

%). The reaction vessel is evacuated and then THF (300 mL) followed by 11.89 g (30

mmol) of tungsten hexachloride (Aldrich, 99+ %) are added. The reaction solution is

vigorously stirred for 4 days (96 h) under an atmosphere of ultra high purity (UHP) N$_2$.

The reaction mixture is filtered through a Celite packed Schlenk filter to remove the Mg

turnings. At this point, orange crystals can be seen on the Celite bed. These crystals are

then dissolved off of the Celite and the initial reaction flask is rinsed with THF (1.5 – 2

L). Once the crystals have been dissolved, the solvent is reduced in volume by half (i.e. to

500 mL) and degassed methanol (300 mL; Acros, anhydrous, 99.8 %) is added. The flask

is cooled to 0 °C for 1 h. The orange micro crystals are then filtered off and re-

crystallized by dissolving them in THF (50 mL). Slight heating may be required to get the crystals fully into solution. After three times as much methanol (150 mL) is added, 13 g (12.54 mmol, 41.8%) of the orange dinitrogen complex is obtained by filtration as an orange crystalline solid.

**Spectroscopic Data**

$^1$H NMR (399.905 MHz, $C_6D_6$): $\delta$ = 2.26 (t, $J(^1H^1H)$ = 8 Hz, 8 H, C$\underline{H}_2$), 7.01 (s, 20 H, C$_6\underline{H}_5$), 7.02 (s, 20 H, C$_6\underline{H}_5$), 7.19 (s, 32 H, C$_6\underline{H}_5$). $^{31}$P (161.884 MHz, $C_6D_6$): $\delta$ = 45.71. IR (CaF$_2$ plates, toluene solvent) $v$(N≡N) 1948.72 (s, sy), 2009.46 (w, as).

**11. Bis(dinitrogen)bis[1,2-bis(di($p$-ethylphenyl)phosphino)benzene]molybdenum(0)[5]**
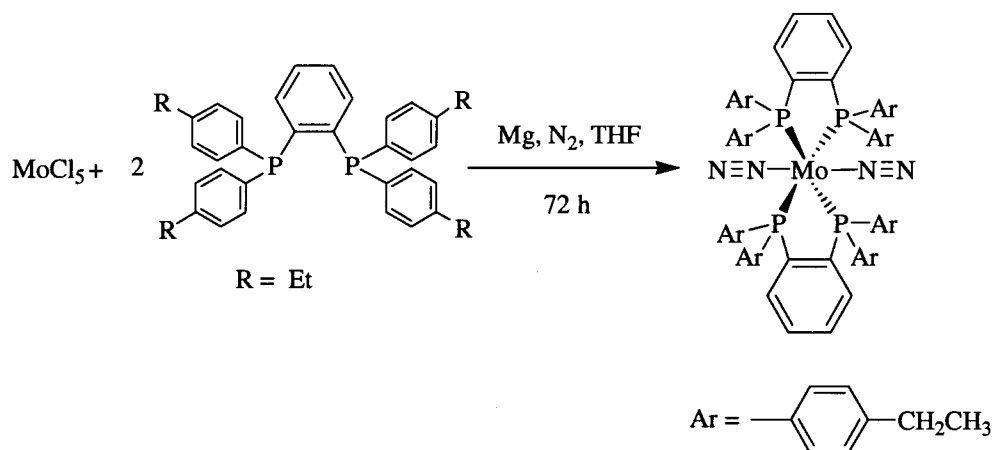


To a 1 L Schlenk flask equipped with a stir bar and stopper, is added 2.38 g (97.9 mmol) of Mg turnings (Aldrich, 99.9+ %; note: it is important that the Mg turnings be as clean as possible) and 6.71 g (12.01 mmol) of 1,2-bis(di($p$-ethylbenzene)phosphino)benzene. The reaction vessel is evacuated and then THF (400

mL) followed by 1.64 g (6.0 mmol) of molybdenum pentachloride (Aldrich, 99+ %) are added. The reaction solution is stirred vigorously for 3 days (72 h) under an atmosphere of ultra high purity (UHP) $N_2$. The reaction mixture is then filtered through a Celite packed Schlenk filter to remove the Mg turnings. Degassed methanol (600 mL; Acros, anhydrous, 99.8%) is then added to precipitate the orange red product. The flask is cooled to 0 °C for 1 h. The suspension is again filtered through Celite. The resulting red-orange dinitrogen complex is dissolved off of the Celite into a different 1000 mL flask using THF (approximately 200 mL) and methanol (600 mL; Acros, anhydrous, 99.8%) is again added to precipitate 5.1 g (4.02 mmol, 66.8%) of the red dinitrogen complex. These crystals are collected on a filter frit and dried *in vacuo*. The purity of the product can be determined by $^1H$ NMR and additional purification by re-crystallization (THF/methanol mixture) can be done if necessary.

**Spectroscopic Data**

$^1H$ NMR (399.905 MHz, $C_6D_6$): δ = 7.21 (d, $J$ ($^1H^1H$) = 7.6 Hz, 20 H, $C_6\underline{H}_5$), 6.94 (d, $J$ ($^1H^1H$) = 8 Hz, 20 H, $C_6\underline{H}_5$), 2.43 (q, $J$ ($^1H^1H$) = 8 Hz, 16 H, $C\underline{H}_2$), 1.07 (t, $J$ ($^1H^1H$) = 7.6 Hz, 24 H, $C\underline{H}_3$). $^{31}P$ NMR (161.884 MHz, $C_6D_6$): δ = 70.10. IR (CaF$_2$ plates, toluene solvent) $v$(N≡N) 1980.54 (s, sy), 2054.78 (w, as).

## 12. Bis(dinitrogen)bis[1,2 bis (di(p-ethylphenyl)phosphino)benzene]tungsten(0)[5]



$$R = Et$$

$$Ar = \text{—} \bigcirc \text{—} CH_2CH_3$$
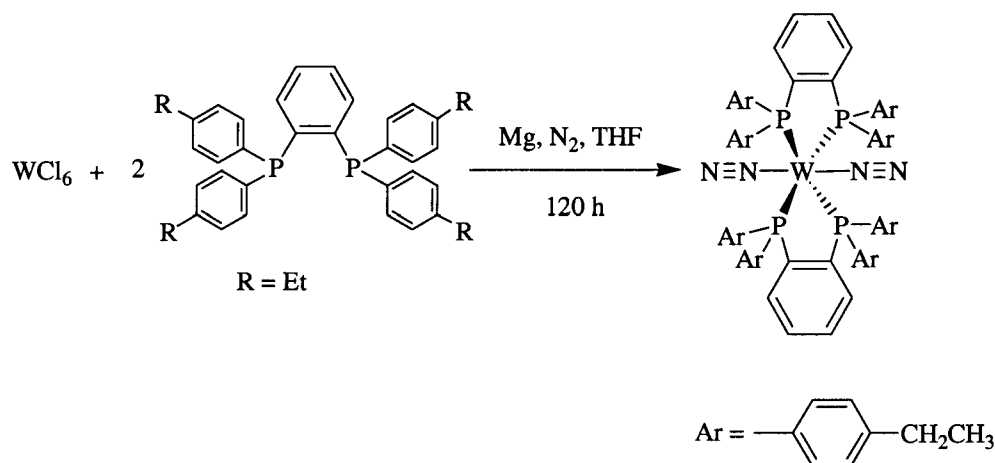
To a 500 mL Schlenk flask equipped with a stir bar and stopper, are added 1.02 g (42 mmol) of Mg turnings (Aldrich, 99.9+ %; note: it is important that the Mg turnings be as clean as possible) and 2.50 g (4.48 mmol) of 1,2 bis(di(p-ethylbenzene)phosphino)benzene. The reaction vessel is evacuated and then THF (300 mL) followed by 0.89 g (2.2 mmol) of tungsten hexachloride (Aldrich, 99+ %) are added. The reaction solution is stirred for 5 days (120 h) under an atmosphere of $N_2$. The reaction mixture is filtered through a Celite packed Schlenk filter to remove the Mg turnings and degassed methanol (800 mL; Acros, anhydrous, 99.8%) is added. The flask is then placed in the freezer (-19 °C) overnight. The solution mixture is again filtered through a Schlenk filter to remove any solid impurities and methanol (800 mL; Acros, anhydrous, 99.8%) is again added to precipitate the complex. These crystals are then collected on a filter frit. $^1$H NMR confirms the product's identity.

**Spectroscopic Data**

$^1$H NMR (399.905 MHz) δ 6.94 (d, J = 8 Hz, 40H, C$_6$H$_5$), 2.43 (q, J = 8 Hz 16H, CH$_2$), 1.07 (t, J = 7.6 Hz, 24H, CH$_3$). IR (CaF$_2$ plates, toluene solvent) ν(N≡N) 1952.57(s, sym), 2023.93 (w, asym).

### 13. *cis*-Bis(1,4-diisocyanobenzene)bis[diphenylphosphinoethane]tungsten(0)
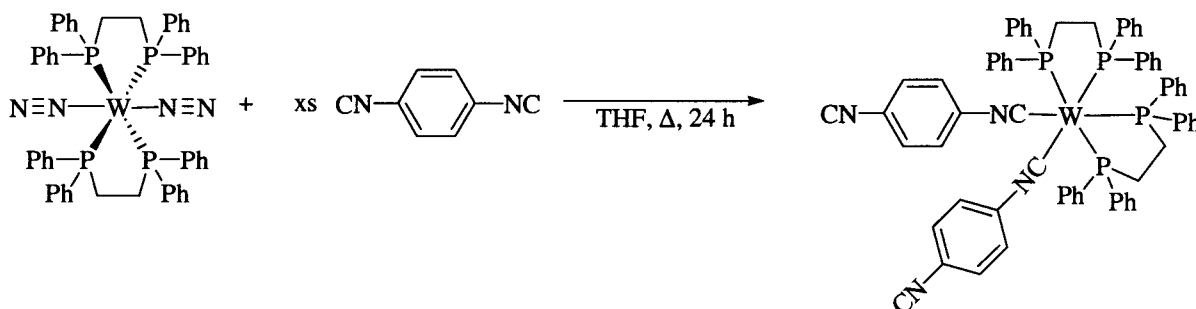


To a 500 mL 3-neck flask equipped with a stir bar, stopper, nitrogen adapter, and reflux condenser, are added 0.60 g. (0.58 mmol) of *trans*-bis(dinitrogen)bis(1,2-bis(diphenylphosphino)ethane)tungsten(0) and 0.74 g (5.8 mmol) of 1,4-diisocyanobenzene. The reaction vessel is evacuated and THF (200 mL) is added. The solution is heated to reflux for 24 h. The solvent is reduced *in vacuo* to 60 mL and 100 mL hexanes are added to precipitate the product as dark red crystals. The mixture is allowed to further crystallize in the refrigerator at 3 °C for 48 h. The mixture is filtered through a Schlenk filter and the resulting crystals are washed with hexane resulting in 0.229 g (0.19 mmol, 32%) of the bis(diisonitrile) complex.

**Spectroscopic Data**

No NMR data was recorded due to the poor solubility of the target complex

## 14. *cis*-Bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[diphenylphosphinoethane]tungsten(0)
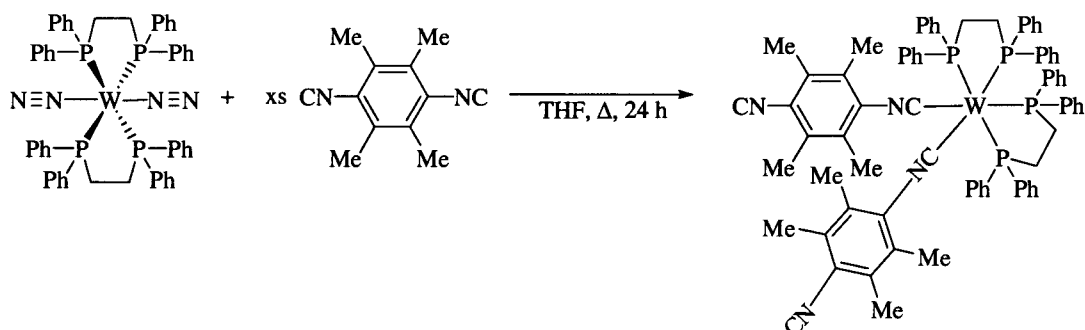


To a 500 mL 3-neck flask equipped with a stir bar, stopper, nitrogen adapter, and reflux condenser are added 0.60 g. (0.58 mmol) of *trans*-bis(dinitrogen)bis(1,2-bis(diphenylphosphino)ethane)tungsten(0) and 1.07 g (5.8 mmol) of 2,3,5,6-tetramethyl-1,4 diisocyanobenzene. The reaction vessel is evacuated and THF (200 mL) is added. The solution is heated to reflux for 24 h. The solvent is reduced *in vacuo* to 60 mL and 100 mL hexanes are added to precipitate the product as dark red crystals. The mixture is allowed to further crystallize in the refrigerator at 3 °C for 48 h. The mixture is collected on a Schlenk filter and the resulting purple crystals are washed with hexane (100 mL). In an attempt to further purify these crystals, THF (2.5 L) was used to dissolve the product (Note: product is only sparingly soluble in polar solvents) and the solution was placed in

the −80 °C freezer and later discarded. The hexane washing were placed in the refrigerator (3 °C). After 5 days, black crystals could be seen in the flask. The target bis(diisonitrile complex was produced in a 34% (0.27 g, 0.20 mmol) yield.

**Spectroscopic Data**

No NMR data due to poor solubility of the complex. X-ray diffraction showed the product to be the *cis* isomer of the target isonitrile complex.

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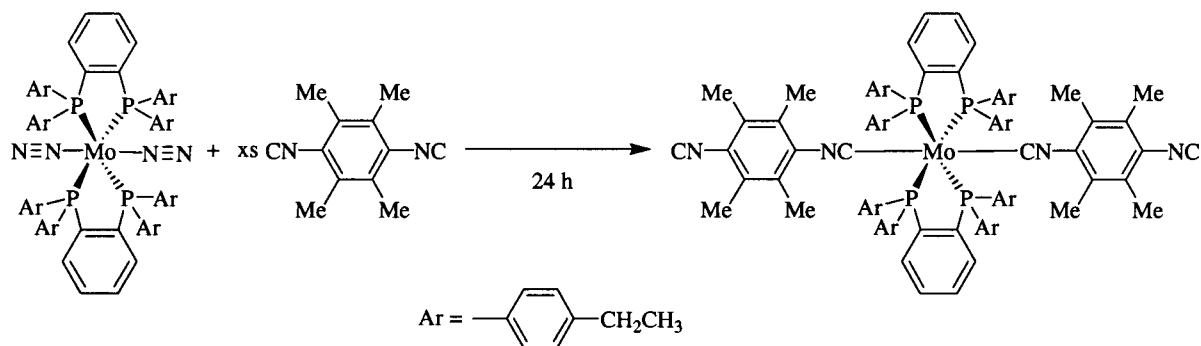


To a 500 mL 3-neck flask equipped with a stir bar, nitrogen adapter, addition funnel, and stopper are added 2.40 g (13.03 mmol) of 2,3,5,6-tetramethyl-1,4-diisocyanobenzene and toluene (120 mL). To the addition funnel are added 1.515 g (1.19 mmol) of bis(dinitrogen)bis[1,2-bis(di(p-ethylphenyl)phosphino)benzene] molybdenum(0) and toluene (60 mL). The flask is cooled to 0 °C with an ice bath and the bis(dinitrogen) bis[1,2-bis(di(p-ethylbenzene)phosphino)benzene]

molybdenum(0)/toluene solution is added drop-wise over the course of 1 h. Toluene (20 mL) is used to rinse the addition funnel and the reaction progress is monitored by IR spectroscopy. The reaction mixture is stirred for a total of 24 h. The solvent is reduced in volume *in vacuo* to 100 mL at which point dark green to blue micro crystals were observed in the flask. The flask is then placed in the freezer (-19 °C) and allowed to crystallize overnight. Hexane (120 mL) is added and the solution is again placed in the freezer to crystallize over the course of two days. The green-blue crystals are collected on a filter frit giving 1.89 g (1.20 mmol, 89.4%) of the bis(diisonitrile) complex.

**Spectroscopic Data**

$^1$H NMR (399.905 MHz, C$_6$D$_6$): δ = 7.88 (s, 10 H, C$_6$H$_5$), 7.21 (d, $J$ ($^1$H$^1$H) = 6.8 Hz, 10 H, C$_6$H$_5$), 7.14 (s, 10 H, C$_6$H$_5$), 6.81 (d, $J$ ($^1$H$^1$H) = 8 Hz, 10 H, C$_6$H$_5$), 2.34 (q, $J$ ($^1$H$^1$H) = 7.6 Hz, 16 H, CH$_2$), 2.00 (s, 12 H, Ar-CH$_3$), 1.00 (t, $J$ ($^1$H$^1$H) = 7.6 Hz, 24 H, CH$_3$), 0.83 (s, 12 H, Ar-CH$_3$). $^{31}$P NMR (161.884 MHz, C$_6$D$_6$): δ = 71.19 (s). IR (CaF$_2$ plates, toluene solvent) $\nu$(N≡C) 1865.79 (s).

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

$Ar = \underset{\text{}}{\bigcirc} -CH_2CH_3$
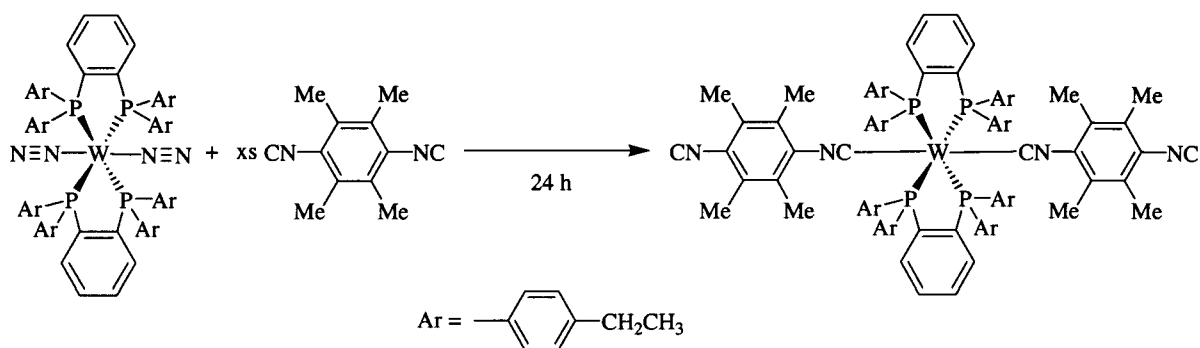
To a 500 mL 3-neck flask equipped with a stir bar, nitrogen adapter and stopper, are added 0.351 g (1.90 mmol) of 2,3,5,6-tetramethyl-1,4-diisocyanobenzene and 0.515 g (0.380 mmol) of bis(dinitrogen)bis[1,2-bis(di(p-ethylphenyl)phosphino)benzene] tungsten(0). The flask is evacuated and toluene (300 mL) is added. The reaction mixture is stirred for a total of 168 h. The solvent is evaporated down to 20 mL and hexane (60 mL) is added. The flask is then placed in the freezer (-19 °C) and the product is allowed to crystallize over the course of five days. The resulting product is shown by $^1$H NMR spectroscopy to be unreacted starting materials. The solvent is reduced to dryness *in vacuo*, toluene (150 mL) is added and the solution is heated to reflux for 18 h. The solution is then allowed to cool to room temperature and the solvent is reduced *in vacuo* to 20 mL. Hexane (100 mL) is added and the solution is again placed in the freezer to crystallize over the course of five days. The brown-to-black crystals are collected on a filter frit giving 0.25 g (0.150 mmol, 39.5%) of the bis(diisonitrile) complex.

**Spectroscopic Data**

$^1$H NMR (399.905 MHz, $C_6D_6$): δ = 7.88 (s, 16 H, $C_6\underline{H}_5$), 7.21 (d, *J* ($^1H^1H$) = 6.8 Hz, 4 H, $C_6\underline{H}_5$), 7.14 (s, 16 H, $C_6\underline{H}_5$), 6.81 (d, *J* ($^1H^1H$) = 8 Hz, 4 H, $C_6\underline{H}_5$), 2.34 (q, *J* ($^1H^1H$) =

7.6 Hz, 16 H, C$\underline{H}_2$), 2.00 (s, 12 H, Ar-C$\underline{H}_3$), 1.00 (t, $J$ ($^1$H$^1$H) = 7.6 Hz, 24 H, C$\underline{H}_3$), 0.83

(s, 12 H, Ar-C$\underline{H}_3$). $^{31}$P NMR (161.884 MHz, $C_6D_6$): $\delta$ = 71.19 (d, $J$ = 42.1 Hz). IR (CaF$_2$

plates, toluene solvent) $\nu$(N≡C) 1858.08 (s).

## 17. Attempted synthesis of bis[1, 2-bis (di{*p*-ethylphenyl})phosphinobenzene] dinitrogencarbonylmolybdenum(0)
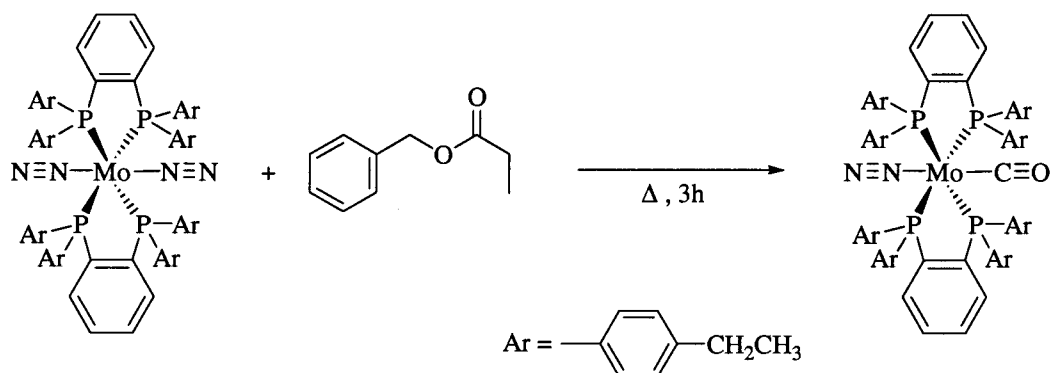


To a 250 mL 3-neck flask fitted with a nitrogen adaptor, stopper, reflux condenser, and stir bar is added 0.205 g (0.169 mmol) of bis(dinitrogen)bis[1,2-bis{di(*p*-ethylphenyl)}phosphinobenzene]molybdenum(0). The flask is evacuated and 10 mL of toluene and 0.30 mL (0.169 mmol) of benzyl propionate are added. The solution is heated to reflux for 3 h. The solution is allowed to cool to room temperature and 65 mL of hexane is added. The flask is placed in the refrigerator at 4 °C to crystallize. After two days, another 60 mL hexane is added in an attempt to crystallize the product. The mixture is placed in the freezer (-19 °C) to crystallize. No product was isolated.

## 18. Attempted synthesis of bis(diphenylphosphinoethane)carbonyl(DMF)tungsten(0)

$$\begin{array}{ccc}
\text{Ph}\diagup\diagdown\text{Ph} & & \text{Ph}\diagup\diagdown\text{Ph} \\
\text{Ph}-\text{P}\quad\text{P}-\text{Ph} & & \text{Ph}-\text{P}\quad\text{P}-\text{Ph} \\
\text{N}\equiv\text{N}-\text{W}-\text{N}\equiv\text{N} \quad + \quad \text{DMF} \xrightarrow{\text{Benzene, }\Delta} & & \text{DMF}-\text{W}-\text{C}\equiv\text{O} \\
\text{Ph}-\text{P}\quad\text{P}-\text{Ph} & & \text{Ph}-\text{P}\quad\text{P}-\text{Ph} \\
\text{Ph}\diagup\diagdown\text{Ph} & & \text{Ph}\diagup\diagdown\text{Ph}
\end{array}$$
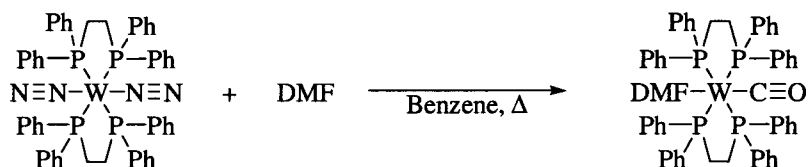
To a 150 mL 3-neck flask fitted with a stir bar, reflux condenser, nitrogen adaptor and stopper are added 0.314 g (0.29 mmol) of bis(1,2-bis(diphenylphosphino)ethane)bis(dinitrogen)tungsten(0). The flask is evacuated and 0.2 mL (0.87 mmol) of DMF, along with 60 mL of benzene are added. The mixture is heated to reflux for 16 h. The solution is allowed to cool to room temperature and 100 mL hexane is added. The mixture is then filtered through a Schlenk filter to remove the impurities and the filtrate was placed in the freezer (-19 °C) to crystallize. A mixture of small red and white crystals is visible after a day in the freezer. The solution is then removed *via* syringe and the crystals are dried under a stream of nitrogen for 2 h. These crystals were found to be starting material by $^1$H NMR.

## 19. μ-C,C'-[bis[bis{di(*p*-ethylphenyl)phosphino}benzene]bis(*p*-diisocyanotetramethylbenzene)molybdenum(0)]bis(pentacarbonylchromium(0))

Ar = —⟨benzene⟩—CH₂CH₃
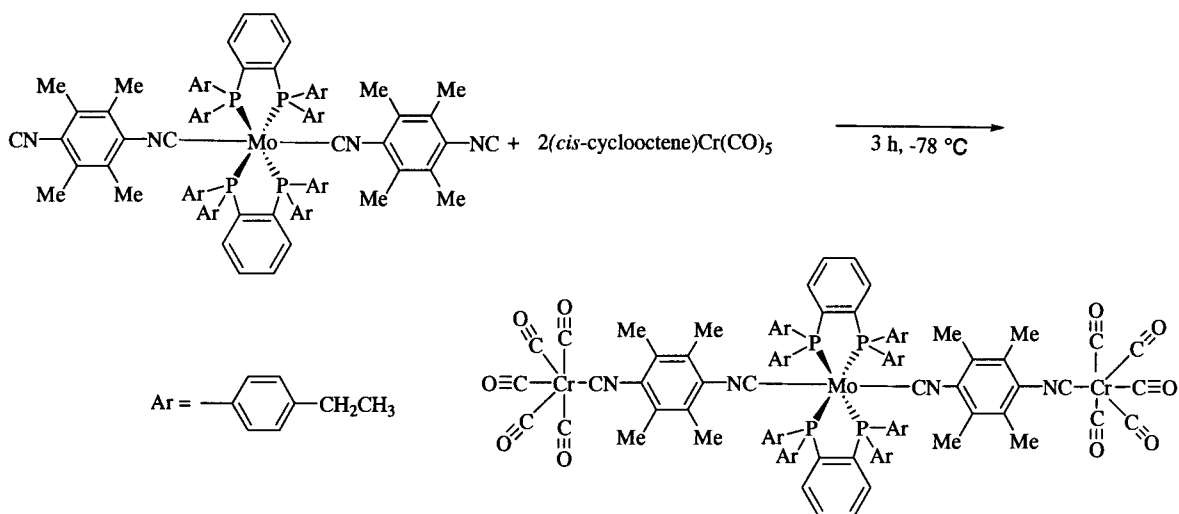
To a 100 mL Schlenck flask are added 0.301 g (0.190 mmol) of bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis{di(*p*-ethylphenyl)}phosphinobenzene]molybdenum(0) and 0.131 g (0.433 mmol) of *cis*-cyclooctenechromiumpentacarbonyl (synthesized by Matthias Zeller). The flask is evacuated and 20 mL of toluene is added. The stirred reaction mixture is cooled with an ethanol/dry ice bath to -30 °C for 3 h. The ethanol/dry ice bath is removed and the mixture is allowed to warm to room temperature over the course of 1 h. Hexane (60 mL) is added and the mixture is placed in the freezer (-19 °C) for three days to crystallize. The mother liquor is then removed *via* canula and the crystals washed with cold hexane (2 × 20 mL) and collected on filter paper to give 0.16 g (0.0814 mmol, 42.8%) of the desired product.

**Spectroscopic Data**

$^1$H NMR (399.905 MHz, C$_6$D$_6$): δ = 7.22 (d, $J$ ($^1$H$^1$H) = 7.6 Hz. 4 H, C$_6$$\underline{H}$$_5$), 6.84 (d, $J$

($^1$H$^1$H) = 8 Hz, 4 H, C$_6$$\underline{H}$$_5$), 2.36 (q, $J$ ($^1$H$^1$H) = 6.4 Hz, 16 H, C$\underline{H}$$_2$), 1.86 (s, 12 H, Ar-

C$\underline{H}$$_3$), 0.99 (t, $J$ ($^1$H$^1$H) = 7.6 Hz, 24 H, C$\underline{H}$$_3$), 0.86 (s, 12 H, Ar-C$\underline{H}$$_3$). IR (CaF$_2$ plates,

toluene solvent) $\nu$(C≡O) 2053.82 (w), $\nu$( C≡O) 1954.50 (s), $\nu$(N≡C)1859.04 (s).

Anal. Calcd Cr, 5.06; C, 64.33; H, 5.10; N, 2.73. Found: Cr, 5.18; C, 63.73; H,

5.38; N, 2.82.

**20. μ-C,C′-[bis[bis{di($p$-ethylphenyl)phosphino}benzene]bis($p$-diisocyanotetramethylbenzene)tungsten(0)]bis(pentacarbonylchromium(0))**
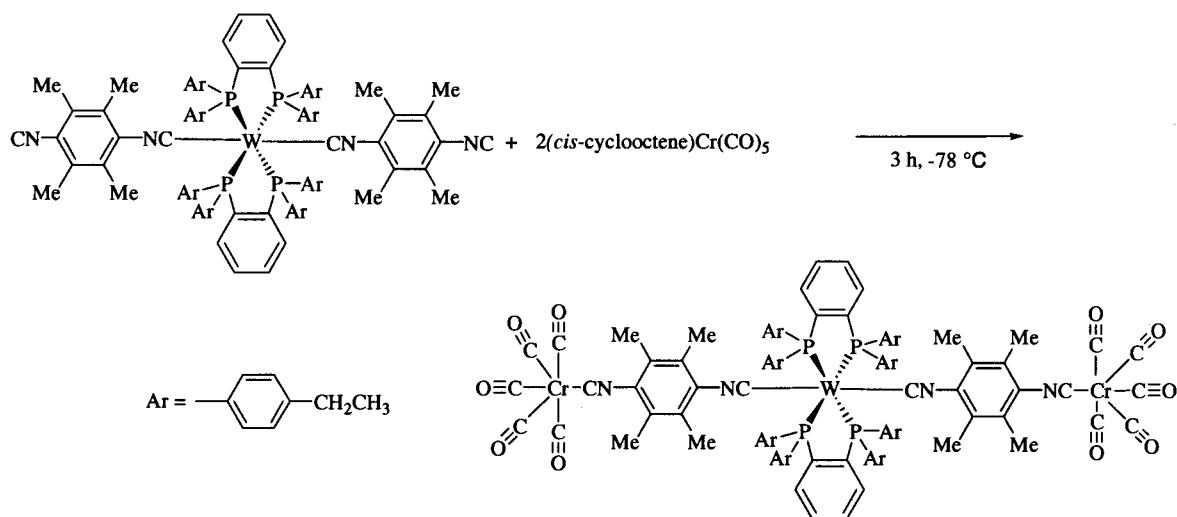


To a 100 mL Schlenck flask are added 0.100 g (0.058 mmol) of bis(2,3,5,6-

tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis{di($p$-

ethylphenyl)}phosphinobenzene]tunsten(0) and 0.039 g (0.128 mmol) of *cis*-cyclooctenechromiumpentacarbonyl. The flask is evacuated and 25 mL of toluene is added. The stirred reaction mixture is cooled with an ethanol/dry ice bath (-78 °C) for 5 h. The ethanol/dry ice bath is removed and the mixture is allowed to warm to room temperature over the course of 1/2 h. The solvent is reduced in volume *in vacuo* to 15 mL, hexane (40 mL) is added, and the mixture is placed in the freezer (-19 °C) for three days to crystallize. The mother liquor is then removed *via* a canula and the crystals washed with cold hexane (2 × 20 mL) and collected on filter paper to give 0.06 g (0.0292 mmol, 48.8%) of the desired product.

**Spectroscopic Data**

$^1$H NMR (399.905 MHz, $C_6D_6$): $\delta$ = 6.84 (d, $J$ ($^1H^1H$) = 8 Hz, 4 H, $C_6\underline{H}_5$), 2.36 (q, $J$ ($^1H^1H$) = 6.4 and 7.6 Hz, 16 H, $C\underline{H}_2$), 1.86 (s, 12 H, Ar-$C\underline{H}_3$), 0.99 (t, $J$ ($^1H^1H$) = 7.6 Hz, 24 H, $C\underline{H}_3$), 0.84 (s, 12 H, Ar-$C\underline{H}_3$). IR (CaF$_2$ plates, toluene solvent) $\nu$( C≡O) 2054.78 (w), $\nu$( C≡O) 1953.54 (s), $\nu$(N≡C) 1851.33 (s).

**21. Attempted synthesis of $\mu$-C,C'-[bis[bis{di($p$-ethylphenyl)phosphino} benzene]bis($p$-diisocyanotetramethylbenzene)molybdenum(0)] bis($\eta^5$-cyclopentadienyl dicarbonylmanganese(0))**

Me Me  Ar P P Ar  Me Me

CN NC Mo CN NC + 2 cis-cycloocteneMnCp(CO)$_2$  →  3 h, -30 °C

Me Me  Ar P P Ar  Me Me

Ar = —◯—CH$_2$CH$_3$

Mn—CN NC Mo CN NC-Mn
O≡C C  Me Me  Ar P P Ar  Me Me  C C≡O
O  O

To a 250 mL Schlenck flask are added 0.202 g (0.131 mmol) of bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis{di(p-ethylphenyl)}phosphinobenzene]molybdenum(0) and 0.078 g (0.270 mmol) of cis-cyclooctene-$\eta^5$-cyclopentadienyldicarbonylmangenese(0) synthesized by Matthias Zeller). The flask is evacuated and 120 mL of toluene is added. The reaction mixture is stirred for 120 h. The solvent is reduced *in vacuo* to 20 mL and hexane (100 mL) is added and the mixture is placed in the freezer (-19 °C) to crystallize. After one week, the reaction vessel was placed in the −80 °C freezer. No product was isolated.

**22. Attempted synthesis of μ-C,C'-[bis[bis{di(p-ethylphenyl)phosphino} benzene] bis(p-diisocyanotetramethylbenzene)molybdenum(0)]bis([bis(di(p-ethylbenzene)phosphino)ethane]carbonylmolybdenum(0))**

Ar = ⟨benzene ring⟩—CH$_2$CH$_3$
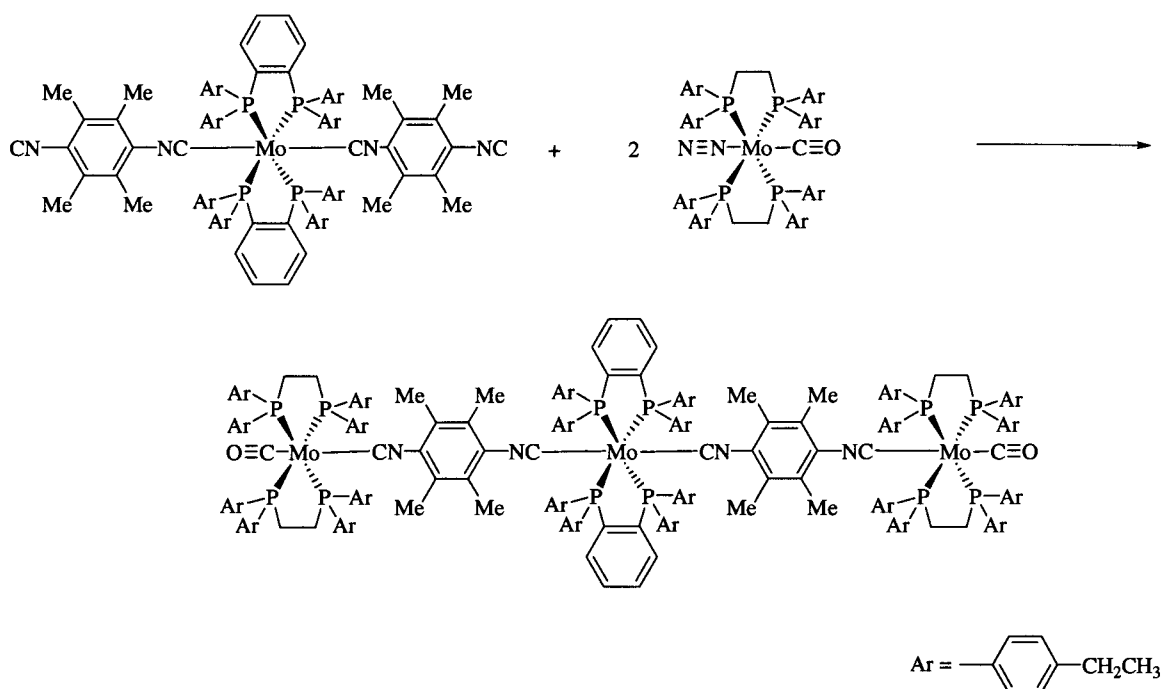
To a 250 mL Schlenck flask that had been cooled in a dry ice/ethanol bath (-78 °C) are added 0.101 g (0.0.64 mmol) of bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis{di($p$-ethylphenyl)}phosphinobenzene]molybdenum(0) and 0.150 g (0.128 mmol) of bis(di($p$-ethylphenyl)dinitrogencarbonylmolybdenum(0). The flask is evacuated and 120 mL of toluene is added. The reaction mixture is allowed to warm to room temperature over the course of 1 h and then stirred for and additional 5 h. The solution is filtered using a canula and filter paper and the solvent is reduced in volume to 20 mL. Hexane (100 mL) is added and the solution is placed in the freezer (-19 °C) to crystallize. After one week, a small amount of small black crystals can be seen in the flask. In an attempt to further crystallize the product, the reaction mixture is placed in the –80 °C freezer. No product was isolated.

# References

1. W. L. F. Armarego, D. D. Perrin. *Puification of Laboratory Chemicals*, 4th ed.; BH: Boston, 1996.

2. E. P. Kyba, S-T. Jui, R. L. Harris. *Organometallics* **1983**, *2*, 1877-1879

3. Adapted from L. Dahenburg, A. Kaunert. *Eur. J. Inorg. Chem.* **1998**, 885-887

4. E. P. Kyba, M. C. Kerby, S. P. Rines. *Organometallics* **1986**, *5*, 1189-1194

5. G. J. Kubas, C. J. Burns, J. Eckert, S. W. Johnson, A. C. Larson, P. J. Vergamini, C. J. Unkefer, G. R. K. Khalsa, S. A. Jackson, O. Eisenstein, *J. Am. Chem. Soc.* **1993**, *115*, 569-581

6. T. A. George, M. E. Noble, *Inorg. Chem.* **1978**, *17*, 1678-1679

# Chapter III –Results and Discussion

## 1. Phosphines

The derivatives of 1, 2-bis(phosphino)benzene were synthesized according to the previously published method by Kyba[1] shown below:



**Equation 3.1.1** Kyba's synthesis of 1,2-bis(phosphino)benzene
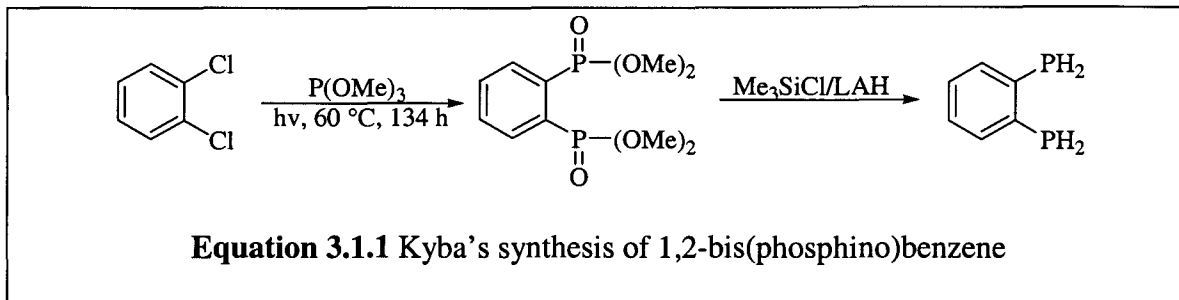
In the first step of this reaction, the two C-Cl bonds in 1,2-dichlorobenzene are photolytically cleaved in the presence of trimethylphosphite, resulting in the formation of 1,2-bis(dimethylphosphoryl)benzene. In the second step of **Equation 3.1.1**, 1,2-bis (dimethylphosphoryl)benzene is reduced to 1,2-bis(phosphino)benzene by a suspension of lithium aluminum hydride, LAH, and trimethylchlorosilane in diethyl ether.

The workup of 1,2-bis(phosphino)benzene uses both water (100 mL) and potassium hydroxide (1N, 250 mL). This must be done with extreme caution, as LAH reacts violently with water. After hydrolysis is complete, extraction can then be done with diethyl ether (approx. 1 L). This extraction is often mechanically difficult due to the amount of solid hydrolysis by-products. In order to deal with this, a piece of filter paper is folded into a cone and inserted into the 3-necked flask. The diethyl ether is then removed *via* syringe through the filter paper.

The first step of **Equation 3.1.1** produces about 20-50 g of the phosphoryl compound in a 14-38% yield after crystallization from acetone. The colorless crystals obtained are air stable. The $^{31}$P NMR spectrum exhibits one peak at -4.63 ppm. The $^{1}$H NMR spectrum shows multiplets with an AA'BB' coupling pattern at 7.90 and 7.41 ppm. A pseudo-doublet at 3.58 ppm is found due to the coupling of the methyl hydrogens with the phosphorus atoms.

In the second step of **Equation 3.1.1**, 1,2-bis(phosphino)benzene is produced in a 28-64% yield after distillation. The colorless to slightly yellow liquid has a boiling point (in oil pump vacuum) of 60 °C and is phyrophoric and extremely air sensitive. The $^{31}$P NMR spectrum exhibits one peak at -147.69 ppm. The $^{1}$H spectrum shows two AA'BB' multiplets at 7.25 and 6.90 ppm. Again, this can be attributed to the aromatic hydrogen atoms. A pseudo-doublet of doublets ($J(^{1}$H$^{31}$P$) = 25.2$ Hz) at 3.90 ppm is likely due to coupling between each of the phosphorous atoms and each hydrogen directly bonded to it.

The isolated yield for 1,2-bis(phosphino)benzene varied drastically from reaction to reaction and was low compared to the yield reported by Kyba (83%). The difference can be attributed to both the extraction process and the extreme sensitivity of the compound. In contast to the findings here, Kyba reports using only 400 mL (2 × 200 mL) of diethyl ether. The phosphine is extremely air sensitive (as a neat compound, it is self-igniting in the presence of oxygen), thus great care must be taken to avoid oxygen during the synthesis. Failure to do so will result in loss of product due to oxidation. With the tedious and lengthy work-up procedure in mind, the diethyl ether must then be separated

from the solid by-products. This is done *via* syringe and may also contribute to the low isolated yield of this compound.

The chlorination reaction of 1,2-bis(phosphino)benzene is adapted from a method published by Dahlenburg *et al.*[2] as illustrated below:
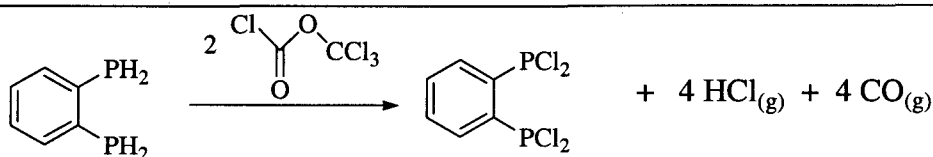


**Equation 3.1.2** Synthesis of 1,2-bis(dichlorophosphino)benzene

Trichloromethyl chloroformate (diphosgene) is used as the chlorination agent and both carbon monoxide and hydrochloric acid gases are produced as by-products. The reaction proceeds smoothly over three hours. The chlorinated species is produced in a 36.8% yield and has a boiling point (in oil pump vacuum) of 85-90 °C. It is interesting to note that independent of the scale of the reaction, the yield is consistently about 37% each time. The side products are higher boiling than 1,2-bis(dichlorophosphino)benzene. Thus it can be surmised that condensation products (dimers, trimer) are formed by the reaction of the P-Cl groups with the unreacted P-H moieties.

1,2-Bis(dichlorophosphino)benzene is the starting compound in the synthesis of a wide range of aryl phosphines. The excellent leaving ability of the chloride ion allows for a wide range of reactions to be performed: Grignard addition and nucleophilic attack are the most common. As mentioned in the introduction, aryl phosphines are preferred over alkyl phosphines because of the $\pi$-back-bonding contributions. Electron withdrawing substituents, such as fluorinated groups, will increase the degree of back-bonding present within the aryl phosphines.

The attempted synthesis of 1,2-bis(di(pentafluorobenzene)phosphino)benzene is shown below:



**Equation 3.1.3** Attempted synthesis of 1,2-bis(di(pentafluorobenzene)phosphino)
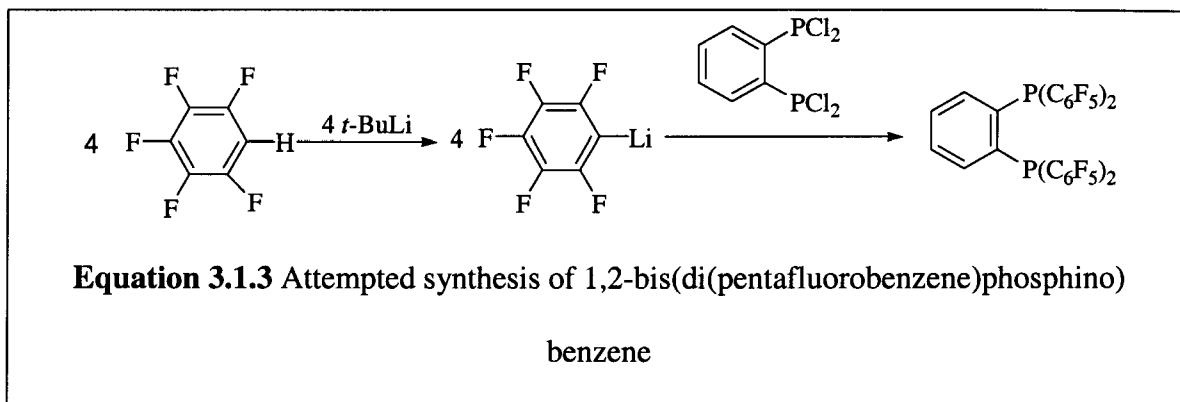
benzene

Pentafluorobenzene is deprotonated in THF using $t$-butyl lithium.[3] The resulting nucleophile was then reacted with 1,2-bis(dichlorophosphino)benzene at -78 °C in an attempt to displace the chlorine atoms in a nuclophilic substitution reaction. After work-up, no product has yet been isolated from the reaction solution. A possible explanation for this is that since the fluorine atoms themselves are highly electronegative, thus they will evenly distribute the negative charge of the carbon atom where deprotonation occurred within the ring. This, in turn, will weaken the strength of the nuclophile to the point where it can no longer displace all of the chlorine atoms, resulting in a mixture of half reacted products or even no product at all.

In a second attempt to synthesis a fluorinated aromatic phosphine, 1,2-bis({3,5-bis(trifluoromethyl)benzene}phosphino)benzene was synthesized by the route shown below:

**Equation 3.1.4** Synthesis of 1,2-bis({3,5bis(trifluoromethyl)benzene}phosphino)benzene
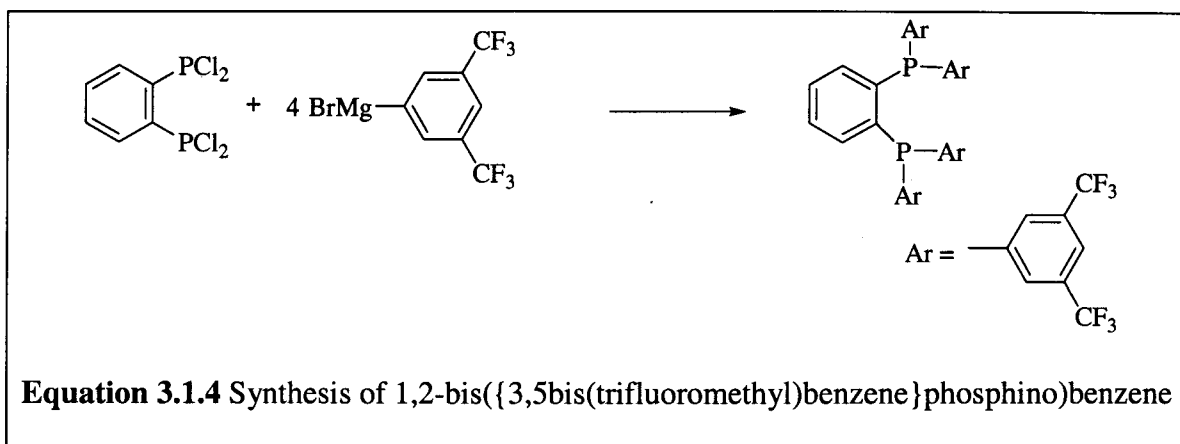
In the first step in this reaction, the Grignard reagent is synthesized. This is done by combining 3,5-bis(trifluoromethyl)bromobenzene and very clean magnesium turnings (99.9+% pure) in THF. It is important to use clean magnesium turnings as conventional magnesium will give poor yields for this step, which will then decrease the overall yield. The next step is a simple Grignard addition/substitution reaction. The resulting solution is hydrolyzed with a 10% solution of $NH_4Cl$ to remove the excess Grignard reagent, and the phosphine is isolated by crystallization from a concentrated toluene solution.

The crystals of the target phosphine are clear and quartz-like in appearance. They are air stable and produced in an 18.5% yield. One molecule of toluene is present in the crystal lattice as shown in **Figure 3.1.1**. The $^1H$ NMR spectrum shows one singlet at 7.88 ppm. This is due to the *para*-hydrogen atoms between the –$CF_3$ groups as they will be the furthest downfield due to the electron withdrawing effect of the two –$CF_3$ groups. There is also a multiplet at 7.57 ppm. This is from the *ortho*-hydrogen atoms next to each one of the –$CF_3$ groups as they would be the next furthest downfield. The final multiplet at 7.11 ppm has to be due to the two AA'BB' type signals of the aromatic hydrogen atoms on the benzene backbone.

X-Ray structure analysis has determined that this phosphine crystallizes in the monoclinic space group P2$_1$/n. The unit cell dimensions are $a$ = 11.367(6) Å, $b$ = 16.374(8) Å, $c$ = 22.225(11) Å, $\alpha$ and $\gamma$ = 90°, and $\beta$ = 94.756(10)°. Some of the trifluoromethyl groups exhibit a pronounced rotational disorder, resulting in the residual electron density being modeled as if these CF$_3$ groups were actually CF$_6$ groups. A final R$_1$ value for all data of 0.0871 and a wR$_2$ for all data of 0.1818 was obtained. Due to the amount of disorder present and the amount of parameters that were used, the overall quality of the structure solution was poor, resulting in such high R values. The ORTEP plot is shown in **Figure 3.1.1**. The table of geometric parameters as well as refinement statistics can be found in Apendix I.
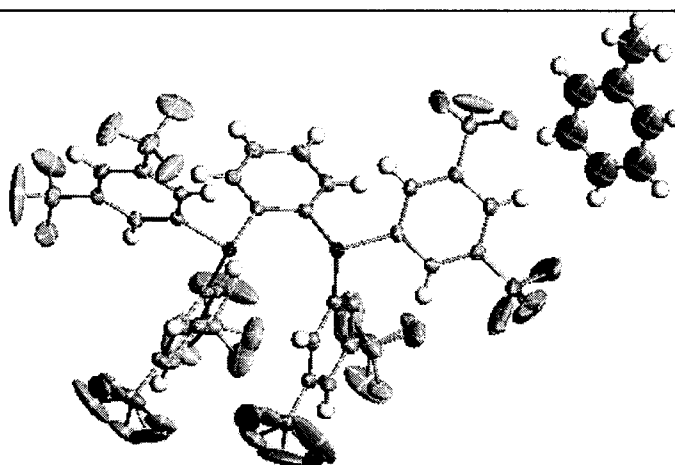


**Figure 3.1.1** ORTEP representation of 1,2-bis(bis{3,5-bis(trifluoromethyl)benzene} phosphino)benzene. The thermal displacement ellipsoids are drawn at the 30% probability level and the disorder of the CF$_3$ groups as well as the one solvate of toluene are shown.

1,2-Bis(di(*p*-anisole)phosphino)benzene was synthesized by the method shown below:



**Equation 3.1.5** Synthesis of 1,2-bis(di(*p*-anisole)phosphino)benzene
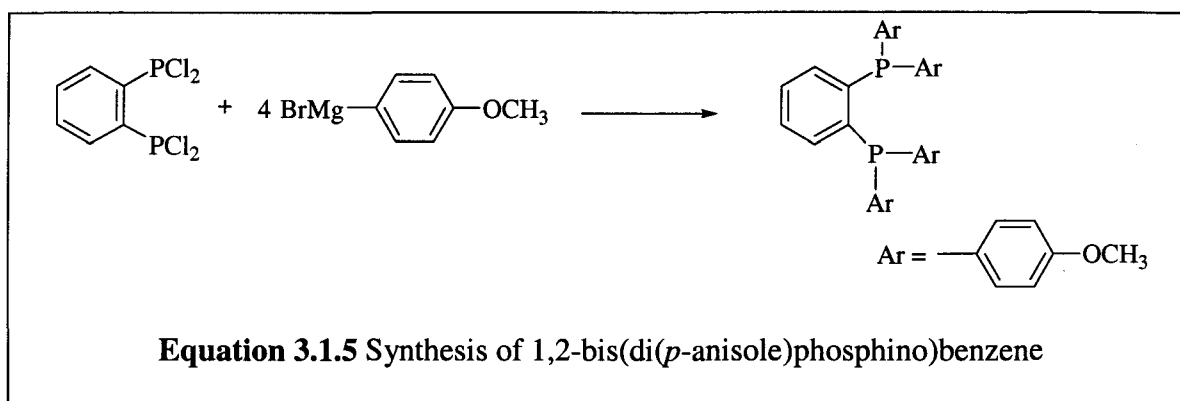
This phosphine is synthesized by a route similar to the one used in **Equation 3.1.4**. The white, air stable phosphine was isolated in a yield of 11.7%. The $^1$H NMR spectrum exhibits two multiplets at 7.26 and 7.09 ppm. These are likely due to the AA'BB' interactions occurring between the hydrogen atoms of the benzene backbone. A doublet is found at 6.74 ppm ($J$ ($^1$H$^1$H) = 8 Hz), due to the hydrogen atoms of the anisole rings. The singlet at 3.78 can be assigned to the methoxy hydrogen atoms.

Overall, the yields of the 1,2-bis(phosphino)benzene derivatives (i.e. those created *via* Grignard reagents) needs to be improved. A useful amount of phosphine would be approximately 20 g. At present, that would need twenty of these syntheses. Scaling these two reactions up may give higher yields. A method for synthesizing the pentafluorinated phosphine also has to be investigated.

## 2. Dinitrogen Complexes

The molybdenum and tungsten dinitrogen complexes are synthesized by a route similar to that published by Hussain *et. al*[4] in which the appropriate metal halide is reduced in the presence of $N_2$ and the desired phosphine by magnesium metal. In a similar method reported by George and Nobel[5] sodium-mercury amalgam was used as the reducing agent. The magnesium route was chosen because of its one distinct advantage over the sodium-mercury amalgam route: mercury has a rather high toxicity level, while magnesium does not. The two routes show usually comparable yields, with the yield from the sodium-mercury amalgam method being slightly (~5%) higher. The magnesium method does, however, require the magnesium turnings to be absolutely clean (99.999+% pure) if one hopes to get reasonable yields. This is because the reduction reaction occurs on the surface of the magnesium metal; the cleaner the surface, the more efficient the reduction reaction will be.

George and Nobel also documented a competing reaction that is present in the method reported by Hussain *et. al*, namely, the formation of the tetrahydride complex (i.e. the two $N_2$ groups are replaced by four hydrogen atoms, $M(R_2PC_xH_xPR_2)_2H_4$). This is a competing reaction in which the source of hydrogen is thought[5] to be from solvent decomposition and traces of humidity on the glass walls.

**Equation 3.2.1** Synthesis of bis(dinitrogen)bis[1,2-bis(di(*p*-ethylphenyl) phosphino) benzene]molybdenum(0) and the tetrahydride by-product.
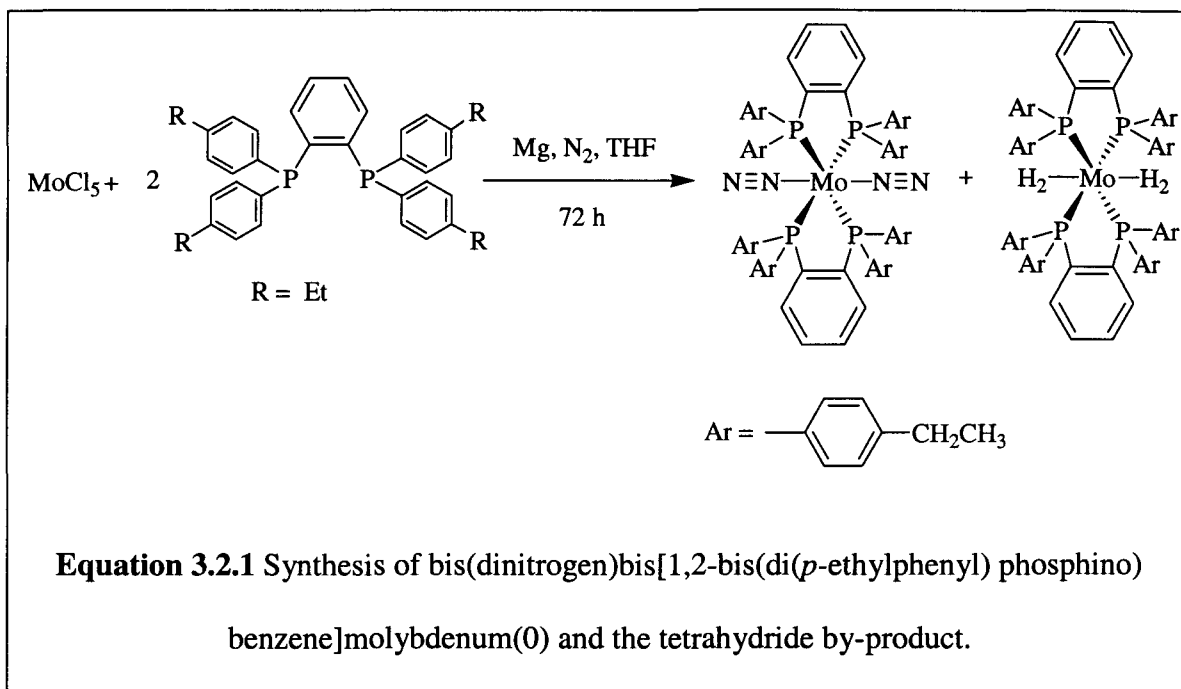
The formation of the tetrahydride complex was not witnessed in the synthesis of the three dinitrogen complexes described in this thesis. Slight modifications in procedure, such as removal of the solvent under high vacuum instead of *via* rotary evaporation and precipitation of the complex at 0 °C instead of at room temperature, may have helped to avoid the formation of the tetrahydride complex.

The first dinitrogen complex synthesized was bis(dinitrogen)bis((1,2-bisdiphenylphosphino)ethane)tungsten (0) by the route shown below:



**Equation 3.2.2** Synthesis of bis(dinitrogen)bis[1,2-bis(diphenylphosphino)ethane] tungsten(0)
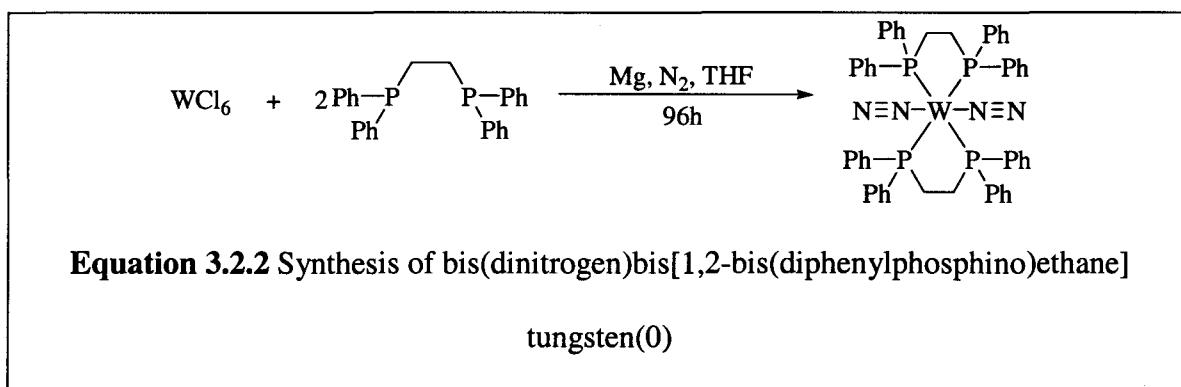
The reaction proceeds as mentioned above. The workup is carried out by first filtering the reaction mixture to remove excess magnesium turnings then reducing the solvent *in vacuo* to half of its original volume, and, finally, precipitating the dinitrogen complex with methanol.

The orange dinitrogen complex is isolated in a 41.8% yield and is air stable as a solid for months, but is air sensitive in solution. The $^{31}$P NMR spectrum shows a single peak at 45.71 ppm, indicating that all four phosphorus atoms are equivalent, thus the complex is the *trans* isomer. The $^1$H NMR spectrum shows three singlets at 7.19, 7.02, and 7.01 ppm which integrate to a 1:2:3 ratio and can be attributed to the three types of aromatic hydrogen atoms present. The pseudo-triplet at 2.26 ppm ($J(^1H^{31}P) = 8$ Hz) are due to the methylene hydrogens forming the bridge between the phosphorus atoms. The two characteristic IR $N{\equiv}N$ stretching frequencies are at 1949 (strong) and 2009 (weak) cm$^{-1}$. In the *trans* isomer, the asymmetric stretching mode is expected to be the more intense of the two, as it has the greatest effect on the dipole moment.

The second dintrogen complex synthesized, bis(dinitrogen)bis[1,2-bis(di(*p*-ethylphenyl)phosphino)benzene]molybdenum(0), was synthesized according to the route shown:

**Equation 3.2.3** Synthesis of bis(dinitrogen)bis[1,2-bis(di($p$-ethylphenyl) phosphino)

benzene]molybdenum(0)
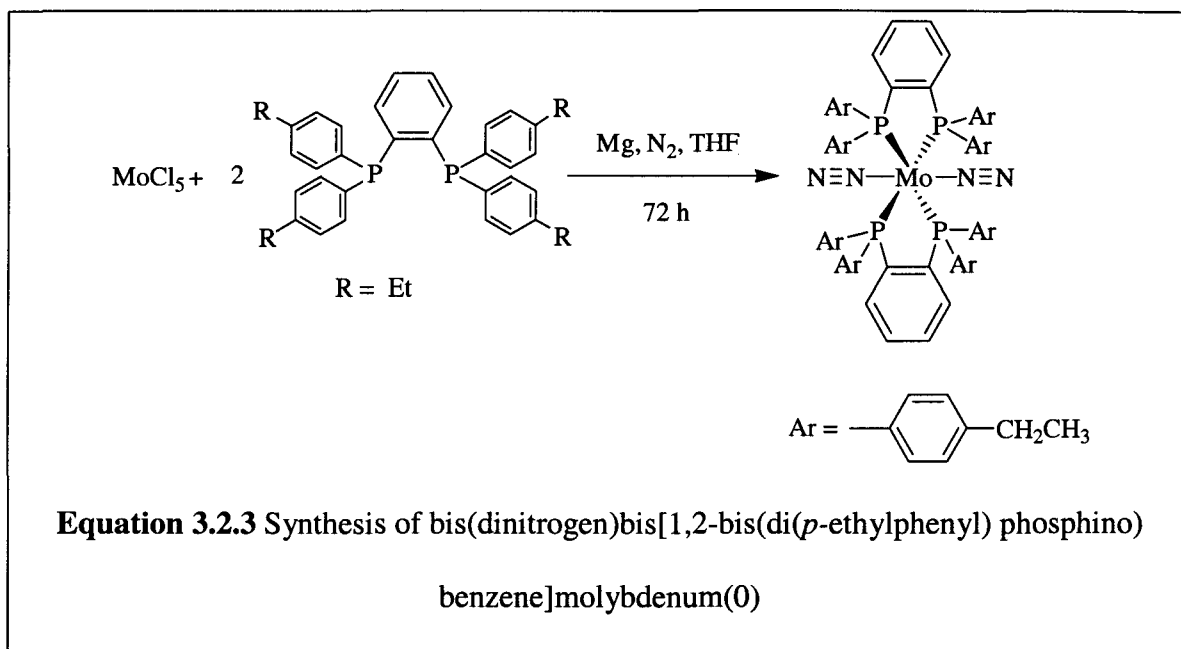
The reaction and work-up is done in the same manner as the procedure outlined

for bis(dinitrogen)bis(1,2-bis(diphenylphosphino)ethane)tungsten(0). The orange to red

dinitrogen complex is isolated in a 66.8% yield. The $^{31}$P NMR spectrum has a singlet at

70.1 ppm, indicating the presence of the *trans* isomer. The $^{1}$H NMR spectrum shows two

pseudo-doublets, which have integration ratios of 1:2, at 7.21 ppm ($J(^{1}H^{1}H) = 7.8$ Hz )

and 6.94 ppm ($J(^{1}H^{1}H) = 7.8$ Hz) representing the aromatic hydrogen atoms of the

benzene backbone and the $p$-ethylphenyl respectively. Two other aromatic proton signals

are not observed, likely due to overlap with one of the above signals or overlap with the

solvent signal. The quartet at 2.43 ppm ($J(^{1}H^{1}H) = 8$ Hz) can be attributed to the

methylene protons of the ethyl groups. The triplet at 1.07 ppm ($J (^{1}H^{1}H) = 7.6$ Hz) is due

to the methyl protons of the ethyl groups. The IR spectrum shows the two characteristic

stretching frequencies of the dintrogen ligand at 1981 and 2055 cm$^{-1}$. Again, the stronger

vibrational mode at 1981 cm$^{-1}$ can be attributed to the asymmetric stretching mode.

The final dintrogen complex synthesized, bis(dinitrogen)bis[1,2-bis(di(*p*-ethylphenyl)phosphino)benzene]tungsten(0), is the tungsten derivative of the previously mentioned molybdenum complex. The reaction conditions and the work-up are the same. The synthetic route is shown below:



**Equation 3.2.4** Synthesis of bis(dinitrogen)bis[1,2-bis(di(*p*-ethylphenyl)phosphino)benzene]tungsten(0)
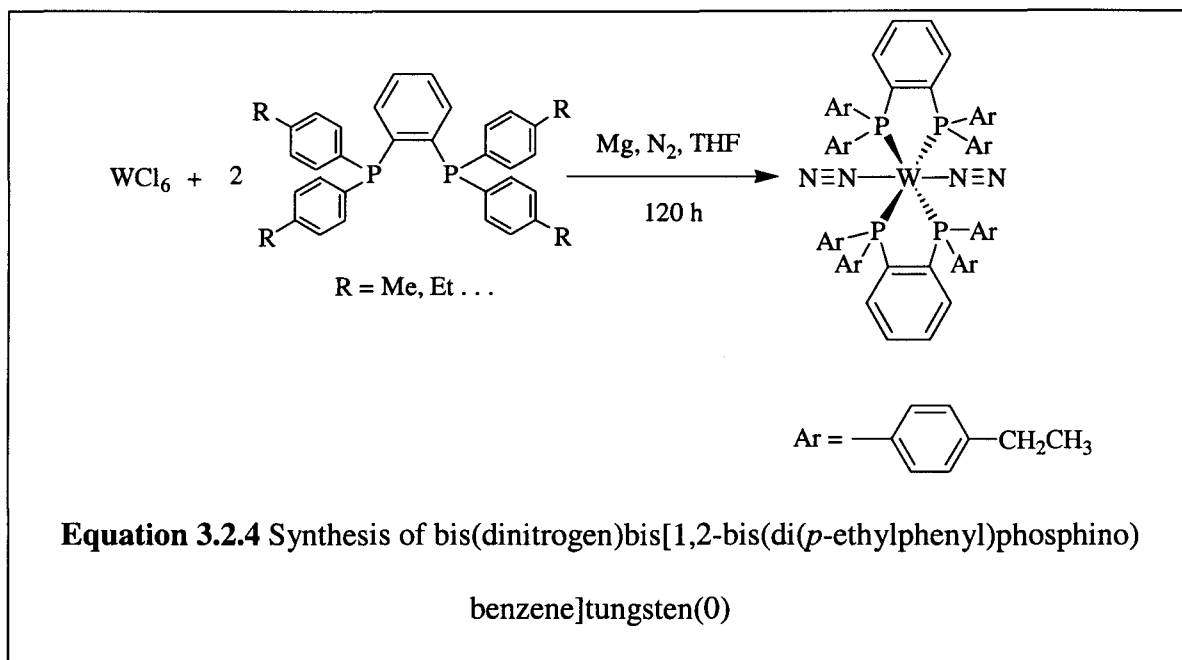
The red fiber-like product is obtained in a 54% yield. It too is air stable as a solid but air-sensitive in solution. The $^1$H NMR spectrum shows a doublet at 6.94 ppm ($J = 8$ Hz). This can be assigned to the aromatic hydrogen atoms. Three aromatic proton signals are missing. This again can be attributed to signal overlap. The quartet at 2.43 ppm ($J = 8$ Hz) is due to the methylene protons of the ethyl groups. The triplet at 1.07 ppm ($J = 7.6$ Hz) can be attributed to the methyl protons of the ethyl groups. The IR spectrum again exhibits the two characteristic dinitrogen stretching frequencies at 1953 and 2024 cm$^{-1}$. X-Ray diffraction shows that this complex is the *trans* isomer, thus the strong band at 1953 cm$^{-1}$ is the asymmetric stretching mode.

X-Ray structure analysis was used to confirm the structure of the ethylphenyldintrogen complex of tungsten. This complex crystallizes in the tetragonal space group I4₁/a. In **Figure 3.3.2,** it can be seen that there are channels present within the unit cell that contains highly disordered (i.e. pseudo liquid) hexane. The unit cell parameters are $a$ = 32.331(16) Å, $b$ = 32.331 Å, $c$ = 13.251(7) Å, $\alpha$ = 90°, $\beta$ = 90° and $\gamma$ = 90°. A final value of 0.0990 for $R_1$ and 0.2085 for $wR_2$ was obtained for all data. The unexpectedly high R values are the result of the disordered hexane present within the channels. The ORTEP plot showing the *trans* configuration of this complex is shown in **Figure 3.3.3.**



**Figure 3.2.2** ORTEP plot of bis(dinitrogen)bis[1,2-bis (di(p-ethylphenyl)phosphino)benzene]tungsten(0) showing the presences of liquid hexane channels. Ellipsoids are drawn at the 30% probability level.
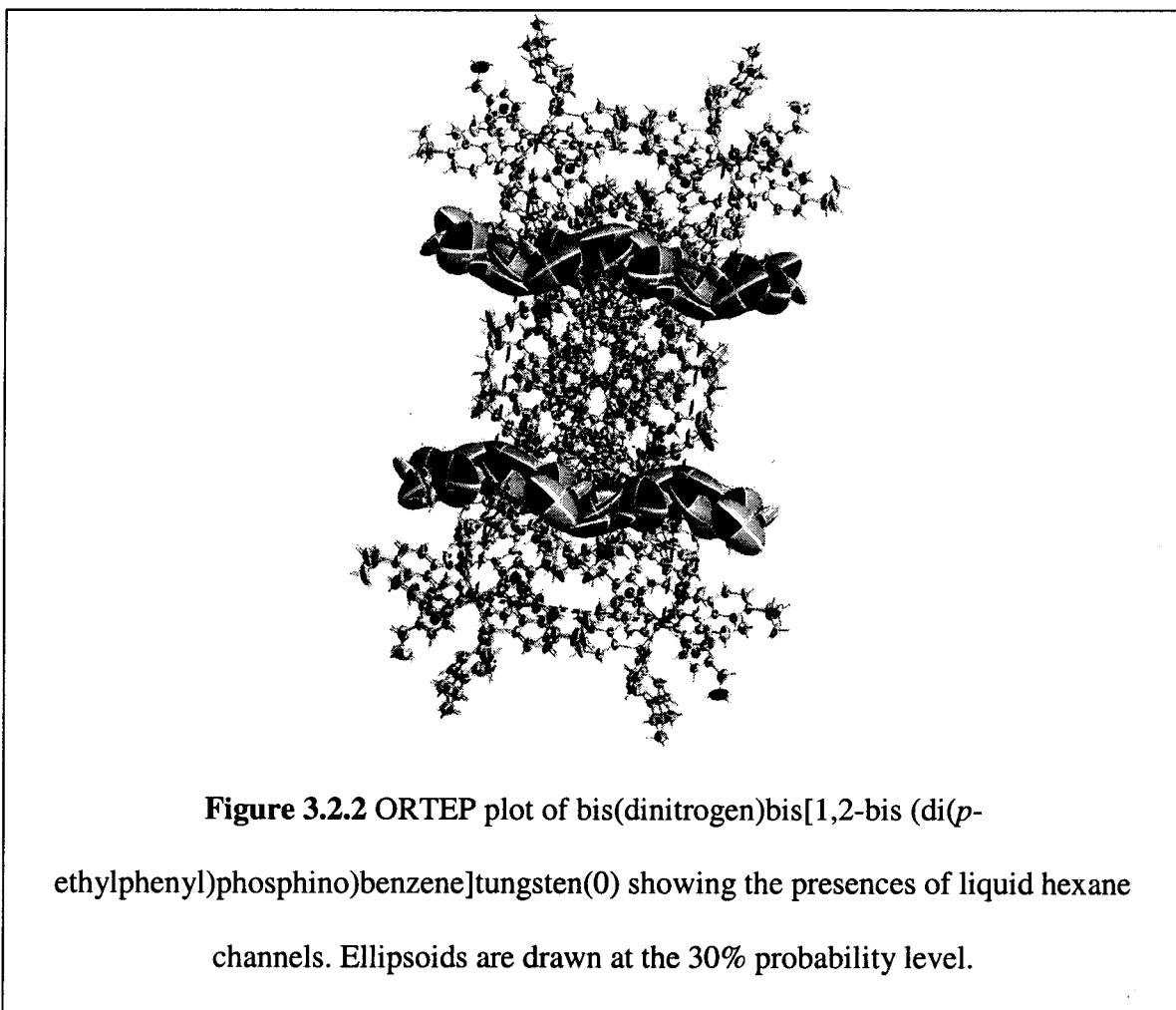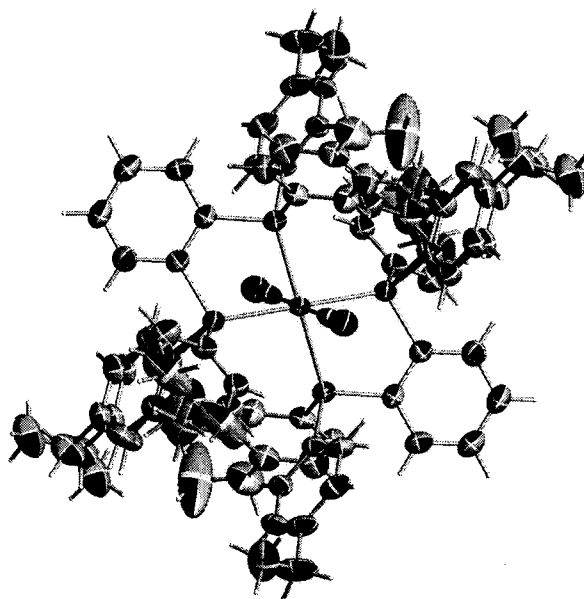
**Figure 3.2.3** ORTEP plot of bis(dinitrogen)bis[1,2-bis (di(*p*-

ethylphenyl)phosphino)benzene]tungsten(0). The hexane channels are omitted for clarity.

Ellipsoids are drawn at the 30% probability level.

Overall, the synthetic routes for the dinitrogen complexes all work according to the literature methods. The bis(dinitrogen)bis(dppe)tungsten(0) complex is only sparingly soluble in the solvents employed (THF, diethyl ether, toluene, and dichloromethane) because of the unsubstituted phenyl rings of the phosphine. This made full characterization of this complex difficult and boded poorly for the solubility of the eventual nanostar products. For this reason, the unsubstituted dppe ligand complex was abandoned as a starting material for future reactions. Bis(dinitrogen)bis[1,2-bis(di(*p*-ethylphenyl)phosphino)benzene]molybdenum(0) and its tungsten derivative did not exhibit the insolubility shown by bis(dinitrogen)bis(dppe)tungsten(0). Thus, the presence

of the alkyl substituents on the phenyl rings of the phosphine greatly enhances the solubility of these complexes. They are soluble in the solvents mentioned above and also standard NMR solvents.

A few important observations can be made concerning the nature of the dinitrogen complexes. In the $^{31}$P NMR, the chemical shift of the tungsten complexes are consistently shifted to higher field than that of the molybdenum complexes which agrees with the expected trends,[6] although the origin of this difference in shift is not fully understood. This difference may likely be due to the lanthanide contraction and, thus, the paramagnetic screening term associated with it.

The next important observation about the dinitrogen complexes is that regardless of what metal is used (Mo or W), the resulting complex has the *trans* configuration. This is important because, when assembling a nanorod, *trans* symmetry is desired so that conjugation between the metal centers will be maximized. A *cis* conformation in nanorods will likely result in reduced conjugation between the metal centers because of the nature of the two metal-isonitrile overlaps.

The final observation regarding the dinitrogen complexes is that the complexes are all orange to red. They are not very intensely colored in solution. This has to do with the type of electronic transitions that are present within the complex. The dinitrogen complexes are $d^6$ complexes with the metal in the zero oxidation state. A charge transfer transition would not occur since there is no strong acceptor molecule. Thus, the metal can act as either a donor or acceptor, the phosphine is a spectator ligand that does nothing more than shield the metal against oxidation, and the dinitrogen ligand is a rather labile ligand that has very little to no $\pi$- acceptor ability. A d-d transition is spin allowed since

promoting one of the paired electrons to the *e* orbital does not create a condition where two electrons have a parallel spin. However, this type of transition is Laporte forbidden since the dinitrogen complex has a center of inversion. Such d-d transitions tend not to be intensely colored, especially those that are not allowed. Even though this d-d transition is not allowed, molecular vibrations resulting in deviation from the perfect octahedral symmetry allows these transitions to be seen, albeit at low intensities. This accounts for the orange to red color of the dinitrogen complexes.

## 3. Bis(diisonitrile) complexes

In general, the bis(diisonitrile) complexes were synthesized using a ten-fold molar excess of isonitrile compared to the dintrogen complex.

The first bis(diisonitrile) complex synthesized was bis(1,4-diisocyanobenzene)bis(1,2-bis(diphenylphosphino)ethane)tungsten(0) by the route shown below:



**Equation 3.3.1** Synthesis of bis(1,4-diisocyanobenzene)bis(1,2-bis(diphenylphosphino)ethane) tunsten(0)
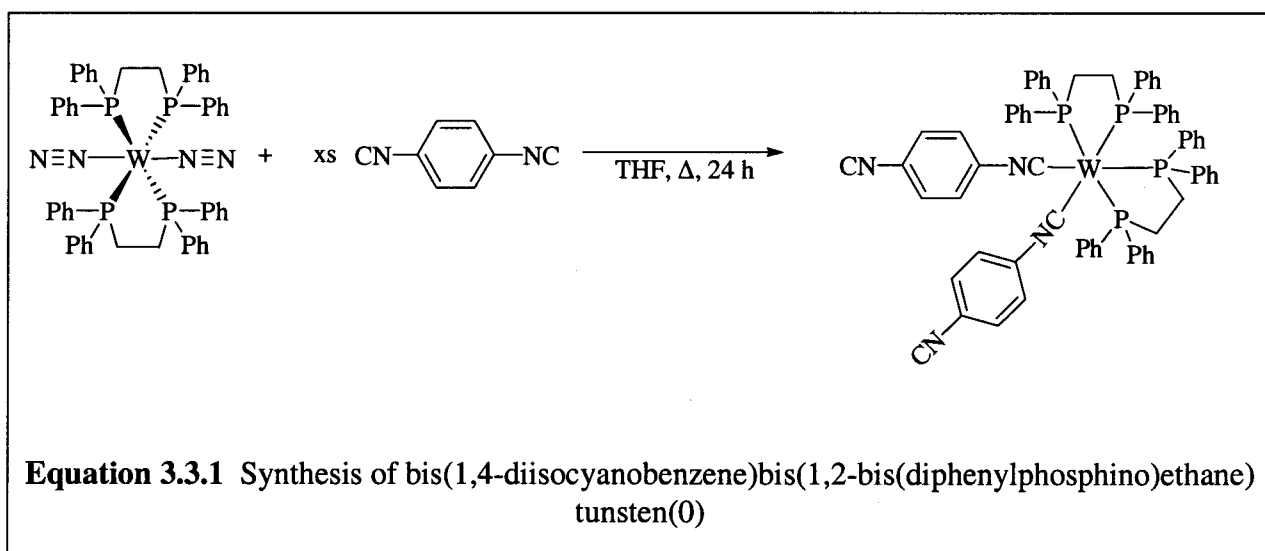
1,4-Diisocyanobenzene[7] is combined with bis(dinitrogen)bis(1,2-bis(diphenylphosphino)ethane)tungsten(0) in THF. This solution is then heated to reflux for 24 h. With molybedum, heating of the reaction mixture is usually not required. However, because of the lower reactivity of the tungsten complexes, heating is required to activate the complex. The solvent is reduced in volume and hexane is added to precipitate the bis(diisonitrile) complex as a dark red, almost black powder in a 32% yield. Due to the insolubility of this material (because of the un-substituted dppe ligand as well as the un-substituted 1,4-diisonitrile ligand), no further reactions were done with this material. Full characterization was also difficult, as this complex was not soluble in standard NMR solvents.

The next bis(isonitrile) complex synthesized was bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis(1,2-bis(diphenylphosphino)ethane)tungsten(0) according to the procedure published by Bennett et al.[8] as illustrated below:



**Equation 3.3.2** Synthesis of bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene) bis(1,2-bis(diphenylphosphino)ethane) tunsten(0)
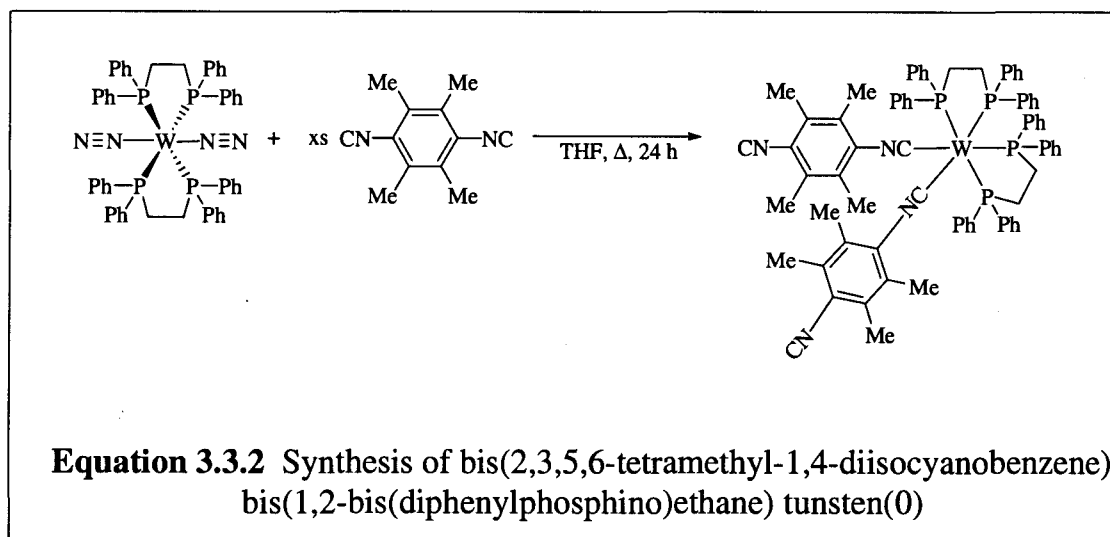
2,3,5,6-Tetramethyl-1,4-diisocyanobenzene was chosen as the bridging isonitrile in an effort to increase the solubility of the eventual product. This reaction was carried

out using the same procedure as that described in **Equation 3.3.1**. The target tungsten bis(isonitrile) complex was produced as a black crystalline solid. Like the complex in **Equation 3.3.1**, this bis(isonitrile) complex also proved to be insoluble in standard NMR solvents and proved to be only sparingly soluble in THF. X-Ray structure analysis was used to confirm the presence of the *cis* isomer in the solid state. Bennett *et* al. report this complex to have *trans* symmetry, based on the spectroscopic data gathered.[8] The $^{31}$P NMR spectrum we collected shows only one peak; IR spectroscopy revealed the C$\equiv$N stretching frequency to be *cis*. Bennett *et. al.* showed that *trans* complexes have stretching frequencies in the range of 1940 to 1970 cm$^{-1}$, while the *cis* isomers exhibit these stretching frequencies in the range of 1740 to 1830 cm$^{-1}$. By comparing the data gathered on this complex and comparing it to data gathered on complexes with known geometries, it was deduced by Bennett *et. al.* that this complex has *trans* symmetry. The origin of this difference is not clear and perhaps reflects preferential crystallization of the *cis* species. This complex crystallizes in the triclinic space group P-1. Two THF molecules and one hexane molecules (per unit cell) have been incorporated into the crystal lattice. The unit cell parameters are $a$ = 12.490(25) Å, $b$ = 14.298(28) Å, $c$ = 21.133(42) Å, $\alpha$ = 71.067(34)°, $\beta$ = 81.897(36)° and $\gamma$ = 82.440(36)°. The ORTEP plot is shown in **Figure 3.3.1**. The geometric parameters and cell data can be found in Appendix II.
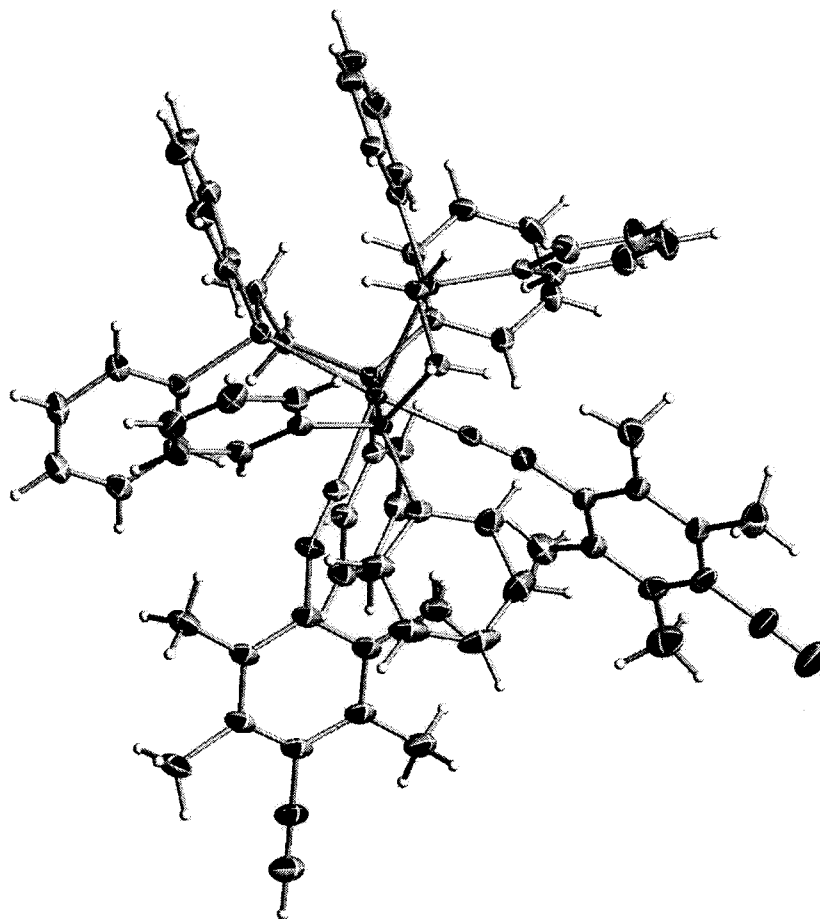
**Figure 3.3.1** ORTEP plot of bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene))bis[1,2-bis(diphenylphosphino)ethane]tungsten(0). Thermal displacement ellipsoids are shown at the 30% probability level. Solvent molecules omitted for clarity.

Bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis(di(*p*-ethylphenyl) phosphino)benzene]molybdenum(0) was synthesized by the route shown below:

**Equation 3.3.3** Synthesis of bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene) bis(1,2-bis(di(*p*- ethylphenyl)phosphino)benzene)molybdenum(0)
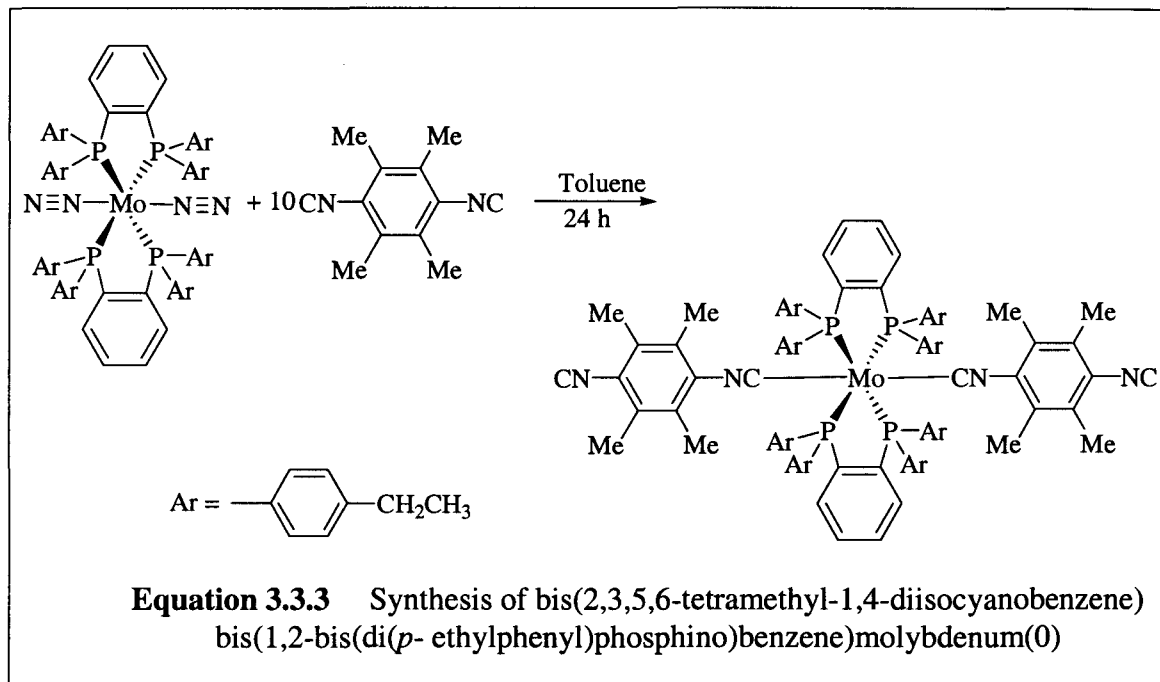
In this reaction, a solution of the molybdenum dinitrogen complex was added drop-wise to a solution of 2,3,5,6-tetramethyl-1,4-diisocyanobenzene in toluene. In order to avoid side reactions, the reaction was carried out at 0 °C. The completeness of the reaction was monitored by IR spectroscopy. Thus, after 24 h, the N≡N stretching frequencies at 1981 and 2055 cm$^{-1}$ were replaced by the C≡N strecting frequencies at 1867 and 2114 cm$^{-1}$.

In the solid state, the bis(diisonitrile) complex is isolated as very dark green to blue microcrystals in a 89.4% yield. The $^{31}$P NMR spectrum has a single peak at 71.19 ppm, indicating that all four phosphorus atoms are in the same environment and, thus, the complex has a *trans* configuration. This is further confirmed by the $^1$H NMR spectrum, in which there is only one set of each type of signals. The broad signals at 7.88 ppm as well as doublets which have integration ration of 1:1 at 7.21 ($J(^1$H$^1$H) = 7.4 Hz) and 6.81 ($J(^1$H$^1$H) = 7.4 Hz) ppm can be assigned to the aromatic hydrogens. A quartet at 2.34

$(J({}^1H{}^1H) = 7.6$ Hz) is due to the methylene protons of the ethyl groups. Singlets at 2.00 and 0.83 ppm are from the two types of methyl groups of the isonitrile: the 2,6 methyl groups and the 3,5 methyl groups, respectively. The triplet at 1.0 $(J({}^1H{}^1H) = 7.6$ Hz) ppm can be attributed to the methyl protons of the ethyl groups.

Bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis(di($p$-ethylphenyl) phosphino)benzene]tungsten(0) was synthesized *via* the route below:



**Equation 3.3.4** Synthesis of bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene) bis(1,2-bis(di($p$- ethylphenyl)phosphino)benzene)tunsten(0)
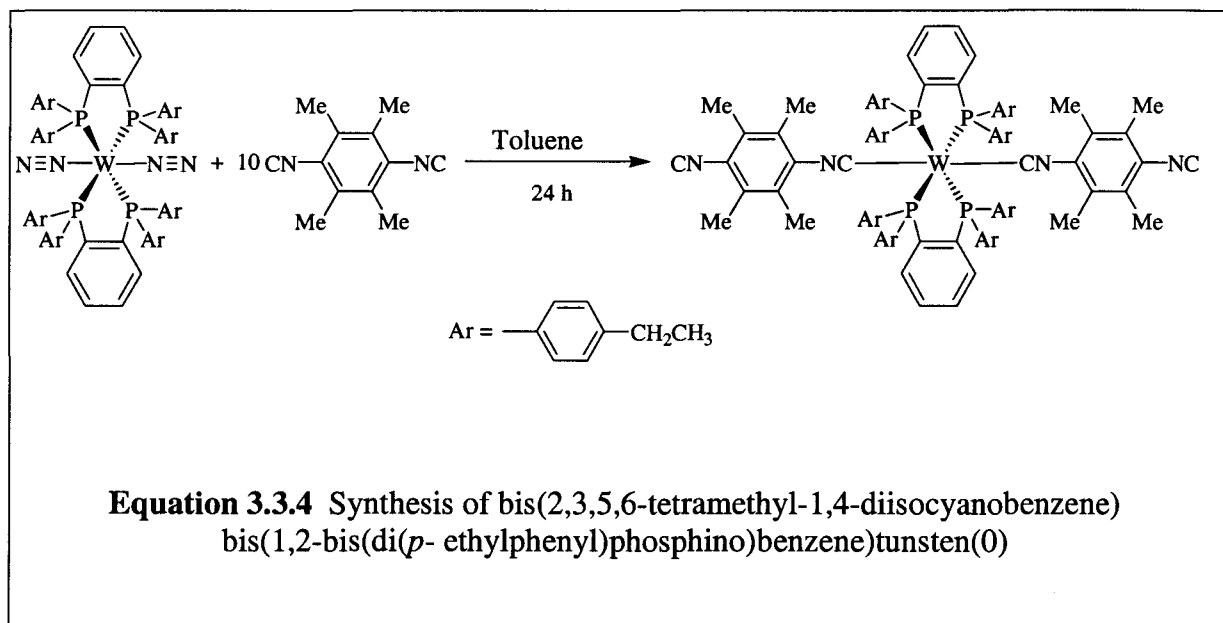
Although this is the tungsten congenor of the product in **Equation 3.3.3** the reaction conditions are slightly different. In particular, the slow reaction kinetics associated with tungsten removes the need to do this reaction at 0 °C. In fact, in order to force this reaction to completion, it was necessary to reflux the reaction mixture. After 18 h of heating, the solution was then allowed to cool to room temperature and it was worked up using the same method as its molybdenum congenor. The crude bis(diisonitrile) complex was isolated in a 39.5% yield.

The bis(diisonitrile) tungsten complex is a $5d^6$ complex, whereas the molybdenum derivative is a $4d^6$ complex. The 5d complexes have a higher activation barrier for substitution due to the Lathanide contraction.

Both tungsten bis(diisonitrile) complexes synthesized with the dppe phosphine, bis (1,4-diisocyanobenzene)bis(1,2-bis(diphenylphosphino)ethane)tungsten(0) and bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis(1,2-bis(diphenylphosphino)ethane) tungsten(0), are only sparingly soluble in common organic solvents (THF, diethyl ether, toluene) and were even less soluble in standard NMR solvents. Bis(1,4-diisocyanobenzene)bis(1,2-bis(diphenylphosphino)ethane)tungsten(0) has both un-substituted phenyl rings on the phosphines and unsubstituted isonitrile arenes. The methyl substituents of the bis(diisonitrile) ligands have only a minor effect on the solubility of bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis(1,2-bis(diphenylphosphino)ethane) tungsten(0), as the tetramethyl isonitrile complex shows only a slight increase in solubility over the perhydro isonitrile complex. Thus, five grams of the tetramethyl complex will dissolve in approximately 1.5 L THF as opposed to five grams of the perhydro complex dissolving in 2.5 L of THF. It can be concluded that the solubility of the bis(diisonitrile) complexes, like that of the corresponding dinitrogen complexes, is influenced more by the solubility properties of the phosphines and that the solubility of the bis(diisonitrile) serves only to augment the solubility dictated by the phosphine ligands. Bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene)bis[1,2-bis(di(p-ethylbenzene) phosphino) benzene]molybdenum(0) and bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene) bis[1,2-bis(di(p-ethylbenzene)phosphino)benzene]tungsten(0) do not exhibit these solubility problem because of the ethyl substituents that are present on the phenyl rings of

the phosphines. Indeed, it appears that the ethyl phosphines increase the solubility of the complex by a factor of 200.

The bis(diisonitrile) complexes all have one thing in common: in solution, they are all very intensely colored, usually dark purple to almost black. This is a major difference from the color found in the dinitrogen complexes and has to do with the types of electronic transitions that are present. As mentioned previously, for the dinitrogen complexes, the only transitions present are Laporte forbidden d-d transitions. The bis(diisonitrile) complexes also posses this transition, but more importantly, the bis(diisonitrile) complexes now have a metal to ligand (MLCT) charge transfer. In order to have these types of charge transfers, there must be a donor species (the metal "d" orbitals in this case) and an acceptor species [the bis(diisonitrile)]. Since the acceptor species has a delocalized $\pi$ system of electrons, this will allow a donated electron to be dispersed throughout the bis(diisonitrile) itself and will enhance the charge transfer.

## 4. Capping Reactions

All wires, whether macroscopic or molecular, must have a distinct starting as well as ending point; the "caps" described in this section will provide these. In a capping reaction, a bis(diisonitrile) complex is combined with a monofunctional, usually organometallic, fragment. This fragment will very often contain one or more carbonyl groups.

The attempted synthesis of bis [1,2-bis(di{p-ethylphenyl})phosphinobenzene] dinitrogencarbonylmolybdenum(0) as a potential capping group is shown below:

**Equation 3.4.1** Synthesis of bis [1, 2-bis (di{p-ethylbenzene})phosphinobenzene]
dinitrogencarbonylmolybdenum(0)
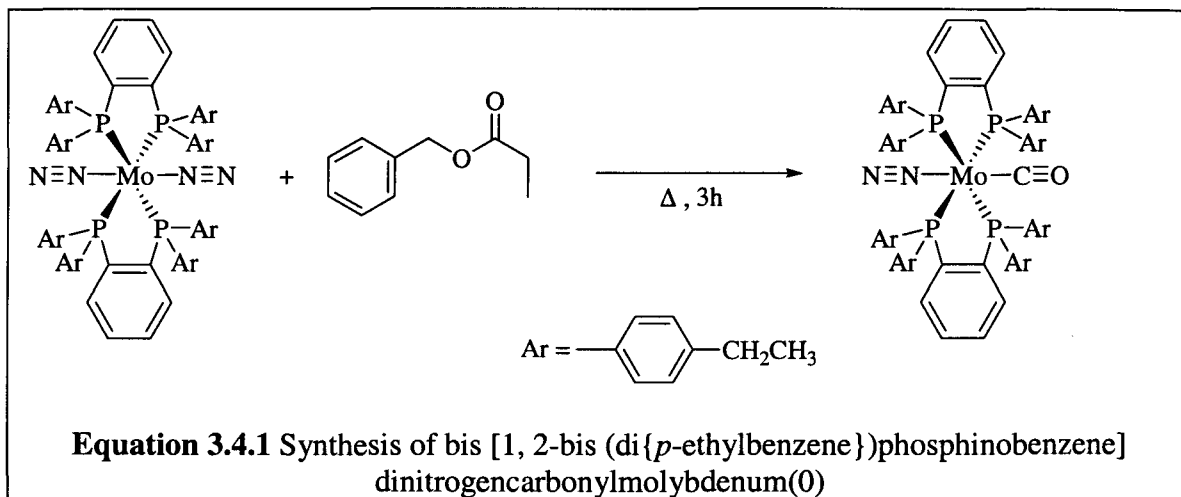
This is an oxidative addition/reductive elimination reaction in which the metal is inserted into either the carbon-carbonyl carbon bond or the oxygen-carbonyl carbon bond. The mechanism of this reaction has not been established. However, it is known that this reaction occurs only when there are two empty 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 3.4.1**. 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 dintrogen ligand. The remaining dintrogen 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 that 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.

**Scheme 3.4.1** Possible mechanistic scheme for the reaction of benzyl propoinate with a

bis(dinitrogen) complex
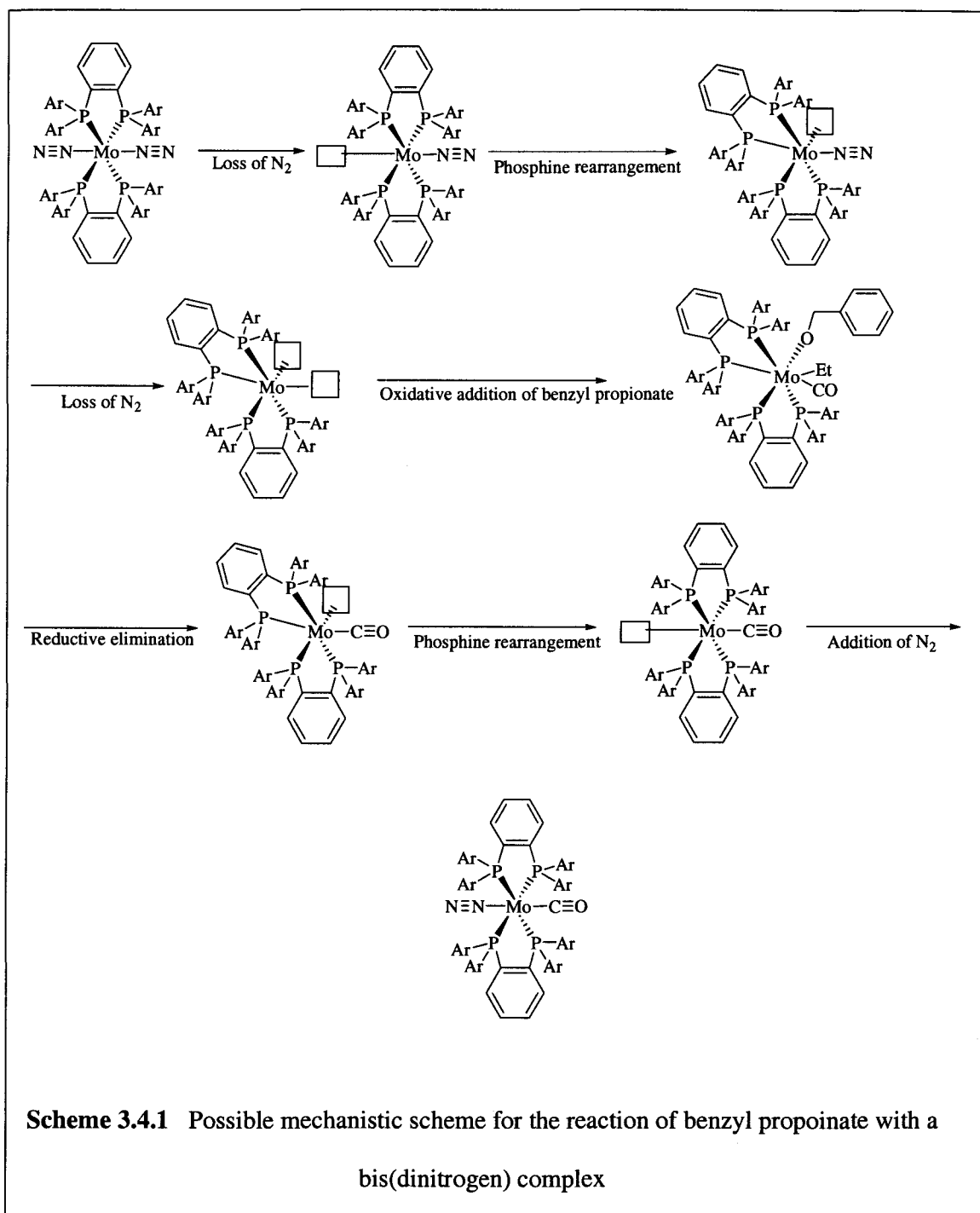
The synthesis of bis(1,2-bis(diphenylphosphino)ethane)carbonyl(DMF) tungsten

(0) was attempted by the route shown:

Ph       Ph
Ph—P     P—Ph

N≡N——W——N≡N  +  DMF  ——Benzene, Δ——▶  DMF——W—C≡O

Ph—P     P—Ph
Ph       Ph

Ph       Ph
Ph—P     P—Ph

Ph—P     P—Ph
Ph       Ph

**Equation 3.4.2** Synthesis of bis(1,2-bis(diphenylphosphino)ethane)carbonyl(DMF)

tungsten(0)
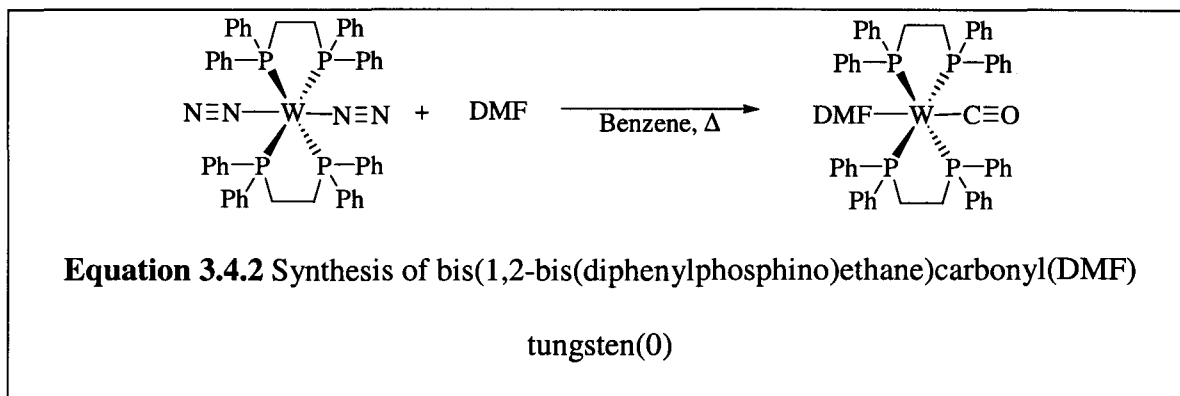
This reaction is very similar to that in **Equation 3.4.1**, with the exception that dinitrogen does not re-attach to the metal because of the more strongly coordinated DMF molecule. A similar reaction in which a large excess of DMF was reacted with bis(dintrogen)bis(1,2-bis(diphenylphosphino)ethane)molybdenum(0) to yield the molybdenum congenor of the product shown in **Equation 3.4.2** was published by Tatsumi et.al.[9] The product recovered after 2 h of reflux proved to be starting material in our case. Even under reflux, the solubility and/or the reactivity of the tungsten dinitrogen complex resulted in no formation of the desired product.

The trimetallic μ-C,C'-[bis(p-diisocyanotetramethylbenzene)bis[1,2-bis{di(p-ethylphenyl)phosphino}benzene]molybdenum(0)]bis(pentacarbonylchromium(0)) was synthesized as shown below:

**Equation 3.4.3** Synthesis of
μ-C,C'-[bis(p-diisocyanotetramethylbenzene)bis[1,2-bis{di(p-ethylphenyl)phosphino}benzene]
molybdenum(0)]bis(pentacarbonylchromium(0))
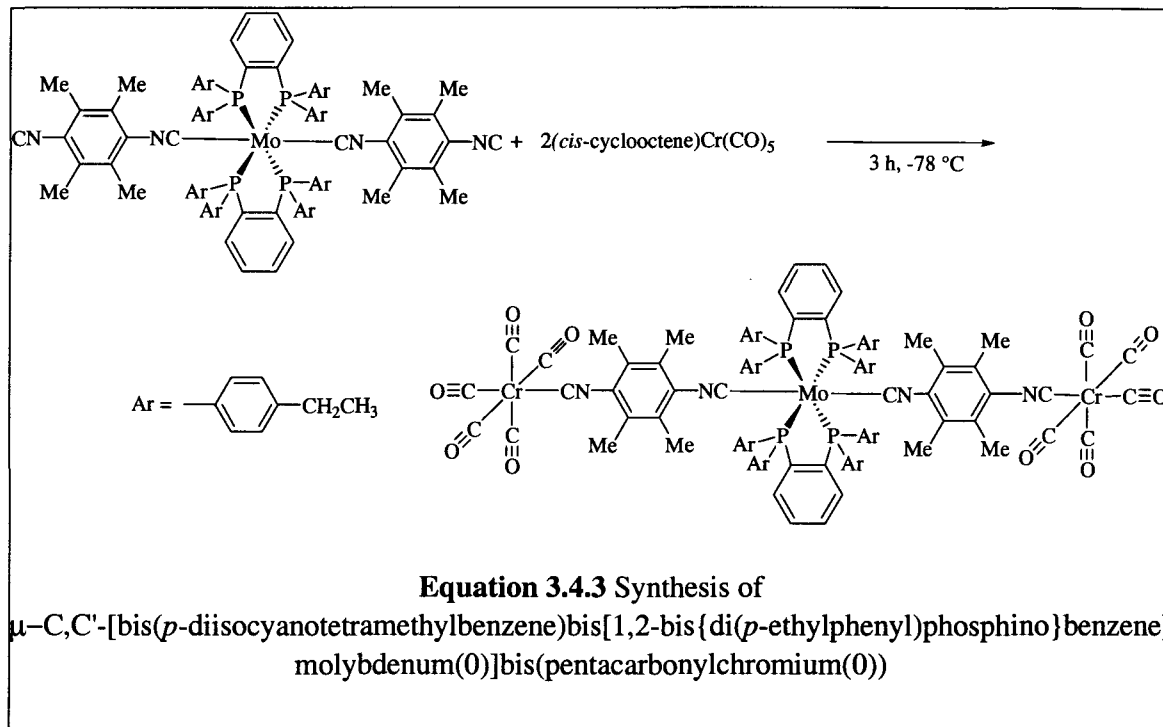
The reaction is carried out at -78 °C in order to minimize any side reactions that may

occur. Two molar equivalents of the chromiumpentacarbonyl complex are added to one

equivalent of the bis(diisonitrile) complex. The reaction is stirred for 3 h at − 78 °C and is

then allowed to warm to room temperature over an additional hour. Hexanes are then

added and the solution is left to crystallize in the freezer.

The trimetallic complex is isolated as black iridescent very thin plates in a yield of

42.8%. The IR spectrum shows one N≡C stretching frequency at 1859 cm$^{-1}$ and two C≡O

stretching vibrations at 2054 and 1955 cm$^{-1}$. The $^1$H NMR spectrum reveals the product

in **Equation 3.4.3** to be exclusively the *trans* isomer as there is only one set of signals.

The doublets at 7.22 ($J(^1H^1H)$ = 7.6 Hz) and 6.84 ($J(^1H^1H)$ = 8 Hz) ppm are due to the

aromatic hydrogen atoms of the phosphine. Two aromatic proton signals are not

observed, apparently due to signal overlap. The quartet at 2.36 ($J$ ($^1H^1H$) = 6.4 Hz) ppm

is from the methylene protons of the ethyl groups. The singlets at 1.86 and 0.86 ppm are from the methyl groups of the bis(diisonitrile) ligands. The triplet at 0.990 $(J(^1H^1H) = 7.6$ Hz) is due to the methyl protons of the ethyl groups.

The trimetallic $\mu$-C,C'-[bis(p-diisocyanotetramethylbenzene)bis[1,2-bis{di(p-ethylphenyl)phosphino}benzene]tungsten(0)]bis(pentacarbonylchromium(0)) was synthesized by a route similar to the one used for its molybdenum congenor:



**Equation 3.4.4** Synthesis of
$\mu$-C,C'-[bi[bis(p-diisocyanotetramethylbenzene)][bis{di(p-ethylphenyl)phosphino}benzene]
tungsten(0)]bis(pentacarbonylchromium(0))
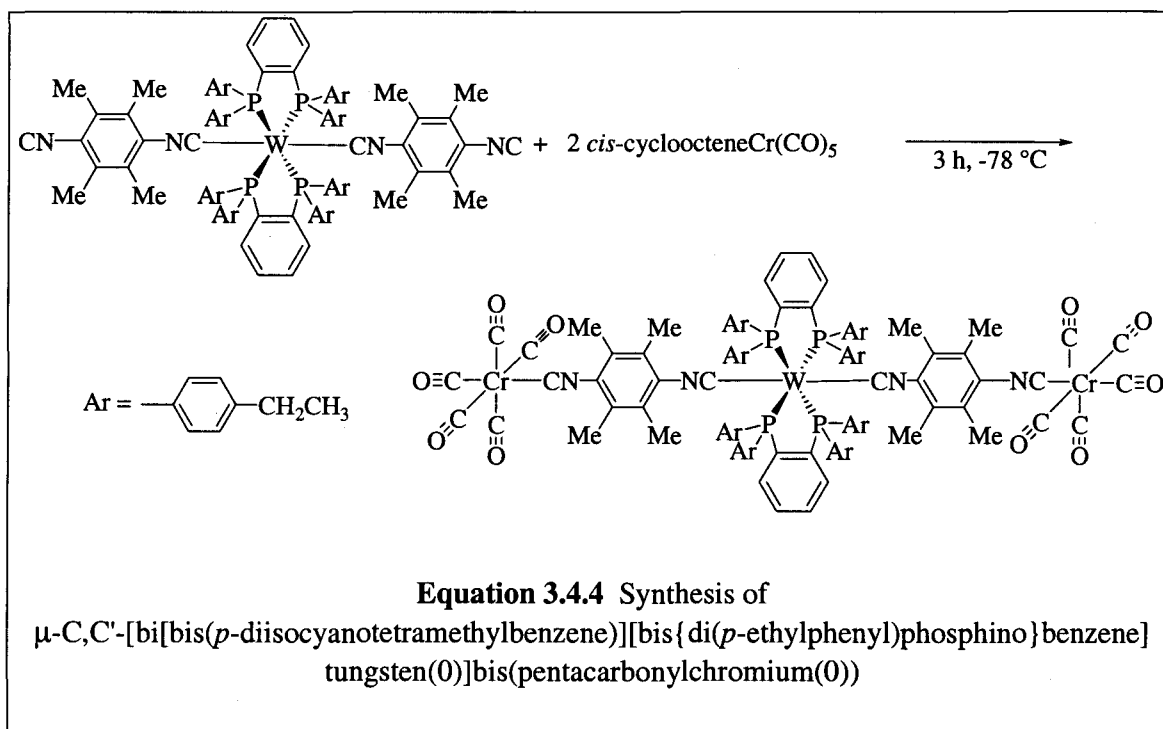
The trimetallic complex was isolated in a 48.8% yield as black iridescent, very thin plates. The IR spectrum shows one $N\equiv C$ stretching frequency at 1851 cm$^{-1}$ and two $C\equiv O$ stretching frequencies at 2055 and 1954 cm$^{-1}$. The $^1H$ NMR spectrum shows this trimetallic to be again exclusively the *trans* isomer. The doublet at 6.84 $(J(^1H^1H) = 8$ Hz) is one of the aromatic proton signals from the phosphine. The other three aromatic proton signals are not observed due to signal overlap. The quartet at 2.36 $(J(^1H^1H) = 7.6$ Hz) is

due to the methylene protons of the ethyl groups. The singlets at 1.86 and 0.84 ppm can be assigned to the methyl groups on the bis(diisonitrile). The triplet at 0.99 ($J$ ($^1H^1H$) = 7.6 Hz) can be assigned to the methyl protons of the ethyl groups.

The attempted synthesis of $\mu$-C,C'-[bis($p$-diisocyanotetramethylbenzene)bis[1,2-bis{di($p$-ethylphenyl)phosphino}benzene]molybdenum(0)]bis($\eta^5$-cyclopentadienyl dicarbonylmanganese(0)) is shown below:



**Equation 3.4.5** Synthesis of
$\mu$-C,C'-[bi[bis($p$-diisocyanotetramethylbenzene)]bis[1,2-bis{di($p$-ethylphenyl)phosphino} benzene]molybdenum(0)] bis($\eta^5$-cyclopentadienyl dicarbonylmanganese(0))
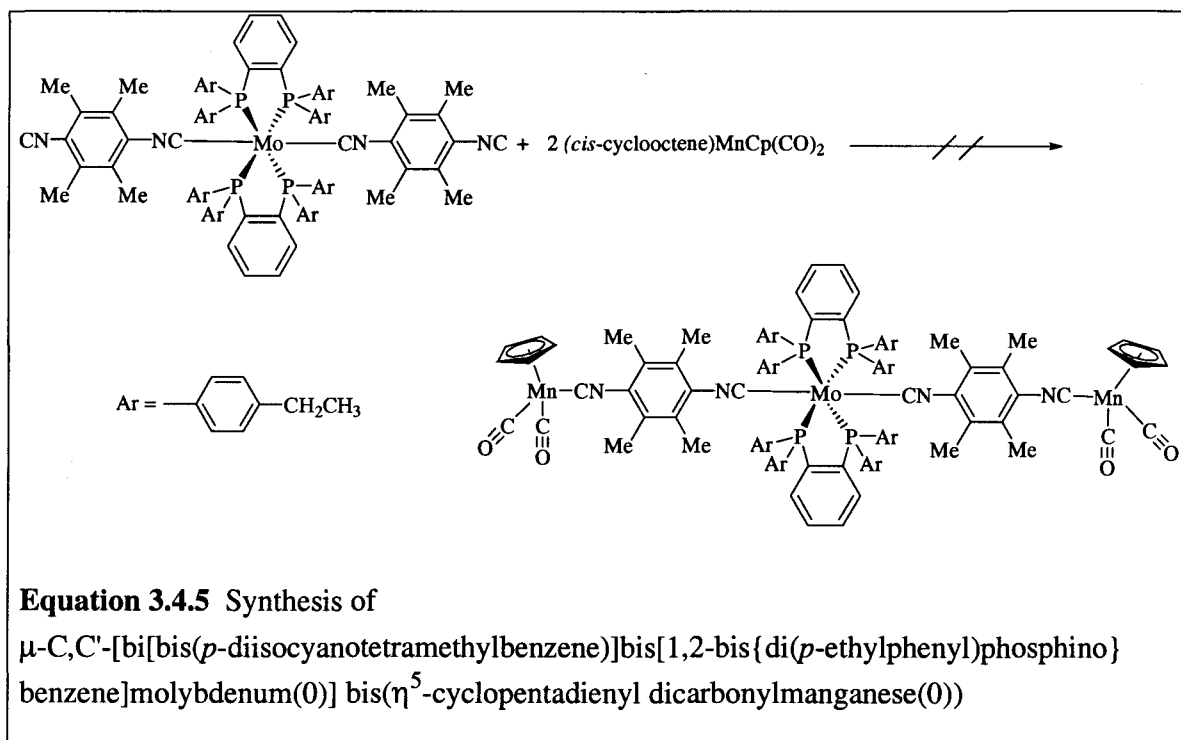
Two molar equivalents of $cis$-cyclooctene-$\eta^5$-cyclopentadienyl-dicarbonylmangenese were combined with one molar equivalent of the bis(isonitrile) complex. Since the manganese reagent does not easily loose its cyclooctene ligand, the reaction was stirred for five days and the reaction was monitored using IR spectroscopy. After five days, hexanes were added in an attempt to crystallize the desired product from the reaction solution. No product crystallized from the pale red-to-pink solution.

The attempted synthesis of μ-C,C'-[bis(p-diisocyanotetramethylbenzene)bis[1,2-bis{di(p-ethylphenyl)phosphino}benzene]molybdenum(0)]bis([1,2-bis(di(p-ethylphenyl)phosphino)ethane]carbonylmolybdenum(0)) is shown below:



**Equation 3.4.6** Synthesis of μ -C,C'-bis(p-diisocyanotetramethylbenzene)[bis[1,2-bis{di(p-ethylphenyl)phosphino} benzene]molybdenum(0)]
bis([1,2-bis(di(p-ethylphenyl)phosphino)ethane]carbonylmolybdenum(0))
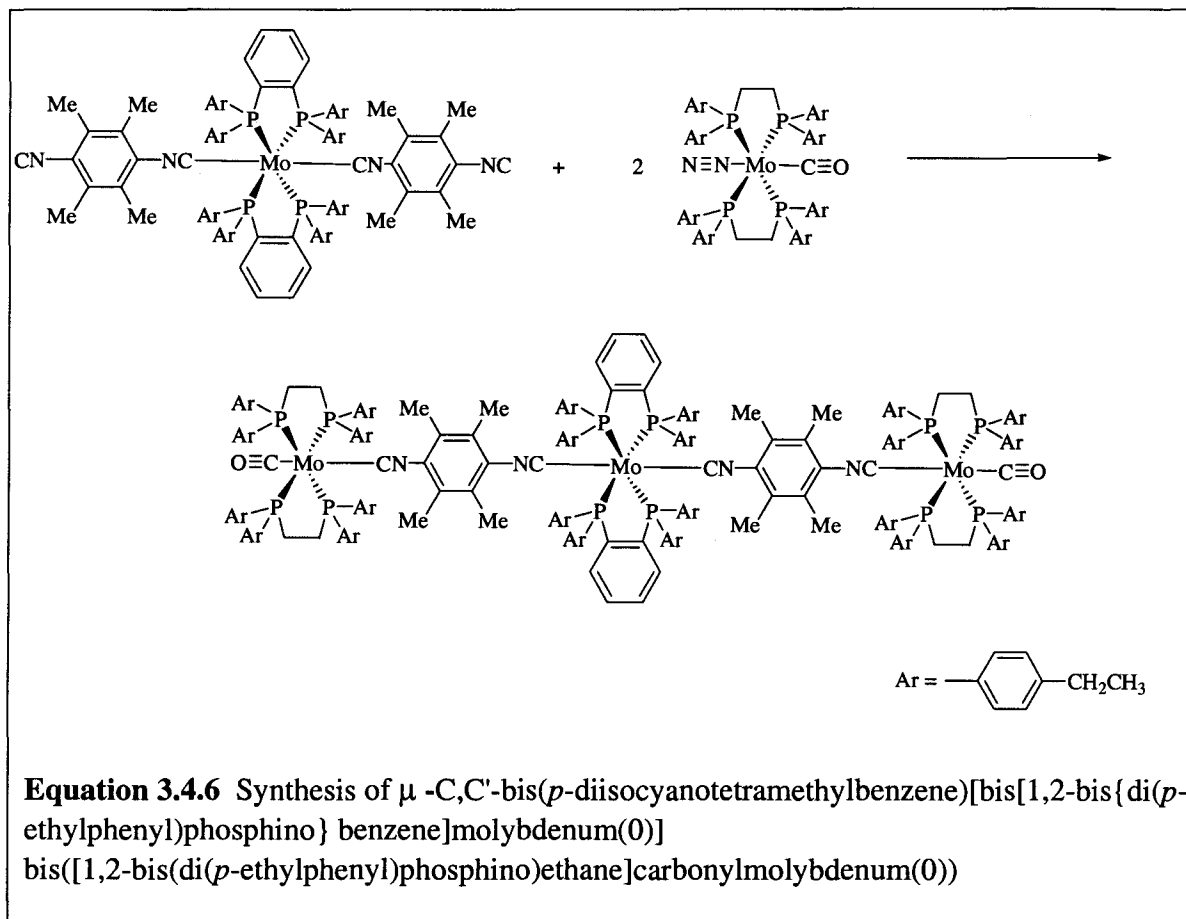
In this reaction, solid bis(tetramethyl-p-diisocyanobenzene)bis[1,2-bis{di(p-ethylbenzene)}phosphinobenzene]molybdenum(0) and solid bis(di(p-ethylbenzene)phosphinoethane)dinitrogencarbonylmolybdenum(0) are combined in a cooled (-78 °C) flask. Toluene is added and the solution is stirred for 6 h (one of which is needed for the solution to warm to room temperature). Hexane is then added in an attempt to crystallize the product. No product was isolated from the dark blue solution.

Like the bis(diisonitrile) complexes, the three trimetallic complexes (those in **Equations 3.4.3**, **4**, and **6**) are very promising. In solution, all three complexes are very dark blue, almost black in color. As solids, all three have a metallic shine to them as well. The color is indicative of either a LMCT or MLCT taking place as in the bis(diisonitrile) complexes. Again, this implies that these complexes are highly conjugated and thus these higher oligomers should be capable of conducting electrons. The iridescent sheen of the solid chromiumpentacarbonyl complexes resembles that found in most metals. With most metals having at least semi-conducting properties, it can be inferred that the chromiumpentacarbonyl complexes might also have semi-conducting properties as well. The goal of synthesizing conducting nanowires becomes even closer with these trimetallic complexes.

# References

1. a) E. P. Kyba, S-T. Jui, R. L. Harris. *Organometallics* **1983**, *2*, 1877-1879, b) E. P.

   Kyba, M. C. Kerby, S. P. Rines. *Organometallics* **1986**, *5*, 1189-1194.

2. Adapted from L. Dahlenburg, A. Kaunert. *Eur. J. Inorg. Chem.* **1998**, 885-887.

3. R. L. Cook and J. G. Morse. *Inorg. Chem.* **1982**, *21*, 4103-4105.

4. W. Hussain, G. J. Leigh, H. M. Ali, J. Pickett, D. Rankin. A. *J. Chem. Soc. Dalton

   Transactions* **1984**, 1703-1708.

5. T. A. George, M. E. Noble. *Inorg. Chem.* **1978**, *17*, 1678-1679.

6. Mtunzi-S. Donovan, M. Hughes, G. J. Leigh, H. Mohd. Ali, R. L. Richards, J. Mason.

   *J. Organomet. Chem.* **1983**, *246*, C1.

7 C. L. Perrine. "0th and 1st Generation Organometallic Nanostars from Ferrocenylamine

   and Ferrocenylaniline." M.S. Thesis. August, **2004**

8 . N. L. Wagner, F. E. Laib, D. W. Bennett. *J. Am. Chem. Soc.* **2000**, *122*, 10856-10867.

9 . T. Tatsumi, H. Tominaga, M. Hidai, Y. Uchida. *J. Organmet. Chem.* **1981**, *215*, 67-

   76.

# Chapter IV- Conclusions

The first step towards the goal of synthesizing electronically conducting nanorods is the synthesis of molybdenum and tungsten dinitrogen complexes. The majority of the dinitrogen complexes containing these metals adopt the *trans* configurations (some are *cis*) as do the bis(diisonitrile) complexes reported here. The bis(diisonitrile) complexes can be made by the direct reaction of the dintrogen complex with an excess of the appropriate bis(diisonitrile), the labile dinitrogen ligand being easily replaced by the stronger coordinating diisonitrile ligands. Trimetallic complexes can then be synthesized from the bis(diisonitrile) complexes. In going from the dinitrogen complexes to the bis(diisonitrile) complexes and then to the trimetallic complexes, charge transfer transitions (indicated by color intensity) become increasingly more important. This points towards an increase in conjugation along the backbone of the metal complexes.

Further studies to be undertaken include electrochemical (CV) analysis, DFT calculations, finding a better synthetic route for the fluorinated phosphines, as well as investigating the exact nature of the transitions that are occurring in both the bis(isonitrile) complexes as well as the trimetallic complexes. A measurement of the UV-Vis spectrum may provide useful information about the type of charge transfer transition and, thus the color changes, occurring in these complexes. The bis(diisonitrile) complexes and the trimetallic complexes both show promise. Thus, with the successful synthesis of the trimetallic complexes, the goal of synthesizing conducting nanowires comes closer.

# Chapter V- Solid Sodium Cyclopentadienide, NaCp

## Section one- Introduction

The cyclopentadienyl anion, $Cp^{\ominus}$, remains one of the most common and widely used ligands in organometallic chemistry. This cyclic polyene ligand can co-ordinate through up to five of its carbon atoms, donating up to six electrons to the metal it is co-coordinated to.[1] The Cp containing complexes can have one, two, or three cyclopentadienyl rings and the dicyclopentadienyl complexes can have either straight or angular (bent) "sandwich" structures ("metallocenes", as in 1 and 2 of Fig. 5.1.1). They can also be derivatives of the sandwich form with other ligands present (Fig. 5.1.1 number 3) or be half sandwich ("piano stool") (Fig. 5.1.1 number 4) complexes.[2,3]
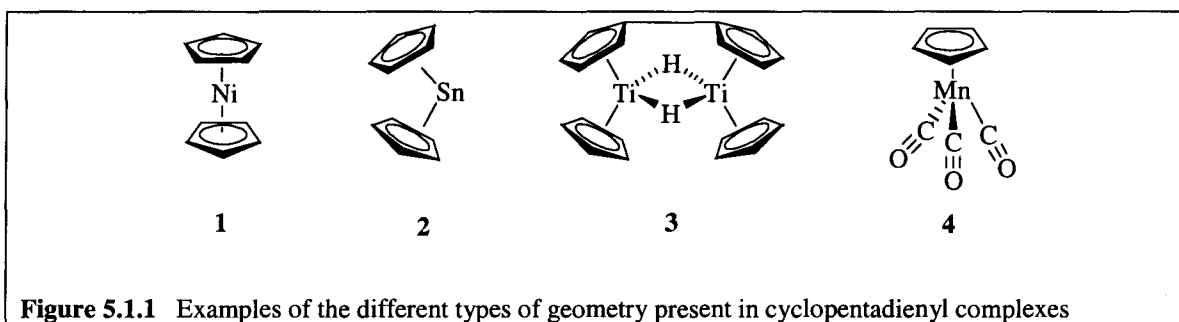


**Figure 5.1.1** Examples of the different types of geometry present in cyclopentadienyl complexes

Cyclopentadiene itself does not usually exist as the free molecule $C_5H_6$, CpH, since the five-membered diene ring has limited thermal stability and readily undergoes dimerization. Instead, the dimeric dicyclopentadiene, $C_{10}H_{12}$, $(CpH)_2$, must be "cracked", meaning it undergoes a retro-Diels-Alder addition reaction to produce the monomeric form of CpH as shown in **Equation 5.1.1**.[2] It is important to use this freshly cracked

CpH as soon as possible as the neat liquid will readily re-dimerize even at room temperature and its solutions are only stable towards dimerization for a few hours at ambient temperature or days in the freezer.



**Equation 5.1.1.**                    The "cracking" of dicyclopentadiene.
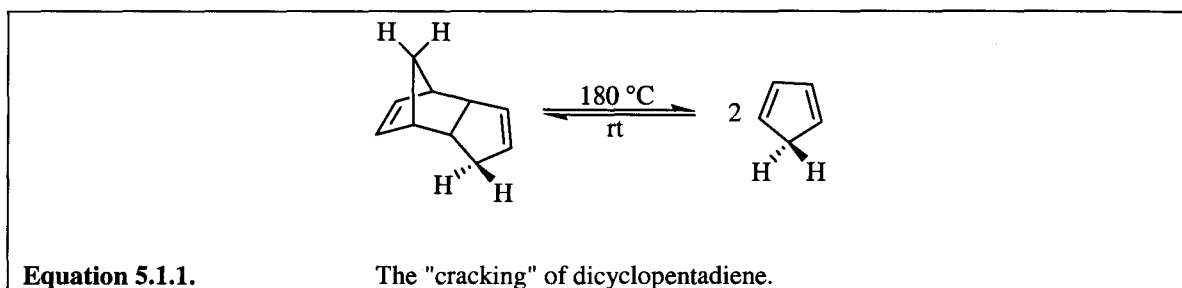
Methylcyclopentadiene, $C_5H_5CH_3$, Cp'H, like the parent compound cyclopentadiene, will also dimerize at or near room temperature (the dimerization of Cp'H is measurable above 0 °C and is complete within two hours at 60 °C).[4] The Cp'H dimer, (Cp'H)$_2$, (CpH, Cp'H, etc., may also form trimers and higher weight oligomers) has the same *endo*-dicyclopentadiene structure as dicyclopentadiene itself. The two dimers also exhibit similar cracking temperatures, namely: 172 °C for the methylcyclopentadiene dimer and 180 °C for dicyclopentadiene.[4] 1,2,3,4,5-Pentamethylcyclopentadiene, $C_5Me_5H$, Cp*H, however, does not show a tendency towards dimerization at room temperature, presumably because it is hindered by the steric bulk of the pentamethylated Cp ring.

Once the monomeric CpH has been produced, it has to be introduced into the coordination sphere of the metal. Cyclopentadiene is a weak acid ( $pK_a = 10^{-15}$), but is still one of the more acidic hydrocarbons. As such, it can easily be deprotonated by a strong base or alkali metals[2] to form the aromatic cyclopentadienyl anion.

**Equation 5.1.2** The deprotonation of cylcopentadiene by (A) strong base and (B) sodium metal.
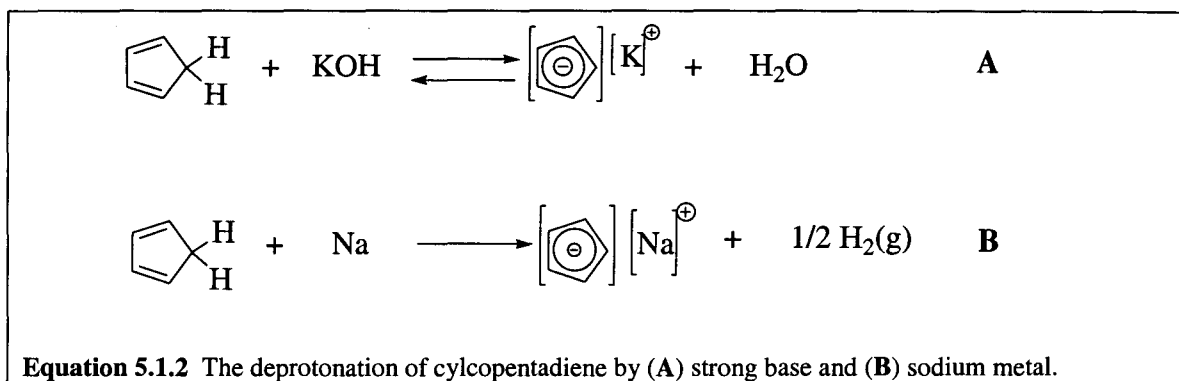
Cp-alkali metal complexes are the most common reagent for the introduction of the Cp ligand into a metal's coordination sphere.[5] The most common such reagent is sodium cyclopentadienide, NaCp. NaCp is the first known Cp-containing complex. It was first synthesized *in situ* by Thiele for use in subsequent reactions[5] in 1900.[6] He later isolated the first pure Cp-alkali metal compound, KCp, which was synthesized from the reaction of cyclopentadiene and potassium metal in benzene.[7]

The metal-Cp bonding in Cp-alkali metal complexes is mainly ionic in character - the value of 80-90% being well established.[8-10] This is to be expected since the bond between an electropositive alkali metal and a less electropositive carbon atom is expected to possess substantial ionic character.[6] The resulting Cp-alkali metal complexes are therefore more accurately described as being ionic clusters in which anion-cation interactions make up the majority of the bonding. The polarity of this bond is not only dependent upon the alkali metal that is present but also on the nature of the organic anion.[6] It has been shown[8, 9] that Cp-alkali metal bonds are more ionic than alkyl-alkali metal bonds. For this reason, Cp-alkali metal complexes are better described as contact ion pairs with no delocalization of the Cp's electron cloud towards the alkali metal.

It has already been mentioned that Cp can have hapticity of up to five. Through a computational haptotropic search in which the lithium cation was moved from side to

side above the Cp anion, it was found[11] that the preference in LiCp is $\eta^5$ coordination. The same type of bonding can be assumed to be present in NaCp since it has been shown *via* the use of high-resolution powder X-ray diffraction[12] that LiCp and NaCp are isomorphous in the solid state, that they show very similar unit cell parameters, and also that they crystallize in the same crystal system and space group.

NaCp, with its highly ionic character and thus its high reactivity, remains the most common reagent through which Cp is introduced into a metal complex. The experimental procedure[2,13] for making NaCp involves three main steps:

(1)    Dicyclopentadiene is "cracked" as mentioned before to give monomeric CpH.

(2)    A sample of metallic sodium is placed in a high boiling inert solvent (under inert atmosphere) which is heated above the melting point of sodium while being vigorously stirred. This gives a suspension of very finely divided sodium. The suspension is then cooled to room temperature while stirring is constant to give sodium sand (care should be taken when using the sodium sand as it is very reactive towards moisture, and is thus air sensitive). The inert solvent is removed by canulation, filtration, etc., to give a finely divided solid. Alternatively, commercial sodium sand in a medium such as paraffin can be heated (below the melting point of sodium) in an inert solvent such as hexanes and then the solvent is removed, the sand washed to give a similar finely divided sodium.

(3)    A solvent that is suitable for dissolving NaCp, typically THF as Cp-alkali metal compounds are insoluble in apolar solvents[5] is then added to the sodium sand and the CpH monomer is added drop-wise. After the reaction to give a colorless (pure) to purple (partially oxidized) solution is complete one has a THF solution of reactive

NaCp(THF). The THF can then be removed *in vacuo* and an alternative solvent added but this solid NaCp is a very air sensitive, pyrophoric material that is very hard to handle. The overall reaction scheme for this is illustrated in **Equation 5.1.3.**



**Equation 5.1.3.**          Experimental route to sodium cyclopentadienide, NaCp
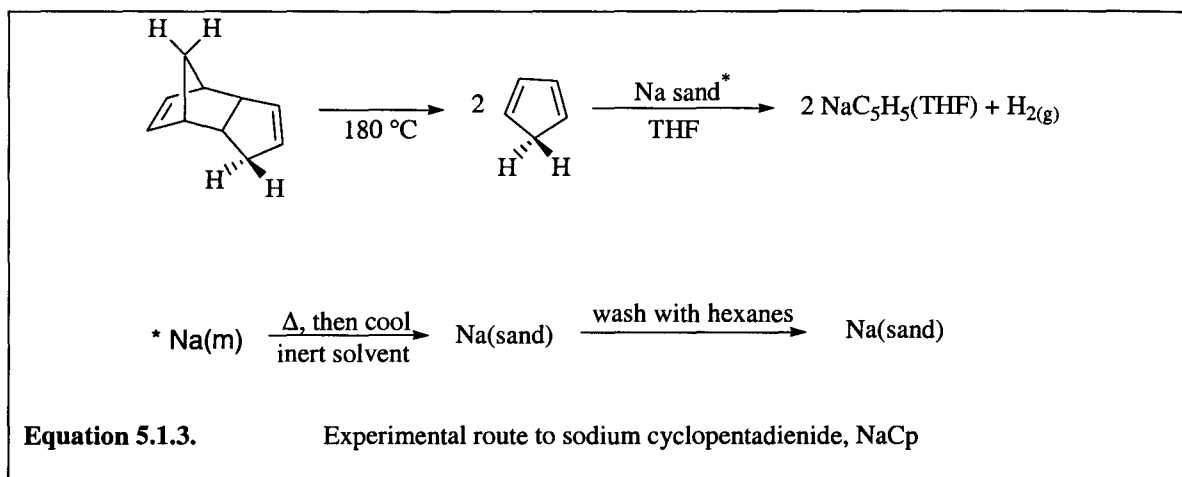
Cyclopentadiene anion can then be introduced into a metal's coordination sphere by reacting a metal precursor (often a metal chloride or carbonyl) with the cyclopentadienyl reagent previously generated (NaCp).[2] This occurs through simple ligand displacement as shown in **Equation 5.1.4.**[1]



**Equation 5.1.4.**          Ligand displacement and introduction of Cp.
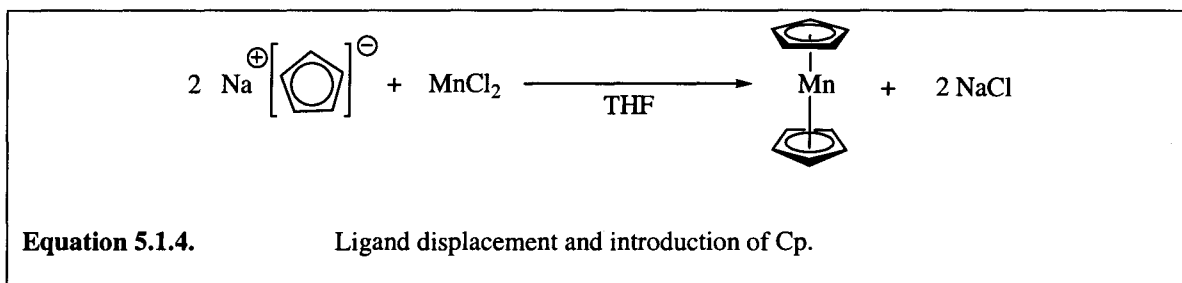
Although the traditional method to make NaCp is reliable (roughly 70% yield), it is rather time consuming. Given the evolution of flammable hydrogen gas, the need to handle pyrophoric sodium sand, multiple reaction steps, and a product that is often rather air sensitive, the need for an easier method is apparent. This chapter deals with such a

method: a one-step, one-pot synthesis of solid NaCp. One can imagine that if a solvent can be chosen that is both inert and has a high enough boiling point, the dicyclopentadiene can be cracked *in situ* while the sodium is being melted and finely divided. The freshly cracked Cp can then immediately react with the sodium droplets. The solvent should also be non-polar so that the NaCp will precipitate from the solution. Collection of the product can then be done *via* filtration under an inert atmosphere or canulation of the supernatant away from the desired product. This new method would both eliminate the multiple steps and might be expected to be safer since the possibility of air getting into the reaction apparatus, the sodium sand catching fire, and/or that the dropping funnel will leak are drastically reduced and/or avoided all together. This new method is basically a "one-pot" reaction: sodium metal, an excess of dicyclopentadiene, and the appropriate solvent are combined in a single flask, heated, and stirred until the sodium metal has been consumed. Butyl ether was chosen as the solvent because it has a pleasant smell, is nonpolar, is relatively inert, and has an appropriately high boiling point of 142-143 °C.

Once it has been determined whether or not the method works, certain fundamental questions will then be investigated and answered. The first of which is how this new method compares to the traditional method, i.e. are the yields similar, how time consuming is it, and how do the products compare (purity, sensitivity, etc.)? The next question is how general is this reaction? To answer this, other ligands in the Cp family will be used (indene and 1,2,3,4,5-pentamethylcyclopentadiene, Cp*). The final question is what kind of transfer properties does the NaCp generated by this new method have (i.e. will a reaction as illustrated in **Equation 5.1.4** work using this new NaCp).

## Section two – Experimental

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of $N_2$ using standard Schlenk techniques. Dicyclopentadiene, indene, 1,2,3,4,5-pentamethylcyclopentadiene, and butyl ether (anhydrous) were purchased commercially through Aldrich chemical company and were degassed by bubbling $N_2$ through them. Solvents were distilled over the appropriate drying agent under a nitrogen atmosphere prior to use (except for butyl ether, which was used without further purification). All of the reactions documented below should be done in a properly working fume hood as dicyclopentadiene has a very pungent odor.

### A. Sodium cyclopentadienide (NaC5H5)[13]
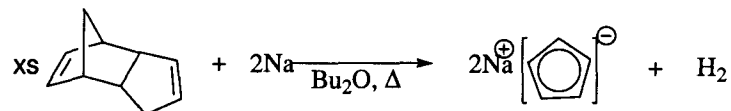


To a 1000 mL 3-necked flask fitted with a septum, reflux condenser with a combination nitrogen inlet/bubbler on top, and nitrogen inlet adapter on the side, are added 400 mL of butyl ether (99.3%, anhydrous, Aldrich) and 30 mL (29.58 g, 223.7 mmol) of dicyclopentadiene (Aldrich). The solution is then degassed by bubbling $N_2$ through it *via* a syringe needle through the septum for 30 minutes. Clean sodium metal, 6.24 g (271.3 mmol) is cut fresh from sodium sticks and added to the flask. The supply of $N_2$ to the side arm is stopped and the suspension is heated to reflux (oil bath temperature

of 120 °C) with vigorous stirring until all of the sodium metal has been consumed (approximately 48 h). No water flow is used in the condenser due to the potential explosion hazard if the apparatus were to break and then water were to come in contact with alkali metals. If the sodium metal is not all consumed after 70 h, additional dicyclopentadiene (in a degassed butyl ether solution) may be added (the reaction mixture is allowed to cool down to room temperature before the addition of additional reagents) and the mixture is heated to reflux for an additional 48 h. [Note: hydrogen gas is generated in this reaction. The pressure that arises from this evolution of gas is alleviated through the use of a mercury bubbler.] After the reaction is finished, the resulting pale yellow suspension is allowed to cool to room temperature and is filtered through a Schlenk filter. The white to beige solid sodium cyclopentadiene is allowed to dry *in vacuo* for 2 h, washed with hexanes (~ 50 mL) and 33.37g (383.2 mmol, 141%) of the air-sensitive NaCp is isolated. Alternatively, the supernatant may be removed by canulation, the solid washed with hexane (3 × 40 mL), and the solid dried *in vacuo*. It is believed that solvent is incorporated in the crystal lattice, resulting in a percent yield above 100.

### B. Sodium Indenide (NaC$_9$H$_7$)[13]
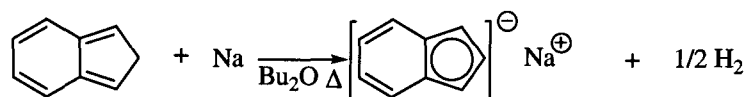
To a 1000 mL 3-necked flask fitted with a septum, reflux condenser with a combination nitrogen inlet/bubbler on top, and nitrogen inlet adapter on the side, are added 300 mL of butyl ether (99.3%, anhydrous, Aldrich) and 25 mL (24.9 g, 214.4 mmol) of indene. The solution is then degassed by bubbling $N_2$ through it *via* a syringe through the septum for 30 minutes. Sodium metal, 3.79 g (164.8 mmol) is cut fresh from sodium sticks and added to the flask. The supply of $N_2$ to the side arm is stopped and the suspension is heated to reflux (with an oil bath temperature of 120 °C) with vigorous stirring until all of the sodium metal is consumed (48 h). After 45min, the solution takes on a brown-yellow color. [Note: hydrogen gas is generated in this reaction. The pressure that arises from this evolution of gas is alleviated through the use of a mercury bubbler.] After the reaction has gone to completion, the solution is allowed to cool down to room temperature. The now greenish solution is filtered t cold hrough a Schlenk filter and placed in the freezer (-19 °C) to crystallize. No product was isolated.

## C. 1,2,3,4,5-Pentamethylcyclopentadienylsodium (NaC$_{10}$H$_{15}$)[13]
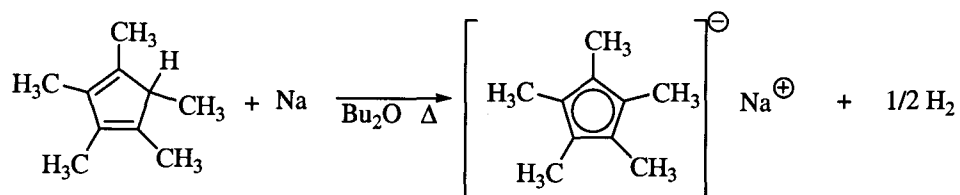


To a 150 mL 3-neck flask fitted with a septum, reflux condenser with a combination nitrogen inlet/bubbler on top, and nitrogen inlet adapter on the side, are added 55 mL of butyl ether (99.3%, anhydrous, Aldrich) and 17 mL (14.79 g, 108.6

mmol) of 1,2,3,4,5-pentamethylcyclopentadiene (Aldrich). The solution is then degassed by bubbling $N_2$ through it *via* a syringe through the septum for 2 h. Sodium metal, 1.7 g (73.95 mmol) is cut fresh from sodium sticks and added to the flask. The supple of $N_2$ to the side arm is stopped and the suspension is heated to reflux (with an oil bath temperature of 120 °C) with vigorous stirring until all of the sodium is consumed (72 h). [Note: hydrogen gas is generated in this reaction. The pressure that arises from this evolution of gas is alleviated through the use of a mercury bubbler.] After the reaction is finished, the resulting suspension is allowed to cool to room temperature and filtered through a Schlenk filter and the slightly gray pentamethylcyclopentadienyl sodium is allowed to dry *in vacuo* for 2 h. 4.30 g (27.2 mmol, 36.8%) of the very air-sensitive product are isolated.

### D. Ferrocene (FeC$_{10}$H$_{10}$)[13]
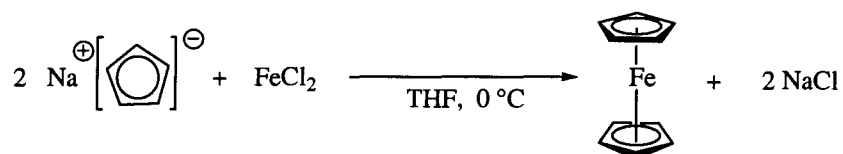


To a 100 mL Schlenk flask is added 0.68 g (5.36 mmol, anhydrous) of $FeCl_2$ and the flask is evacuated and filled with nitrogen. To a second 100 mL Schlenk flask are added 1.18 g (13.55 mmol) of sodium cyclopentadienide and 25 mL of THF. This solution is then added to the $FeCl_2$ along with an additional 25 mL of THF. The solution is stirred at 0 °C for 18 h. The THF is evaporated off, leaving crude yellow-orange ferrocene. The product is purified by dissolving the crystals in diethyl ether (Aldrich) and

then by sublimation *in vacuo* at 80 °C for 2 h. 0.35 g (2.08 mmol, 35%) of the air-stable,

yellow-orange ferrocene are obtained.

# Section three - Results and Discussion

## 1. Synthesis and physical properties of sodium cyclopentadienide, NaCp

As was previously mentioned[13], the traditional route to sodium cyclopentadienide is very tedious and involves multiple steps. In these multiple steps, the possibility that the reaction apparatus is not air tight, thus allowing humid air to enter and, consequently, oxidize or hydrolyze the desired product, is a major concern. This new one-step, one-pot method seems to have eliminated this concern. On the average, once the starting materials have been combined in the reaction vessel, the reaction needs to be run for ninety-six hours (four days). Although this is a longer reaction time than the traditional method, the advantages are obvious: the possibility that air can enter the reaction vessel has been drastically reduced and the investigator is not doing multiple steps that take up his/her time and equipment. The investigator needs only to ensure that the joints of the glassware are tight upon initial set-up only. The traditional method also requires the removal of the solvent from the sodium sand after it is created and then the addition of another nonpolar solvent so that the NaCp product may precipitate from solution. This removal/addition process not only leaves the newly-formed and highly activated sodium sand exposed to possible oxidation, but it also creates a potential explosion hazard if any moisture or halogenated solvents are present. Again, the new method alleviates this problem since there is no removal of the solvent after the sodium sand is created. The sodium sand is created in an inert solvent that is relatively nonpolar so that the NaCp may precipitate from it and the sodium sand is all consumed in the reaction flask.

The sodium cyclopentadienide created by the traditional method is typically pyrophoric. The NaCp created by the new method did not exhibit this pyrophoric nature. In fact, the off-white to beige product showed remarkable stability: it remained exposed to air for a period of one hour before any decomposition effects were demonstrated. The decomposition of the NaCp created *via* the new method was not violent in nature; the product simply "melted" to give a clear, brown liquid that had an odor similar to that of dicyclopentadiene. This enhanced stability may be explained by first examining the percent yield for this reaction. Upon doing the calculation to determine the percent yield, it is noticed that a percent yield of well over a hundred is obtained. This is usually an indication that the product is still "wet", meaning that the solvent has not been completely removed by drying the product using an oil pump vacuum. One possible explanation could be that the solvent has been incorporated into the crystal lattice. In the traditional method, it is not uncommon for at least one solvent molecule to be incorporated into the crystal lattice of NaCp.[4] This solvent molecule is usually a polar one, coordinating to the sodium cation. These polar solvent molecules interact with the alkali metal electrostatically; a large electrostatic component (cation-dipole interaction) and a smaller polarization component (cation-induced dipole interaction) are present with negligible ligand-to-metal charge transfer effects. [4,14,15] This "solvent effect" serves only to shield the relatively inert cation, leaving the reactive anion readily accessible to oxidation or hydrolysis. The accessibility of the electron-rich anion results in the pyrophoric decomposition event often exhibited by Cp-alkali metal complexes synthesized by the traditional method. The new method, however, does not leave the reactive anion as unprotected. It uses butyl ether, a large and relatively nonpolar solvent,

which may, if incorporated into the crystal lattice, create a protective barrier for the sensitive cyclopentadienyl anion. This can be accomplished in two ways. There could be no interaction between the solvent and the NaCp - the solvent simply fills holes present in the crystal lattice, thus providing added "bulk" around the anion. Alternatively, the butyl ether could be co-coordinated to the sodium through the oxygen atom, in a manner similar to THF. The bulky butyl groups could then create a shield around either side of the Cp anion. A diagram of this proposed shielding effect is shown below in **Fig. 5.3.1.**



| **Figure 5.3.1.** | One possible solvation effect of butyl ether on NaCp. |
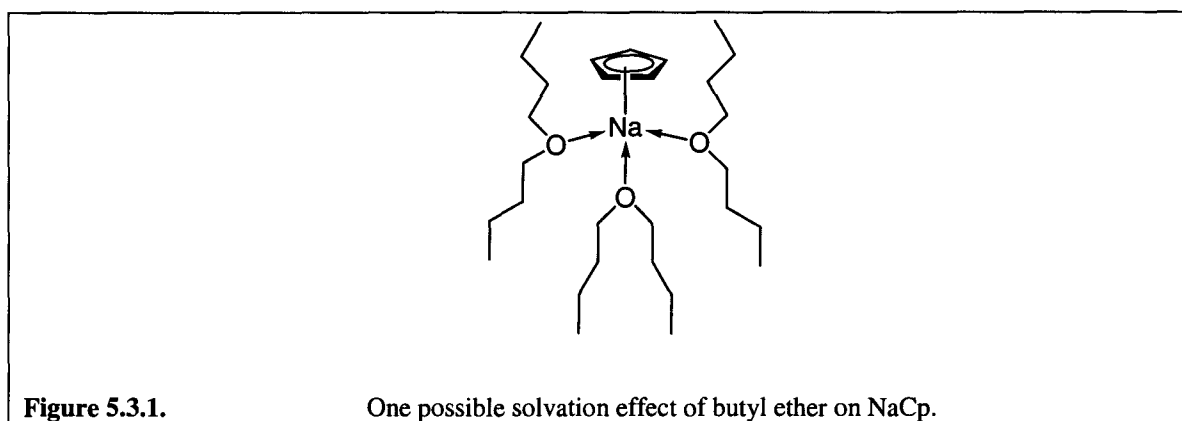
This shielding effect partially stabilizes the cyclopentadienyl anion, resulting in a decomposition event that is a much milder overall.

The cyclopentadienyl ring transfer capability is now called into question. The way that the ring transfer capability was tested was by synthesizing ferrocene from ferrous chloride and two equivalents of NaCp. The textbook yield for this reaction can be as high as 90%, with the average yield being 67-73%.[16] For the new method to even be considered viable, an atom transfer rate at least equal to that of the old method must be obtained. When this synthesis was done, a yield of 35% was obtained. This is half of the standard literature value for this reaction. While this low yield is discouraging, it can be attributed to the inexperience of the investigator since yields of 90+% have been reported by other individuals using solid NaCp in more demanding reactions.

## 2. Synthesis and physical properties of pentamethylcyclopentadienyl sodium,

## NaCp*

Pentamethylcyclopentadienyl sodium was produced as an off white-to-gray powder in a 38.6% yield. The use of a non-polar solvent seemed to have had no effect on the stability of the product, as the powder remained pyrophoric and air sensitive: the NaCp* would "crackle" and spark simply upon transferring the material from one flask to the other. The product is also moisture sensitive. During the writing of this thesis, a flask with ca. two grams of NaCp* that was stored in the freezer leaked. This resulted in not only air getting into the flask, but moisture as well. The violent reaction that followed not only blew the freezer door open, it also melted the plastic clamp that held the glass stopper on, and shot the stopper across the room. An explanation for the higher reactivity of NaCp* compared to NaCp are the methyl ring substituents. A methyl group is electron donating in character. It will then donate electron density to the cyclopentadienyl ring. The cyclopentadienyl ring now has more electron density localized in the aromatic ring, making it more reactive towards oxidation and/or hydrolyses. Thus, when decomposition occurs, the event is rapid, resulting in a more violent event overall. In contrast to NaCp, no stabilizing effect of the butyl ether was observed for NaCp*. An explanation for this is that steric repulsion between the ring substituents and the butyl ether prohibits the butyl ether from forming the "protective wall" close enough to the cyclopentadienyl anion. No attempts to investigate the ring transfer capabilities were undertaken due to the pyrophoric nature of the product as well as the inconclusive results achieved from the NaCp study.

# Section four- Conclusions

This study has shown that, while the new method presents fewer hazards to the investigator and does indeed produce NaCp that is remarkably air-stable, the cyclopentadiene ring transfer capabilities of only 50% of literature values for the synthesis of ferrocene can be attributed to the inexperience of the investigator. NaCp is used as a transfer reagent because of its reactivity and relatively inexpensive cost. The new method yields NaCp that is more stable. This method did not, however, yield NaCp* that showed enhanced stability. Other Cp-like ligands, such as indene, resisted isolation. This could have been due to isolation issues, with the sodium indenide being soluble in the butyl ether (another solvent, such as decane, may be better suited to this reaction due to its lower polarity). Further investigations are needed to determine exactly what effects the solvent does have on both the stability and the reactivity of the NaCp that is produced in this one-step-one-pot method.

During the writing of this thesis, another research group did, in fact, investigate this one-pot synthesis for both NaCp and KCp. Instead of using a non-polar solvent, their reaction was carried out in neat dicyclopentadiene, resulting in the formation of analytically pure NaCp in excellent yield (99%).[17]

# Section five- References

1. D.F Shiver, P.W Atkins. *Inorganic Chemistry*, 3$^{rd}$ ed.; Oxford University Press: New York, 1999; Chapter 16.

2. C. Elschenbroich, A Salzer. *Organometallics A Concise Introduction*, 2$^{nd}$ rev. ed.; VCH: New York, 1992; Chapter 15.

3. T. Aoyagi, H.M.M. Shearer, K. Wade, G. Whitehead. *J. Organomet. Chem.* **1979**, *175*, 21.

4. S.M. Csicsery. *J. Org. Chem.* **1960**, *25*, 518-521.

5. J. Thiele. *Dtsch. Chem. Ges.* **1900**, *33*, 666.

6. S. Harder. *Coordination Chemistry Reviews* **1998**, *176*, 17-66.

7. J. Thiele. *Dtsch. Chem. Ges.* **1901**, *34*, 68.

8. C. Lambert, P. von R. Schleyer. *Angew. Chem.* **1994**, *106*, 1187.

9. C. Lambert, P. von R. Schleyer. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129.

10. S. Harder. Ph.D. Thesis, University of Ultrescht, The Netherlands, 1990, p.2.

11. S. Alexandratos, A. Streitwieser, H. F. Schaefer III. *J. Am. Chem. Soc.* **1976**, *98*, 7959.

12. R. E. Dinnebier, U. Behrens, F. Olbrich. *Organometallics* **1997**, *16*, 3855.

13. A. D. Hunter. "Evaluation of Air Stable Cyclopentadienyl Ligands". Grant proposal 2002

14. G. Corongui, E. P. Clementi, W. Simone. *J. Chem. Phys.* **1980**, *72*, 3096.

15. E. Kaufmann, B. Tidor, P. von R. Schleyer. *J. Comput. Chem.* **1986**, *7*, 334.

16. G. Wilkinson. Ferrocene. In *Organic Syntheses Collective Volume*, 2nd Ed.; Rabjogn, N.; Wiley: New York, 1963, 4, 473-477.

17. T. K. Panda, M. T. Gamer, P. W. Roesky. *Organometallics*. **2003**, *22*, 877-878.

# Chapter VI- Crystallography

# Section one- Introduction

## SubSection One-Crystals

### 6.1.1a. Crystal growth

There are a variety of methods that can be used to grow crystals suitable for X-ray diffraction studies. These different methods all share the same basic steps for crystal growth: nucleation, growth, and termination.

Nucleation is the process of forming the initial aggregate that growth will occur from.[1] This aggregate is formed by the chance association of molecules in solution that happen to have the same orientation or, more commonly, on the surface of the vessel or an adventitious solid. The number of nucleation sites that form play an important role in the crystallization process. Too many sites will result in micro crystals that are not suitable (too small) for X-ray diffraction. Only a few nucleation sites should be present to obtain X-ray quality crystals.

Once the initial nucleus has been formed, crystal growth can now take place by deposition of material onto that nucleus. The strength of the interaction between molecules or ions determines whether or not growth will occur.[1] These interactions tend to be stronger at defect sites. These "defect sites" are sites at which there is a "hole" or "ledge" present from the asymmetrical growth of the crystal as shown in **Figure 6.1.1**. The new material can then "fill the gap". Crystals of suitable quality are formed when the

rate at which material is deposited onto the nucleation site and the rate at which the curing of these defect in the crystal's growth is approximately equal. Rapid deposition may cause growth in too many directions (i.e. formation of dendrites), while a rapid rate of curing of the defect sites may result in early termination of the crystal's growth (i.e. there is still material left in solution, but it will not deposit onto the crystal because of weak interactions).[1]
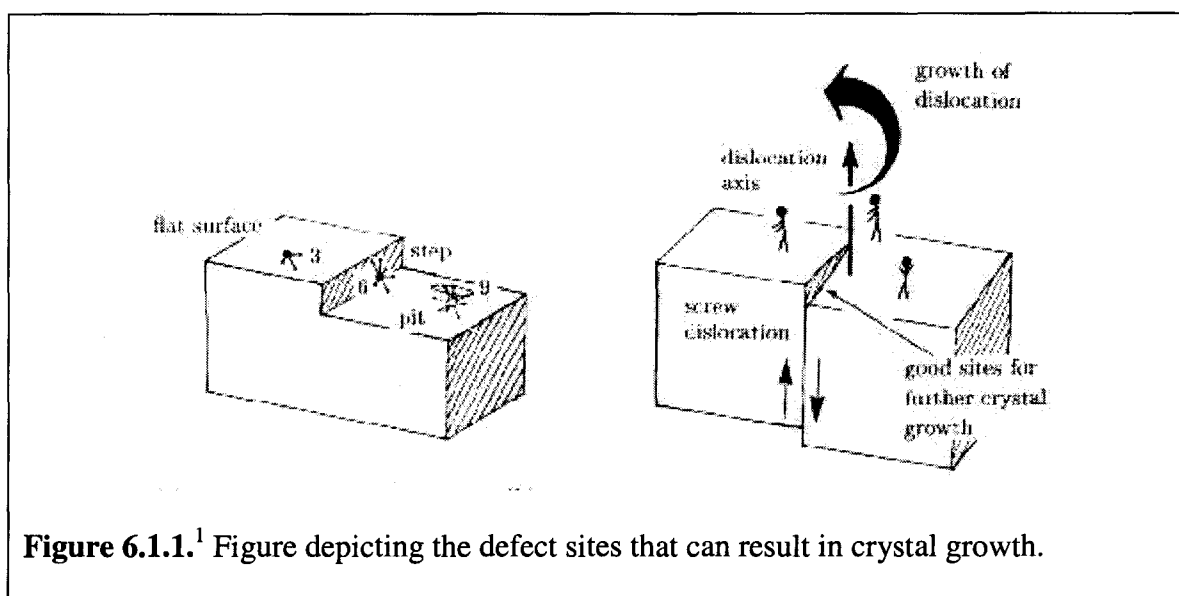


**Figure 6.1.1.**[1] Figure depicting the defect sites that can result in crystal growth.

Termination of the crystal's growth can occur by two methods. As mentioned above, termination can occur when the rate at which the healing of the defect sites is high. More commonly, termination occurs when there is simply no more material left to deposit onto the crystal because the solution is no longer supersaturated.

The most common method for growing crystals of small molecules (also the method used exclusively throughout the course of this work) is crystallization by slow solvent evaporation. A saturated solution of the compound to be crystallized is first made

from an appropriate solvent. A second solvent that the compound of interest is not soluble in is then layered on top of the first solvent and that second solvent is allowed to slowly diffuse into the mixture. The mixture is then allowed to stand undisturbed (usually in the refrigerator of freezer to decrease the solubility of the compound of interest) and, as the name implies, the rate of crystal growth is dependent upon the rate at which the solvent evaporates. Ideally, slow evaporation is desired in order to produce well defined, X-ray diffraction quality crystals. Fast solvent evaporation often produces crystals that have grown together and are of too low quality for diffraction studies.

Crystallization by hanging/sitting drop methods is the preferred method for growing crystals of proteins.[1] In this method, 5-15 μL of a concentrated protein solution containing insoluble precipitates is suspended from a silicone-treated glass slide and placed over a spot place reservoir that contains an addition 500 μL of the concentrated precipitate solution. Protein crystals form as equilibrium between the hanging drop and the solution is reached.[1]

**6.1.1b. Crystal Selection**

Crystal selection is often the hardest aspect of an X-ray diffraction study. Many different factors need to be considered when choosing a crystal: size, morphology, etc. Internal properties (i.e. ordering of the unit cell, solvent molecules incorporated into the crystal lattice, rotational freedoms of functional groups present) of the crystal will also play a role in whether or not it is suitable for diffraction studies. For this reason, just

because a crystal appears to be well defined and of the right size does not mean that that crystal will be suitable for X-ray diffraction studies.

In general, a suitable crystal should be no larger than 0.5 mm × 0.5 mm × 0.5 mm and no smaller than 0.1 mm in all dimensions (these numbers only provide a guideline; smaller or larger crystals can be evaluated on a case-by-case basis). If the crystal is too small in one or more dimensions, the X-ray beam is not diffracted off of the crystal sufficiently strongly. This then, results in the loss of data, as the number of reflections that should be present from that particular orientation of the crystal are dramatically lowered, possibly to the point of none being present at all. If the crystal is too big in one of the dimensions, it projects outside of the homogeneous region of the X-ray or eventually out of the beam which will also badly systematically bias the data.

As noted, the internal properties of the crystal also play a role in whether or not a crystal is suitable for diffraction studies. A crystal may appear to be suitable, but when the diffraction study is done, the crystal is found to be unsuitable for a number of reasons. A crystal that appears to be crystalline can be made up of many micro crystals. This will result in the crystal giving a diffraction pattern which resembles that given by a powder with a greater or lesser degree of preferential alignment of the crystallites. Rotational disorder and/or flip disorder may be present within the crystal (i.e. $CF_3$ groups exhibit rotation disorder, while flip disorder can be seen in thiophene rings). Rotational disorder, like the name suggests, arises from the motion of atoms within the solid crystal. Flip disorder is seen primarily in compounds that contain substituents in the form of rings (i.e. thiophenes, phenyl, etc.). Flip disorder is much like rotational disorder, except that instead of the ring rotating, the ring is flipping back and forth rapidly. Although both

types of dynamic disorder (motion within a crystal) can usually be accommodated for, depending on the overall amount of disorder present, it may still have an effect on how well the structure of that given compound can be determined (i.e. the thermal displacement parameters of the atoms effected by the disorder may be abnormally large).

**Subsection Two-Diffraction**

### 6.1.2a Components of a Diffractometer

#### A. X-ray generators

The most common (and least inexpensive) type of X-ray generators is the sealed X-ray tube. Within these vacuum sealed tubes, a high DC voltage is used to accelerate electrons towards a metal anode target.[1, 2] Upon striking the metal target, a 1s electron is ejected and sharp X-ray bands ($K_\alpha$ waves) are produced as electrons fall from the n = 2 quantum shell to the n = 1 shell.[2] The $K_\alpha$ wavelengths produced are dependant upon the metal being used as the target. Two suitable metals are Cu and Mo, which produce $K_\alpha$ waves at 1.54179 Å and 0.71073 Å, respectively (i.e. these are the composite values of the $K_{\alpha 1}$ and $K_{\alpha 2}$ of each).

The maximum power level of the X-ray tubes is limited primarily by how quickly heat can be removed from the tube.[1, 2] As the electrons collide with the metal target and with themselves, heat is produced. This heat, if not properly dissipated, can melt the metal target. In order to remove this heat, the X-ray tubes are cooled by circulated water running through the back of the tube past the metal target. The tubes are not typically run at a power rating of 100%, but rather at 80% to extend the life of the tubes. This translates into a voltage of 40 kV and a current of 40 mA (1600 W of total power, 2000 W maximum power) for Cu tubes and 40 kV and 50 mA (2000 W of total power, 2500 W maximum power) for Mo tubes in our lab.

Another type of X-ray generator is the rotating anode generator. The workings of this tube are very similar to that of the sealed tubes except that the metal target now rotates. The advantages of this type of generator are that the heat is removed over a much larger area due to the tube rotation. Because of the increased power now useable, the signal-to-noise (S/N) ratio may increase up to six times that obtained by a sealed tube generator, resulting in a better data set. The disadvantages, however, outweigh the advantages for many applications. These types of generators are more costly, much bigger, and require much more user maintenance to keep them functioning properly (i.e. monthly). Since the metal target rotates while under high voltage and vacuum and with water flowing through it, it is much less reliable.

## B. Detectors

The simplest type of detector used is the scintillation or point detector. This detector relies on directly measuring the X-ray beam flux rather than measuring the effects of the beam (i.e. the effects of the X-ray beam on photographic film).[1] The X-ray beam enters the detector and strikes a compound that emits photons of visible light, such as NaI.[1] The intensity of the emitted light is proportional to the intensity of the X-ray beam and is measured by a photomultiplier tube (PMT).[1] Although these types of detectors have very high counting efficiencies and are very reliable, they can only collect data on one single point at a time. Therefore, collection time tends to be rather long when a point detector is employed.

Multi-wire detectors are in the category of area detectors. Area detectors can collect a wide range of reflections at one time, meaning that the collection time when an area detector is used is much shorter than when a point detector is used. Because these types of detectors are flat, the data must be corrected to account for the differences in path length of the refracted X-ray beam. In a multi-wire detector, a wire anode array is sandwiched between two wire cathode arrays. The chamber is filled with a mixture of $Xe/CO_2$. The Xe is ionized upon X-rays entering the detector; the $Xe^+$ ions migrate to the cathode while the electrons produced from the ionization migrate towards the anode (the $CO_2$ serves to absorb UV light which can erroneously activate the signal cascade). The electronic potential generated is then recorded by the detector.[1]

A charge-coupled device, CCD, detector also belongs to the area detector family. Upon entering the detectors, X-rays strike a phosphor (usually doped ZnS) that emits visible light. This light is then transferred to a photocathode either directly (our APEX CCD) or *via* a fiber optic taper (other CCDs). One potential problem inherent to a CCD is that signal loss can occur through the fiber optic taper. Recent advance have corrected this problem and have also allowed for 1:1 imaging.

### C. Monochromator and Collimator

A graphite crystal monochromator is often used to filter out the undesired radiation bands (Bremstralung, $K_\beta$, etc.) from the desired $K_\alpha$ band. The undesired bands are absorbed, while the $K_\alpha$ bands are allowed to pass through the monochromator.[2] This process also produces some collimation.

The collimator is a hollow tube with an internal diameter of 0.1 to 1.0 mm (0.5 mm diameter set by "pinholes" was used in the work herein).[1, 2] The collimator reduces the angular spread of the X-ray beam and makes it nearly collinear.[2] The diameter of the collimator's pin holes also determines the maximum size of the crystal. Thus, the size of the crystal cannot exceed the width of the X-ray beam as mentioned previously in this introduction.

### D. Goniometer and Goniometer heads

Once a crystal has been selected, it needs to be held in place and oriented in the X-ray beam. This is done by the goniometer and the goniometer head. The crystal (if air stable) is first glued on the end of a very thin glass capillary (if the crystal is air sensitive, it can be sealed inside of a capillary tube). The capillary is fixed into a brass pin with epoxy which is then inserted into the goniometer head. This head is adjustable and allows for precise centering of the crystal so that it will constantly remain in the center of the X-ray beam. The goniometer head is then attached to the $\chi$ circle. There are four axes through which the crystal can be oriented by the goniometer: $\varphi$ (spindle axis of the goniometer head), $\omega$ (the angle between the diffraction vector and the plane of the $\chi$ circle), $\chi$ (the angle between the $\varphi$ axis and the base of the diffractometer), and $2\theta$ (angle between the incident and diffracted beams). The goniometer, through direction from the host computer, can then orient the crystal at any or almost any, depending on the goniometer design, arbitrary angle along these axes.[1, 2]

### 6.1.2b. Basic Principles of Diffraction

X-rays can be diffracted by electrons just as light can be diffracted by very small objects.[1] When X-rays are diffracted, a path difference is created between X-rays diffracting off of different parts of the lattice that is dependent upon the angle at which these beams are diffracted. Either constructive or deconstructive interference is then a result of the path differences.

One can think of a crystal lattice as having an infinite number of parallel planes running through it where these planes are spaced by a distance, d, from each other. The angle of the incidence of radiation is given by 90°- θ and is set equal to the angle of reflection.[1] For the $n$th reflection then, the difference in path length is given by

$$n\lambda = 2d\sin\theta$$

**Equation 6.2.1.** Bragg's Law

This equation is known as Bragg's Law. In order for coherent diffraction (diffraction in which the wavelength of the diffracted beam does not change, only the phase changes) to occur, the Bragg Equation must be met.[1] Since only a small number of reflections are diffracted at angles that satisfy Bragg's Law, the crystal is rotated through a number of different angular positions as described above in **subsection 1D**.

Using the analogy of diffraction of visible light by a series of slits, just as the diffraction pattern of the visible light is a result of the periodicity of the slits, the diffraction pattern of X-rays is a result of the periodicity of the crystal lattice.[1] The diffraction pattern for X-rays is determined by the atoms and the spacing of the atoms that are diffracting the X-ray beams. The diffraction pattern of X-rays by a crystal can then be further simplified into the sampling of the lattice points of an individual unit cell (smallest repeating unit in a crystal) within the crystal lattice.[1] The directions in space and the intensity of the diffracted beams can then be measured and attributed to the geometry and the arrangement of the atoms within the unit cell, respectively.

# Section two- Experimental

## 1. 4-bromothiophene-2-carboxaldehyde
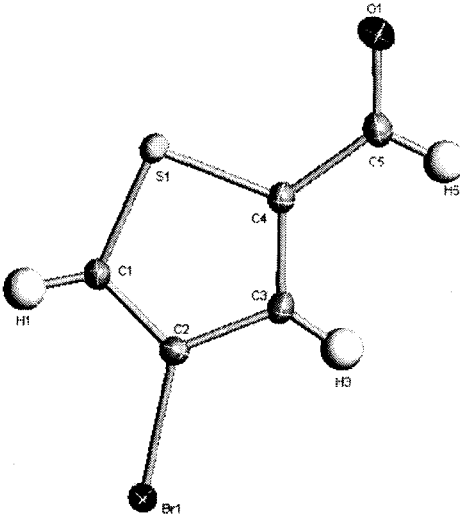
**Comment**

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from ethanol at 273 K.

All H atoms were placed in calculated positions, with C–H distances of 0.93 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom. This constraint was necessary due to the presences of the heavy atom bromine as the heavy atom would mask the presences of the hydrogen atoms next to it.

| Table 6.2.1a. Crystal data for 03JU06am | Table 6.2.1b. Data collection |
|---|---|
| $C_5H_3BrOS$ | Bruker SMART CCD area-detector |
| $Mr = 191.04$ | diffractometer |
| Monoclinic, $P2_1/c$ | $\omega$ scans |
| $a = 4.1169$ (4) Å | Absorption correction: multi-scan |
| $b = 8.4929$ (8) Å | $T_{min} = 0.141$, $T_{max} = 0.159$ |
| $c = 17.1626$ (16) Å | 5955 measured reflections |
| $\beta = 90.788$ (2) ° | 1499 independent reflections |
| $V = 600.02$ (10) Å$^3$ | 1408 reflections with $I > 2\sigma(I)$ |
| $Z = 4$ | $R_{int} = 0.034$ |
| $D_x = 2.115$ Mg m$^{-3}$ | $\theta_{max} = 28.3°$ |

| Mo K$_\alpha$ radiation | h = -5 $\rightarrow$ 5 |
|---|---|
| Cell parameters from 5955 reflections | k = -11 $\rightarrow$ 11 |
| $\theta$ = 2.4±28.3° | l = -22 $\rightarrow$ 22 |
| $\mu$ = 7.08 mm$^{-1}$ | |
| $T$ = 100 (2) K | |
| Cube, colorless | |
| 0.26 × 0.26 × 0.26 mm | |

| Table 6.2.1c. Refinement | Figure 6.2.1. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ |  |
| $R[F^2 > 2\sigma(F^2)] = 0.019$ | |
| $wR(F^2) = 0.047$ | |
| $S = 1.05$ | |
| 1499 reflections | |
| 73 parameters | |
| H-atom parameters constrained | |
| $w = 1/[\sigma^2(F_o^2) + (0.0039P)^2 + 0.449P]$ | |
| where P = $(F_o^2 + 2F_c^2)/3$ | |
| $(\Delta/\sigma)_{max} = 0.004$ | |
| $\Delta\rho_{max} = 0.50$ e×Å$^{-3}$ | |

| $\Delta\rho_{min} = -0.32\ e\times\text{Å}^{-3}$ | |
|---|---|

**Table 6.2.1d**

Selected geometric parameters (Å, °).

| | |
|---|---|
| Br1–C4 1.8804 (18) | C4–C5–S1 111.27 (14) |
| C5–C4 1.371 (2) | C5–C4–C3 113.67 (16) |
| C5–S1 1.7118 (19) | C5–C4–Br1 123.40 (14) |
| C4–C3 1.414 (2) | C3–C4–Br1 122.92 (13) |
| C3–C2 1.374 (2) | C2–C3–C4 111.23 (16) |
| C2–C1 1.457 (2) | C3–C2–C1 125.71 (16) |
| C2–S1 1.7218 (17) | C3–C2–S1 112.23 (13) |
| O1–C1 1.213 (2) | C1–C2–S1 122.03 (14) |
| | C5–S1–C2 91.61 (9) |
| | O1–C1–C2 124.39 (18) |

## 2. Zinc di(pyridin-2-yl)methanone diiodide
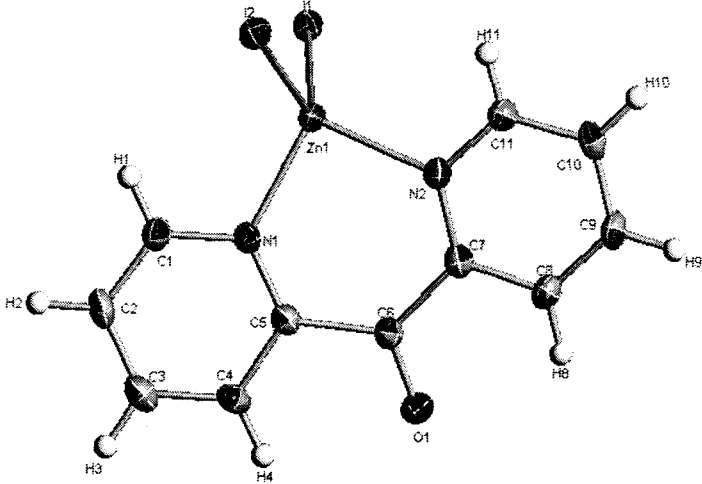
**Comment**

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from 1-butanol.

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H)$ = $1.2U_{eq}$ of the adjacent carbon atom. This constraint was necessary due to the presences of the heavy atom iodine as the heavy atom would mask the presences of the hydrogen atoms next to it.

| Table 6.2.2a. Crystal data for 03JU07am | Table 6.2.2b. Data collection |
|---|---|
| $C_{11}H_8I_2N_2OZn$ | Bruker SMART CCD area-detector |
| Mr = 503.36 | diffractometer |
| Monoclinic, $P2_1/c$ | $\omega$ scans |
| $a$ = 12.6266 (5) Å | Absorption correction: multi-scan |
| $b$ = 8.3959 (3) Å | $T_{min}$ = 0.42557, $T_{max}$ = 0.73 |
| $c$ = 13.1079 (5) Å | 13480 measured reflections |
| $\beta$ = 103.6490 (10)° | 3344 independent reflections |
| $V$ = 1350.35 (9) Å$^3$ | 3114 reflections with I > 2σ(I) |
| $Z$ = 4 | $R_{int}$ = 0.0344 |
| $D_x$ = 2.476 Mg m$^{-3}$ | $\theta_{max}$ = 28.28° |
| Mo K$_\alpha$ radiation | h = -16 → 16 |

| Cell parameters from 9564 reflections | k = -11 → 11 |
|---|---|
| $\theta = 2.906 \pm 28.271°$ | l = -17 → 17 |
| $\mu = 6.376\ mm^{-1}$ | |
| $T = 100\ (2)\ K$ | |
| Plate, yellow | |
| $0.29 \times 0.14 \times 0.05\ mm$ | |

| Table 6.2.2c. Refinement | Figure 6.2.2. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ <br><br> $R[F^2 > 2\sigma(F^2)] = 0.0281$ <br><br> $wR(F^2) = 0.0742$ <br><br> $S = 1.070$ <br><br> 3344 reflections <br><br> 186 parameters <br><br> H-atom parameters constrained <br><br> $w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 2.3356P]$ <br><br> where $P = (F_o^2 + 2F_c^2)/3$ <br><br> $(\Delta/\sigma)_{max} = 0.001$ <br><br> $\Delta\rho_{max} = 1.768\ e\times Å^{-3}$ |  |

| $\Delta\rho_{min} = -0.618\ e\times\text{Å}^{-3}$ | |
|---|---|

**Table 6.2.2d.**

Selected geometric parameters (Å, °).

| | |
|---|---|
| I1—Zn1 2.5321 (5) | N2—C1—H1 118 (2) |
| I2—Zn1 2.5520 (5) | C2—C1—H1 120 (2) |
| Zn1—N1 2.036 (3) | C11—N1—C7 118.4 (3) |
| Zn1—N2 2.042 (3) | C11—N1—Zn1 114.9 (2) |
| C1—N2 1.337 (5) | C7—N1—Zn1 126.6 (2) |
| C1—C2 1.389 (5) | O1—C6—C5 117.0 (3) |
| C1—H1 0.94 (4) | O1—C6—C7 117.4 (3) |
| N1—C11 1.342 (5) | C5—C6—C7 125.5 (3) |
| N1—C7 1.346 (5) | C11—C10—C9 118.6 (3) |
| C6—O1 1.212 (5) | C11—C10—H10 115 (3) |
| C6—C5 1.516 (5) | C9—C10—H10 127 (3) |
| C6—C7 1.522 (5) | N2—C5—C4 121.4 (3) |
| C10—C11 1.375 (5) | N2—C5—C6 123.1 (3) |
| C10—C9 1.387 (6) | C4—C5—C6 115.6 (3) |
| C10—H10 0.97 (6) | C1—N2—C5 118.9 (3) |
| C5—N2 1.353 (5) | C1—N2—Zn1 115.0 (2) |
| C5—C4 1.386 (5) | C5—N2—Zn1 125.9 (2) |
| C9—C8 1.375 (5) | C8—C9—C10 118.9 (4) |

| | |
|---|---|
| C9—H9 0.84 (5) | C8—C9—H9 117 (3) |
| C3—C2 1.381 (6) | C10—C9—H9 124 (3) |
| C3—C4 1.392 (5) | C2—C3—C4 119.3 (3) |
| C3—H3 0.93 (5) | C2—C3—H3 121 (3) |
| C11—H11 0.85 (5) | C4—C3—H3 119 (3) |
| C4—H4 0.92 (4) | N1—C11—C10 123.1 (4) |
| C8—C7 1.393 (5) | N1—C11—H11 111 (4) |
| C8—H8 0.91 (4) | C10—C11—H11 126 (4) |
| C2—H2 1.05 (5) | C5—C4—C3 119.2 (4) |
| N1—Zn1—N2 93.89 (12) | C5—C4—H4 119 (3) |
| N1—Zn1—I1 113.98 (8) | C3—C4—H4 122 (3) |
| N2—Zn1—I1 111.35 (8) | C9—C8—C7 119.6 (4) |
| N1—Zn1—I2 108.79 (9) | C9—C8—H8 119 (3) |
| N2—Zn1—I2 112.14 (8) | C7—C8—H8 121 (3) |
| I1—Zn1—I2 114.860 (17) | C3—C2—C1 118.3 (3) |
| N2—C1—C2 122.9 (3) | C3—C2—H2 121 (3) |
| | C1—C2—H2 120 (3) |
| | N1—C7—C8 121.3 (3) |
| | N1—C7—C6 122.7 (3) |
| | C8—C7—C6 115.9 (3) |

### 3. Zinc di(pyridin-2-yl)methanone dibromide

**Comment**

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from an acetonitrile/dichloromethane mixture.

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

The bromine analogue, like the iodine version, crystallizes in $P2_1/c$. The cell parameters are on average 0.3 Å shorter than that of its iodine brethren, as are the Zn-Br bond distances compared to the Zn-I bond distances. This is to be expected, as iodine is bigger than bromine. The iodine analogue appears to have refined better (judging by the R values) than its bromine counterpart.

| Table 6.2.3a. Crystal data for 03JU13am | Table 6.2.3b. Data collection |
|---|---|
| $C_{11}H_8N_2Br_2OZn$ | Bruker SMART CCD area-detector |
| Mr = 409.38 | diffractometer |
| Monoclinic, $P2_1/c$ | $\omega$ scans |
| $a = 12.300\ (2)$ Å | Absorption correction: multi-scan |
| $b = 8.0699\ (16)$ Å | $T_{min} = 0.15,\ T_{max} = 0.27$ |
| $c = 12.751\ (3)$ Å | 11266 measured reflections |

| | |
|---|---|
| $\beta = 103.229 \ (3)^\circ$ | 3052 independent reflections |
| $V = 1232.1 \ (4) \ \text{Å}^3$ | 2600 reflections with $I > 2\sigma(I)$ |
| $Z = 4$ | $R_{int} = 0.0579$ |
| $D_x = 2.207 \ \text{Mg m}^{-3}$ | $\theta_{max} = 28.36^\circ$ |
| Mo $K_\alpha$ radiation | $h = -16 \rightarrow 16$ |
| Cell parameters from 7592 reflections | $k = -10 \rightarrow 10$ |
| $\theta = 2.62 \pm 28.381^\circ$ | $l = -16 \rightarrow 17$ |
| $\mu = 8.461 \ \text{mm}^{-1}$ | |
| $T = 100 \ (2) \ \text{K}$ | |
| Block, colorless | |
| $0.264 \times 0.195 \times 0.152 \ \text{mm}$ | |

| Table 6.2.3c. Refinement | Figure 6.2.3. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ <br><br> $R[F^2 > 2\sigma(F^2)] = 0.0408$ <br><br> $wR(F^2) = 0.1005$ <br><br> $S = 1.003$ <br><br> 3052 reflections <br><br> 154 parameters <br><br> H-atom parameters constrained <br><br> $w = 1/[\sigma^2(F_o^2) +$ <br><br> $(0.0605P)^2 + 0.0000P]$ <br><br> where $P = (F_o^2 + 2F_c^2)/3$ <br><br> $(\Delta/\sigma)_{max} = 0.001$ <br><br> $\Delta\rho_{max} = 1.973$ e×Å$^{-3}$ <br><br> $\Delta\rho_{min} = -1.356$ e×Å$^{-3}$ |  |
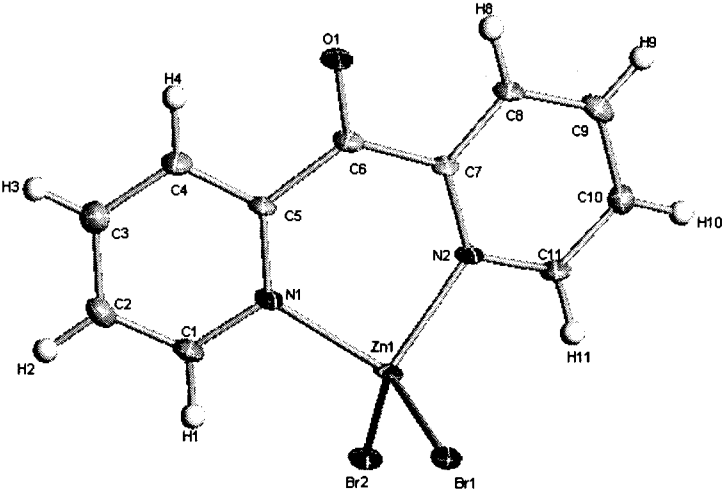
**Table 6.2.3d.**

Selected geometric parameters (Å, °).

| | |
|---|---|
| Br1—Zn1 2.3435 (7) | C1—N1—C5 118.1 (3) |
| Br2—Zn1 2.3658 (7) | C1—N1—Zn1 115.2 (3) |
| Zn1—N1 2.029 (3) | C5—N1—Zn1 126.7 (3) |
| Zn1—N2 2.040 (3) | O1—C6—C7 116.9 (3) |
| N2—C11 1.346 (5) | O1—C6—C5 116.8 (3) |
| N2—C7 1.357 (5) | C7—C6—C5 126.0 (3) |
| N1—C1 1.347 (5) | N2—C7—C8 120.8 (3) |
| N1—C5 1.359 (5) | N2—C7—C6 122.7 (3) |
| C6—O1 1.213 (5) | C8—C7—C6 116.6 (3) |
| C6—C7 1.518 (5) | N1—C1—C2 123.1 (4) |
| C6—C5 1.521 (5) | N1—C1—H1 118.4 |
| C7—C8 1.395 (5) | C2—C1—H1 118.4 |
| C1—C2 1.382 (6) | C1—C2—C3 118.7 (4) |
| C1—H1 0.9500 | C1—C2—H2 120.6 |
| C2—C3 1.383 (6) | C3—C2—H2 120.6 |
| C2—H2 0.9500 | N1—C5—C4 121.6 (3) |
| C5—C4 1.386 (5) | N1—C5—C6 122.0 (3) |
| C3—C4 1.388 (6) | C4—C5—C6 116.4 (3) |
| C3—H3 0.9500 | C2—C3—C4 119.0 (4) |
| C11—C10 1.386 (5) | C2—C3—H3 120.5 |
| C11—H11 0.9500 | C4—C3—H3 120.5 |

| | |
|---|---|
| C9—C10 1.380 (6) | N2—C11—C10 122.5 (4) |
| C9—C8 1.384 (5) | N2—C11—H11 118.7 |
| C9—H9 0.9500 | C10—C11—H11 118.7 |
| C8—H8 0.9500 | C10—C9—C8 119.1 (4) |
| C10—H10 0.9500 | C10—C9—H9 120.5 |
| C4—H4 0.9500 | C8—C9—H9 120.5 |
| N1—Zn1—N2 94.16 (13) | C9—C8—C7 119.8 (4) |
| N1—Zn1—Br1 113.32 (9) | C9—C8—H8 120.1 |
| N2—Zn1—Br1 110.52 (9) | C7—C8—H8 120.1 |
| N1—Zn1—Br2 108.42 (9) | C9—C10—C11 118.9 (4) |
| N2—Zn1—Br2 111.46 (9) | C9—C10—H10 120.6 |
| Br1—Zn1—Br2 116.72 (2) | C11—C10—H10 120.6 |
| C11—N2—C7 118.9 (3) | C5—C4—C3 119.5 (4) |
| C11—N2—Zn1 115.1 (2) | C5—C4—H4 120.2 |
| C7—N2—Zn1 125.9 (3) | C3—C4—H4 120.2 |

## 4. N-(9 H-fluoren-9-ylidene)-N-(4-methoxyphenyl)amine

## Comment

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was made by heating 9-fluorenone, 4-methoxyaniline, $p$-toluenesulfonic acid and toluene under reflux for 24 h.

All H atoms were placed in calculated positions, with aromatic and methyl C–H distances of 0.95 and 0.98 Å, respectively, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

| Table 6.2.4a. Crystal data for 03JU10am | Table 6.2.4b. Data collection |
|---|---|
| $C_{20}H_{15}NO$ | Bruker SMART CCD area-detector |
| Mr = 285.33 | diffractometer |
| Monoclinic, C2/c | $\omega$ scans |
| $a$ = 19.0275 (10) Å | Absorption correction: multi-scan |
| $b$ = 9.8262 (5) Å | $T_{min}$ = 0.922, $T_{max}$ = 0.968 |
| $c$ = 17.4862 (10) Å | 14415 measured reflections |
| $\beta$ = 118.4860 (10)° | 3565 independent reflections |
| $V$ = 2873.5 (3) Å$^3$ | 3287 reflections with I > 2σ(I) |
| $Z$ = 8 | $R_{int}$ = 0.042 |
| $D_x$ = 1.319 Mg m$^{-3}$ | $\theta_{max}$ = 28.3° |
| Mo K$_\alpha$ radiation | h = -25 → 25 |
| Cell parameters from 14878 reflections | k = -13 → 13 |

| $\theta = 2.4\pm28.3°$ | $l = -23 \rightarrow 23$ |
|---|---|
| $\mu = 0.08$ mm$^{-1}$ | |
| $T = 100$ (2) K | |
| Parallelepiped, orange | |
| $0.60 \times 0.56 \times 0.35$ mm | |

| Table 6.2.4c.<br><br>Refinement | Figure 6.2.4. ORTEP plot of title compound. Ellipsoids are at<br><br>the 50% probability level. |
|---|---|
| Refinement on $F^2$<br><br>$R[F^2 > 2\sigma(F^2)] = 0.042$<br><br>$wR(F^2) = 0.115$<br><br>$S = 1.08$<br><br>3287 reflections<br><br>199 parameters<br><br>H-atom parameters<br><br>constrained<br><br>$w = 1/[\sigma^2(F_o^2) +$<br><br>$(0.0646P)^2 + 1.5364P]$<br><br>where $P = (F_o^2 +$<br><br>$2F_c^2)/3$<br><br>$(\Delta/\sigma)_{max} = 0.003$<br><br>$\Delta\rho_{max} = 0.37$ e×Å$^{-3}$ |  |

| $\Delta\rho_{min} = -0.28$ e×Å$^{-3}$ | |
|---|---|
| | |

**Table 6.2.4d.**

Selected geometric parameters (Å, °).

| | |
|---|---|
| O1—C14 1.3758 (11) | C31—C32—C33 132.28 (9) |
| O1—C17 1.4235 (12) | C27—C32—C33 107.71 (8) |
| N1—C33 1.2816 (12) | C16—C11—C12 118.84 (9) |
| N1—C11 1.4186 (12) | C16—C11—N1 121.79 (9) |
| C16—C11 1.3914 (13) | C12—C11—N1 118.93 (9) |
| C16—C15 1.3953 (13) | C13—C12—C11 120.59 (9) |
| C16—H16 0.973 (14) | C13—C12—H12 119.8 (8) |
| C33—C21 1.4874 (13) | C11—C12—H12 119.6 (8) |
| C33—C32 1.4983 (12) | C12—C13—C14 119.99 (9) |
| C15—C14 1.3915 (13) | C12—C13—H13 121.0 (8) |
| C15—H15 0.955 (14) | C14—C13—H13 119.0 (8) |
| C32—C31 1.3904 (13) | C24—C23—C22 120.45 (9) |
| C32—C27 1.4125 (13) | C24—C23—H23 117.9 (8) |
| C11—C12 1.4008 (13) | C22—C23—H23 121.6 (8) |
| C12—C13 1.3853 (14) | C25—C26—C21 120.57 (9) |
| C12—H12 0.961 (14) | C25—C26—C27 131.06 (9) |
| C13—C14 1.3966 (13) | C21—C26—C27 108.27 (8) |
| C13—H13 0.982 (14) | C22—C21—C26 121.30 (9) |

| | |
|---|---|
| C23—C24 1.3950 (14) | C22—C21—C33 129.55 (9) |
| C23—C22 1.3955 (14) | C26—C21—C33 109.12 (8) |
| C23—H23 0.966 (14) | C26—C25—C24 118.06 (9) |
| C26—C25 1.3881 (13) | C26—C25—H25 120.6 (8) |
| C26—C21 1.4025 (13) | C24—C25—H25 121.3 (8) |
| C26—C27 1.4717 (13) | O1—C14—C15 124.18 (8) |
| C21—C22 1.3846 (13) | O1—C14—C13 115.74 (8) |
| C25—C24 1.3962 (14) | C15—C14—C13 120.08 (9) |
| C25—H25 0.991 (14) | C27—C28—C29 118.36 (9) |
| C28—C27 1.3855 (13) | C27—C28—H28 120.5 (8) |
| C28—C29 1.3934 (14) | C29—C28—H28 121.1 (8) |
| C28—H28 0.979 (14) | C32—C31—C30 118.54 (9) |
| C31—C30 1.3994 (13) | C32—C31—H31 121.5 (8) |
| C31—H31 0.995 (14) | C30—C31—H31 120.0 (8) |
| C29—C30 1.3920 (14) | C28—C27—C32 121.45 (9) |
| C29—H29 0.995 (16) | C28—C27—C26 129.11 (9) |
| C30—H30 1.001 (14) | C32—C27—C26 109.30 (8) |
| C22—H22 0.998 (15) | C30—C29—C28 120.63 (9) |
| C24—H24 0.982 (14) | C30—C29—H29 119.1 (9) |
| C17—H1C 0.977 (16) | C28—C29—H29 120.2 (9) |
| C17—H1B 1.015 (16) | C29—C30—C31 121.19 (9) |
| C17—H1A 0.980 (16) | C29—C30—H30 120.6 (8) |
| C14—O1—C17 116.75 (7) | C31—C30—H30 118.2 (8) |

| | |
|---|---|
| C33—N1—C11 122.13 (8) | C21—C22—C23 118.28 (9) |
| C11—C16—C15 121.02 (9) | C21—C22—H22 121.5 (9) |
| C11—C16—H16 120.4 (8) | C23—C22—H22 120.2 (9) |
| C15—C16—H16 118.6 (8) | C23—C24—C25 121.32 (9) |
| N1—C33—C21 121.05 (8) | C23—C24—H24 119.1 (8) |
| N1—C33—C32 133.31 (9) | C25—C24—H24 119.6 (8) |
| C21—C33—C32 105.59 (7) | O1—C17—H1C 109.5 (9) |
| C14—C15—C16 119.44 (9) | O1—C17—H1B 110.2 (9) |
| C14—C15—H15 121.0 (8) | H1C—C17—H1B 110.2 (13) |
| C16—C15—H15 119.5 (8) | O1—C17—H1A 106.6 (9) |
| C31—C32—C27 119.80 (9) | H1C—C17—H1A 108.5 (13) |
| | H1B—C17—H1A 111.7 (12) |

### 5. 2,3-bis(5-bromothien-2-yl)quinoxaline
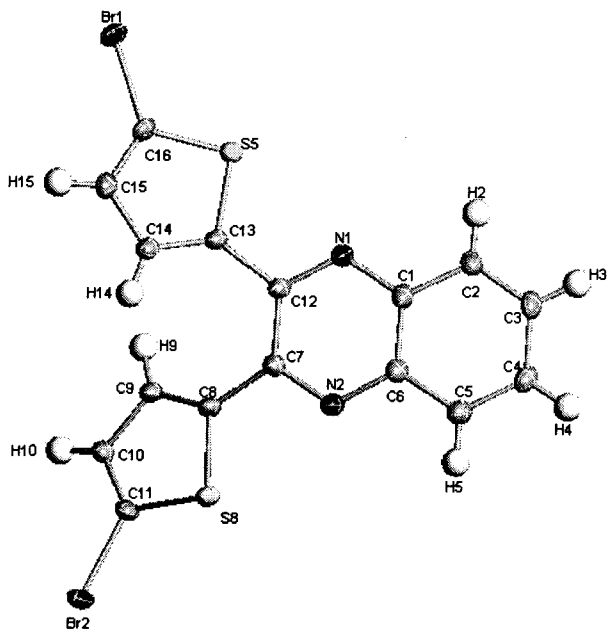
## Comment

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was made by reacting 1,2-phenylenediamine and 1,2-bis(5-bromothien-2-yl)-1,2-ethanedione in boiling ethanol.

All H atoms were placed in calculated positions, with C–H distance of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

| Table 6.2.5a. Crystal data for 03JU11am | Table 6.2.5b. Data collection |
|---|---|
| $C_{16}H_8Br_2N_2S_2$ | Bruker SMART CCD area-detector |
| $Mr = 452.18$ | diffractometer |
| Triclinic, $P\bar{1}$ | $\omega$ scans |
| $a = 8.8701\ (9)$ Å | Absorption correction: multi-scan |
| $b = 9.0664\ (9)$ Å | $T_{min} = 0.018,\ T_{max} = 0.466$ |
| $c = 11.1751\ (11)$ Å | 7531 measured reflections |
| $\beta = 79.998\ (2)^{\circ}$ | 3818 independent reflections |
| $V = 781.51\ (13)$ Å$^3$ | 3126 reflections with $I > 2\sigma(I)$ |
| $Z = 2$ | $R_{int} = 0.044$ |
| $D_x = 1.922$ Mg m$^{-3}$ | $\theta_{max} = 28.4^{\circ}$ |

| Mo K$_\alpha$ radiation | h = -11 → 11 |
|---|---|
| Cell parameters from 7531 reflections | k = -12 → 12 |
| $\theta$ = 1.9±28.4° | l = -14 → 14 |
| $\mu$ = 5.45 mm$^{-1}$ | |
| T = 100 (2) K | |
| Thick plate, yellow | |
| 0.88 × 0.35 × 0.14 mm | |

| Table 6.2.5c. Refinement | Figure 6.2.5. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ <br><br> $R[F^2 > 2\sigma(F^2)] = 0.044$ <br><br> $wR(F^2) = 0.119$ <br><br> $S = 0.85$ <br><br> 3818 reflections <br><br> 199 parameters <br><br> H-atom parameters constrained <br><br> $w = 1/[\sigma^2(F_o^2) + (0.0927P)^2]$ <br><br> where P = $(F_o^2 + 2F_c^2)/3$ |  |

| $(\Delta/\sigma)_{max} = 0.001$ | |
|---|---|
| $\Delta\rho_{max} = 1.39\ e\times\text{Å}^{-3}$ | |
| $\Delta\rho_{min} = -1.08\ e\times\text{Å}^{-3}$ | |

**Table 6.2.5d.**

Selected geometric parameters (Å, °).

| | |
|---|---|
| Br2—C18 1.875 (3) | N1—C10—C15 114.6 (3) |
| Br1—C14 1.877 (3) | C1—C10—C15 124.2 (3) |
| S2—C18 1.721 (3) | C1—N2—C3 118.6 (3) |
| S2—C15 1.730 (3) | N1—C8—C3 120.8 (3) |
| S1—C14 1.722 (3) | N1—C8—C7 120.1 (3) |
| S1—C11 1.736 (3) | C3—C8—C7 119.1 (3) |
| C13—C14 1.350 (5) | C10—N1—C8 118.2 (3) |
| C13—C12 1.424 (4) | C11—C12—C13 113.4 (3) |
| C13—H13 0.9500 | C11—C12—H12 123.3 |
| C10—N1 1.318 (4) | C13—C12—H12 123.3 |
| C10—C1 1.451 (4) | C17—C18—S2 113.1 (2) |
| C10—C15 1.477 (4) | C17—C18—Br2 127.0 (3) |
| N2—C1 1.326 (4) | S2—C18—Br2 119.70 (18) |
| N2—C3 1.362 (4) | C15—C16—C17 113.3 (3) |
| C8—N1 1.361 (4) | C15—C16—H16 123.4 |
| C8—C3 1.418 (5) | C17—C16—H16 123.4 |

| | |
|---|---|
| C8—C7 1.423 (4) | C16—C15—C10 131.1 (3) |
| C12—C11 1.371 (4) | C16—C15—S2 111.4 (2) |
| C12—H12 0.9500 | C10—C15—S2 117.1 (2) |
| C18—C17 1.360 (5) | C12—C11—C1 131.6 (3) |
| C16—C15 1.370 (4) | C12—C11—S1 110.9 (2) |
| C16—C17 1.415 (5) | C1—C11—S1 117.0 (2) |
| C16—H16 0.9500 | C7—C6—C5 121.3 (3) |
| C11—C1 1.465 (4) | C7—C6—H6 119.4 |
| C6—C7 1.368 (5) | C5—C6—H6 119.4 |
| C6—C5 1.413 (5) | N2—C3—C4 119.5 (3) |
| C6—H6 0.9500 | N2—C3—C8 120.1 (3) |
| C3—C4 1.412 (5) | C4—C3—C8 120.1 (3) |
| C4—C5 1.376 (5) | C5—C4—C3 119.5 (3) |
| C4—H4 0.9500 | C5—C4—H4 120.2 |
| C5—H5 0.9500 | C3—C4—H4 120.2 |
| C17—H17 0.9500 | N2—C1—C10 120.1 (3) |
| C7—H7 0.9500 | N2—C1—C11 114.5 (3) |
| C18—S2—C15 90.67 (15) | C10—C1—C11 125.4 (3) |
| C14—S1—C11 90.77 (15) | C4—C5—C6 120.4 (3) |
| C14—C13—C12 111.4 (3) | C4—C5—H5 119.8 |
| C14—C13—H13 124.3 | C6—C5—H5 119.8 |
| C12—C13—H13 124.3 | C18—C17—C16 111.5 (3) |
| C13—C14—S1 113.4 (2) | C18—C17—H17 124.2 |

| | |
|---|---|
| C13—C14—Br1 126.4 (2) | C16—C17—H17 124.2 |
| S1—C14—Br1 120.16 (19) | C6—C7—C8 119.5 (3) |
| N1—C10—C1 121.1 (3) | C6—C7—H7 120.3 |
| | C8—C7—H7 120.3 |

## 6. 5,10,15,20-tetrakis(5'-methylthien-2'-yl)porphyrin

**Comment**
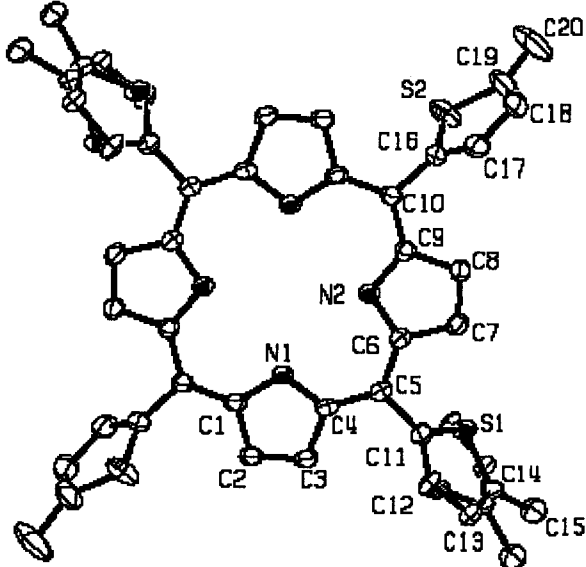
G. Crundwell from Central Connecticut State University provided the crystal investigated. It was prepared by the condensation of pyrrole and 5-methyl-2-thiophenecarboxaldehyde.

All H atoms were placed in calculated positions, with aromatic and methyl C–H distances of 0.95- 0.98 Å, respectively, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2\text{-}1.5U_{eq}$ of the adjacent carbon atom. The placement of the imino hydrogen on N1 was arbitrary, or from a difference map (i.e. Q peaks): placement on N1 over N2 had no significant effect on the refinement.

The major and minor components of ring 1 were modeled to be structurally equivalent. Thus, restraints were applied so that the overall geometry of the two component rings were identical. Due to the closeness of some of the disordered atoms, it also became necessary to define the thermal displacement parameters (and consequently their thermal ellipsoids) to be the same (e.g. C11 and C11B were given the same displacement parameters, as were C12 and C12B, C13 and C13B, seven sets of atoms in total).

| Table 6.2.6a. Crystal data for 03JU12am | Table 6.2.6b. Data collection |
|---|---|
| $C_{40}H_{30}N_4S_4$ <br><br> Mr = 452.18 | Bruker SMART CCD area-detector <br><br> diffractometer |

| | |
|---|---|
| Triclinic, $P\bar{1}$ | $\omega$ scans |
| $a = 6.5126 \ (7)$ Å | Absorption correction: multi-scan |
| $b = 10.499 \ (1)$ Å | $T_{min} = 0.659241$, $T_{max} = 1$ |
| $c = 12.635 \ (1)$ Å | 8653 measured reflections |
| $\beta = 79.141 \ (2)°$ | 4124 independent reflections |
| $V = 846.7 \ (16)$ Å$^3$ | 3692 reflections with $I > 2\sigma(I)$ |
| $Z = 1$ | $R_{int} = 0.0314$ |
| $D_x = 1.363$ Mg m$^{-3}$ | $\theta_{max} = 28.29°$ |
| Mo K$_\alpha$ radiation | $h = -8 \rightarrow 8$ |
| Cell parameters from 7344 reflections | $k = -13 \rightarrow 13$ |
| $\theta = 2.5095 \pm 28.2875°$ | $l = -16 \rightarrow 16$ |
| $\mu = 0.317$ mm$^{-1}$ | |
| $T = 100 \ (2)$ K | |
| Thin plate, purple | |
| $0.7 \times 0.6 \times 0.033$ mm | |

| Table 6.2.6c. Refinement | Figure 6.2.6. ORTEP plot of title compound. |
|---|---|
| | Ellipsoids are at the 50% probability level. |
| Refinement on $F^2$<br><br>$R[F^2 > 2\sigma(F^2)] = 0.0579$<br><br>$wR(F^2) = 0.149$<br><br>$S = 1.087$<br><br>4124 reflections<br><br>255 parameters<br><br>H-atom parameters constrained<br><br>$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.7520P]$<br><br>where $P = (F_o^2 + 2F_c^2)/3$<br><br>$(\Delta/\sigma)_{max} = 0.000$<br><br>$\Delta\rho_{max} = 0.536$ e×Å$^{-3}$<br><br>$\Delta\rho_{min} = -0.516$ e×Å$^{-3}$ |  |

| Table 6.2.6d. | |
|---|---|
| Selected geometric parameters (Å, °). | |
| S1—C16 1.685 (3) | C5—C16A—C17A 120.56 (14) |
| S1—C19 1.743 (3) | C18A—C17A—C16A 115.1 |
| C16—C5 1.467 (3) | C18A—C17A—H17A 122.4 |
| C16—C17 1.473 (4) | C16A—C17A—H17A 122.4 |
| C17—C18 1.289 (5) | C17A—C18A—C19A 113.6 |

| | |
|---|---|
| C17—H17 0.9500 | C17A—C18A—H18A 123.2 |
| C18—C19 1.340 (4) | C19A—C18A—H18A 123.2 |
| C18—H18 0.9500 | C20A—C19A—C18A 124.6 |
| C19—C20 1.506 (3) | C20A—C19A—S1A 125.15 (11) |
| C20—H20A 0.9800 | C18A—C19A—S1A 105.4 |
| C20—H20B 0.9800 | C19A—C20A—H20D 109.5 |
| C20—H20C 0.9800 | C19A—C20A—H20E 109.5 |
| S1A—C16A 1.4121 | H20D—C20A—H20E 109.5 |
| S1A—C19A 1.7787 | C19A—C20A—H20F 109.5 |
| C16A—C5 1.516 (3) | H20D—C20A—H20F 109.5 |
| C16A—C17A 1.7087 | H20E—C20A—H20F 109.5 |
| C17A—C18A 1.0785 | C11—S2—C14 92.56 (15) |
| C17A—H17A 0.9500 | C6—N2—C9 106.16 (18) |
| C18A—C19A 1.5079 | C6—N2—H1B 120 (7) |
| C18A—H18A 0.9500 | C9—N2—H1B 133 (7) |
| C19A—C20A 1.4940 (16) | C1—N1—C4 109.62 (17) |
| C20A—H20D 0.9800 | C1—N1—H1A 126 (3) |
| C20A—H20E 0.9800 | C4—N1—H1A 125 (3) |
| C20A—H20F 0.9800 | N2—C6—C5 126.39 (19) |
| S2—C11 1.729 (3) | N2—C6—C7 110.29 (18) |
| S2—C14 1.729 (3) | C5—C6—C7 123.32 (19) |
| N2—C6 1.365 (3) | C4—C5—C6 125.38 (19) |
| N2—C9 1.369 (3) | C4—C5—C16 116.6 (2) |

| | |
|---|---|
| N2—H1B 0.66 (8) | C6—C5—C16 118.0 (2) |
| N1—C1 1.366 (3) | C4—C5—C16A 116.5 (3) |
| N1—C4 1.372 (3) | C6—C5—C16A 118.1 (3) |
| N1—H1A 0.79 (4) | C16—C5—C16A 1.3 (2) |
| C6—C5 1.409 (3) | N2—C9—C10 125.80 (19) |
| C6—C7 1.448 (3) | N2—C9—C8 110.00 (18) |
| C5—C4 1.401 (3) | C10—C9—C8 124.21 (19) |
| C9—C10 1.407 (3) | C2—C3—C4 107.63 (19) |
| C9—C8 1.448 (3) | C2—C3—H3 128.6 (16) |
| C3—C2 1.358 (3) | C4—C3—H3 123.7 (16) |
| C3—C4 1.439 (3) | N1—C4—C5 126.18 (18) |
| C3—H3 0.95 (3) | N1—C4—C3 107.31 (18) |
| C10—C1i 1.399 (3) | C5—C4—C3 126.43 (19) |
| C10—C11 1.480 (3) | C1i—C10—C9 125.65 (19) |
| C1—C10i 1.399 (3) | C1i—C10—C11 116.85 (18) |
| C1—C2 1.436 (3) | C9—C10—C11 117.50 (19) |
| C7—C8 1.350 (3) | N1—C1—C10i 126.69 (18) |
| C7—H7 0.94 (3) | N1—C1—C2 107.44 (18) |
| C2—H2 0.93 (3) | C10i—C1—C2 125.68 (19) |
| C8—H8 0.93 (3) | C8—C7—C6 106.64 (19) |
| C11—C12 1.362 (3) | C8—C7—H7 128.2 (16) |
| C14—C13 1.336 (5) | C6—C7—H7 125.0 (16) |
| C14—C15 1.506 (5) | C3—C2—C1 107.99 (19) |

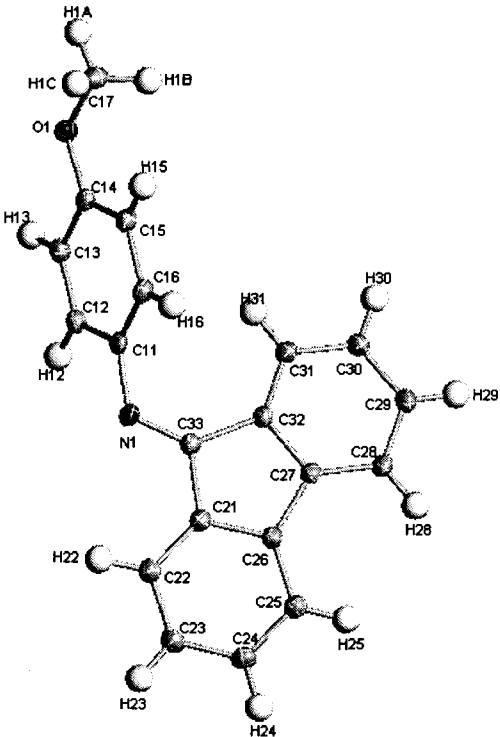| | |
|---|---|
| C12—C13 1.425 (4) | C3—C2—H2 130.9 (17) |
| C12—H12 0.92 (3) | C1—C2—H2 121.0 (17) |
| C13—H13 0.94 (4) | C7—C8—C9 106.91 (19) |
| C15—H15A 0.9800 | C7—C8—H8 128.0 (16) |
| C15—H15B 0.9800 | C9—C8—H8 125.1 (16) |
| C15—H15C 0.9800 | C12—C11—C10 130.2 (2) |
| C16—S1—C19 93.57 (14) | C12—C11—S2 110.00 (19) |
| C5—C16—C17 130.4 (3) | C10—C11—S2 119.71 (17) |
| C5—C16—S1 124.6 (2) | C13—C14—C15 130.1 (3) |
| C17—C16—S1 105.0 (2) | C13—C14—S2 110.5 (2) |
| C18—C17—C16 117.3 (3) | C15—C14—S2 119.5 (3) |
| C18—C17—H17 121.3 | C11—C12—C13 112.9 (3) |
| C16—C17—H17 121.3 | C11—C12—H12 125.9 (18) |
| C17—C18—C19 113.4 (3) | C13—C12—H12 121.2 (18) |
| C17—C18—H18 123.3 | C14—C13—C12 114.0 (3) |
| C19—C18—H18 123.3 | C14—C13—H13 126 (2) |
| C18—C19—C20 129.3 (3) | C12—C13—H13 120 (2) |
| C18—C19—S1 110.74 (19) | C14—C15—H15A 109.5 |
| C20—C19—S1 119.9 (2) | C14—C15—H15B 109.5 |
| C16A—S1A—C19A 97.7 | H15A—C15—H15B 109.5 |
| S1A—C16A—C5 132.19 (14) | C14—C15—H15C 109.5 |
| S1A—C16A—C17A 107.2 | H15A—C15—H15C 109.5 |
| | H15B—C15—H15C 109.5 |

## 7. 1,2-bis(4-bromothiopen-2-yl)ethane-1,2-dione

**Comment**

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from ethanol.

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

| Table 6.2.7a. Crystal data for 03JU15am | Table 6.2.7b. Data collection |
|---|---|
| $C_{10}H_4S_2Br_2O_2$ | Bruker SMART CCD area-detector |
| $Mr = 380.07$ | diffractometer |
| Orthorhombic, $P2_12_12$ | $\omega$ scans |
| $a = 8.522$ (2) Å | Absorption correction: multi-scan |
| $b = 16.890$ (4) Å | $T_{min} = 0.0936$, $T_{max} = 0.28$ |
| $c = 3.89331$ (9) Å | 5622 measured reflections |
| $V = 560.4$ (2) Å $^3$ | 1402 independent reflections |
| $Z = 2$ | 1368 reflections with $I > 2\sigma(I)$ |
| $D_x = 2.253$ Mg m$^{-3}$ | $R_{int} = 0.0750$ |
| Mo $K_\alpha$ radiation | $\theta_{max} = 28.31°$ |
| Cell parameters from 5567 reflections | $h = -11 \rightarrow 11$ |
| $\theta = 2.390\pm28.3075°$ | $k = -22 \rightarrow 22$ |

| $\mu = 7.583$ mm$^{-1}$ | $l = -5 \rightarrow 5$ |
|---|---|
| $T = 100\ (2)$ K | |
| Block, colorless | |
| $0.49 \times 0.27 \times 0.17$ mm | |

| Table 6.2.7c. Refinement | Figure 6.2.7. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ |  |
| $R[F^2 > 2\sigma(F^2)] = 0.0303$ | |
| $wR(F^2) = 0.0758$ | |
| $S = 1.064$ | |
| 1402 reflections | |
| 73 parameters | |
| H-atom parameters constrained | |
| $w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.0000P]$ | |
| where P $= (F_o^2 + 2F_c^2)/3$ | |
| $(\Delta/\sigma)_{max} = 0.001$ | |
| $\Delta\rho_{max} = 0.946$ e×Å$^{-3}$ | |
| $\Delta\rho_{min} = -0.801$ e×Å$^{-3}$ | |
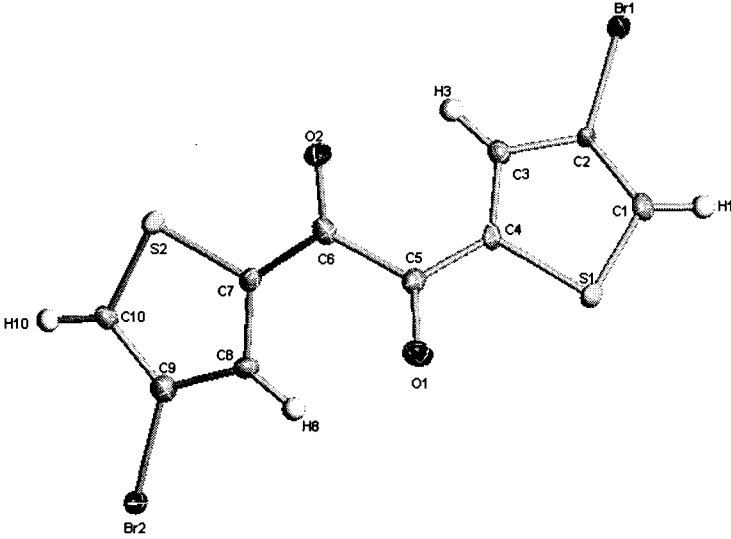
**Table 6.2.7d.**

Selected geometric parameters (Å, °).

| | |
|---|---|
| Br1—C3 1.886 (3) | C4—C3—Br1 124.1 (2) |
| S1—C4 1.712 (3) | C2—C3—Br1 121.9 (2) |
| S1—C1 1.730 (3) | C2—C1—C5 129.0 (3) |
| C3—C4 1.363 (4) | C2—C1—S1 112.0 (2) |
| C3—C2 1.414 (4) | C5—C1—S1 119.0 (2) |
| C1—C2 1.377 (4) | C3—C4—S1 111.5 (2) |
| C1—C5 1.462 (4) | C3—C4—H4 124.3 |
| C4—H4 0.9500 | S1—C4—H4 124.3 |
| C2—H2 0.9500 | C1—C2—C3 111.0 (3) |
| O1—C5 1.226 (4) | C1—C2—H2 124.5 |
| C5—C5i 1.531 (6) | C3—C2—H2 124.5 |
| C4—S1—C1 91.42 (15) | O1—C5—C1 123.4 (3) |
| C4—C3—C2 114.1 (3) | O1—C5—C5i 120.0 (3) |
| | C1—C5—C5i 116.6 (3) |

## 8. 5-nitro-2-thiophenecarboxaldehyde

### Comment

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown by re-crystallizing commercially available material from benzene (material purchased from Aldrich).

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) =$ 1.2$U_{eq}$ of the adjacent carbon atom.

| Table 6.2.8a. Crystal data for 04JU06a | Table 6.2.8b. Data collection |
|---|---|
| $C_5H_3SNO_3$ | Bruker SMART CCD area-detector |
| Mr = 157.14 | diffractometer |
| Orthorhombic, $Pn_{a2(1)}$ | $\omega$ scans |
| $a$ = 11.409 (5) Å | Absorption correction: multi-scan |
| $b$ = 13.936 (6) Å | $T_{min}$ = 0.77, $T_{max}$ = 0.9 |
| $c$ = 3.8479 (17) Å | 5484 measured reflections |
| $V$ = 611.8 (5) Å$^3$ | 1513 independent reflections |
| $Z$ = 4 | 1482 reflections with I > 2σ(I) |
| $D_x$ = 1.706 Mg m$^{-3}$ | $R_{int}$ = 0.0555 |
| Mo K$_\alpha$ radiation | $\theta_{max}$ = 28.35° |
| Cell parameters from 5589 reflections | h = -14 → 14 |

| $\theta = 2.307 \pm 28.348°$ | k = -18 → 18 |
|---|---|
| $\mu = 0.463$ mm$^{-1}$ | l = -5 → 5 |
| $T = 100$ (2) K | |
| Block, brown | |
| 0.55 × 0.24 × 0.24 mm | |

| **Table 6.2.8c.**<br><br>**Refinement** | **Figure 6.2.8.** ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$<br><br>$R[F^2 > 2\sigma(F^2)] = 0.0377$<br><br>$wR(F^2) = 0.0951$<br><br>$S = 1.067$<br><br>1513 reflections<br><br>103 parameters<br><br>H-atom parameters constrained<br><br>$w = 1/[\sigma^2(F_o^2) +$<br><br>$(0.0664P)^2 + 0.0662P]$<br><br>where P = $(F_o^2 + 2F_c^2)/3$<br><br>$(\Delta/\sigma)_{max} = 0.001$<br><br>$\Delta\rho_{max} = 0.482$ e×Å$^{-3}$<br><br>$\Delta\rho_{min} = -0.337$ e×Å$^{-3}$ |  |
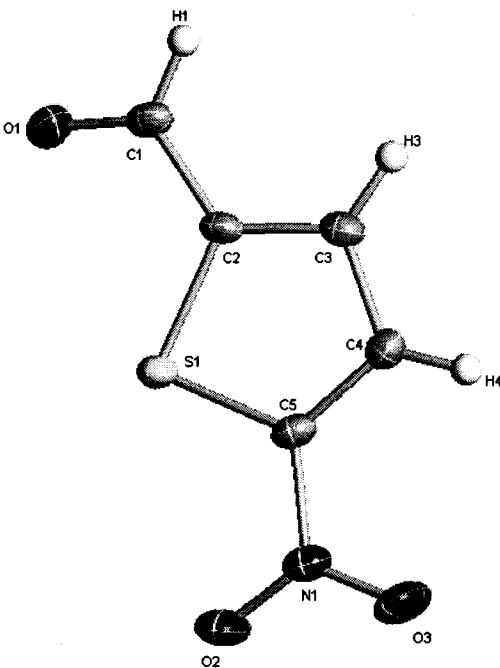
**Table 6.2.8d.**

Selected geometric parameters (Å, °).

| | |
|---|---|
| S1—C5 1.7103 (19) | C2—C1—H1 114.5 (19) |
| S1—C2 1.7247 (19) | C5—C4—C3 110.45 (18) |
| O1—C1 1.213 (3) | C5—C4—H4 122.7 (16) |
| O2—N1 1.222 (2) | C3—C4—H4 126.9 (16) |
| C1—C2 1.463 (3) | C2—C3—C4 111.98 (17) |
| C1—H1 0.91 (3) | C2—C3—H3 124.4 (16) |
| C4—C5 1.357 (3) | C4—C3—H3 123.7 (16) |
| C4—C3 1.414 (2) | C3—C2—C1 126.74 (17) |
| C4—H4 0.95 (2) | C3—C2—S1 113.20 (14) |
| O3—N1 1.220 (2) | C1—C2—S1 120.03 (15) |
| C3—C2 1.378 (3) | O3—N1—O2 124.77 (17) |
| C3—H3 0.93 (3) | O3—N1—C5 117.56 (17) |
| N1—C5 1.444 (2) | O2—N1—C5 117.67 (16) |
| C5—S1—C2 88.84 (10) | C4—C5—N1 124.95 (17) |
| O1—C1—C2 122.77 (19) | C4—C5—S1 115.53 (15) |
| O1—C1—H1 122.7 (19) | N1—C5—S1 119.50 (14) |

## 9. *N*-(9 H-fluoren-9-ylidene)-3,4-dimethylbenzenamine

**Comment**

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from hexane.

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

| Table 6.2.9a. Crystal data for 04JU07a | Table 6.2.9b. Data collection |
|---|---|
| $C_{21}H_{17}N$ | Bruker SMART CCD area-detector |
| Mr = 283.355 | diffractometer |
| Triclinic, $P\bar{1}$ | $\omega$ scans |
| $a$ = 8.476 (3) Å | Absorption correction: multi-scan |
| $b$ = 8.870 (3) Å | $T_{min}$ = 0.972, $T_{max}$ = 0.993 |
| $c$ = 10.376 (4) Å | 7401 measured reflections |
| $V$ = 752.095 (8) Å $^3$ | 3722 independent reflections |
| $Z$ = 2 | 3472 reflections with I > 2σ(I) |
| $D_x$ = 1.251 Mg m$^{-3}$ | $R_{int}$ = 0.0351 |
| Mo K$_\alpha$ radiation | $\theta_{max}$ = 28.47° |
| Cell parameters from 6350 reflections | h = -11 → 11 |
| $\theta$ = 2.342 ± 28.366° | k = -11 → 11 |

| $\mu = 0.07$ mm$^{-1}$ | $1 = -13 \rightarrow 13$ |
|---|---|
| $T = 100\ (2)$ K | |
| Block, orange | |
| $0.40 \times 0.34 \times 0.10$ mm | |

| Table 6.2.9c. Refinement | Figure 6.2.9. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ | |
| $R[F^2 > 2\sigma(F^2)] = 0.0543$ | |
| $wR(F^2) = 0.1463$ | |
| $S = 1.032$ | |
| 3722 reflections | |
| 201 parameters | |
| H-atom parameters constrained | |
| $w = 1/[\sigma^2(F_o^2) + (0.0808P)^2 + 0.24P]$ | |
| where P $= (F_o^2 + 2F_c^2)/3$ | |
| $(\Delta/\sigma)_{max} = 0.000$ | |
| $\Delta\rho_{max} = 0.49$ e×Å$^{-3}$ | |
| $\Delta\rho_{min} = -0.28$ e×Å$^{-3}$ | |
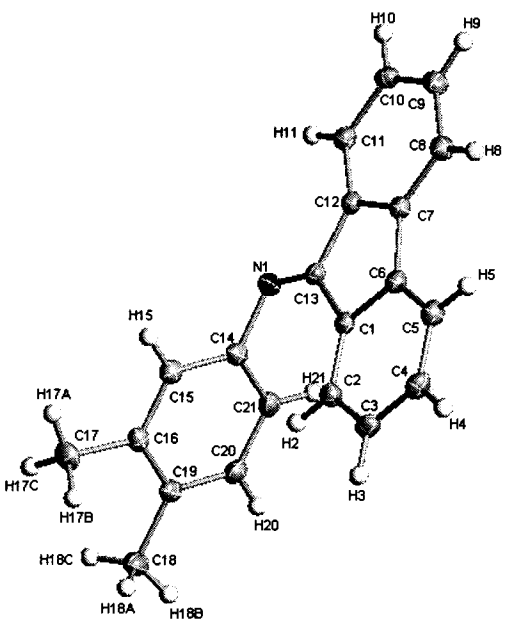


Figure 6.2.9. ORTEP plot of title compound. Ellipsoids are at the 50% probability level.

**Table 6.2.9d.**

Selected geometric parameters (Å, °).

| N(1)-C(8) | 1.2745(15) | N(1)-C(8)-C(9) | 132.58(10) |
|---|---|---|---|
| N(1)-C(7) | 1.4234(15) | C(20)-C(8)-C(9) | 105.45(9) |
| C(5)-C(4) | 1.3922(16) | C(13)-C(14)-C(9) | 120.82(10) |
| C(5)-C(7) | 1.3939(16) | C(13)-C(14)-C(15) | 129.77(10) |
| C(5)-H(5) | 0.983(16) | C(9)-C(14)-C(15) | 109.41(9) |
| C(4)-C(2) | 1.4046(17) | C(6)-C(3)-C(2) | 121.77(11) |
| C(4)-C(21) | 1.5057(17) | C(6)-C(3)-H(3) | 118.8(10) |
| C(2)-C(3) | 1.3912(17) | C(2)-C(3)-H(3) | 119.4(10) |
| C(2)-C(1) | 1.5054(16) | C(6)-C(7)-C(5) | 119.42(10) |
| C(15)-C(16) | 1.3866(16) | C(6)-C(7)-N(1) | 120.25(10) |
| C(15)-C(20) | 1.4035(15) | C(5)-C(7)-N(1) | 120.21(10) |
| C(15)-C(14) | 1.4712(16) | C(2)-C(1)-H(1B) | 110.7(10) |
| C(8)-C(20) | 1.4885(15) | C(2)-C(1)-H(1C) | 111.0(12) |
| C(8)-C(9) | 1.4982(15) | H(1B)-C(1)-H(1C) | 107.7(15) |
| C(14)-C(13) | 1.3885(15) | C(2)-C(1)-H(1A) | 111.1(12) |
| C(14)-C(9) | 1.4088(15) | H(1B)-C(1)-H(1A) | 107.2(15) |
| C(3)-C(6) | 1.3896(16) | H(1C)-C(1)-H(1A) | 109.0(17) |
| C(3)-H(3) | 0.981(16) | C(10)-C(9)-C(14) | 120.47(10) |
| C(7)-C(6) | 1.3891(17) | C(10)-C(9)-C(8) | 131.69(10) |
| C(1)-H(1B) | 0.995(18) | C(14)-C(9)-C(8) | 107.84(9) |

| | | | |
|---|---|---|---|
| C(1)-H(1C) | 1.02(2) | C(19)-C(20)-C(15) | 121.06(10) |
| C(1)-H(1A) | 1.00(2) | C(19)-C(20)-C(8) | 129.78(10) |
| C(9)-C(10) | 1.3901(16) | C(15)-C(20)-C(8) | 109.15(10) |
| C(20)-C(19) | 1.3842(16) | C(17)-C(18)-C(19) | 120.47(11) |
| C(18)-C(17) | 1.3937(16) | C(17)-C(18)-H(18) | 119.2(9) |
| C(18)-C(19) | 1.3953(16) | C(19)-C(18)-H(18) | 120.4(9) |
| C(18)-H(18) | 0.960(16) | C(15)-C(16)-C(17) | 118.47(11) |
| C(16)-C(17) | 1.3970(17) | C(15)-C(16)-H(16) | 121.3(9) |
| C(16)-H(16) | 0.991(16) | C(17)-C(16)-H(16) | 120.2(9) |
| C(6)-H(6) | 0.979(17) | C(7)-C(6)-C(3) | 119.43(11) |
| C(13)-C(12) | 1.3931(17) | C(7)-C(6)-H(6) | 118.6(9) |
| C(13)-H(13) | 0.992(17) | C(3)-C(6)-H(6) | 122.0(9) |
| C(11)-C(12) | 1.3894(18) | C(14)-C(13)-C(12) | 118.40(11) |
| C(11)-C(10) | 1.3983(16) | C(14)-C(13)-H(13) | 121.0(9) |
| C(11)-H(11) | 0.999(17) | C(12)-C(13)-H(13) | 120.6(9) |
| C(19)-H(19) | 0.990(17) | C(12)-C(11)-C(10) | 120.91(11) |
| C(10)-H(10) | 0.984(17) | C(12)-C(11)-H(11) | 120.2(10) |
| C(17)-H(17) | 1.004(16) | C(10)-C(11)-H(11) | 118.9(10) |
| C(12)-H(12) | 0.996(18) | C(20)-C(19)-C(18) | 118.56(10) |
| C(21)-H(21A) | 1.019(19) | C(20)-C(19)-H(19) | 120.0(10) |
| C(21)-H(21C) | 1.014(19) | C(18)-C(19)-H(19) | 121.5(10) |
| C(21)-H(21B) | 1.00(2) | C(9)-C(10)-C(11) | 118.39(11) |
| C(8)-N(1)-C(7) | 119.72(10) | C(9)-C(10)-H(10) | 121.9(10) |

| | | | | |
|---|---|---|---|---|
| C(4)-C(5)-C(7) | 121.23(11) | | C(11)-C(10)-H(10) | 119.8(10) |
| C(4)-C(5)-H(5) | 119.4(9) | | C(18)-C(17)-C(16) | 120.98(11) |
| C(7)-C(5)-H(5) | 119.4(9) | | C(18)-C(17)-H(17) | 118.4(10) |
| C(5)-C(4)-C(2) | 119.40(10) | | C(16)-C(17)-H(17) | 120.6(10) |
| C(5)-C(4)-C(21) | 119.76(11) | | C(11)-C(12)-C(13) | 121.01(11) |
| C(2)-C(4)-C(21) | 120.82(11) | | C(11)-C(12)-H(12) | 119.1(10) |
| C(3)-C(2)-C(4) | 118.72(10) | | C(13)-C(12)-H(12) | 119.9(10) |
| C(3)-C(2)-C(1) | 120.56(11) | | C(4)-C(21)-H(21A) | 110.9(11) |
| C(4)-C(2)-C(1) | 120.70(11) | | C(4)-C(21)-H(21C) | 111.2(11) |
| C(16)-C(15)-C(20) | 120.45(10) | | H(21A)-C(21)-H(21C) | 108.9(15) |
| C(16)-C(15)-C(14) | 131.40(10) | | C(4)-C(21)-H(21B) | 112.7(11) |
| C(20)-C(15)-C(14) | 108.15(10) | | H(21A)-C(21)-H(21B) | 104.5(15) |
| N(1)-C(8)-C(20) | 121.96(10) | | H(21C)-C(21)-H(21B) | 108.4(15) |

## 10. Bis(2,3-di(5-bromothiophen-2-yl)quinoxaline)silver nitrate

**Comment**

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from methanol.

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

| Table 6.2.10a. Crystal data for 04JU10am | Table 6.2.10b. Data collection |
|---|---|
| $C_{32}H_{16}N_5AgBr_4O_3S_4$ | Bruker SMART CCD area-detector |
| Mr = 1074.25 | diffractometer |
| Triclinic, $P\bar{1}$ | $\omega$ scans |
| $a$ = 8.765 (11) Å | Absorption correction: multi-scan |
| $b$ = 13.871 (17) Å | $T_{min}$ = 0.203, $T_{max}$ = 0.642 |
| $c$ = 15.192 (19) Å | 17117 measured reflections |
| $V$ = 1710.774 (4) Å$^3$ | 8404 independent reflections |
| $Z$ = 2 | 7507 reflections with I > 2σ(I) |
| $D_x$ = 2.085 Mg m$^{-3}$ | $R_{int}$ = 0.0418 |
| Mo K$_\alpha$ radiation | $\theta_{max}$ = 28.31° |
| Cell parameters from 12478 reflections | h = -11 → 11 |

| | |
|---|---|
| $\theta = 2.316\pm28.31°$ | k = -18 → 18 |
| $\mu = 5.548$ mm$^{-1}$ | l = -20 → 20 |
| $T = 100$ (2) K | |
| Plate, yellow | |
| $0.45 \times 0.25 \times 0.08$ mm | |

| Table 6.2.10c. Refinement | Figure 6.2.10. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ | |
| $R[F^2 > 2\sigma(F^2)] = 0.0437$ | |
| $wR(F^2) = 0.1017$ |  |
| $S = 1.024$ | |
| 8404 reflections | |
| 442 parameters | |
| H-atom parameters constrained | |
| $w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 1.1808P]$ where P = $(F_o^2 + 2F_c^2)/3$ | |
| $(\Delta/\sigma)_{max} = 0.001$ | |
| $\Delta\rho_{max} = 1.510$ e×Å$^{-3}$ | |
| $\Delta\rho_{min} = -1.324$ e×Å$^{-3}$ | |
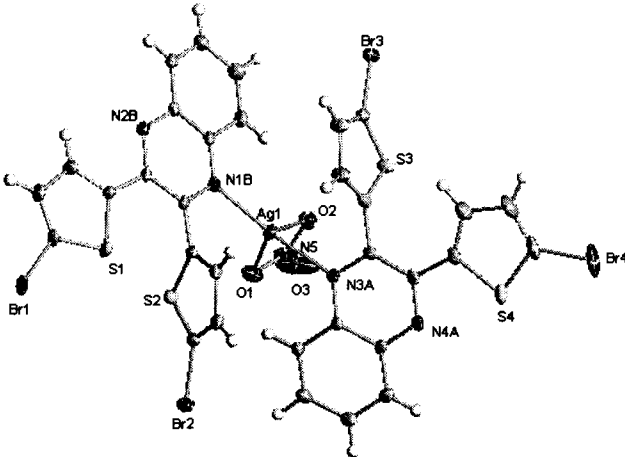
**Table 6.2.10d.**

Geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ag(1)-N(1B) | 2.209(2) | C(6)-N(1B)-C(11) | 119.0(2) |
| Ag(1)-N(3A) | 2.248(2) | C(6)-N(1B)-Ag(1) | 117.45(19) |
| Ag(1)-O(2) | 2.481(2) | C(11)-N(1B)-Ag(1) | 123.53(19) |
| Ag(1)-O(1) | 2.535(3) | C(9)-C(10)-S(2) | 112.7(2) |
| Br(3)-C(21) | 1.870(3) | C(9)-C(10)-Br(2) | 126.5(2) |
| Br(2)-C(10) | 1.873(3) | S(2)-C(10)-Br(2) | 120.73(17) |
| Br(1)-C(1) | 1.874(3) | C(5)-N(2B)-C(16) | 118.9(3) |
| Br(4)-C(30) | 1.869(3) | C(26)-N(4A)-C(31) | 118.5(3) |
| S(2)-C(10) | 1.716(3) | N(4A)-C(31)-C(36) | 120.8(3) |
| S(2)-C(7) | 1.731(3) | N(4A)-C(31)-C(32) | 119.7(3) |
| S(4)-C(30) | 1.713(4) | C(36)-C(31)-C(32) | 119.4(3) |
| S(4)-C(27) | 1.742(3) | N(5)-O(2)-Ag(1) | 96.07(18) |
| S(1)-C(1) | 1.714(3) | C(25)-N(3A)-C(36) | 118.5(2) |
| S(1)-C(4) | 1.735(3) | C(25)-N(3A)-Ag(1) | 117.03(18) |
| S(3)-C(21) | 1.723(3) | C(36)-N(3A)-Ag(1) | 123.90(18) |
| S(3)-C(24) | 1.732(3) | C(23)-C(24)-C(25) | 129.0(3) |
| C(35)-C(34) | 1.378(4) | C(23)-C(24)-S(3) | 111.4(2) |
| C(35)-C(36) | 1.415(4) | C(25)-C(24)-S(3) | 119.3(2) |
| C(35)-H(35) | 0.9500 | N(3A)-C(25)-C(26) | 120.9(3) |
| C(28)-C(27) | 1.363(4) | N(3A)-C(25)-C(24) | 114.8(3) |

| | | | | |
|---|---|---|---|---|
| C(28)-C(29) | 1.418(5) | C(26)-C(25)-C(24) | 124.2(3) | |
| C(28)-H(28) | 0.9500 | C(2)-C(1)-S(1) | 113.4(2) | |
| C(8)-C(7) | 1.371(4) | C(2)-C(1)-Br(1) | 126.4(2) | |
| C(8)-C(9) | 1.424(4) | S(1)-C(1)-Br(1) | 120.19(17) | |
| C(8)-H(8) | 0.9500 | C(24)-C(23)-C(22) | 113.0(3) | |
| C(26)-N(4A) | 1.327(4) | C(24)-C(23)-H(23) | 123.5 | |
| C(26)-C(25) | 1.436(4) | C(22)-C(23)-H(23) | 123.5 | |
| C(26)-C(27) | 1.458(4) | C(28)-C(27)-C(26) | 133.8(3) | |
| N(1B)-C(6) | 1.325(4) | C(28)-C(27)-S(4) | 110.5(2) | |
| N(1B)-C(11) | 1.368(4) | C(26)-C(27)-S(4) | 115.7(2) | |
| C(10)-C(9) | 1.359(4) | N(2B)-C(16)-C(15) | 120.0(3) | |
| N(2B)-C(5) | 1.327(4) | N(2B)-C(16)-C(11) | 121.0(3) | |
| N(2B)-C(16) | 1.361(4) | C(15)-C(16)-C(11) | 118.9(3) | |
| N(4A)-C(31) | 1.359(4) | C(32)-C(33)-C(34) | 120.7(3) | |
| C(31)-C(36) | 1.411(4) | C(32)-C(33)-H(33) | 119.7 | |
| C(31)-C(32) | 1.412(4) | C(34)-C(33)-H(33) | 119.7 | |
| O(2)-N(5) | 1.255(4) | N(3A)-C(36)-C(31) | 120.1(3) | |
| N(3A)-C(25) | 1.324(4) | N(3A)-C(36)-C(35) | 119.8(3) | |
| N(3A)-C(36) | 1.372(3) | C(31)-C(36)-C(35) | 120.1(3) | |
| C(24)-C(23) | 1.356(4) | N(5)-O(1)-Ag(1) | 93.34(18) | |
| C(24)-C(25) | 1.483(4) | C(29)-C(30)-S(4) | 112.8(3) | |
| C(1)-C(2) | 1.356(4) | C(29)-C(30)-Br(4) | 127.9(3) | |
| C(23)-C(22) | 1.425(4) | S(4)-C(30)-Br(4) | 119.2(2) | |

| | | | |
|---|---|---|---|
| C(23)-H(23) | 0.9500 | C(8)-C(7)-C(6) | 128.7(3) |
| C(16)-C(15) | 1.414(4) | C(8)-C(7)-S(2) | 111.3(2) |
| C(16)-C(11) | 1.418(4) | C(6)-C(7)-S(2) | 120.0(2) |
| C(33)-C(32) | 1.370(4) | C(13)-C(12)-C(11) | 119.0(3) |
| C(33)-C(34) | 1.412(5) | C(13)-C(12)-H(12) | 120.5 |
| C(33)-H(33) | 0.9500 | C(11)-C(12)-H(12) | 120.5 |
| O(1)-N(5) | 1.260(4) | C(14)-C(15)-C(16) | 119.8(3) |
| C(30)-C(29) | 1.347(6) | C(14)-C(15)-H(15) | 120.1 |
| C(7)-C(6) | 1.477(4) | C(16)-C(15)-H(15) | 120.1 |
| C(12)-C(13) | 1.371(4) | C(1)-C(2)-C(3) | 110.9(3) |
| C(12)-C(11) | 1.410(4) | C(1)-C(2)-H(2) | 124.6 |
| C(12)-H(12) | 0.9500 | C(3)-C(2)-H(2) | 124.6 |
| C(15)-C(14) | 1.364(4) | C(22)-C(21)-S(3) | 112.1(2) |
| C(15)-H(15) | 0.9500 | C(22)-C(21)-Br(3) | 126.8(2) |
| C(2)-C(3) | 1.421(4) | S(3)-C(21)-Br(3) | 121.13(17) |
| C(2)-H(2) | 0.9500 | C(33)-C(32)-C(31) | 119.8(3) |
| C(21)-C(22) | 1.359(4) | C(33)-C(32)-H(32) | 120.1 |
| C(32)-H(32) | 0.9500 | C(31)-C(32)-H(32) | 120.1 |
| C(3)-C(4) | 1.362(4) | C(4)-C(3)-C(2) | 114.2(3) |
| C(3)-H(3) | 0.9500 | C(4)-C(3)-H(3) | 122.9 |
| C(9)-H(9) | 0.9500 | C(2)-C(3)-H(3) | 122.9 |
| C(34)-H(34) | 0.9500 | C(10)-C(9)-C(8) | 112.0(3) |
| C(14)-C(13) | 1.416(5) | C(10)-C(9)-H(9) | 124.0 |

| | | | | |
|---|---|---|---|---|
| C(14)-H(14) | 0.9500 | C(8)-C(9)-H(9) | 124.0 |
| C(4)-C(5) | 1.473(4) | C(35)-C(34)-C(33) | 120.7(3) |
| C(13)-H(13) | 0.9500 | C(35)-C(34)-H(34) | 119.6 |
| C(6)-C(5) | 1.438(4) | C(33)-C(34)-H(34) | 119.6 |
| C(22)-H(22) | 0.9500 | C(15)-C(14)-C(13) | 121.1(3) |
| O(3)-N(5) | 1.239(4) | C(15)-C(14)-H(14) | 119.5 |
| C(29)-H(29) | 0.9500 | C(13)-C(14)-H(14) | 119.5 |
| N(1B)-Ag(1)-N(3A) | 141.77(8) | C(3)-C(4)-C(5) | 124.3(3) |
| N(1B)-Ag(1)-O(2) | 122.55(8) | C(3)-C(4)-S(1) | 110.5(2) |
| N(3A)-Ag(1)-O(2) | 90.47(8) | C(5)-C(4)-S(1) | 125.2(2) |
| N(1B)-Ag(1)-O(1) | 116.18(9) | C(12)-C(13)-C(14) | 120.6(3) |
| N(3A)-Ag(1)-O(1) | 99.12(8) | C(12)-C(13)-H(13) | 119.7 |
| O(2)-Ag(1)-O(1) | 51.07(8) | C(14)-C(13)-H(13) | 119.7 |
| C(10)-S(2)-C(7) | 91.22(14) | N(1B)-C(6)-C(5) | 121.2(3) |
| C(30)-S(4)-C(27) | 91.12(17) | N(1B)-C(6)-C(7) | 115.3(2) |
| C(1)-S(1)-C(4) | 91.06(14) | C(5)-C(6)-C(7) | 123.6(2) |
| C(21)-S(3)-C(24) | 91.25(14) | C(21)-C(22)-C(23) | 112.2(3) |
| C(34)-C(35)-C(36) | 119.1(3) | C(21)-C(22)-H(22) | 123.9 |
| C(34)-C(35)-H(35) | 120.5 | C(23)-C(22)-H(22) | 123.9 |
| C(36)-C(35)-H(35) | 120.5 | N(1B)-C(11)-C(12) | 119.9(3) |
| C(27)-C(28)-C(29) | 113.4(3) | N(1B)-C(11)-C(16) | 119.5(3) |
| C(27)-C(28)-H(28) | 123.3 | C(12)-C(11)-C(16) | 120.6(3) |
| C(29)-C(28)-H(28) | 123.3 | N(2B)-C(5)-C(6) | 120.3(3) |

| | | | | |
|---|---|---|---|---|
| C(7)-C(8)-C(9) | 112.7(3) | N(2B)-C(5)-C(4) | 115.4(2) |
| C(7)-C(8)-H(8) | 123.6 | C(6)-C(5)-C(4) | 124.3(2) |
| C(9)-C(8)-H(8) | 123.6 | O(3)-N(5)-O(2) | 120.0(3) |
| N(4A)-C(26)-C(25) | 120.7(3) | O(3)-N(5)-O(1) | 121.4(3) |
| N(4A)-C(26)-C(27) | 114.6(3) | O(2)-N(5)-O(1) | 118.6(3) |
| | | C(30)-C(29)-C(28) | 112.1(3) |

## 11. Bis(2,3-di(thiophen-2-yl)quinoxaline)silver nitrate

### Comment

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from methanol.

Three of the four thiophene rings exhibit flip disorder (the rings are rapidly flipping from "right-handed" to left handed"). The major and minor components were refined to be the same: restraints were applied so that the geometry of the two component rings was identical. Due to the flip disorder, it also became necessary for the thermal displacement parameter of the disordered atoms (thus their thermal ellipsoids) to be set the same.

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

| Table 6.2.11a. Crystal data for 04JU11am | Table 6.2.11b. Data collection |
|---|---|
| $C_{32}H_{16}N_5AgO_3S_4$ | Bruker SMART CCD area-detector |
| Mr = 758.64 | diffractometer |
| Triclinic, $P\bar{1}$ | $\omega$ scans |
| $a = 10.4991\ (7)$ Å | Absorption correction: multi-scan |
| $b = 11.9510\ (8)$ Å | $T_{min} = 0.683$, $T_{max} = 0.885$ |
| $c = 12.5195\ (8)$ Å | 15097 measured reflections |

| | |
|---|---|
| $V = 1467.81\ (17)\ \text{Å}^3$ | 7234 independent reflections |
| $Z = 2$ | 6833 reflections with $I > 2\sigma(I)$ |
| $D_x = 1.717\ \text{Mg m}^{-3}$ | $R_{int} = 0.0164$ |
| Mo $K_\alpha$ radiation | $\theta_{max} = 28.32°$ |
| Cell parameters from 12561 reflections | h = -13 $\rightarrow$ 13 |
| $\theta = 2.43 \pm 28.306°$ | k = -15 $\rightarrow$ 15 |
| $\mu = 1.017\ \text{mm}^{-1}$ | l = -16 $\rightarrow$ 16 |
| $T = 100\ (2)\ \text{K}$ | |
| Block, yellow | |
| $0.40 \times 0.32 \times 0.12$ mm | |

| Table 6.2.11c.<br><br>**Refinement** | **Figure 6.2.11.** ORTEP plot of title compound. Ellipsoids are at the 50% probability level. The flip disorder is also modeled. |
|---|---|
| Refinement on $F^2$<br><br>$R[F^2 > 2\sigma(F^2)] = 0.0372$<br><br>$wR(F^2) = 0.0954$<br><br>$S = 1.048$<br><br>7234 reflections<br><br>416 parameters<br><br>H-atom parameters constrained<br><br>$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 2.32P]$<br><br>where $P = (F_o^2 + 2F_c^2)/3$<br><br>$(\Delta/\sigma)_{max} = 0.000$<br><br>$\Delta\rho_{max} = 1.769$ e×Å$^{-3}$<br><br>$\Delta\rho_{min} = -0.818$ e×Å$^{-3}$ |  |
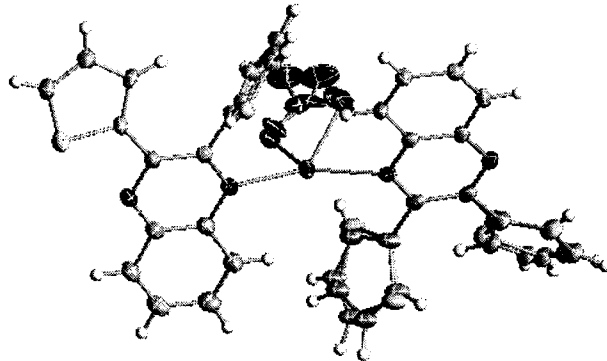
**Table 6.2.11d.**

Geometric parameters (Å, °).

| Ag(1)-N(4) | 2.226(2) | N(1)-C(8)-C(9) | 113.6(3) |
|---|---|---|---|
| Ag(1)-N(2) | 2.226(2) | C(13)-C(8)-C(9) | 124.8(3) |

| | | | | |
|---|---|---|---|---|
| Ag(1)-O(2) | 2.489(12) | | N(1)-C(8)-C(9B) | 121.5(5) |
| Ag(1)-O(1B) | 2.56(3) | | C(13)-C(8)-C(9B) | 116.6(5) |
| C(1)-N(2) | 1.370(3) | | C(9)-C(8)-C(9B) | 10.8(5) |
| C(1)-C(2) | 1.411(3) | | C(10)-C(9)-C(8) | 137.5(4) |
| C(1)-C(6) | 1.416(3) | | C(10)-C(9)-S(3) | 100.1(3) |
| C(2)-C(3) | 1.372(3) | | C(8)-C(9)-S(3) | 120.1(3) |
| C(2)-H(2) | 0.9500 | | C(11)-C(10)-C(9) | 130.4(6) |
| C(3)-C(4) | 1.414(3) | | C(11)-C(10)-H(10) | 114.8 |
| C(3)-H(3) | 0.9500 | | C(9)-C(10)-H(10) | 114.8 |
| C(4)-C(5) | 1.366(4) | | C(10)-C(11)-C(12) | 103.9(4) |
| C(4)-H(4) | 0.9500 | | C(10)-C(11)-H(11) | 128.1 |
| C(5)-C(6) | 1.418(3) | | C(12)-C(11)-H(11) | 128.1 |
| C(5)-H(5) | 0.9500 | | C(11)-C(12)-S(3) | 114.1(3) |
| C(6)-N(1) | 1.362(3) | | C(11)-C(12)-H(12) | 123.0 |
| N(1)-C(8) | 1.322(3) | | S(3)-C(12)-H(12) | 123.0 |
| C(8)-C(13) | 1.440(3) | | C(9)-S(3)-C(12) | 89.3(2) |
| C(8)-C(9) | 1.467(5) | | C(10B)-C(9B)-C(8) | 146.6(10) |
| C(8)-C(9B) | 1.513(11) | | C(10B)-C(9B)-S(3B) | 105.0(9) |
| C(9)-C(10) | 1.365(7) | | C(8)-C(9B)-S(3B) | 108.3(6) |
| C(9)-S(3) | 1.737(4) | | C(11B)-C(10B)-C(9B) | 125.7(14) |
| C(10)-C(11) | 1.214(6) | | C(11B)-C(10B)-H(10B) | 117.1 |
| C(10)-H(10) | 0.9500 | | C(9B)-C(10B)-H(10B) | 117.1 |
| C(11)-C(12) | 1.333(6) | | C(10B)-C(11B)-C(12B) | 105.7(11) |

| | | | | |
|---|---|---|---|---|
| C(11)-H(11) | 0.9500 | C(10B)-C(11B)-H(11B) | 127.1 |
| C(12)-S(3) | 1.761(4) | C(12B)-C(11B)-H(11B) | 127.1 |
| C(12)-H(12) | 0.9500 | C(11B)-C(12B)-S(3B) | 115.3(7) |
| C(9B)-C(10B) | 1.423(15) | C(11B)-C(12B)-H(12B) | 122.4 |
| C(9B)-S(3B) | 1.709(11) | S(3B)-C(12B)-H(12B) | 122.4 |
| C(10B)-C(11B) | 1.213(14) | C(9B)-S(3B)-C(12B) | 86.4(5) |
| C(10B)-H(10B) | 0.9500 | N(2)-C(13)-C(8) | 120.7(2) |
| C(11B)-C(12B) | 1.332(12) | N(2)-C(13)-C(14) | 116.3(2) |
| C(11B)-H(11B) | 0.9500 | C(8)-C(13)-C(14) | 123.0(2) |
| C(12B)-S(3B) | 1.829(9) | C(15)-C(14)-C(13) | 130.0(3) |
| C(12B)-H(12B) | 0.9500 | C(15)-C(14)-S(4) | 106.0(3) |
| C(13)-N(2) | 1.325(3) | C(13)-C(14)-S(4) | 123.3(2) |
| C(13)-C(14) | 1.474(4) | C(16)-C(15)-C(14) | 119.3(5) |
| C(14)-C(15) | 1.413(7) | C(16)-C(15)-H(15A) | 120.4 |
| C(14)-S(4) | 1.706(3) | C(14)-C(15)-H(15A) | 120.4 |
| C(15)-C(16) | 1.346(7) | C(15)-C(16)-C(17) | 108.1(5) |
| C(15)-H(15A) | 0.9500 | C(15)-C(16)-H(16) | 126.0 |
| C(16)-C(17) | 1.352(6) | C(17)-C(16)-H(16) | 126.0 |
| C(16)-H(16) | 0.9500 | C(16)-C(17)-S(4) | 114.0(4) |
| C(17)-S(4) | 1.729(5) | C(16)-C(17)-H(17) | 123.0 |
| C(17)-H(17) | 0.9500 | S(4)-C(17)-H(17) | 123.0 |
| C(15B)-C(16B) | 1.426(13) | C(14)-S(4)-C(17) | 91.8(2) |
| C(15B)-H(15B) | 0.9500 | C(16B)-C(15B)-H(15B) | 125.0 |

| | | | | |
|---|---|---|---|---|
| C(16B)-C(17B) | 1.356(11) | C(17B)-C(16B)-C(15B) | 108.7(9) |
| C(16B)-H(16B) | 0.9500 | C(17B)-C(16B)-H(16B) | 125.7 |
| C(17B)-S(4B) | 1.775(9) | C(15B)-C(16B)-H(16B) | 125.7 |
| C(17B)-H(17B) | 0.9500 | C(16B)-C(17B)-S(4B) | 115.4(8) |
| C(18)-N(4) | 1.369(3) | C(16B)-C(17B)-H(17B) | 122.3 |
| C(18)-C(19) | 1.410(4) | S(4B)-C(17B)-H(17B) | 122.3 |
| C(18)-C(23) | 1.411(3) | N(4)-C(18)-C(19) | 119.7(2) |
| C(19)-C(20) | 1.371(4) | N(4)-C(18)-C(23) | 119.7(2) |
| C(19)-H(19) | 0.9500 | C(19)-C(18)-C(23) | 120.6(2) |
| C(20)-C(21) | 1.409(4) | C(20)-C(19)-C(18) | 119.6(3) |
| C(20)-H(20) | 0.9500 | C(20)-C(19)-H(19) | 120.2 |
| C(21)-C(22) | 1.368(4) | C(18)-C(19)-H(19) | 120.2 |
| C(21)-H(21) | 0.9500 | C(19)-C(20)-C(21) | 120.0(3) |
| C(22)-C(23) | 1.425(3) | C(19)-C(20)-H(20) | 120.0 |
| C(22)-H(22) | 0.9500 | C(21)-C(20)-H(20) | 120.0 |
| C(23)-N(3) | 1.355(3) | C(22)-C(21)-C(20) | 121.6(2) |
| N(3)-C(25) | 1.327(3) | C(22)-C(21)-H(21) | 119.2 |
| C(25)-C(30) | 1.441(3) | C(20)-C(21)-H(21) | 119.2 |
| C(25)-C(26) | 1.466(3) | C(21)-C(22)-C(23) | 119.4(2) |
| C(26)-C(27) | 1.419(3) | C(21)-C(22)-H(22) | 120.3 |
| C(26)-S(2) | 1.726(2) | C(23)-C(22)-H(22) | 120.3 |
| C(27)-C(28) | 1.437(3) | N(3)-C(23)-C(18) | 121.4(2) |
| C(27)-H(27) | 0.9500 | N(3)-C(23)-C(22) | 119.9(2) |

| | | | | |
|---|---|---|---|---|
| C(28)-C(29) | 1.358(4) | C(18)-C(23)-C(22) | 118.6(2) |
| C(28)-H(28) | 0.9500 | C(25)-N(3)-C(23) | 118.4(2) |
| C(29)-S(2) | 1.697(3) | N(3)-C(25)-C(30) | 120.7(2) |
| C(29)-H(29) | 0.9500 | N(3)-C(25)-C(26) | 115.5(2) |
| C(30)-N(4) | 1.322(3) | C(30)-C(25)-C(26) | 123.8(2) |
| C(30)-C(31) | 1.481(3) | C(27)-C(26)-C(25) | 132.1(2) |
| C(31)-C(32) | 1.409(6) | C(27)-C(26)-S(2) | 111.36(18) |
| C(31)-S(5) | 1.687(3) | C(25)-C(26)-S(2) | 116.48(17) |
| C(32)-C(33) | 1.393(7) | C(26)-C(27)-C(28) | 109.8(2) |
| C(32)-H(32) | 0.9500 | C(26)-C(27)-H(27) | 125.1 |
| C(33)-C(34) | 1.359(6) | C(28)-C(27)-H(27) | 125.1 |
| C(33)-H(33) | 0.9500 | C(29)-C(28)-C(27) | 113.9(2) |
| C(34)-S(5) | 1.730(5) | C(29)-C(28)-H(28) | 123.0 |
| C(34)-H(34) | 0.9500 | C(27)-C(28)-H(28) | 123.0 |
| C(32B)-C(33B) | 1.362(10) | C(28)-C(29)-S(2) | 112.5(2) |
| C(32B)-H(32B) | 0.9500 | C(28)-C(29)-H(29) | 123.7 |
| C(33B)-C(34B) | 1.351(8) | S(2)-C(29)-H(29) | 123.7 |
| C(33B)-H(33B) | 0.9500 | N(4)-C(30)-C(25) | 120.7(2) |
| C(34B)-S(5B) | 1.732(7) | N(4)-C(30)-C(31) | 115.6(2) |
| C(34B)-H(34B) | 0.9500 | C(25)-C(30)-C(31) | 123.7(2) |
| N(5)-O(3) | 1.245(10) | C(32)-C(31)-C(30) | 127.1(3) |
| N(5)-O(1) | 1.248(10) | C(32)-C(31)-S(5) | 109.9(3) |
| N(5)-O(2) | 1.249(10) | C(30)-C(31)-S(5) | 123.08(18) |

| | | | | |
|---|---|---|---|---|
| N(5B)-O(2B) | 1.236(14) | C(33)-C(32)-C(31) | 115.5(5) |
| N(5B)-O(3B) | 1.239(14) | C(33)-C(32)-H(32) | 122.3 |
| N(5B)-O(1B) | 1.247(14) | C(31)-C(32)-H(32) | 122.3 |
| N(4)-Ag(1)-N(2) | 151.74(7) | C(34)-C(33)-C(32) | 109.0(5) |
| N(4)-Ag(1)-O(2) | 83.7(3) | C(34)-C(33)-H(33) | 125.5 |
| N(2)-Ag(1)-O(2) | 123.9(3) | C(32)-C(33)-H(33) | 125.5 |
| N(4)-Ag(1)-O(1B) | 131.2(6) | C(33)-C(34)-S(5) | 114.3(4) |
| N(2)-Ag(1)-O(1B) | 76.0(5) | C(33)-C(34)-H(34) | 122.8 |
| O(2)-Ag(1)-O(1B) | 54.8(5) | S(5)-C(34)-H(34) | 122.8 |
| N(2)-C(1)-C(2) | 119.8(2) | C(31)-S(5)-C(34) | 91.2(2) |
| N(2)-C(1)-C(6) | 119.8(2) | C(33B)-C(32B)-H(32B) | 122.6 |
| C(2)-C(1)-C(6) | 120.4(2) | C(34B)-C(33B)-C(32B) | 108.7(8) |
| C(3)-C(2)-C(1) | 119.5(2) | C(34B)-C(33B)-H(33B) | 125.7 |
| C(3)-C(2)-H(2) | 120.3 | C(32B)-C(33B)-H(33B) | 125.7 |
| C(1)-C(2)-H(2) | 120.3 | C(33B)-C(34B)-S(5B) | 116.0(6) |
| C(2)-C(3)-C(4) | 120.3(2) | C(33B)-C(34B)-H(34B) | 122.0 |
| C(2)-C(3)-H(3) | 119.9 | S(5B)-C(34B)-H(34B) | 122.0 |
| C(4)-C(3)-H(3) | 119.9 | C(13)-N(2)-C(1) | 118.6(2) |
| C(5)-C(4)-C(3) | 121.3(2) | C(13)-N(2)-Ag(1) | 120.38(17) |
| C(5)-C(4)-H(4) | 119.4 | C(1)-N(2)-Ag(1) | 118.97(15) |
| C(3)-C(4)-H(4) | 119.4 | C(30)-N(4)-C(18) | 119.0(2) |
| C(4)-C(5)-C(6) | 119.7(2) | C(30)-N(4)-Ag(1) | 119.23(15) |
| C(4)-C(5)-H(5) | 120.2 | C(18)-N(4)-Ag(1) | 120.86(16) |

| | | | | |
|---|---|---|---|---|
| C(6)-C(5)-H(5) | 120.2 | O(3)-N(5)-O(1) | 119.9(13) | |
| N(1)-C(6)-C(1) | 121.5(2) | O(3)-N(5)-O(2) | 120.5(11) | |
| N(1)-C(6)-C(5) | 119.6(2) | O(1)-N(5)-O(2) | 119.3(11) | |
| C(1)-C(6)-C(5) | 118.9(2) | N(5)-O(2)-Ag(1) | 103.6(7) | |
| C(8)-N(1)-C(6) | 117.7(2) | O(2B)-N(5B)-O(3B) | 122.8(18) | |
| N(1)-C(8)-C(13) | 121.6(2) | O(2B)-N(5B)-O(1B) | 119.4(16) | |
| | | O(3B)-N(5B)-O(1B) | 117.3(17) | |

## 12. Nitroanthracene

## Comment

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from hexane.

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

| Table 6.2.12a. Crystal data for 04JU12a | Table 6.2.12b. Data collection |
|---|---|
| $C_{14}H_9NO_2$ | Bruker SMART CCD area-detector |
| Mr = 268.22 | diffractometer |
| Monoclinic, $P2_1/c$ | $\omega$ scans |
| $a$ = 10.5117 (7) Å | Absorption correction: multi-scan |
| $b$ = 13.5401 (9) Å | $T_{min}$ = 0.981, $T_{max}$ = 0.984 |
| $c$ = 7.4285 (5) Å | 10391 measured reflections |
| $\beta$ = 103.1970 (10)° | 2545 independent reflections |
| $V$ = 1029.37 (12) Å$^3$ | 2182 reflections with I > 2σ(I) |
| $Z$ = 3 | $R_{int}$ = 0.0247 |
| $D_x$ = 1.298 Mg m$^{-3}$ | $\theta_{max}$ = 28.29° |
| Mo K$_\alpha$ radiation | h = -14 → 14 |
| Cell parameters from 5299 reflections | k = -18 → 18 |

| $\theta = 2.495 \pm 28.283°$ | $l = -9 \rightarrow 9$ |
|---|---|
| $\mu = 0.098$ mm$^{-1}$ | |
| $T = 100$ (2) K | |
| Needle, yellow | |
| $0.40 \times 0.16 \times 0.16$ mm | |

| **Table 6.2.12c.** **Refinement** | **Figure 6.2.12.** ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ | |
| $R[F^2 > 2\sigma(F^2)] = 0.0438$ | |
| $wR(F^2) = 0.1255$ | |
| $S = 1.066$ | |
| 2545 reflections | |
| 154 parameters | |
| H-atom parameters constrained | |
| $w = 1/[\sigma^2(F_o^2) +$ $(0.0791P)^2 + 0.20P]$ | |
| where P = $(F_o^2 + 2F_c^2)/3$ | |
| $(\Delta/\sigma)_{max} = 0.000$ | |

| $\Delta\rho_{max} = 0.471$ e×Å$^{-3}$ | |
|---|---|
| $\Delta\rho_{min} = -0.202$ e×Å$^{-3}$ | |

**Table 6.2.12d.**

Geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| C(11)-C(12) | 1.3989(14) | C(11)-C(12)-N(1) | 117.82(9) |
| C(11)-C(10) | 1.4284(14) | C(12)-C(13)-C(14) | 124.39(10) |
| C(11)-C(6) | 1.4343(15) | C(12)-C(13)-C(4) | 116.81(9) |
| C(4)-C(5) | 1.3972(14) | C(14)-C(13)-C(4) | 118.78(9) |
| C(4)-C(3) | 1.4274(14) | C(6)-C(5)-C(4) | 122.07(10) |
| C(4)-C(13) | 1.4325(14) | C(6)-C(5)-H(5) | 119.0 |
| C(12)-C(13) | 1.3976(14) | C(4)-C(5)-H(5) | 119.0 |
| C(12)-N(1) | 1.4728(13) | C(5)-C(6)-C(7) | 121.84(10) |
| C(13)-C(14) | 1.4297(14) | C(5)-C(6)-C(11) | 119.56(9) |
| C(5)-C(6) | 1.3950(15) | C(7)-C(6)-C(11) | 118.60(10) |
| C(5)-H(5) | 0.9500 | C(2)-C(3)-C(4) | 121.10(10) |
| C(6)-C(7) | 1.4286(14) | C(2)-C(3)-H(3) | 119.4 |
| C(3)-C(2) | 1.3592(16) | C(4)-C(3)-H(3) | 119.4 |
| C(3)-H(3) | 0.9500 | C(9)-C(10)-C(11) | 120.32(11) |
| C(10)-C(9) | 1.3608(15) | C(9)-C(10)-H(10) | 119.8 |
| C(10)-H(10) | 0.9500 | C(11)-C(10)-H(10) | 119.8 |
| N(1)-O(2) | 1.2170(13) | O(2)-N(1)-O(1) | 123.25(10) |

| | | | | |
|---|---|---|---|---|
| N(1)-O(1) | 1.2201(12) | O(2)-N(1)-C(12) | 118.55(9) |
| C(7)-C(8) | 1.3591(16) | O(1)-N(1)-C(12) | 118.20(9) |
| C(7)-H(7) | 0.9500 | C(8)-C(7)-C(6) | 120.86(11) |
| C(14)-C(1) | 1.3619(15) | C(8)-C(7)-H(7) | 119.6 |
| C(14)-H(14) | 0.9500 | C(6)-C(7)-H(7) | 119.6 |
| C(8)-C(9) | 1.4213(18) | C(1)-C(14)-C(13) | 120.35(10) |
| C(8)-H(8) | 0.9500 | C(1)-C(14)-H(14) | 119.8 |
| C(9)-H(9) | 0.9500 | C(13)-C(14)-H(14) | 119.8 |
| C(2)-C(1) | 1.4194(17) | C(7)-C(8)-C(9) | 120.33(10) |
| C(2)-H(2) | 0.9500 | C(7)-C(8)-H(8) | 119.8 |
| C(1)-H(1A) | 0.9500 | C(9)-C(8)-H(8) | 119.8 |
| C(12)-C(11)-C(10) | 124.13(10) | C(10)-C(9)-C(8) | 120.99(10) |
| C(12)-C(11)-C(6) | 116.96(9) | C(10)-C(9)-H(9) | 119.5 |
| C(10)-C(11)-C(6) | 118.90(10) | C(8)-C(9)-H(9) | 119.5 |
| C(5)-C(4)-C(3) | 121.64(10) | C(3)-C(2)-C(1) | 120.11(10) |
| C(5)-C(4)-C(13) | 119.77(9) | C(3)-C(2)-H(2) | 119.9 |
| C(3)-C(4)-C(13) | 118.59(9) | C(1)-C(2)-H(2) | 119.9 |
| C(13)-C(12)-C(11) | 124.81(10) | C(14)-C(1)-C(2) | 121.06(10) |
| C(13)-C(12)-N(1) | 117.37(9) | | |

### 13. *o*-1-nitro-2-ethylbenzene and *p*-methylbenzensulfonate

### Comment

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from hexane and was the starting material of the intended compound.

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

| Table 6.2.13a. Crystal data for 04JU25am | Table 6.2.13b. Data collection |
|---|---|
| $C_{15}H_{19}NO_3S$ | Bruker SMART CCD area-detector |
| Mr = 293.37 | diffractometer |
| Monoclinic, $P2_1/c$ | $\omega$ scans |
| $a = 5.9374$ (7) Å | Absorption correction: multi-scan |
| $b = 21.805$ (2) Å | $T_{min} = 0.905$, $T_{max} = 0.984$ |
| $c = 11.5549$ (13) Å | 12891 measured reflections |
| $\beta = 95.057$ (2)° | 3618 independent reflections |
| $V = 1490.1$ (3) Å$^3$ | 3527 reflections with $I > 2\sigma(I)$ |
| $Z = 4$ | $R_{int} = 0.0381$ |
| $D_x = 1.308$ Mg m$^{-3}$ | $\theta_{max} = 28.30°$ |

| Mo $K_\alpha$ radiation | $h = -7 \rightarrow 7$ |
|---|---|
| Cell parameters from 13010 reflections | $k = -29 \rightarrow 29$ |
| $\theta = 2.573 \pm 28.289°$ | $l = -15 \rightarrow 15$ |
| $\mu = 0.224$ mm$^{-1}$ | |
| $T = 100\ (2)$ K | |
| Plate, colorless | |
| $0.60 \times 0.37 \times 0.07$ mm | |

| Table 6.2.13c. Refinement | Figure 6.2.13. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ <br><br> $R[F^2 > 2\sigma(F^2)] = 0.0614$ <br><br> $wR(F^2) = 0.1356$ <br><br> $S = 1.292$ <br><br> 3618 reflections <br><br> 184 parameters <br><br> H-atom parameters constrained <br><br> $w = 1/[\sigma^2(F_o^2) + (0.0206P)^2 + 2.1666P]$ <br><br> where $P = (F_o^2 + 2F_c^2)/3$ <br><br> $(\Delta/\sigma)_{max} = 0.000$ <br><br> $\Delta\rho_{max} = 0.43$ e $\times$ Å$^{-3}$ <br><br> $\Delta\rho_{min} = -0.44$ e $\times$ Å$^{-3}$ |  |

| Table 6.2.13d. | | | | |
|---|---|---|---|---|
| Geometric parameters (Å, °). | | | | |
| C(15)-H(15B) | 0.9800 | H(4A)-N(1)-H(4C) | 109.5 | |
| C(15)-H(15C) | 0.9800 | H(4B)-N(1)-H(4C) | 109.5 | |
| S(1)-O(1) | 1.4574(18) | C(5)-C(4)-C(3) | 122.8(2) | |

| | | | |
|---|---|---|---|
| S(1)-O(3) | 1.4587(17) | C(5)-C(4)-N(1) | 118.3(2) |
| S(1)-O(2) | 1.4635(17) | C(3)-C(4)-N(1) | 119.0(2) |
| S(1)-C(9) | 1.774(2) | C(8)-C(3)-C(4) | 116.8(2) |
| N(1)-C(4) | 1.467(3) | C(8)-C(3)-C(2) | 123.6(2) |
| N(1)-H(4A) | 0.9100 | C(4)-C(3)-C(2) | 119.6(2) |
| N(1)-H(4B) | 0.9100 | C(6)-C(7)-C(8) | 120.2(2) |
| N(1)-H(4C) | 0.9100 | C(6)-C(7)-H(7) | 119.9 |
| C(4)-C(5) | 1.386(3) | C(8)-C(7)-H(7) | 119.9 |
| C(4)-C(3) | 1.398(3) | C(4)-C(5)-C(6) | 119.1(2) |
| C(3)-C(8) | 1.392(3) | C(4)-C(5)-H(5) | 120.4 |
| C(3)-C(2) | 1.516(3) | C(6)-C(5)-H(5) | 120.4 |
| C(7)-C(6) | 1.387(4) | C(3)-C(2)-C(1) | 116.2(2) |
| C(7)-C(8) | 1.394(4) | C(3)-C(2)-H(2A) | 108.2 |
| C(7)-H(7) | 0.9500 | C(1)-C(2)-H(2A) | 108.2 |
| C(5)-C(6) | 1.387(4) | C(15)-C(12) | 1.508(3) |
| C(5)-H(5) | 0.9500 | C(15)-H(15A) | 0.9800 |
| C(2)-C(1) | 1.522(3) | C(3)-C(2)-H(2B) | 108.2 |
| C(2)-H(2A) | 0.9900 | C(1)-C(2)-H(2B) | 108.2 |
| C(2)-H(2B) | 0.9900 | H(2A)-C(2)-H(2B) | 107.4 |
| C(1)-H(1A) | 0.9800 | C(2)-C(1)-H(1A) | 109.5 |
| C(1)-H(1B) | 0.9800 | C(2)-C(1)-H(1B) | 109.5 |
| C(1)-H(1C) | 0.9800 | H(1A)-C(1)-H(1B) | 109.5 |
| C(8)-H(8) | 0.9500 | C(2)-C(1)-H(1C) | 109.5 |

| | | | | |
|---|---|---|---|---|
| C(6)-H(6) | 0.9500 | H(1A)-C(1)-H(1C) | 109.5 |
| C(12)-C(11) | 1.392(3) | H(1B)-C(1)-H(1C) | 109.5 |
| C(12)-C(13) | 1.401(3) | C(3)-C(8)-C(7) | 121.4(2) |
| C(14)-C(9) | 1.389(3) | C(3)-C(8)-H(8) | 119.3 |
| C(14)-C(13) | 1.392(3) | C(7)-C(8)-H(8) | 119.3 |
| C(14)-H(14) | 0.9500 | C(5)-C(6)-C(7) | 119.7(2) |
| C(11)-C(10) | 1.394(3) | C(5)-C(6)-H(6) | 120.1 |
| C(11)-H(11) | 0.9500 | C(7)-C(6)-H(6) | 120.1 |
| C(13)-H(13) | 0.9500 | C(11)-C(12)-C(13) | 118.6(2) |
| C(10)-C(9) | 1.393(3) | C(11)-C(12)-C(15) | 120.9(2) |
| C(10)-H(10) | 0.9500 | C(13)-C(12)-C(15) | 120.6(2) |
| C(12)-C(15)-H(15A) | 109.5 | C(9)-C(14)-C(13) | 119.5(2) |
| C(12)-C(15)-H(15B) | 109.5 | C(9)-C(14)-H(14) | 120.2 |
| H(15A)-C(15)-H(15B) | 109.5 | C(13)-C(14)-H(14) | 120.2 |
| C(12)-C(15)-H(15C) | 109.5 | C(12)-C(11)-C(10) | 121.5(2) |
| H(15A)-C(15)-H(15C) | 109.5 | C(12)-C(11)-H(11) | 119.3 |
| H(15B)-C(15)-H(15C) | 109.5 | C(10)-C(11)-H(11) | 119.3 |
| O(1)-S(1)-O(3) | 113.02(11) | C(14)-C(13)-C(12) | 120.7(2) |
| O(1)-S(1)-O(2) | 110.53(10) | C(14)-C(13)-H(13) | 119.6 |
| O(3)-S(1)-O(2) | 112.31(10) | C(12)-C(13)-H(13) | 119.6 |
| O(1)-S(1)-C(9) | 107.22(10) | C(9)-C(10)-C(11) | 118.8(2) |
| O(3)-S(1)-C(9) | 106.30(10) | C(9)-C(10)-H(10) | 120.6 |
| O(2)-S(1)-C(9) | 107.06(10) | C(11)-C(10)-H(10) | 120.6 |

| | | | | |
|---|---|---|---|---|
| C(4)-N(1)-H(4A) | 109.5 | | C(14)-C(9)-C(10) | 120.9(2) |
| C(4)-N(1)-H(4B) | 109.5 | | C(14)-C(9)-S(1) | 119.76(17) |
| H(4A)-N(1)-H(4B) | 109.5 | | C(10)-C(9)-S(1) | 119.28(17) |
| C(4)-N(1)-H(4C) | 109.5 | | | |

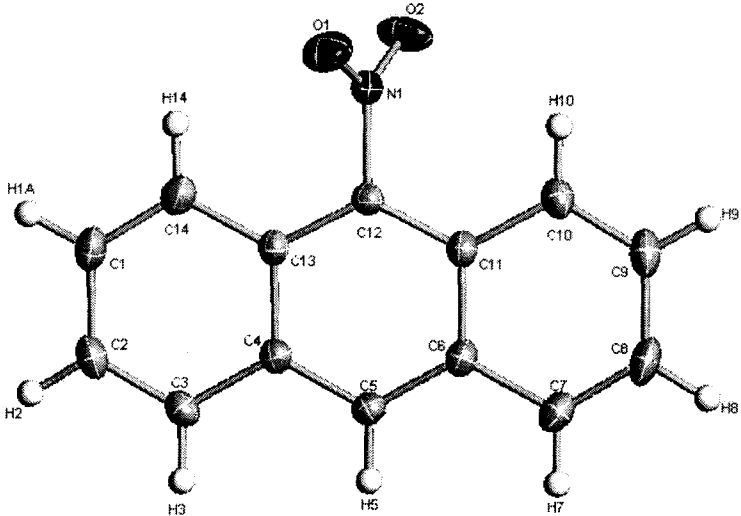## 14. Fluoren-9-ylidene-(4-nitrophenyl)-amine
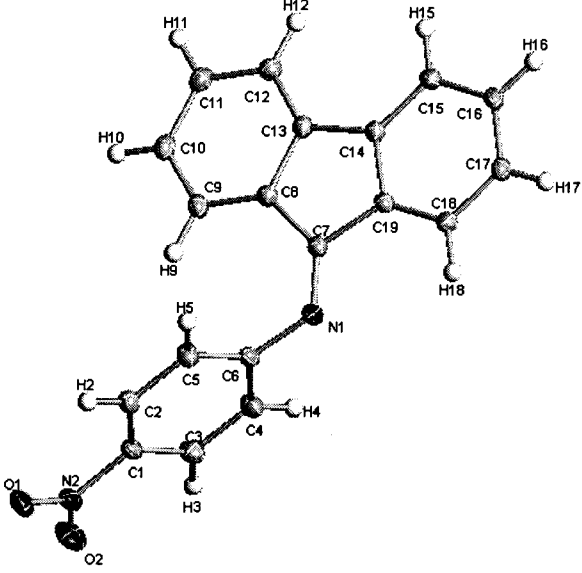
**Comment**

G. Crundwell from Central Connecticut State University provided the crystal investigated. It was grown from hexane.

All H atoms were placed in calculated positions, with C–H distances of 0.95 Å, and were included in the refinement in riding-motion approximation, with $U_{iso}(H) = 1.2U_{eq}$ of the adjacent carbon atom.

| Table 6.2.14a. Crystal data for 04JU26am | Table 6.2.14b. Data collection |
|---|---|
| $C_{19}H_{12}N_2O_2$ | Bruker SMART CCD area-detector |
| Mr = 293.37 | diffractometer |
| Triclinic, $P\bar{1}$ | $\omega$ scans |
| $a = 8.0894\ (12)$ Å | Absorption correction: multi-scan |
| $b = 9.0445\ (14)$ Å | $T_{min} = 0.950,\ T_{max} = 0.955$ |
| $c = 9.8573\ (15)$ Å | 7381 measured reflections |
| $\beta = 85.417\ (3)$ ° | 3496 independent reflections |
| $V = 707.70\ (19)$ Å$^3$ | 3277 reflections with I > 2σ(I) |
| $Z = 2$ | $R_{int} = 0.0292$ |
| $D_x = 1.409$ Mg m$^{-3}$ | $\theta_{max} = 28.35°$ |
| Mo K$_\alpha$ radiation | h = -10 → 10 |

| Cell parameters from 6491 reflections | k = -12 → 12 |
|---|---|
| $\theta$ = 2.285 ± 28.35° | l = -13→ 12 |
| $\mu$ = 0.093 mm$^{-1}$ | |
| $T$ = 100 (2) K | |
| Block, yellow | |
| 0.55 × 0.55 × 0.50 mm | |

| Table 6.2.14c. Refinement | Figure 6.2.14. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. |
|---|---|
| Refinement on $F^2$ <br><br> $R[F^2 > 2\sigma(F^2)]$ = 0.0443 <br><br> $wR(F^2)$ = 0.1189 <br><br> $S$ = 1.036 <br><br> 3496 reflections <br><br> 256 parameters <br><br> H-atom parameters constrained <br><br> $w = 1/[\sigma^2(F_o^2) +$ <br><br> $(0.0723P)^2 + 0.2346P]$ <br><br> where P = $(F_o^2 + 2F_c^2)/3$ <br><br> $(\Delta/\sigma)_{max}$ = 0.000 <br><br> $\Delta\rho_{max}$ = 0.40 e × Å$^{-3}$ |  |

| $\Delta\rho_{min} = -0.30 \, e \times \text{Å}^{-3}$ | |
|---|---|

**Table 6.2.14d.**

Geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| N(1)-C(7) | 1.2766(14) | C(6)-C(4)-H(4) | 120.2(10) |
| N(1)-C(6) | 1.4102(13) | C(17)-C(16)-C(15) | 120.78(9) |
| O(1)-N(2) | 1.2296(13) | C(17)-C(16)-H(16) | 119.9(9) |
| N(2)-O(2) | 1.2266(13) | C(15)-C(16)-H(16) | 119.3(9) |
| N(2)-C(1) | 1.4636(13) | C(15)-C(14)-C(19) | 120.54(9) |
| C(1)-C(2) | 1.3861(15) | C(15)-C(14)-C(13) | 130.94(9) |
| C(1)-C(3) | 1.3864(15) | C(19)-C(14)-C(13) | 108.51(9) |
| C(6)-C(4) | 1.3968(15) | C(12)-C(13)-C(8) | 121.15(9) |
| C(6)-C(5) | 1.3976(15) | C(12)-C(13)-C(14) | 129.80(9) |
| C(4)-C(3) | 1.3856(15) | C(8)-C(13)-C(14) | 109.04(9) |
| C(4)-H(4) | 0.957(17) | C(14)-C(15)-C(16) | 118.47(9) |
| C(16)-C(17) | 1.3927(15) | C(14)-C(15)-H(15) | 120.9(9) |
| C(16)-C(15) | 1.3966(14) | C(16)-C(15)-H(15) | 120.6(9) |
| C(16)-H(16) | 0.992(16) | N(1)-C(7)-C(19) | 121.95(9) |
| C(14)-C(15) | 1.3867(14) | N(1)-C(7)-C(8) | 132.47(9) |
| C(14)-C(19) | 1.4030(14) | C(19)-C(7)-C(8) | 105.56(8) |
| C(14)-C(13) | 1.4744(13) | C(4)-C(3)-C(1) | 118.61(10) |
| C(13)-C(12) | 1.3849(14) | C(4)-C(3)-H(3) | 119.8(9) |

| | | | | |
|---|---|---|---|---|
| C(13)-C(8) | 1.4096(14) | | C(1)-C(3)-H(3) | 121.5(9) |
| C(15)-H(15) | 0.983(15) | | C(1)-C(2)-C(5) | 118.55(10) |
| C(7)-C(19) | 1.4899(13) | | C(1)-C(2)-H(2) | 120.8(10) |
| C(7)-C(8) | 1.4985(14) | | C(5)-C(2)-H(2) | 120.7(10) |
| C(3)-H(3) | 0.989(16) | | C(2)-C(5)-C(6) | 120.34(10) |
| C(2)-C(5) | 1.3878(14) | | C(2)-C(5)-H(5) | 119.8(9) |
| C(2)-H(2) | 0.965(16) | | C(6)-C(5)-H(5) | 119.8(9) |
| C(5)-H(5) | 0.971(16) | | C(9)-C(8)-C(13) | 120.26(9) |
| C(8)-C(9) | 1.3914(14) | | C(9)-C(8)-C(7) | 131.70(10) |
| C(17)-C(18) | 1.3992(14) | | C(13)-C(8)-C(7) | 107.99(9) |
| C(17)-H(17) | 0.950(16) | | C(16)-C(17)-C(18) | 120.95(9) |
| C(10)-C(11) | 1.3922(16) | | C(16)-C(17)-H(17) | 119.6(9) |
| C(10)-C(9) | 1.3981(15) | | C(18)-C(17)-H(17) | 119.4(9) |
| C(10)-H(10) | 0.988(16) | | C(11)-C(10)-C(9) | 120.90(10) |
| C(18)-C(19) | 1.3856(14) | | C(11)-C(10)-H(10) | 119.4(9) |
| C(18)-H(18) | 0.988(16) | | C(9)-C(10)-H(10) | 119.7(9) |
| C(9)-H(9) | 0.962(15) | | C(19)-C(18)-C(17) | 117.97(9) |
| C(11)-C(12) | 1.3979(15) | | C(19)-C(18)-H(18) | 121.2(9) |
| C(11)-H(11) | 0.978(16) | | C(17)-C(18)-H(18) | 120.9(9) |
| C(12)-H(12) | 0.972(16) | | C(8)-C(9)-C(10) | 118.51(10) |
| C(7)-N(1)-C(6) | 122.24(9) | | C(8)-C(9)-H(9) | 121.9(9) |
| O(2)-N(2)-O(1) | 123.27(9) | | C(10)-C(9)-H(9) | 119.6(9) |
| O(2)-N(2)-C(1) | 118.31(9) | | C(18)-C(19)-C(14) | 121.27(9) |

| | | | |
|---|---|---|---|
| O(1)-N(2)-C(1) | 118.41(9) | C(18)-C(19)-C(7) | 129.86(9) |
| C(2)-C(1)-C(3) | 122.34(10) | C(14)-C(19)-C(7) | 108.87(9) |
| C(2)-C(1)-N(2) | 118.85(10) | C(10)-C(11)-C(12) | 120.85(10) |
| C(3)-C(1)-N(2) | 118.79(9) | C(10)-C(11)-H(11) | 120.9(9) |
| C(4)-C(6)-C(5) | 119.74(10) | C(12)-C(11)-H(11) | 118.2(9) |
| C(4)-C(6)-N(1) | 119.73(10) | C(13)-C(12)-C(11) | 118.32(10) |
| C(5)-C(6)-N(1) | 120.23(9) | C(13)-C(12)-H(12) | 122.0(9) |
| C(3)-C(4)-C(6) | 120.40(10) | C(11)-C(12)-H(12) | 119.6(9) |
| C(3)-C(4)-H(4) | 119.4(10) | | |

# Section three- References

1 J.P. Glusker, M. Lewis, M. Rossi. *Crystal Structure Analysis for Chemists and Biologists*; Wiley-VCH: New York, 1994.

2 A.D. Hunter. *X-ray Structure Analysis Lab Manual: A Beginner's Introduction*, 1998

# Appendix I

**X-Ray crystal data for 1,2-bis[{3,5-bis(trifluoromethyl)benzene}phosphino]benzene**

| Table A1a. Crystal data for 03JU01a | Table A1b. Data collection |
|---|---|
| $C_{38}H_{16}F_{24}P_2$ | Bruker SMART CCD area-detector |
| Mr = 990.45 | diffractometer |
| Monoclinic, $P2_1/n$ | $\omega$ scans |
| $a$ = 11.3667 (6) Å | Absorption correction: multi-scan |
| $b$ = 16.3738 (8) Å | $T_{min}$ = 0.942, $T_{max}$ = 0.964 |
| $c$ = 22.2252 (11) Å | 42957 measured reflections |
| $\beta$ = 94.756 (1) ° | 10226 independent reflections |
| $V$ = 4122.22 (10) Å$^3$ | 32068 reflections with I > 2σ(I) |
| $Z$ = 4 | $R_{int}$ = 0.0394 |
| $D_x$ = 1.596 Mg m$^{-3}$ | $\theta_{max}$ = 28.3° |
| Mo K$_\alpha$ radiation | h = -15 → 15 |
| Cell parameters from 17838 reflections | k = -21 → 21 |
| $\theta$ = 2.22±28.3° | l = -29 → 29 |
| $\mu$ = 0.24 mm$^{-1}$ | |
| $T$ = 100 (2) K | |
| Rectangular, colorless | |
| 0.15 × 0.20 × 0.27 mm | |

| | | | |
|---|---|---|---|
| C(5)-H(5) | 0.94(4) | C(28)-C(27)-C(26) | 121.4(3) |
| C(6)-H(6) | 0.95(3) | C(28)-C(27)-C(38) | 118.9(3) |
| C(7)-C(12) | 1.394(4) | C(26)-C(27)-C(38) | 119.7(3) |
| C(7)-C(8) | 1.401(4) | C(29)-C(28)-C(27) | 118.2(3) |
| C(8)-C(9) | 1.384(4) | C(29)-C(28)-H(28) | 122(2) |
| C(8)-H(8) | 0.97(3) | C(27)-C(28)-H(28) | 120(2) |
| C(9)-C(10) | 1.387(4) | C(28)-C(29)-C(30) | 121.4(3) |
| C(9)-C(31) | 1.498(4) | C(28)-C(29)-C(37) | 119.8(3) |
| C(10)-C(11) | 1.386(4) | C(30)-C(29)-C(37) | 118.7(3) |
| C(10)-H(10) | 0.92(4) | C(29)-C(30)-C(25) | 120.5(3) |
| C(11)-C(12) | 1.390(4) | C(29)-C(30)-H(30) | 120(2) |
| C(11)-C(32) | 1.503(4) | C(25)-C(30)-H(30) | 119(2) |
| C(12)-H(12) | 0.90(4) | F(31C)-C(31)-F(31B) | 106.1(3) |
| C(13)-C(14) | 1.394(4) | F(31C)-C(31)-F(31A) | 106.8(3) |
| C(13)-C(18) | 1.401(4) | F(31B)-C(31)-F(31A) | 106.2(3) |
| C(14)-C(15) | 1.387(4) | F(31C)-C(31)-C(9) | 112.9(3) |
| C(14)-H(14) | 0.90(4) | F(31B)-C(31)-C(9) | 113.1(3) |
| C(15)-C(16) | 1.387(5) | F(31A)-C(31)-C(9) | 111.3(3) |
| C(15)-C(34) | 1.498(4) | F(32A)-C(32)-F(32E) | 92.7(12) |
| C(16)-C(17) | 1.383(4) | F(32A)-C(32)-F(32B) | 108.8(13) |
| C(16)-H(16) | 0.93(4) | F(32E)-C(32)-F(32B) | 19.5(16) |
| C(17)-C(18) | 1.391(4) | F(32A)-C(32)-F(32D) | 17.6(17) |
| C(17)-C(33) | 1.508(5) | F(32E)-C(32)-F(32D) | 105.1(12) |

| | | | | |
|---|---|---|---|---|
| C(19)-C(20) | 1.388(4) | F(32B)-C(32)-F(32D) | 118.0(9) |
| C(19)-C(24) | 1.394(4) | F(32A)-C(32)-F(32F) | 119.9(14) |
| C(20)-C(21) | 1.386(4) | F(32E)-C(32)-F(32F) | 109.0(12) |
| C(20)-H(20) | 0.93(4) | F(32B)-C(32)-F(32F) | 91.1(9) |
| C(21)-C(22) | 1.392(4) | F(32D)-C(32)-F(32F) | 103.4(7) |
| C(21)-C(36) | 1.500(4) | F(32A)-C(32)-F(32C) | 110.3(13) |
| C(22)-C(23) | 1.382(4) | F(32E)-C(32)-F(32C) | 119.4(12) |
| C(22)-H(22) | 0.99(3) | F(32B)-C(32)-F(32C) | 102.4(8) |
| C(23)-C(24) | 1.385(4) | F(32D)-C(32)-F(32C) | 93.2(8) |
| C(23)-C(35) | 1.502(4) | F(32F)-C(32)-F(32C) | 12.5(8) |
| C(24)-H(24) | 0.93(3) | F(32A)-C(32)-C(11) | 109.8(9) |
| C(25)-C(30) | 1.390(4) | F(32E)-C(32)-C(11) | 111.5(7) |
| C(25)-C(26) | 1.401(4) | F(32B)-C(32)-C(11) | 113.8(7) |
| C(26)-C(27) | 1.387(4) | F(32D)-C(32)-C(11) | 114.9(6) |
| C(26)-H(26) | 0.96(4) | F(32F)-C(32)-C(11) | 112.2(6) |
| C(27)-C(28) | 1.381(4) | F(32C)-C(32)-C(11) | 111.4(7) |
| C(27)-C(38) | 1.501(5) | F(33D)-C(33)-F(33C) | 111(2) |
| C(28)-C(29) | 1.380(4) | F(33D)-C(33)-F(33A) | 87.7(18) |
| C(28)-H(28) | 0.94(4) | F(33C)-C(33)-F(33A) | 113.9(16) |
| C(29)-C(30) | 1.385(4) | F(33D)-C(33)-F(33E) | 118(2) |
| C(29)-C(37) | 1.503(4) | F(33C)-C(33)-F(33E) | 11(3) |
| C(30)-H(30) | 0.91(3) | F(33A)-C(33)-F(33E) | 104.1(16) |
| C(31)-F(31C) | 1.315(4) | F(33D)-C(33)-F(33F) | 106.6(13) |

| | | | | |
|---|---|---|---|---|
| C(31)-F(31B) | 1.324(4) | F(33C)-C(33)-F(33F) | 107(2) |
| C(31)-F(31A) | 1.327(4) | F(33A)-C(33)-F(33F) | 18.9(15) |
| C(32)-F(32A) | 1.300(11) | F(33E)-C(33)-F(33F) | 96(2) |
| C(32)-F(32E) | 1.301(10) | F(33D)-C(33)-F(33B) | 21(2) |
| C(32)-F(32B) | 1.308(9) | F(33C)-C(33)-F(33B) | 96.0(14) |
| C(32)-F(32D) | 1.312(9) | F(33A)-C(33)-F(33B) | 107.0(9) |
| C(32)-F(32F) | 1.316(8) | F(33E)-C(33)-F(33B) | 104.8(13) |
| C(32)-F(32C) | 1.323(9) | F(33F)-C(33)-F(33B) | 126.0(14) |
| C(33)-F(33D) | 1.306(11) | F(33D)-C(33)-C(17) | 114.9(9) |
| C(33)-F(33C) | 1.313(11) | F(33C)-C(33)-C(17) | 110.8(9) |
| C(33)-F(33A) | 1.323(10) | F(33A)-C(33)-C(17) | 116.5(10) |
| C(33)-F(33E) | 1.331(10) | F(33E)-C(33)-C(17) | 112.9(7) |
| C(33)-F(33F) | 1.339(13) | F(33F)-C(33)-C(17) | 105.7(11) |
| C(33)-F(33B) | 1.354(7) | F(33B)-C(33)-C(17) | 110.5(6) |
| C(34)-F(34F) | 1.283(15) | F(34F)-C(34)-F(34D) | 107(2) |
| C(34)-F(34D) | 1.287(14) | F(34F)-C(34)-F(34A) | 35(3) |
| C(34)-F(34A) | 1.305(5) | F(34D)-C(34)-F(34A) | 127.5(13) |
| C(34)-F(34B) | 1.315(5) | F(34F)-C(34)-F(34B) | 128.4(18) |
| C(34)-F(34E) | 1.326(14) | F(34D)-C(34)-F(34B) | 61(2) |
| C(34)-F(34C) | 1.343(5) | F(34A)-C(34)-F(34B) | 108.5(4) |
| C(35)-F(35A) | 1.318(4) | F(34F)-C(34)-F(34E) | 103(3) |
| C(35)-F(35B) | 1.321(4) | F(34D)-C(34)-F(34E) | 102(3) |
| C(35)-F(35C) | 1.330(5) | F(34A)-C(34)-F(34E) | 71(4) |

| | | | | |
|---|---|---|---|---|
| C(36)-F(36C) | 1.287(4) | F(34B)-C(34)-F(34E) | 44(4) |
| C(36)-F(36A) | 1.301(4) | F(34F)-C(34)-F(34C) | 73(3) |
| C(36)-F(36B) | 1.302(4) | F(34D)-C(34)-F(34C) | 44(2) |
| C(37)-F(37D) | 1.276(11) | F(34A)-C(34)-F(34C) | 106.3(4) |
| C(37)-F(37C) | 1.291(7) | F(34B)-C(34)-F(34C) | 104.7(4) |
| C(37)-F(37E) | 1.310(8) | F(34E)-C(34)-F(34C) | 137.7(18) |
| C(37)-F(37B) | 1.310(7) | F(34F)-C(34)-C(15) | 116.9(15) |
| C(37)-F(37A) | 1.356(6) | F(34D)-C(34)-C(15) | 117.4(12) |
| C(37)-F(37F) | 1.369(10) | F(34A)-C(34)-C(15) | 114.0(3) |
| C(38)-F(38A) | 1.198(8) | F(34B)-C(34)-C(15) | 111.8(3) |
| C(38)-F(38F) | 1.241(10) | F(34E)-C(34)-C(15) | 107.8(12) |
| C(38)-F(38D) | 1.283(7) | F(34C)-C(34)-C(15) | 111.1(3) |
| C(38)-F(38C) | 1.297(8) | F(35A)-C(35)-F(35B) | 108.1(3) |
| C(38)-F(38B) | 1.434(8) | F(35A)-C(35)-F(35C) | 105.8(3) |
| C(38)-F(38E) | 1.456(8) | F(35B)-C(35)-F(35C) | 106.0(3) |
| C(41)-C(40)-C(45) | 120.0 | F(35A)-C(35)-C(23) | 112.5(3) |
| C(41)-C(40)-H(40) | 120.0 | F(35B)-C(35)-C(23) | 112.7(3) |
| C(45)-C(40)-H(40) | 120.0 | F(35C)-C(35)-C(23) | 111.3(3) |
| C(42)-C(41)-C(40) | 120.0 | F(36C)-C(36)-F(36A) | 106.6(4) |
| C(42)-C(41)-H(41) | 120.0 | F(36C)-C(36)-F(36B) | 104.9(3) |
| C(40)-C(41)-H(41) | 120.0 | F(36A)-C(36)-F(36B) | 104.9(3) |
| C(41)-C(42)-C(43) | 120.0 | F(36C)-C(36)-C(21) | 113.2(3) |
| C(41)-C(42)-H(42) | 120.0 | F(36A)-C(36)-C(21) | 113.0(3) |

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|---|---|---|---|---|
| C(43)-C(42)-H(42) | 120.0 | F(36B)-C(36)-C(21) | 113.5(3) |
| C(44)-C(43)-C(42) | 120.0 | F(37D)-C(37)-F(37C) | 125.2(8) |
| C(44)-C(43)-H(43) | 120.0 | F(37D)-C(37)-F(37E) | 117.0(12) |
| C(42)-C(43)-H(43) | 120.0 | F(37C)-C(37)-F(37E) | 68.4(11) |
| C(43)-C(44)-C(45) | 120.0 | F(37D)-C(37)-F(37B) | 21.5(10) |
| C(43)-C(44)-H(44) | 120.0 | F(37C)-C(37)-F(37B) | 108.8(6) |
| C(45)-C(44)-H(44) | 120.0 | F(37E)-C(37)-F(37B) | 127.9(8) |
| C(44)-C(45)-C(40) | 120.0 | F(37D)-C(37)-F(37A) | 83.8(9) |
| C(44)-C(45)-C(46) | 129.0(8) | F(37C)-C(37)-F(37A) | 107.2(5) |
| C(40)-C(45)-C(46) | 111.0(8) | F(37E)-C(37)-F(37A) | 41.1(12) |
| C(13)-P(1)-C(7) | 101.08(12) | F(37B)-C(37)-F(37A) | 102.6(6) |
| C(13)-P(1)-C(1) | 99.05(12) | F(37D)-C(37)-F(37F) | 102.1(8) |
| C(7)-P(1)-C(1) | 103.34(12) | F(37C)-C(37)-F(37F) | 34.4(4) |
| C(6)-C(1)-C(2) | 118.9(2) | F(37E)-C(37)-F(37F) | 101.5(9) |
| C(6)-C(1)-P(1) | 123.7(2) | F(37B)-C(37)-F(37F) | 81.5(7) |
| C(2)-C(1)-P(1) | 117.35(19) | F(37A)-C(37)-F(37F) | 135.2(7) |
| C(25)-P(2)-C(2) | 101.60(12) | F(37D)-C(37)-C(29) | 112.6(8) |
| C(25)-P(2)-C(19) | 101.43(12) | F(37C)-C(37)-C(29) | 113.0(4) |
| C(2)-P(2)-C(19) | 103.09(12) | F(37E)-C(37)-C(29) | 113.6(4) |
| C(3)-C(2)-C(1) | 119.2(2) | F(37B)-C(37)-C(29) | 114.5(5) |
| C(3)-C(2)-P(2) | 122.4(2) | F(37A)-C(37)-C(29) | 110.0(3) |
| C(1)-C(2)-P(2) | 118.23(19) | C(14)-C(13)-C(18) | 118.8(3) |
| C(4)-C(3)-C(2) | 121.2(3) | C(14)-C(13)-P(1) | 118.9(2) |

| | | | | |
|---|---|---|---|---|
| C(4)-C(3)-H(3) | 118(2) | | C(18)-C(13)-P(1) | 122.3(2) |
| C(2)-C(3)-H(3) | 120(2) | | C(15)-C(14)-C(13) | 120.2(3) |
| C(5)-C(4)-C(3) | 119.4(3) | | C(15)-C(14)-H(14) | 122(2) |
| C(5)-C(4)-H(4) | 122(2) | | C(13)-C(14)-H(14) | 118(2) |
| C(3)-C(4)-H(4) | 119(2) | | C(16)-C(15)-C(14) | 121.1(3) |
| C(4)-C(5)-C(6) | 120.4(3) | | C(16)-C(15)-C(34) | 118.3(3) |
| C(4)-C(5)-H(5) | 120(2) | | C(14)-C(15)-C(34) | 120.5(3) |
| C(6)-C(5)-H(5) | 120(2) | | F(37F)-C(37)-C(29) | 108.3(6) |
| C(5)-C(6)-C(1) | 120.8(3) | | F(38A)-C(38)-F(38F) | 121.1(9) |
| C(5)-C(6)-H(6) | 119(2) | | F(38A)-C(38)-F(38D) | 52.7(10) |
| C(1)-C(6)-H(6) | 121(2) | | F(38F)-C(38)-F(38D) | 116.4(8) |
| C(12)-C(7)-C(8) | 118.1(2) | | F(38A)-C(38)-F(38C) | 113.3(10) |
| C(12)-C(7)-P(1) | 122.0(2) | | F(38F)-C(38)-F(38C) | 22.6(10) |
| C(8)-C(7)-P(1) | 119.4(2) | | F(38D)-C(38)-F(38C) | 131.3(6) |
| C(9)-C(8)-C(7) | 120.7(3) | | F(38A)-C(38)-F(38B) | 108.1(9) |
| C(9)-C(8)-H(8) | 121.5(19) | | F(38F)-C(38)-F(38B) | 72.9(9) |
| C(7)-C(8)-H(8) | 117.8(19) | | F(38D)-C(38)-F(38B) | 58.7(5) |
| C(8)-C(9)-C(10) | 121.0(3) | | F(38C)-C(38)-F(38B) | 95.4(6) |
| C(8)-C(9)-C(31) | 120.0(3) | | F(38A)-C(38)-F(38E) | 43.8(11) |
| C(10)-C(9)-C(31) | 119.0(3) | | F(38F)-C(38)-F(38E) | 100.1(9) |
| C(11)-C(10)-C(9) | 118.6(3) | | F(38D)-C(38)-F(38E) | 96.2(5) |
| C(11)-C(10)-H(10) | 120(2) | | F(38C)-C(38)-F(38E) | 81.3(6) |
| C(9)-C(10)-H(10) | 122(2) | | F(38B)-C(38)-F(38E) | 143.2(5) |

| | | | | |
|---|---|---|---|---|
| C(10)-C(11)-C(12) | 120.9(3) | F(38A)-C(38)-C(27) | 117.2(5) |
| C(10)-C(11)-C(32) | 120.0(3) | F(38F)-C(38)-C(27) | 117.9(7) |
| C(12)-C(11)-C(32) | 119.0(3) | F(38D)-C(38)-C(27) | 114.5(4) |
| C(11)-C(12)-C(7) | 120.6(3) | F(38C)-C(38)-C(27) | 112.5(5) |
| C(11)-C(12)-H(12) | 121(2) | F(38B)-C(38)-C(27) | 107.7(4) |
| C(7)-C(12)-H(12) | 119(2) | F(38E)-C(38)-C(27) | 107.3(4) |
| C(17)-C(16)-C(15) | 118.8(3) | C5–S1–C2 | 91.61 (9) |
| C(17)-C(16)-H(16) | 123(2) | O1–C1–C2 | 124.39 (18) |

# Appendix II

**X-Ray crystal data for *cis*-bis(2,3,5,6-tetramethyl-1,4-diisocyanobenzene) bis[1,2-bis(diphenylphosphino)ethane]tungsten(0)**

| Table A2a. Crystal data for 03Mz48am | Table A2b. Data collection |
|---|---|
| $C_{85}H_{89}N_4P_4W$ | Bruker SMART CCD area-detector |
| $Mr = 1498.33$ | diffractometer |
| Triclinic, P-1 | $\omega$ scans |
| $a = 12.486\ (3)$ Å | Absorption correction: multi-scan |
| $b = 14.298\ (3)$ Å | $T_{min} = 0.741$, $T_{max} = 0.837$ |
| $c = 21.133\ (4)$ Å | 36248 measured reflections |
| $\alpha = 71.067\ (3)\ °$ | 17391 independent reflections |
| $\beta = 81.897\ (4)\ °$ | 14642 reflections with $I > 2\sigma(I)$ |
| $\gamma = 82.440\ (4)\ °$ | $R_{int} = 0.0388$ |
| $V = 3518.1\ (12)$ Å$^3$ | $\theta_{max} = 28.313°$ |
| $Z = 2$ | $h = -16 \rightarrow 16$ |
| $D_x = 1.414$ Mg m$^{-3}$ | $k = -19 \rightarrow 19$ |
| Mo K$_\alpha$ radiation | $l = -28 \rightarrow 28$ |
| Cell parameters from 19900 reflections | |
| $\theta = 2.342 \pm 28.313°$ | |
| $\mu = 1.785$ mm$^{-1}$ | |
| $T = 100\ (2)$ K | |
| Rectangular, colorless | |
| $0.10 \times 0.14 \times 0.30$ mm | |

| Table A2c. Refinement | Figure A2a. ORTEP plot of title compound. Ellipsoids are at the 50% probability level. Solvent molecules of THF and hexane are also shown. |
|---|---|
| Refinement on $F^2$<br><br>$R[F^2 > 2\sigma(F^2)] = 0.0530$<br><br>$wR(F^2) = 0.1033$<br><br>$S = 1.026$<br><br>17391 reflections<br><br>862 parameters<br><br>H-atom parameters constrained<br><br>$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 0.0000P]$<br><br>where $P = (F_o^2 + 2F_c^2)/3$<br><br>$(\Delta/\sigma)_{max} = 0.002$<br><br>$\Delta\rho_{max} = 3.679\ e\times Å^{-3}$<br><br>$\Delta\rho_{min} = -0.924\ e\times Å^{-3}$ |  |
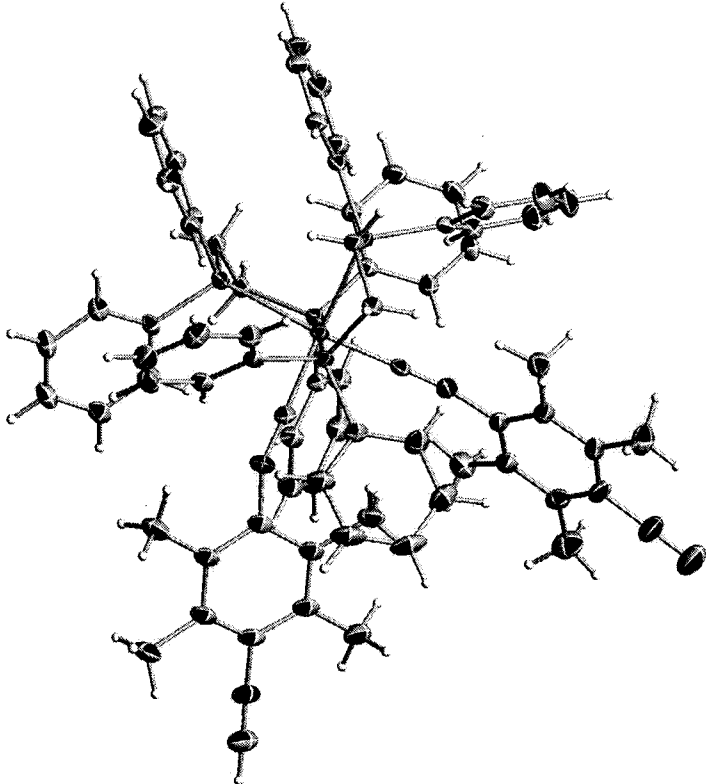
**Table A2d**

Selected geometric parameters (Å, °).

| W(1)-C(1) | 1.973(4) | C(29)-C(22)-C(28) | 121.4(3) |
|---|---|---|---|
| W(1)-C(8) | 2.000(4) | C(30)-C(23)-C(29) | 118.5(3) |
| W(1)-P(2) | 2.4347(9) | C(30)-C(23)-C(69) | 122.0(4) |
| W(1)-P(4) | 2.4669(9) | C(29)-C(23)-C(69) | 119.5(4) |
| W(1)-P(3) | 2.5252(10) | C(26)-C(24)-C(9) | 121.2(4) |
| W(1)-P(1) | 2.5358(9) | C(26)-C(24)-H(24) | 119.4 |

| | | | | |
|---|---|---|---|---|
| P(2)-C(25) | 1.832(3) | C(9)-C(24)-H(24) | 119.4 | |
| P(2)-C(5) | 1.838(4) | C(17)-C(25)-P(2) | 106.6(2) | |
| P(2)-C(7) | 1.843(4) | C(17)-C(25)-H(25A) | 110.4 | |
| P(4)-C(11) | 1.837(4) | P(2)-C(25)-H(25A) | 110.4 | |
| P(4)-C(27) | 1.843(4) | C(17)-C(25)-H(25B) | 110.4 | |
| P(4)-C(6) | 1.857(4) | P(2)-C(25)-H(25B) | 110.4 | |
| P(1)-C(3) | 1.838(4) | H(25A)-C(25)-H(25B) | 108.6 | |
| P(1)-C(17) | 1.843(3) | C(24)-C(26)-C(57) | 120.1(4) | |
| P(1)-C(4) | 1.844(4) | C(24)-C(26)-H(26) | 120.0 | |
| P(3)-C(10) | 1.848(4) | C(57)-C(26)-H(26) | 120.0 | |
| P(3)-C(9) | 1.851(3) | C(15)-C(27)-P(4) | 111.0(2) | |
| P(3)-C(15) | 1.861(4) | C(15)-C(27)-H(27A) | 109.4 | |
| C(3)-C(42) | 1.395(5) | P(4)-C(27)-H(27A) | 109.4 | |
| C(3)-C(12) | 1.399(5) | C(15)-C(27)-H(27B) | 109.4 | |
| C(1)-N(2) | 1.221(4) | P(4)-C(27)-H(27B) | 109.4 | |
| C(4)-C(31) | 1.386(5) | H(27A)-C(27)-H(27B) | 108.0 | |
| C(4)-C(20) | 1.396(5) | C(48)-C(28)-C(22) | 118.9(3) | |
| C(5)-C(16) | 1.387(5) | C(48)-C(28)-C(60) | 120.0(3) | |
| C(5)-C(34) | 1.392(5) | C(22)-C(28)-C(60) | 121.0(3) | |
| C(6)-C(43) | 1.385(5) | C(23)-C(29)-C(22) | 119.0(3) | |
| C(6)-C(13) | 1.392(5) | C(23)-C(29)-C(37) | 119.5(3) | |
| C(7)-C(56) | 1.388(6) | P(3)-C(15)-H(15B) | 109.6 | |
| C(7)-C(18) | 1.390(5) | H(15A)-C(15)-H(15B) | 108.1 | |

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|---|---|---|---|---|
| N(1)-C(8) | 1.187(5) | C(62)-C(16)-C(5) | 121.3(4) |
| N(1)-C(22) | 1.393(5) | C(62)-C(16)-H(16) | 119.3 |
| C(9)-C(14) | 1.382(5) | C(5)-C(16)-H(16) | 119.3 |
| C(9)-C(24) | 1.400(5) | C(25)-C(17)-P(1) | 107.8(2) |
| C(10)-C(19) | 1.387(5) | C(25)-C(17)-H(17A) | 110.1 |
| C(10)-C(36) | 1.403(5) | P(1)-C(17)-H(17A) | 110.1 |
| C(11)-C(21) | 1.393(5) | C(25)-C(17)-H(17B) | 110.1 |
| C(11)-C(32) | 1.397(5) | P(1)-C(17)-H(17B) | 110.1 |
| C(12)-C(67) | 1.372(5) | H(17A)-C(17)-H(17B) | 108.5 |
| C(12)-H(12) | 0.9500 | N(1)-C(8)-W(1) | 171.1(3) |
| C(13)-C(39) | 1.382(5) | C(71)-C(18)-C(7) | 120.2(4) |
| C(13)-H(13) | 0.9500 | C(71)-C(18)-H(18) | 119.9 |
| C(14)-C(45) | 1.395(5) | C(22)-C(29)-C(37) | 121.5(3) |
| C(14)-H(14) | 0.9500 | C(48)-C(30)-C(23) | 123.3(3) |
| C(15)-C(27) | 1.509(5) | C(48)-C(30)-N(3) | 118.3(4) |
| C(15)-H(15A) | 0.9900 | C(23)-C(30)-N(3) | 118.4(4) |
| C(15)-H(15B) | 0.9900 | C(4)-C(31)-C(47) | 119.9(4) |
| C(16)-C(62) | 1.382(5) | C(4)-C(31)-H(31) | 120.0 |
| C(16)-H(16) | 0.9500 | C(47)-C(31)-H(31) | 120.0 |
| C(17)-C(25) | 1.533(5) | C(35)-C(32)-C(11) | 121.0(3) |
| C(17)-H(17A) | 0.9900 | C(35)-C(32)-H(32) | 119.5 |
| C(17)-H(17B) | 0.9900 | C(11)-C(32)-H(32) | 119.5 |
| C(18)-C(71) | 1.389(6) | C(54)-C(33)-C(20) | 120.3(4) |

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|---|---|---|---|---|
| C(18)-H(18) | 0.9500 | C(54)-C(33)-H(33) | 119.9 |
| C(19)-C(46) | 1.383(5) | C(20)-C(33)-H(33) | 119.9 |
| C(19)-H(19) | 0.9500 | C(41)-C(34)-C(5) | 120.6(4) |
| C(20)-C(33) | 1.391(5) | C(41)-C(34)-H(34) | 119.7 |
| C(20)-H(20) | 0.9500 | C(5)-C(34)-H(34) | 119.7 |
| C(21)-C(49) | 1.396(5) | C(32)-C(35)-C(50) | 120.3(4) |
| C(21)-H(21) | 0.9500 | C(32)-C(35)-H(35) | 119.8 |
| N(2)-C(38) | 1.386(5) | C(50)-C(35)-H(35) | 119.8 |
| C(22)-C(29) | 1.406(5) | C(66)-C(36)-C(10) | 120.5(4) |
| C(22)-C(28) | 1.411(5) | C(66)-C(36)-H(36) | 119.8 |
| C(23)-C(30) | 1.390(6) | C(10)-C(36)-H(36) | 119.8 |
| C(23)-C(29) | 1.391(5) | C(29)-C(37)-H(37A) | 109.5 |
| C(23)-C(69) | 1.507(5) | C(29)-C(37)-H(37B) | 109.5 |
| C(24)-C(26) | 1.386(5) | H(37A)-C(37)-H(37B) | 109.5 |
| C(24)-H(24) | 0.9500 | C(29)-C(37)-H(37C) | 109.5 |
| C(25)-H(25A) | 0.9900 | H(37A)-C(37)-H(37C) | 109.5 |
| C(25)-H(25B) | 0.9900 | H(37B)-C(37)-H(37C) | 109.5 |
| C(26)-C(57) | 1.389(6) | C(77)-N(3)-C(30) | 178.9(5) |
| C(26)-H(26) | 0.9500 | N(2)-C(38)-C(52) | 118.9(4) |
| C(27)-H(27A) | 0.9900 | N(2)-C(38)-C(44) | 119.8(3) |
| C(27)-H(27B) | 0.9900 | C(52)-C(38)-C(44) | 121.3(3) |
| C(28)-C(48) | 1.389(5) | C(40)-C(39)-C(13) | 120.0(4) |
| C(28)-C(60) | 1.519(5) | C(40)-C(39)-H(39) | 120.0 |

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|---|---|---|---|---|
| C(29)-C(37) | 1.498(5) | C(13)-C(39)-H(39) | 120.0 | |
| C(30)-C(48) | 1.386(6) | C(39)-C(40)-C(61) | 119.4(4) | |
| C(30)-N(3) | 1.407(5) | C(39)-C(40)-H(40) | 120.3 | |
| C(31)-C(47) | 1.400(5) | C(61)-C(40)-H(40) | 120.3 | |
| C(31)-H(31) | 0.9500 | C(55)-C(41)-C(34) | 120.1(4) | |
| C(32)-C(35) | 1.384(5) | C(55)-C(41)-H(41) | 119.9 | |
| C(32)-H(32) | 0.9500 | C(34)-C(41)-H(41) | 119.9 | |
| C(33)-C(54) | 1.379(6) | C(70)-C(42)-C(3) | 120.8(4) | |
| C(33)-H(33) | 0.9500 | C(70)-C(42)-H(42) | 119.6 | |
| C(34)-C(41) | 1.387(6) | C(3)-C(42)-H(42) | 119.6 | |
| C(34)-H(34) | 0.9500 | C(61)-C(43)-C(6) | 121.5(4) | |
| C(35)-C(50) | 1.386(6) | C(61)-C(43)-H(43) | 119.3 | |
| C(35)-H(35) | 0.9500 | C(6)-C(43)-H(43) | 119.3 | |
| C(36)-C(66) | 1.390(6) | C(51)-C(44)-C(38) | 119.1(4) | |
| C(36)-H(36) | 0.9500 | C(51)-C(44)-C(65) | 121.8(4) | |
| C(37)-H(37A) | 0.9800 | C(38)-C(44)-C(65) | 119.1(3) | |
| C(37)-H(37B) | 0.9800 | C(57)-C(45)-C(14) | 120.3(4) | |
| C(37)-H(37C) | 0.9800 | C(57)-C(45)-H(45) | 119.8 | |
| N(3)-C(77) | 1.142(6) | C(14)-C(45)-H(45) | 119.8 | |
| C(38)-C(52) | 1.405(5) | C(19)-C(46)-C(68) | 120.0(4) | |
| C(38)-C(44) | 1.407(6) | C(19)-C(46)-H(46) | 120.0 | |
| C(39)-C(40) | 1.373(6) | C(68)-C(46)-H(46) | 120.0 | |
| C(39)-H(39) | 0.9500 | C(54)-C(47)-C(31) | 120.7(4) | |

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|---|---|---|---|---|
| C(40)-C(61) | 1.394(6) | C(54)-C(47)-H(47) | 119.7 |
| C(40)-H(40) | 0.9500 | C(31)-C(47)-H(47) | 119.7 |
| C(41)-C(55) | 1.381(6) | C(30)-C(48)-C(28) | 118.6(3) |
| C(41)-H(41) | 0.9500 | C(30)-C(48)-C(76) | 120.3(4) |
| C(42)-C(70) | 1.380(6) | C(28)-C(48)-C(76) | 121.1(4) |
| C(42)-H(42) | 0.9500 | C(50)-C(49)-C(21) | 119.9(4) |
| C(43)-C(61) | 1.381(5) | C(50)-C(49)-H(49) | 120.0 |
| C(43)-H(43) | 0.9500 | C(21)-C(49)-H(49) | 120.0 |
| C(44)-C(51) | 1.396(5) | C(49)-C(50)-C(35) | 119.8(4) |
| C(44)-C(65) | 1.510(5) | C(49)-C(50)-H(50) | 120.1 |
| C(45)-C(57) | 1.389(6) | C(35)-C(50)-H(50) | 120.1 |
| C(45)-H(45) | 0.9500 | C(53)-C(51)-C(44) | 118.1(4) |
| C(46)-C(68) | 1.391(6) | C(53)-C(51)-C(59) | 120.7(4) |
| C(46)-H(46) | 0.9500 | C(44)-C(51)-C(59) | 121.3(4) |
| C(47)-C(54) | 1.379(6) | C(58)-C(52)-C(38) | 118.5(4) |
| C(47)-H(47) | 0.9500 | C(58)-C(52)-C(64) | 121.4(4) |
| C(48)-C(76) | 1.510(6) | C(38)-C(52)-C(64) | 120.1(3) |
| C(49)-C(50) | 1.377(6) | C(72)-N(4)-C(53) | 179.4(5) |
| C(49)-H(49) | 0.9500 | C(58)-C(53)-C(51) | 123.3(3) |
| C(50)-H(50) | 0.9500 | C(58)-C(53)-N(4) | 118.4(4) |
| C(51)-C(53) | 1.392(6) | C(51)-C(53)-N(4) | 118.3(4) |
| C(51)-C(59) | 1.498(6) | C(33)-C(54)-C(47) | 119.6(4) |
| C(52)-C(58) | 1.402(5) | C(33)-C(54)-H(54) | 120.2 |

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|---|---|---|---|---|
| C(52)-C(64) | 1.496(6) | C(47)-C(54)-H(54) | 120.2 |
| N(4)-C(72) | 1.141(5) | C(41)-C(55)-C(62) | 120.0(4) |
| N(4)-C(53) | 1.405(5) | C(41)-C(55)-H(55) | 120.0 |
| C(53)-C(58) | 1.384(6) | C(62)-C(55)-H(55) | 120.0 |
| C(54)-H(54) | 0.9500 | C(7)-C(56)-C(75) | 120.9(4) |
| C(55)-C(62) | 1.382(6) | C(7)-C(56)-H(56) | 119.6 |
| C(55)-H(55) | 0.9500 | C(75)-C(56)-H(56) | 119.6 |
| C(56)-C(75) | 1.389(6) | C(26)-C(57)-C(45) | 119.2(4) |
| C(56)-H(56) | 0.9500 | C(26)-C(57)-H(57) | 120.4 |
| C(57)-H(57) | 0.9500 | C(45)-C(57)-H(57) | 120.4 |
| C(58)-C(63) | 1.507(6) | C(53)-C(58)-C(52) | 118.8(4) |
| C(59)-H(59A) | 0.9800 | C(53)-C(58)-C(63) | 120.6(4) |
| C(59)-H(59B) | 0.9800 | C(52)-C(58)-C(63) | 120.6(4) |
| C(59)-H(59C) | 0.9800 | C(51)-C(59)-H(59A) | 109.5 |
| C(60)-H(60A) | 0.9800 | C(51)-C(59)-H(59B) | 109.5 |
| C(60)-H(60B) | 0.9800 | H(59A)-C(59)-H(59B) | 109.5 |
| C(60)-H(60C) | 0.9800 | C(51)-C(59)-H(59C) | 109.5 |
| C(61)-H(61) | 0.9500 | H(59A)-C(59)-H(59C) | 109.5 |
| C(62)-H(62) | 0.9500 | H(59B)-C(59)-H(59C) | 109.5 |
| C(63)-H(63A) | 0.9800 | C(28)-C(60)-H(60A) | 109.5 |
| C(63)-H(63B) | 0.9800 | C(28)-C(60)-H(60B) | 109.5 |
| C(63)-H(63C) | 0.9800 | H(60A)-C(60)-H(60B) | 109.5 |
| C(64)-H(64A) | 0.9800 | C(28)-C(60)-H(60C) | 109.5 |

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|---|---|---|---|---|
| C(64)-H(64B) | 0.9800 | H(60A)-C(60)-H(60C) | 109.5 |
| C(64)-H(64C) | 0.9800 | H(60B)-C(60)-H(60C) | 109.5 |
| C(65)-H(65A) | 0.9800 | C(43)-C(61)-C(40) | 120.0(4) |
| C(65)-H(65B) | 0.9800 | C(43)-C(61)-H(61) | 120.0 |
| C(65)-H(65C) | 0.9800 | C(40)-C(61)-H(61) | 120.0 |
| C(66)-C(68) | 1.369(6) | C(16)-C(62)-C(55) | 119.7(4) |
| C(66)-H(66) | 0.9500 | C(16)-C(62)-H(62) | 120.2 |
| C(67)-C(73) | 1.377(6) | C(55)-C(62)-H(62) | 120.2 |
| C(67)-H(67) | 0.9500 | C(58)-C(63)-H(63A) | 109.5 |
| C(68)-H(68) | 0.9500 | C(58)-C(63)-H(63B) | 109.5 |
| C(69)-H(69A) | 0.9800 | H(63A)-C(63)-H(63B) | 109.5 |
| C(69)-H(69B) | 0.9800 | C(58)-C(63)-H(63C) | 109.5 |
| C(69)-H(69C) | 0.9800 | H(63A)-C(63)-H(63C) | 109.5 |
| C(70)-C(73) | 1.383(7) | H(63B)-C(63)-H(63C) | 109.5 |
| C(70)-H(70) | 0.9500 | C(52)-C(64)-H(64A) | 109.5 |
| C(71)-C(74) | 1.375(7) | C(52)-C(64)-H(64B) | 109.5 |
| C(71)-H(71) | 0.9500 | H(64A)-C(64)-H(64B) | 109.5 |
| C(72)-H(72) | 0.9500 | C(52)-C(64)-H(64C) | 109.5 |
| C(73)-H(73) | 0.9500 | H(64A)-C(64)-H(64C) | 109.5 |
| C(74)-C(75) | 1.374(7) | H(64B)-C(64)-H(64C) | 109.5 |
| C(74)-H(74) | 0.9500 | C(44)-C(65)-H(65A) | 109.5 |
| C(75)-H(75) | 0.9500 | C(44)-C(65)-H(65B) | 109.5 |
| C(76)-H(76A) | 0.9800 | H(65A)-C(65)-H(65B) | 109.5 |

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|---|---|---|---|---|
| C(76)-H(76B) | 0.9800 | C(44)-C(65)-H(65C) | 109.5 |
| C(76)-H(76C) | 0.9800 | H(65A)-C(65)-H(65C) | 109.5 |
| C(77)-H(77) | 0.9500 | H(65B)-C(65)-H(65C) | 109.5 |
| O(1)-C(81) | 1.436(8) | C(68)-C(66)-C(36) | 120.4(4) |
| O(1)-C(78) | 1.445(6) | C(68)-C(66)-H(66) | 119.8 |
| C(78)-C(79) | 1.515(7) | C(36)-C(66)-H(66) | 119.8 |
| C(78)-H(78A) | 0.9900 | C(12)-C(67)-C(73) | 120.3(4) |
| C(78)-H(78B) | 0.9900 | C(12)-C(67)-H(67) | 119.8 |
| C(79)-C(80) | 1.496(8) | C(73)-C(67)-H(67) | 119.8 |
| C(79)-H(79A) | 0.9900 | C(66)-C(68)-C(46) | 119.9(4) |
| C(79)-H(79B) | 0.9900 | C(66)-C(68)-H(68) | 120.1 |
| C(80)-C(81) | 1.442(10) | C(46)-C(68)-H(68) | 120.1 |
| C(80)-H(80A) | 0.9900 | C(23)-C(69)-H(69A) | 109.5 |
| C(80)-H(80B) | 0.9900 | C(23)-C(69)-H(69B) | 109.5 |
| C(81)-H(81A) | 0.9900 | H(69A)-C(69)-H(69B) | 109.5 |
| C(81)-H(81B) | 0.9900 | C(23)-C(69)-H(69C) | 109.5 |
| C(85)-C(86) | 1.556(18) | H(69A)-C(69)-H(69C) | 109.5 |
| C(85)-C(84) | 1.76(2) | H(69B)-C(69)-H(69C) | 109.5 |
| C(85)-H(85A) | 0.9900 | C(42)-C(70)-C(73) | 120.6(4) |
| C(85)-H(85B) | 0.9900 | C(42)-C(70)-H(70) | 119.7 |
| C(84)-C(84)#1 | 1.48(2) | C(73)-C(70)-H(70) | 119.7 |
| C(84)-H(84A) | 0.9900 | C(74)-C(71)-C(18) | 120.9(4) |
| C(84)-H(84B) | 0.9900 | C(74)-C(71)-H(71) | 119.6 |

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|---|---|---|---|---|
| C(86)-H(86A) | 0.9800 | | C(18)-C(71)-H(71) | 119.6 |
| C(86)-H(86B) | 0.9800 | | N(4)-C(72)-H(72) | 180.0 |
| C(86)-H(86C) | 0.9800 | | C(67)-C(73)-C(70) | 119.3(4) |
| O(2)-C(91)#2 | 0.19(3) | | C(67)-C(73)-H(73) | 120.3 |
| O(2)-C(92)#2 | 1.35(2) | | C(70)-C(73)-H(73) | 120.3 |
| O(2)-C(93) | 1.440(16) | | C(75)-C(74)-C(71) | 119.4(4) |
| O(2)-C(90) | 1.441(16) | | C(75)-C(74)-H(74) | 120.3 |
| O(2)-C(90)#2 | 1.55(2) | | C(71)-C(74)-H(74) | 120.3 |
| C(90)-C(93)#2 | 0.758(14) | | C(74)-C(75)-C(56) | 120.3(4) |
| C(90)-C(92)#2 | 0.784(13) | | C(74)-C(75)-H(75) | 119.9 |
| C(90)-O(2)#2 | 1.55(2) | | C(56)-C(75)-H(75) | 119.9 |
| C(90)-C(91) | 1.565(13) | | C(48)-C(76)-H(76A) | 109.5 |
| C(90)-C(91)#2 | 1.617(17) | | C(48)-C(76)-H(76B) | 109.5 |
| C(90)-C(90)#2 | 2.02(2) | | H(76A)-C(76)-H(76B) | 109.5 |
| C(91)-O(2)#2 | 0.19(3) | | C(48)-C(76)-H(76C) | 109.5 |
| C(91)-C(93)#2 | 1.361(19) | | H(76A)-C(76)-H(76C) | 109.5 |
| C(91)-C(92) | 1.490(13) | | H(76B)-C(76)-H(76C) | 109.5 |
| C(91)-C(90)#2 | 1.617(17) | | N(3)-C(77)-H(77) | 180.0 |
| C(92)-C(90)#2 | 0.784(13) | | C(81)-O(1)-C(78) | 107.1(5) |
| C(92)-O(2)#2 | 1.35(2) | | O(1)-C(78)-C(79) | 106.0(4) |
| C(92)-C(93) | 1.449(13) | | O(1)-C(78)-H(78A) | 110.5 |
| C(93)-C(90)#2 | 0.758(14) | | C(79)-C(78)-H(78A) | 110.5 |
| C(93)-C(91)#2 | 1.361(19) | | O(1)-C(78)-H(78B) | 110.5 |

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| C(1)-W(1)-C(8) | 89.57(14) | C(79)-C(78)-H(78B) | 110.5 | |
| C(1)-W(1)-P(2) | 78.92(10) | H(78A)-C(78)-H(78B) | 108.7 | |
| C(8)-W(1)-P(2) | 94.05(10) | C(80)-C(79)-C(78) | 101.4(5) | |
| C(1)-W(1)-P(4) | 96.18(10) | C(80)-C(79)-H(79A) | 111.5 | |
| C(8)-W(1)-P(4) | 84.05(10) | C(78)-C(79)-H(79A) | 111.5 | |
| P(2)-W(1)-P(4) | 174.78(3) | C(80)-C(79)-H(79B) | 111.5 | |
| C(1)-W(1)-P(3) | 95.41(11) | C(78)-C(79)-H(79B) | 111.5 | |
| C(8)-W(1)-P(3) | 162.65(10) | H(79A)-C(79)-H(79B) | 109.3 | |
| P(2)-W(1)-P(3) | 103.21(3) | C(81)-C(80)-C(79) | 105.1(5) | |
| P(4)-W(1)-P(3) | 78.90(3) | C(81)-C(80)-H(80A) | 110.7 | |
| C(1)-W(1)-P(1) | 156.84(10) | C(79)-C(80)-H(80A) | 110.7 | |
| C(8)-W(1)-P(1) | 92.75(10) | C(81)-C(80)-H(80B) | 110.7 | |
| P(2)-W(1)-P(1) | 77.94(3) | C(79)-C(80)-H(80B) | 110.7 | |
| P(4)-W(1)-P(1) | 106.97(3) | H(80A)-C(80)-H(80B) | 108.8 | |
| P(3)-W(1)-P(1) | 89.18(3) | O(1)-C(81)-C(80) | 108.9(5) | |
| C(25)-P(2)-C(5) | 103.22(17) | O(1)-C(81)-H(81A) | 109.9 | |
| C(25)-P(2)-C(7) | 102.85(16) | C(80)-C(81)-H(81A) | 109.9 | |
| C(5)-P(2)-C(7) | 101.30(16) | O(1)-C(81)-H(81B) | 109.9 | |
| C(25)-P(2)-W(1) | 111.21(11) | C(80)-C(81)-H(81B) | 109.9 | |
| C(5)-P(2)-W(1) | 119.39(12) | H(81A)-C(81)-H(81B) | 108.3 | |
| C(7)-P(2)-W(1) | 116.76(12) | C(86)-C(85)-C(84) | 91.4(11) | |
| C(11)-P(4)-C(27) | 103.02(16) | C(86)-C(85)-H(85A) | 113.4 | |
| C(11)-P(4)-C(6) | 99.26(16) | C(84)-C(85)-H(85A) | 113.4 | |

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| C(27)-P(4)-C(6) | 98.43(16) | | C(86)-C(85)-H(85B) | 113.4 |
| C(11)-P(4)-W(1) | 121.21(11) | | C(84)-C(85)-H(85B) | 113.4 |
| C(27)-P(4)-W(1) | 111.38(12) | | H(85A)-C(85)-H(85B) | 110.7 |
| C(6)-P(4)-W(1) | 120.02(12) | | C(84)#1-C(84)-C(85) | 102.1(17) |
| C(3)-P(1)-C(17) | 101.44(16) | | C(84)#1-C(84)-H(84A) | 111.4 |
| C(3)-P(1)-C(4) | 98.82(15) | | C(85)-C(84)-H(84A) | 111.4 |
| C(17)-P(1)-C(4) | 101.92(16) | | C(84)#1-C(84)-H(84B) | 111.4 |
| C(3)-P(1)-W(1) | 119.65(11) | | C(85)-C(84)-H(84B) | 111.4 |
| C(17)-P(1)-W(1) | 107.71(11) | | H(84A)-C(84)-H(84B) | 109.2 |
| C(4)-P(1)-W(1) | 123.98(11) | | C(85)-C(86)-H(86A) | 109.5 |
| C(10)-P(3)-C(9) | 99.72(16) | | C(85)-C(86)-H(86B) | 109.5 |
| C(10)-P(3)-C(15) | 100.39(16) | | H(86A)-C(86)-H(86B) | 109.5 |
| C(9)-P(3)-C(15) | 99.55(16) | | C(85)-C(86)-H(86C) | 109.5 |
| C(10)-P(3)-W(1) | 125.84(11) | | H(86A)-C(86)-H(86C) | 109.5 |
| C(9)-P(3)-W(1) | 118.86(12) | | H(86B)-C(86)-H(86C) | 109.5 |
| C(15)-P(3)-W(1) | 108.20(12) | | C(91)#2-O(2)-C(92)#2 | 132(10) |
| C(42)-C(3)-C(12) | 117.5(3) | | C(91)#2-O(2)-C(93) | 63(7) |
| C(42)-C(3)-P(1) | 124.4(3) | | C(92)#2-O(2)-C(93) | 131.3(19) |
| C(12)-C(3)-P(1) | 118.1(3) | | C(91)#2-O(2)-C(90) | 153(10) |
| N(2)-C(1)-W(1) | 168.4(3) | | C(92)#2-O(2)-C(90) | 32.4(7) |
| C(31)-C(4)-C(20) | 119.0(3) | | C(93)-O(2)-C(90) | 109.5(12) |
| C(31)-C(4)-P(1) | 124.4(3) | | C(91)#2-O(2)-C(90)#2 | 92(8) |
| C(20)-C(4)-P(1) | 116.6(3) | | C(92)#2-O(2)-C(90)#2 | 114.1(15) |

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| C(16)-C(5)-C(34) | 118.3(3) | C(93)-O(2)-C(90)#2 | 29.1(7) |
| C(16)-C(5)-P(2) | 118.5(3) | C(90)-O(2)-C(90)#2 | 85.0(11) |
| C(34)-C(5)-P(2) | 123.1(3) | C(93)#2-C(90)-C(92)#2 | 140(2) |
| C(43)-C(6)-C(13) | 117.4(3) | C(93)#2-C(90)-O(2) | 144(2) |
| C(43)-C(6)-P(4) | 123.4(3) | C(92)#2-C(90)-O(2) | 67.6(15) |
| C(13)-C(6)-P(4) | 119.1(3) | C(93)#2-C(90)-O(2)#2 | 67.6(14) |
| C(56)-C(7)-C(18) | 118.4(4) | C(92)#2-C(90)-O(2)#2 | 150(2) |
| C(56)-C(7)-P(2) | 118.3(3) | O(2)-C(90)-O(2)#2 | 95.0(11) |
| C(18)-C(7)-P(2) | 123.3(3) | C(93)#2-C(90)-C(91) | 60.4(14) |
| C(8)-N(1)-C(22) | 159.4(4) | C(92)#2-C(90)-C(91) | 156(2) |
| C(14)-C(9)-C(24) | 118.1(3) | O(2)-C(90)-C(91) | 101.3(10) |
| C(14)-C(9)-P(3) | 123.8(3) | O(2)#2-C(90)-C(91) | 7.1(11) |
| C(24)-C(9)-P(3) | 118.1(3) | C(93)#2-C(90)-C(91)#2 | 146.6(19) |
| C(19)-C(10)-C(36) | 118.2(3) | C(92)#2-C(90)-C(91)#2 | 66.6(11) |
| C(19)-C(10)-P(3) | 118.8(3) | O(2)-C(90)-C(91)#2 | 3.2(19) |
| C(36)-C(10)-P(3) | 122.9(3) | O(2)#2-C(90)-C(91)#2 | 94.6(11) |
| C(21)-C(11)-C(32) | 117.9(3) | C(91)-C(90)-C(91)#2 | 101.1(8) |
| C(21)-C(11)-P(4) | 122.8(3) | C(93)#2-C(90)-C(90)#2 | 106.6(16) |
| C(32)-C(11)-P(4) | 119.3(3) | C(92)#2-C(90)-C(90)#2 | 112.9(15) |
| C(67)-C(12)-C(3) | 121.4(4) | O(2)-C(90)-C(90)#2 | 49.7(8) |
| C(67)-C(12)-H(12) | 119.3 | O(2)#2-C(90)-C(90)#2 | 45.3(7) |
| C(3)-C(12)-H(12) | 119.3 | C(91)-C(90)-C(90)#2 | 51.7(6) |
| C(39)-C(13)-C(6) | 121.7(4) | C(91)#2-C(90)-C(90)#2 | 49.4(6) |

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| C(39)-C(13)-H(13) | 119.1 | O(2)#2-C(91)-C(93)#2 | 110(8) |
| C(6)-C(13)-H(13) | 119.1 | O(2)#2-C(91)-C(92) | 43(10) |
| C(9)-C(14)-C(45) | 121.0(4) | C(93)#2-C(91)-C(92) | 126.3(12) |
| C(9)-C(14)-H(14) | 119.5 | O(2)#2-C(91)-C(90) | 81(8) |
| C(45)-C(14)-H(14) | 119.5 | C(93)#2-C(91)-C(90) | 29.0(6) |
| C(27)-C(15)-P(3) | 110.3(2) | C(92)-C(91)-C(90) | 105.7(9) |
| C(27)-C(15)-H(15A) | 109.6 | O(2)#2-C(91)-C(90)#2 | 24(10) |
| P(3)-C(15)-H(15A) | 109.6 | C(93)#2-C(91)-C(90)#2 | 104.1(10) |
| C(27)-C(15)-H(15B) | 109.6 | C(92)-C(91)-C(90)#2 | 28.9(5) |
| C(7)-C(18)-H(18) | 119.9 | C(90)-C(91)-C(90)#2 | 78.9(8) |
| C(46)-C(19)-C(10) | 121.0(4) | C(90)#2-C(92)-O(2)#2 | 80.0(15) |
| C(46)-C(19)-H(19) | 119.5 | C(90)#2-C(92)-C(93) | 19.6(11) |
| C(10)-C(19)-H(19) | 119.5 | O(2)#2-C(92)-C(93) | 97.2(13) |
| C(33)-C(20)-C(4) | 120.5(4) | C(90)#2-C(92)-C(91) | 84.5(13) |
| C(33)-C(20)-H(20) | 119.7 | O(2)#2-C(92)-C(91) | 5.6(18) |
| C(4)-C(20)-H(20) | 119.7 | C(93)-C(92)-C(91) | 102.2(9) |
| C(11)-C(21)-C(49) | 121.1(4) | C(90)#2-C(93)-C(91)#2 | 90.6(16) |
| C(11)-C(21)-H(21) | 119.4 | C(90)#2-C(93)-O(2) | 83.3(16) |
| C(49)-C(21)-H(21) | 119.4 | C(91)#2-C(93)-O(2) | 7.3(12) |
| C(1)-N(2)-C(38) | 143.9(4) | C(90)#2-C(93)-C(92) | 20.3(11) |
| N(1)-C(22)-C(29) | 119.8(3) | C(91)#2-C(93)-C(92) | 110.0(11) |
| N(1)-C(22)-C(28) | 118.7(3) | O(2)-C(93)-C(92) | 102.9(12) |