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CHEMICAL SCIENCES DIVISION

I. Redox Chemistry of Bimetallic Fulvalene Complexes II. Oligocyclopentadienyl Complexes

D.S. Brown
(Ph.D. Thesis)

November 1993



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I. Redox Chemistry of Bimetallic Fulvalene Complexes
II. Oligocyclopentadienyl Complexes

David Stephen Brown
Ph.D. Thesis

Department of Chemistry
University of California

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

November 1993

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Abstract

I. Redox Chemistry of Bimetallic Fulvalene Complexes
II. Oligocyclopentadienyl Complexes

by

David Stephen Brown

Doctor of Philosophy in Chemistry

University of California at Berkeley

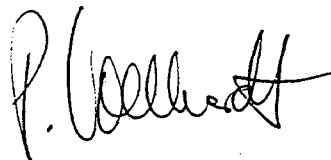
Professor K. Peter C. Vollhardt, Chair

The electrochemistry of the heterobimetallic complexes (fulvalene)WFe(CO)₅ (**30**) and (fulvalene)WRu(CO)₅ (**31**) has been investigated. Compound **30** is reduced in two one-electron processes, and this behavior was exploited synthetically to prepare the tetranuclear dimer **98** by selective metal reduction. Complex **31** displayed a distinction between the metals upon reoxidation of the dianion, allowing the formation of the dimer **103** by selective metal anion oxidation. The dianions of both **30** and **31** were prepared and trapped as the corresponding dimethyl complexes **99** and **102**, respectively.

The redox behavior of **30** led to an investigation of the use of electrocatalysis to effect metal-specific ligand substitution. It was found that reduction of **30** with a catalytic amount of CpFe(C₆Me₆) **97** in the presence of excess P(OMe)₃ or PMe₃ led to the formation of the zwitterions (fulvalene)[W(CO)₃]⁻[Fe(CO)PR₃]⁺ (**107**, R = P(OMe)₃; **108**, R = PMe₃). X-ray crystallography was used to confirm the structure of **107**. This electrocatalytic process was extended to the homobimetallic species (fulvalene)Mo₂(CO)₆ **93** and (fulvalene)W₂(CO)₆ **94**, allowing the preparation of the previously reported zwitterions **117** and **118**, respectively. It was also shown that selective metal substitution could be achieved with the heterobimetallic compounds (fulvalene)MoRu(CO)₅ **95** and **31**. Compound **31** also displayed unique behavior with different reducing agents, as the

monosubstituted zwitterion (fulvalene)[W(CO)₃]⁻[Ru(CO)₂(PMe₃)⁺] **123** was obtained when **97** was used while the disubstituted complex (fulvalene)[W(CO)₃]⁻[Ru(CO)(PMe₃)₂]⁺ **122** was produced when Cp*Fe(C₆Me₆) was the catalyst.

Potential synthetic routes to quatercyclopentadienyl complexes were also explored. Various attempts to couple heterobimetallic fulvalene compounds proved to be unsuccessful. The use of a pinacol coupling reaction on the enone (3-oxo-1-cyclopentenyl)cyclopentadienyltungstentricarbonyl methyl **22** with SmI₂ produced the corresponding diols **170a** and **b** in quantitative yield, but efforts to convert the diols to quatercyclopentadienyl species by dehydration were unsuccessful. Attempts to couple the anion of (cyclopentadienyl)cyclopentadienyltungstentricarbonyl methyl **24** also failed to give the desired quatercyclopentadienyl species.



Acknowledgments

I would like to thank all of the people who helped to make this work possible. First, I am indebted to Peter Vollhardt for his support and approach to chemistry, which made for a unique independent learning experience. I also wish to extend special thanks to Didier Astruc, whose creativity underlies much of this work and whose enthusiasm for chemistry I hope to emulate. Additionally, I want to express my deep appreciation for the contributions of Marie-Hélène Delville, who provided all of the cyclic voltammetry investigations which are presented in this text. Special thanks are also due to my group mentors Andy Kahn, Randy Myrabo, and Andrew Van Sickle, as their experience proved invaluable in the completion of this work. I extend my thanks to all the members of the Vollhardt group, especially Debbie Mohler, Jean-Pierre and Véronique Gotteland, Rüdiger Faust, Cristina Azevedo, Alvin Negron, Ansgar Nonn, Mike Malaska, Mike West, and Martin Ruppelt, who made my graduate career more interesting and rewarding. Finally, I want to express my deep gratitude to my parents, who were always supportive throughout my educational pursuits.

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Chapter One

Introduction

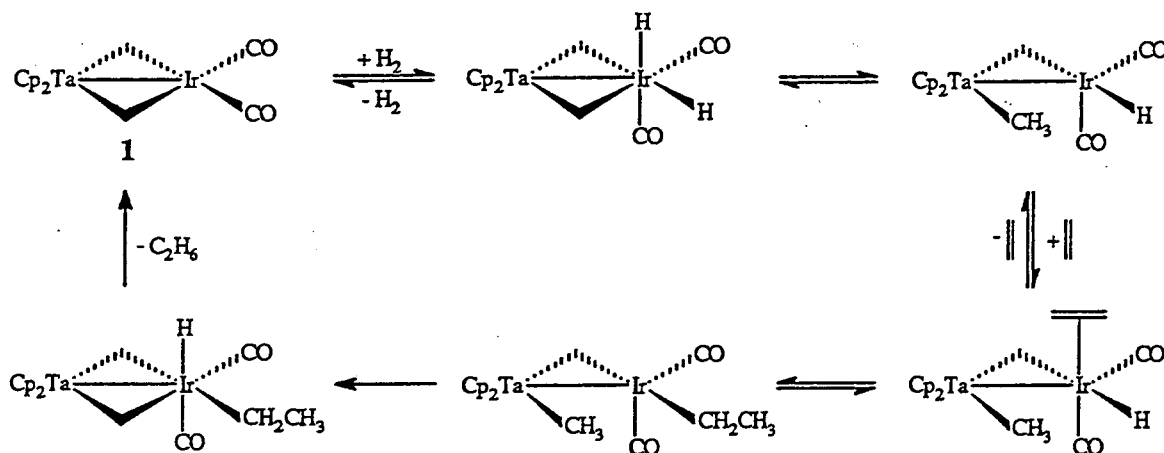
The first part of this thesis will discuss the electrochemical behavior of some heterobimetallic fulvalene complexes. This work is part of the ongoing effort to explore the reactivity of complexes containing two different metal centers. Since relevant introductory material is presented at the beginning of each chapter, this general introduction will focus on the reasons for the interest in heterobimetallic complexes. Some representative examples from the recent literature will be cited, and the latest developments in fulvalene chemistry itself will be emphasized.

One of the primary reasons for the interest in complexes containing two metal centers is that these compounds may serve as models for metal surfaces, thereby leading to an improved understanding of many important heterogeneous reactions. For example, the strong metal support interaction (SMSI), in which a late transition metal film displays enhanced catalytic activity when combined with an early transition metal support,¹ has generated a significant amount of work on the synthesis of early-late heterobimetallic complexes which might display the same effect in solution.² Bergman has recently provided detailed studies of the reactivity of some early-late heterobimetallic complexes,³ and a proposed mechanism for the hydrogenation of ethylene by the tantalum-iridium complex **1** is shown in Scheme 1.1. According to this mechanism, the role of the tantalum center is to allow the reductive elimination of one of the bridging methylene groups so that catalysis occurs without dissociation of the iridium carbonyls.

Another reason for the significant amount of interest in heterobimetallic compounds is the possibility that these compounds will display cooperative interactions between the metal centers.⁴ Such synergistic effects could give rise to novel reactivity compared to monometallic analogs. Garland has explored this concept in heterometallic clusters by

comparing the catalyst precursors $\text{CoRh}(\text{CO})_7$ and $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ with the homometallic clusters $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ in the hydroformylation of 3,3-dimethylbut-1-ene.⁵ In this case, it was found that the heterometallic clusters showed significantly shorter induction periods, but this effect was attributed to the facile fragmentation of these compounds rather than any cooperative interactions between the different metals. Each compound gave rise to the same active catalyst, which was a mononuclear rhodium species. Garland's work illustrates a common problem encountered with heterobimetallic clusters, as these compounds frequently undergo fragmentation reactions to give mononuclear species.⁶

Scheme 1.1



In order to circumvent the problem of cluster fragmentation, a wide variety of bridging ligands have been employed as a means of linking the metal centers, and some recent examples of these types of compounds are shown in Figure 1.1.⁷ There is considerable evidence that heterobimetallic species with bridging ligands can display enhanced or novel reactivity. For example, the catalytic hydrogenation of cyclohexene by the ruthenium-iridium heterobimetallic complexes **8** and **9** has been examined by Oro.^{7E} Synergism which produced enhanced catalytic activity compared to mononuclear analogs was observed, and the ruthenium center in each case was postulated to serve as a center of

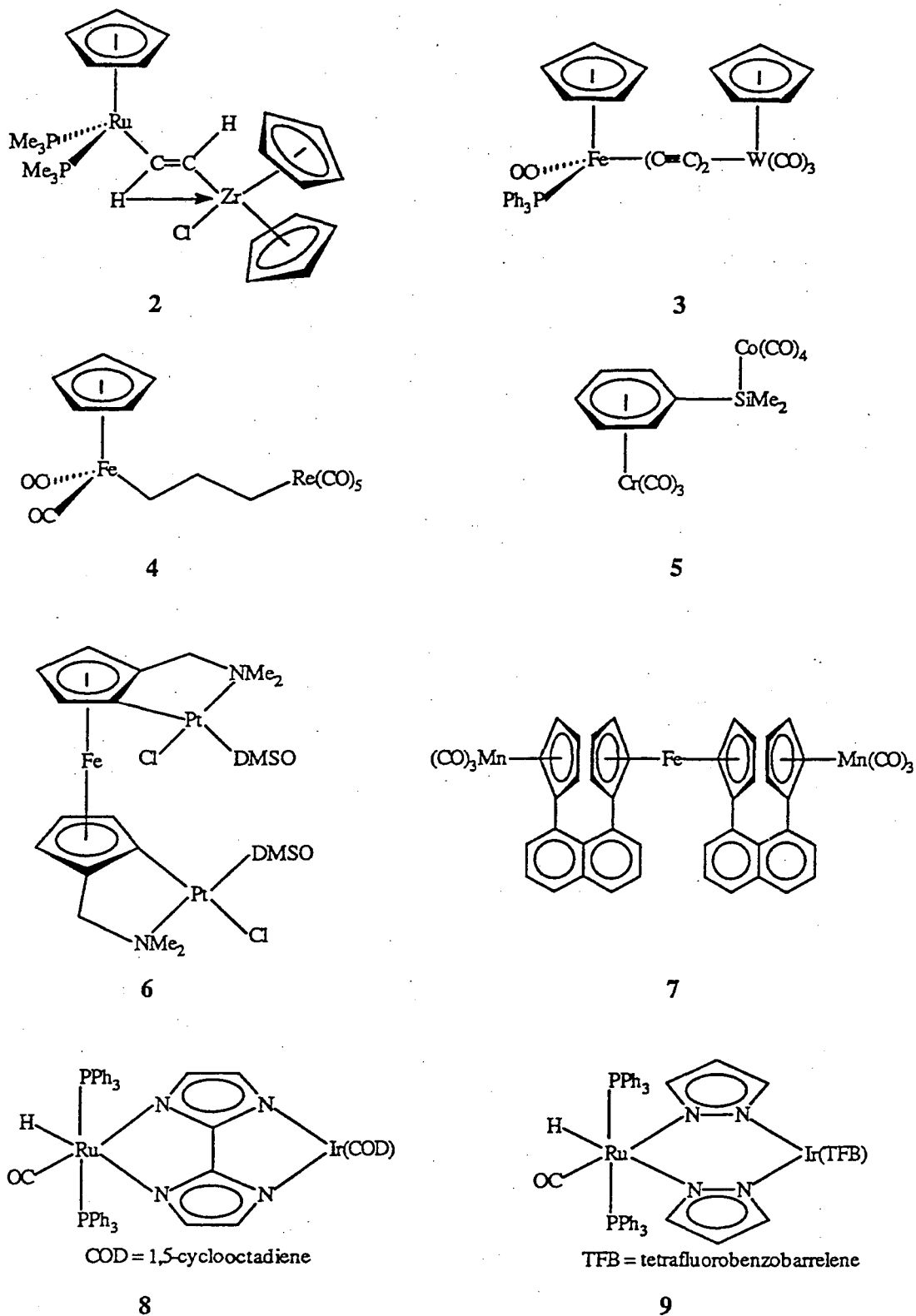
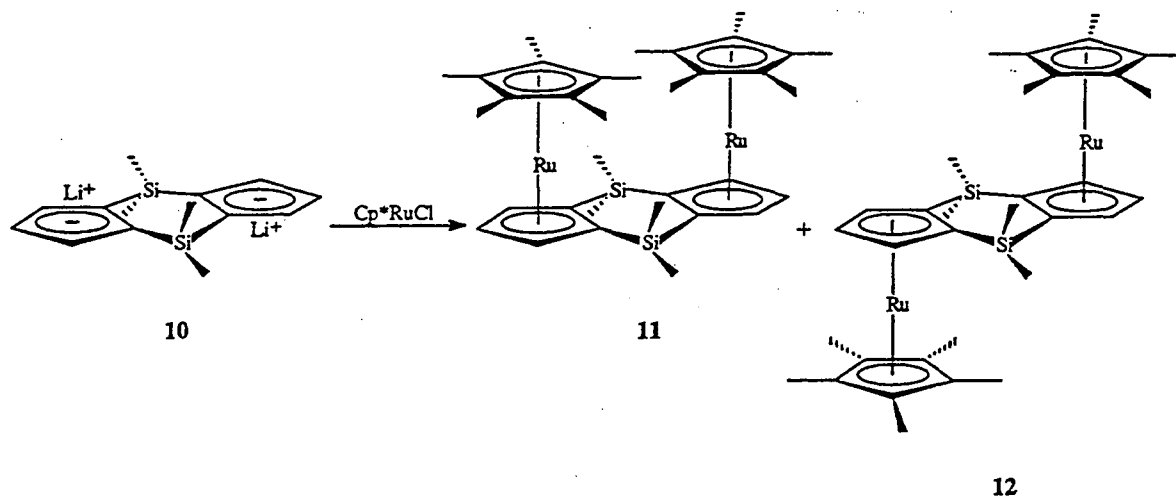


Figure 1.1. Heterobimetallic complexes with bridging ligands: (2) alkenediyl;^{7a} (3) butadienediyl;^{7b} (4) alkanediyl;^{7c} (5) arene-dimethylsilyl;^{7d} (6) 1,1'-bis(*N,N*-dimethylaminomethyl)ferrocenyl;^{7e} (7) 1,1'-bis(8-cyclopentadienyl-1-naphthyl)ferrocenyl;^{7f} (8) 2,2'-biimidazole;^{7g} (9) pyrazolate.^{7g}

variable electron density which helped to activate the iridium center. Thus, the origin of the synergism was ascribed to an indirect cooperative interaction between the metal centers via electronic communication through the bridging ligands.

There are a number of points to be considered when using bridging ligands. First, the metal-ligand bonds should be sufficiently strong to ensure that dissociation to mononuclear fragments does not occur. Second, the bridging ligand should allow electronic communication between the metal centers, as was observed by Oro. Additionally, the ligand should hold the metal centers in close proximity to allow for direct metal-metal interactions, and finally, the ligand must allow for the selective introduction of the metals so that heterobimetallic compounds can be prepared efficiently.

Scheme 1.2

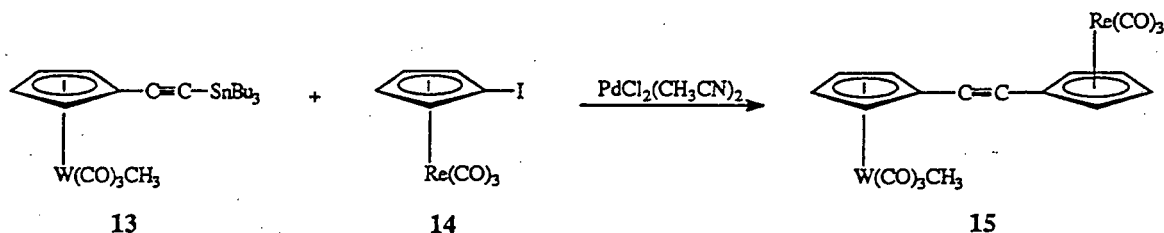


There are very few ligand systems which satisfy all of the above concerns. For example, bidentate phosphines suffer from the limitation of relatively weak metal-phosphorus bonds, which are typically on the order of 30-40 kcal/mol.⁸ A variety of bridging ligands have been developed which employ linked cyclopentadienyl (Cp) rings, which are particularly attractive due to the strong Cp-metal bonds (90-118 kcal/mol)⁹ and the fact that Cp complexes are known for all the transition metals. However, most of these systems suffer from other limitations. The doubly-bridged cyclopentadienyl system

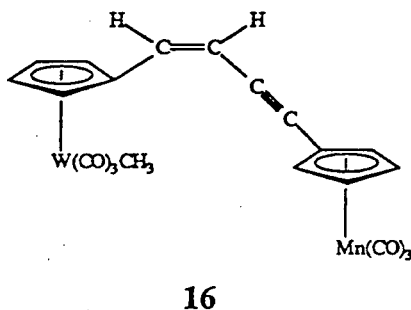
10,¹⁰ for example, affords the possibility of electronic communication mediated by the $\text{Si}(\text{CH}_3)_2$ units¹¹ but gives mixtures of cis and trans products when treated with metal reagents (Scheme 1.2). Furthermore, the system is not amenable to the synthesis of heterobimetallic compounds in that it does not allow selective complexation of the Cp rings.

An elegant approach to heterobimetallic compounds, in which palladium-mediated coupling is utilized (Scheme 1.3), has been provided by Stille.¹² In this case, the acetylene bridge can allow electronic communication between the metals as well as serve as a site of further reactivity, and the synthetic route allows the preparation of numerous complexes.

Scheme 1.3

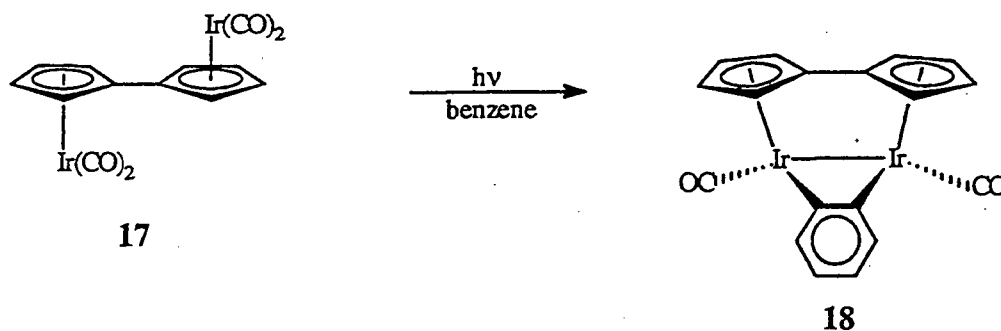


Unfortunately, the rigid acetylene bridge also caused the distance between the metal centers to be too large to allow for intramolecular metal-metal interactions. In an effort to circumvent this problem, an additional ethylene bridge was introduced to bend the linkage and bring the metal centers closer together to give compounds such as 16.¹³ However, this approach gave viscous oils which were difficult to purify and characterize, and no crystallographic information was obtained to indicate the distance between the metal centers.



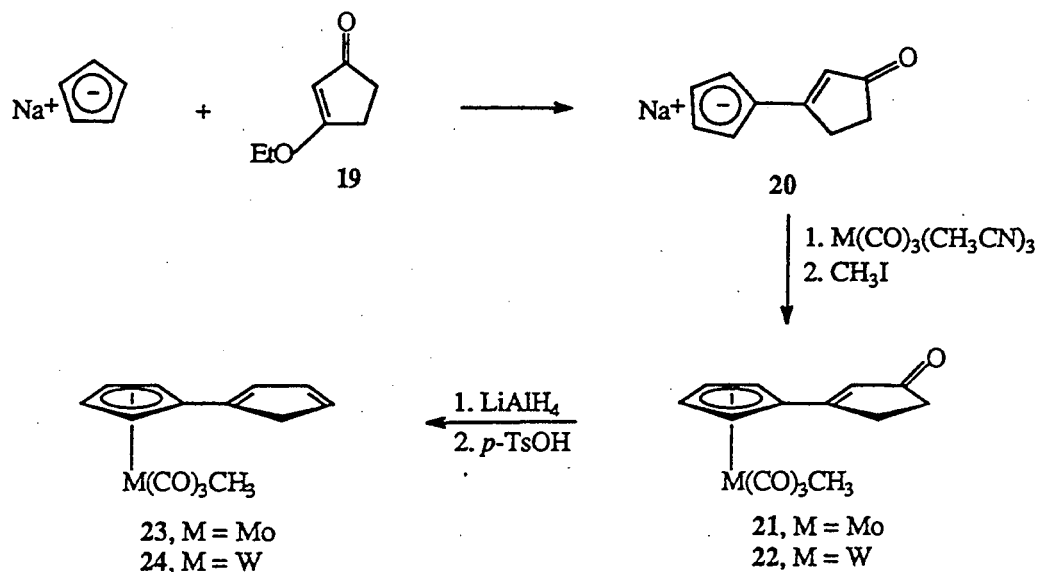
In contrast to the foregoing examples, the fulvalene ligand provides an ideal template on which to bind metal centers. This ligand offers the advantage of strong Cp-metal bonds, but the direct linkage of the rings forces the metal centers to be in close proximity, allowing the formation of metal-metal bonds. The relatively short distance between the metals also affords the possibility of cooperative interactions even in the absence of a metal-metal bond, as was illustrated in the study of the double C-H activation chemistry of the diiridium complex **17** (Scheme 1.4).¹⁴ The delocalized system of π -electrons in the fulvalene ligand permits electronic communication between the metals in the absence of a metal-metal bond, an aspect which has been investigated and confirmed by Astruc,¹⁵ Hendrickson,¹⁶ and Mueller-Westerhoff.¹⁷ Additionally, the fulvalene ligand has proven to be extremely versatile in the preparation of heterobimetallic complexes.

Scheme 1.4



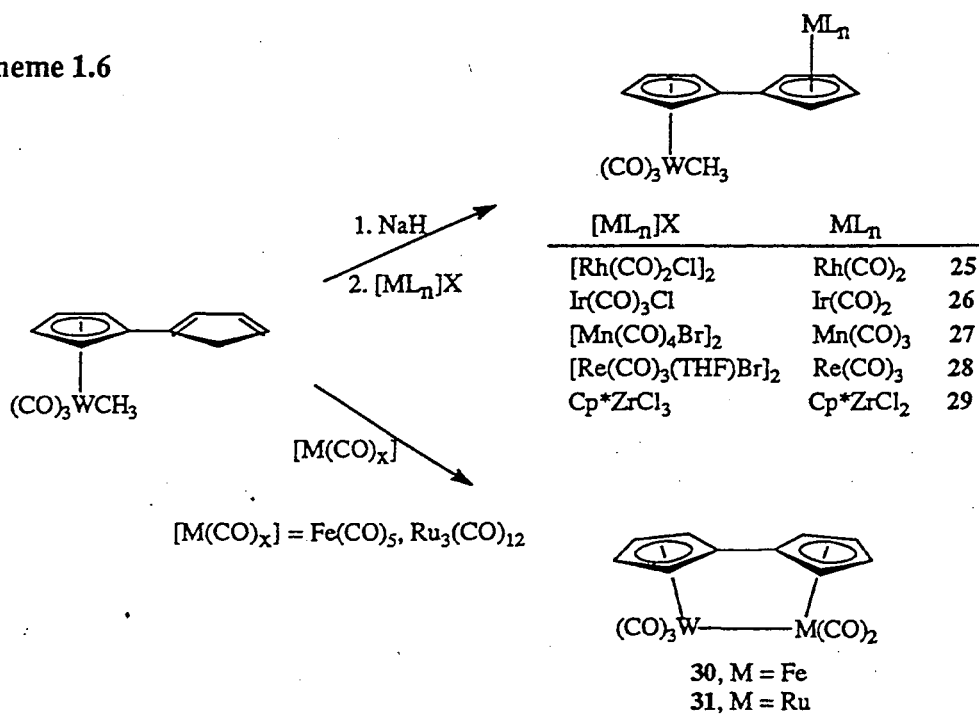
Although there have been numerous reports of homobimetallic fulvalene compounds,¹⁸ the synthesis of heterobimetallic derivatives presented the much more difficult challenge of finding a means of selectively complexing one ring while the other remained unchanged. This problem was solved by the development of a synthetic route utilizing a cyclopentenone moiety as a masked Cp unit (Scheme 1.5).¹⁹ In this sequence, 3-ethoxy-2-cyclopentenone is added to a solution of sodium cyclopentadienide to give enone **20** by a conjugate addition-elimination reaction. The resulting enone is then treated with a metal reagent to introduce the first metal center selectively. Elaboration of the

Scheme 1.5



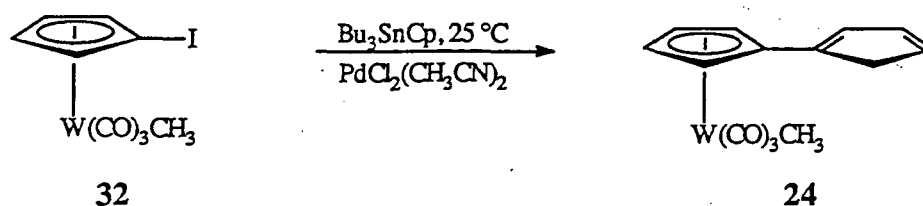
cyclopentenone unit to give the second Cp ring is accomplished by reduction with lithium aluminum hydride followed by catalytic dehydration with *p*-toluenesulfonic acid (*p*-TsOH), giving the precursors 23 and 24. The versatility of 24 was illustrated by the preparation of a variety of heterobimetallic complexes, both with and without metal-metal bonds (Scheme 1.6).^{19b}

Scheme 1.6



In an effort to expand the available routes to heterobimetallic fulvalene complexes, the extension of Stille's palladium-mediated coupling reaction to the preparation of fulvalene compounds was investigated.²⁰ This method was found to give an efficient route to the precursor **24** (Scheme 1.7). Although Stille had found this type of reaction to be applicable with several different metals, there were limitations in the fulvalene case. The reaction worked well to produce the molybdenum and tungsten precursors **23** and **24**, but the extension to other metals proved unsuccessful. As a result, this approach was deemed to be inferior to the previous route and was not pursued further for the preparation of fulvalene complexes.

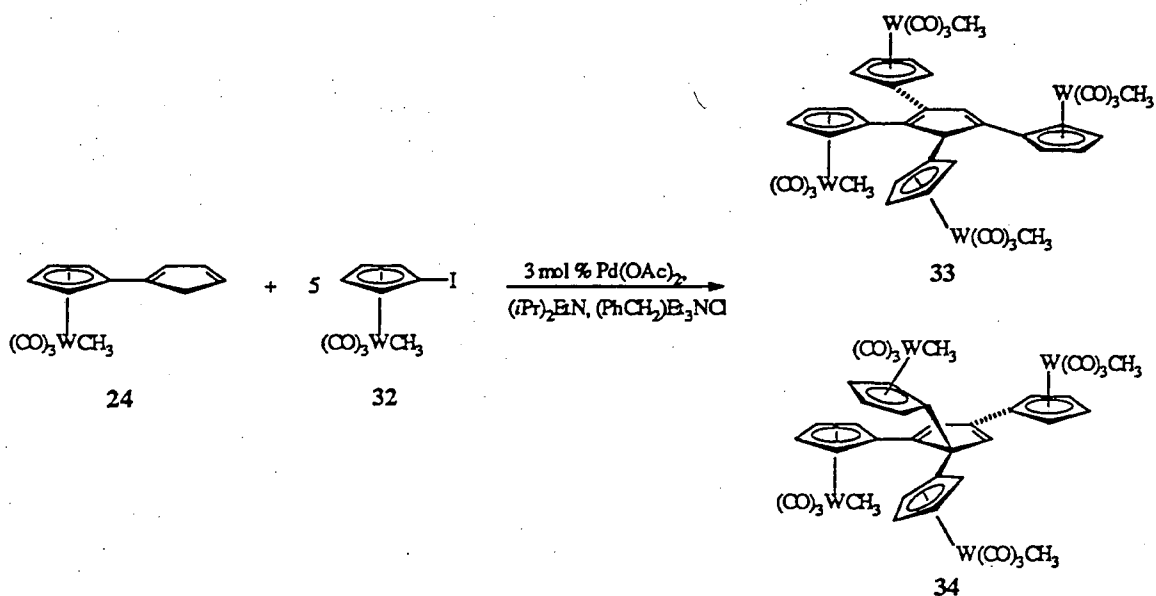
Scheme 1.7



The utility of the palladium-mediated coupling methodology for the preparation of heterotrimetallic tercyclopentadienyl compounds was also studied, but in this case a surprising result was obtained.²⁰ Instead of the expected tercyclopentadienyl isomers, a low yield of the tetrametallic complex **33** was produced, resulting from the addition of three $\text{CpW}(\text{CO})_3(\text{CH}_3)$ units to the starting material. Subsequent development of this reaction led to an optimized yield of 60% for the two isomers **33** and **34** (Scheme 1.8). The failure to add a fourth $\text{CpW}(\text{CO})_3(\text{CH}_3)$ unit was attributed to the severe steric crowding around the central Cp ring, and an x-ray structure of isomer **34** supported this hypothesis. Unfortunately, the steric problem also seemed to prevent further reactions of **33** and **34**, such as the metallation of the central ring. This coupling reaction showed some generality, as the analogous manganese and iron complexes could be prepared,

although the yield with iron was low (6%). Additionally, mixed coupling reactions could be achieved by varying the iodocyclopentadienylmetal reagent in Scheme 1.8.²¹

Scheme 1.8

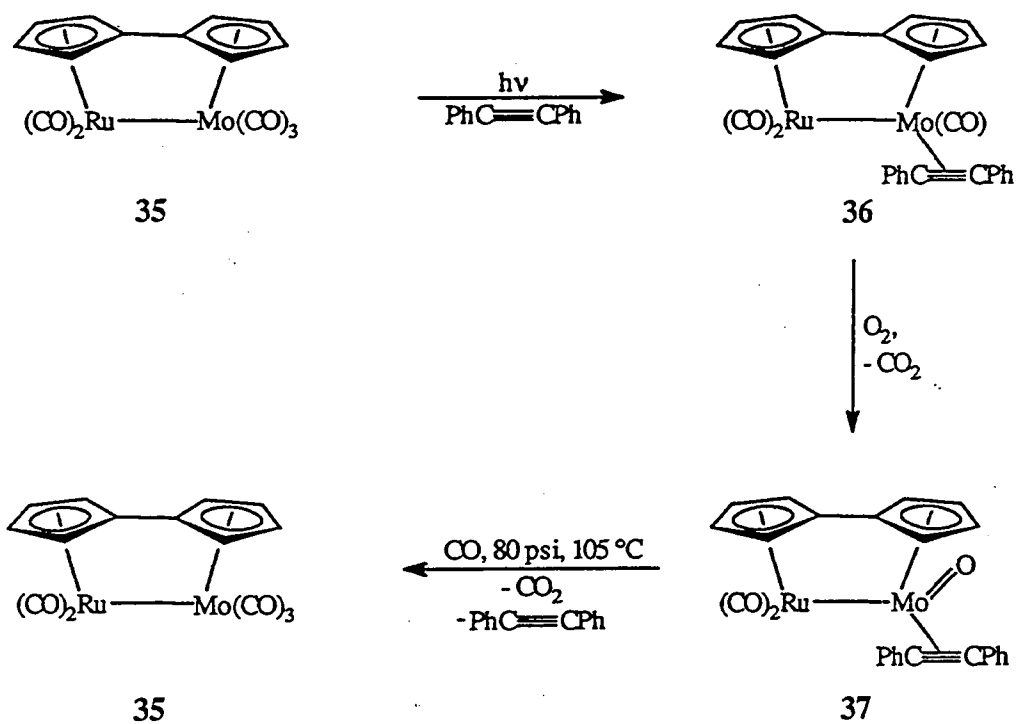


With the emphasis placed on developing methodology for the preparation of heterobimetallic fulvalene complexes, the reaction chemistry of this class of compounds remains largely unexplored. In cases where reaction chemistry has been studied, however, fascinating results have been obtained. The most significant example occurred with the molybdenum-ruthenium complex 35.²² This compound was found to undergo substitution with diphenylacetylene selectively at the molybdenum center, and oxidation with oxygen gave the molybdenum-oxo species 37, which could then be converted back to the starting material under moderate pressures of carbon monoxide (Scheme 1.9). Overall, the sequence represents a model for the catalytic oxidation of carbon monoxide by oxygen to give carbon dioxide, and it confirms the hypothesis that synergistic effects can be observed in heterobimetallic fulvalene compounds.

In order to expand the understanding of the reactivity of heterobimetallic fulvalene complexes, some representative examples were chosen for further study. Chapter 2 will

describe the exploration of the redox behavior of some of these compounds, and Chapter 3 will detail the extension of the redox chemistry to metal-specific ligand substitution. Chapter 4 will present efforts to apply the knowledge gained in the synthesis of fulvalene compounds to the preparation of quatercyclopentadienyl systems.

Scheme 1.9

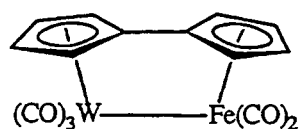


Chapter Two

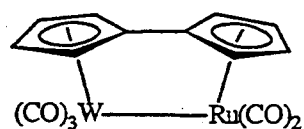
Redox Properties of Heterobimetallic Fulvalene Complexes with Metal-Metal Bonds

2.1 Background

This chapter will describe the investigation of the electrochemical behavior of the heterobimetallic fulvalene complexes **30** and **31**. One of the most extensively studied aspects of bimetallic compounds is their redox properties, particularly in the area of intramolecular electron transfer.²³ As such, a general treatment of this subject is beyond the scope of this text, but several reviews are available.²⁴ Instead, this introduction will focus on the electrochemistry of bimetallic cyclopentadienyl-metal complexes containing metal-metal bonds, as these compounds provide a good basis of comparison for the fulvalene analogs. Previous examinations of electron transfer in fulvalene complexes will also be emphasized.



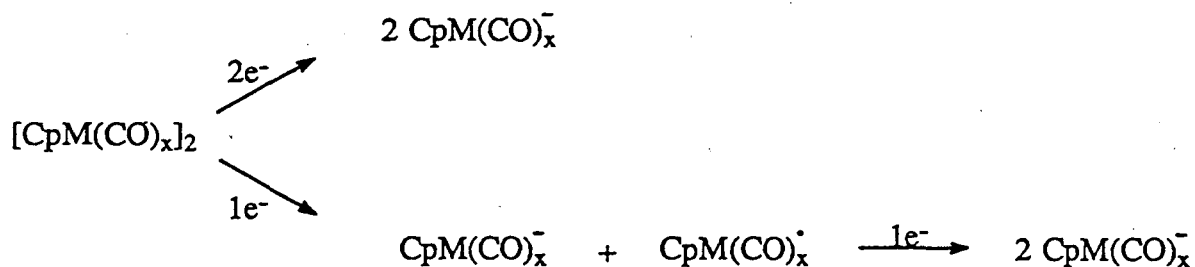
30



31

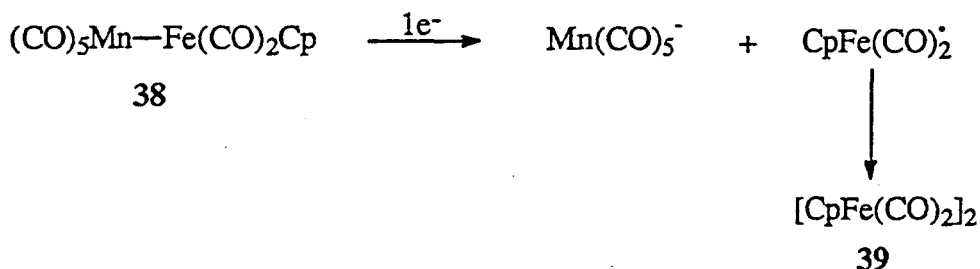
Some of the earliest investigations of the redox properties of Cp compounds were performed by Dessy, who published a series of papers on organometallic electrochemistry.²⁵ The behavior of metal-metal bonds upon reduction was emphasized, and an extensive list of compounds was examined.^{25b} This work led to several generalizations about this class of compounds. Dessy proposed that the reduction of metal-metal bonded complexes could lead to cleavage of the metal-metal bond by two routes, which are illustrated in Scheme 2.1 for a general Cp-metal dimer. The first route involves transfer of two electrons to the dimer to give the dianion, which then undergoes cleavage of the metal-metal bond to give two mononuclear anions, thereby representing an EC process. The second path assumes transfer of only one electron to give a radical

Scheme 2.1



anion. Scission of the metal-metal bond then gives a mononuclear anion and a mononuclear radical, with the radical undergoing rapid reduction to the corresponding anion to give an overall ECE sequence. Dessy went on to state that homobimetallic systems underwent reduction exclusively by the first pathway, while heterobimetallic compounds could be reduced by either route. Furthermore, when a heterobimetallic compound was reduced by the second path, the resulting anionic fragment could be predicted based on a knowledge of the reduction potentials of the two analogous homobimetallic complexes. For example, compound 38 gave a manganese anion and an iron radical upon one-electron reduction because $\text{Mn}_2(\text{CO})_{10}$ is more easily reduced than $[\text{CpFe}(\text{CO})_2]_2$ (Scheme 2.2).

Scheme 2.2

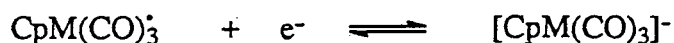
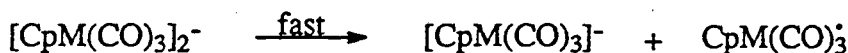
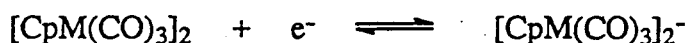


Recently, some of Dessy's generalizations have been questioned, particularly his contention that homobimetallic compounds are always reduced by an EC mechanism. Since Dessy did not provide any detailed mechanistic studies in his survey of bimetallic compounds, several systems have been reinvestigated. Kadish has examined both the reduction and oxidation of the dimers $[\text{CpM}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$),²⁶ and both reactions followed an ECE mechanism (Scheme 2.3). The rate determining step was the first

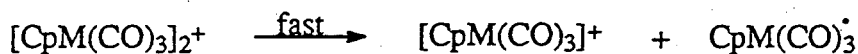
electron transfer in each case, as the resulting radicals were rapidly reduced (or oxidized) to the corresponding anions (or cations). Evidence for the intermediate 17-electron radicals was obtained by ESR spectroscopy.

Scheme 2.3

Reduction

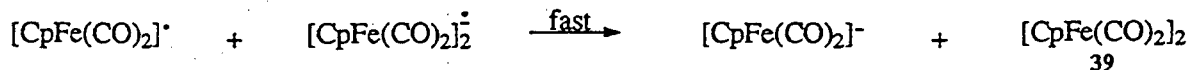
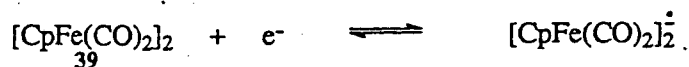


Oxidation



In a further test of Dessy's hypothesis, Davies and Parker studied the reduction of $[\text{CpFe}(\text{CO})_2]_2$,²⁷ and an ECE mechanism was proposed on the basis of data obtained by derivative cyclic voltammetry (Scheme 2.4). In this case, however, the rate determining step was proposed to be the cleavage of the metal-metal bond in the radical anion. The activation energy for this process was 15.7 kcal mol⁻¹, while the entropy of activation was 11 cal (K mol)⁻¹. The positive entropy of activation was reasoned to be the driving force for this facile reaction, which had a rate constant of 1060 s⁻¹ at 273 K.

Scheme 2.4

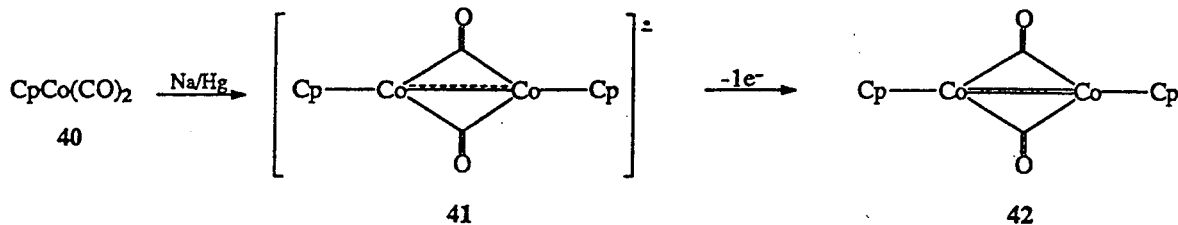


The results obtained by Parker were confirmed by Murray,²⁸ who examined the reduction of $[\text{CpM}(\text{CO})_2]_2$ ($\text{M} = \text{Fe}, \text{Ru}$) and $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ ($\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadiene}$). By utilizing cyclic voltammetry at low temperature, Murray was able to observe a one-electron transfer reaction to give the dimer radical anions for both iron compounds, and these radical anions were found to be stable on the voltammetric time scale. Additional kinetic studies indicated that the two-electron reduction proceeded through the radical anion, which dissociated to give a mononuclear anion and a radical. The radical was then reduced by electron transfer from another dimer radical anion. The rate constant for the Cp compound was found to be two orders of magnitude greater than that for the Cp* complex, while the rate constant for the ruthenium analog was estimated to be at least four orders of magnitude greater than that for the Cp* compound. In fact, the ruthenium reaction proved to be too fast to allow observation of a mono-reduced species, even at low temperature, but the assumption of an ECE path was made in analogy to the iron compounds. Furthermore, neither electron transfer step was rate-determining, although the exact nature of the rate determining chemical reaction step could not be ascertained. Nevertheless, the large differences in the rate constants for the three compounds indicated substantial differences in the reactivities of the three radical anions.

One of the more extensively studied series of bimetallic complexes is a group of structurally similar dicobalt compounds. Bergman showed that the reduction of $\text{CpCo}(\text{CO})_2$ with Na/Hg amalgam led to the formation of the dimer **41**,²⁹ which existed as a radical anion (Scheme 2.5). ESR studies showed that both cobalt centers were equivalent, indicating the delocalization of the unpaired electron over the cobalt atoms. X-ray crystallography revealed a Co-Co distance of 2.36 Å, which was somewhat shorter than reported Co-Co single bonds, and this result was reasoned to support the formulation of **41** as having a Co-Co bond order of 1.5. Compound **41** underwent a one-electron oxidation to the corresponding neutral complex (Scheme 2.5), but further reduction gave NaCp as the only identifiable product. Later, Bergman reported that the rhodium analog

of **41** could be reduced by Na/K alloy to the dianion, which was characterized by x-ray crystallography.³⁰

Scheme 2.5



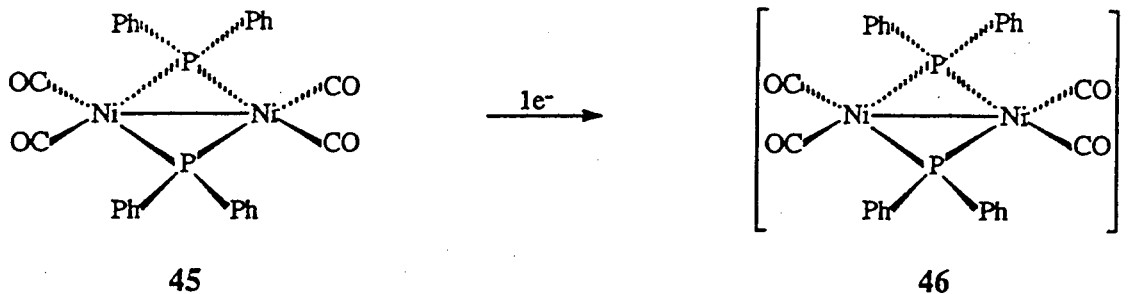
In complementary investigations, other researchers discovered that nitrosylation of CpCo(CO)_2 could produce the analogous mononitrosyl- (**43**)³¹ and dinitrosyl-bridged (**44**)³² dimers, both of which were characterized by x-ray crystallography.³³ Complex **43**, which is isoelectronic with **41**, was found to undergo a reversible one-electron reduction, while compound **44** underwent a reversible one-electron oxidation. Structural data for the oxidation product were not provided, but the crystal structure was later presented by Brintzinger,³⁴ who obtained the cation of **44** by treating CpCo(CO)_2 with NOPF_6 and illustrated its redox properties. The reduction of **44** was irreversible, and it was postulated that the resulting anion would undergo metal-metal bond cleavage, as in $[\text{CpFe(CO)}_2]_2$ and $[\text{CpMo(CO)}_3]_2$. Although the electrochemistry of these compounds seemed to be straightforward, the structural details were perplexing. In order to obtain an 18-electron configuration at each cobalt center in **44**, **41**, and **42**, the metal-metal bond orders should be 1, 1.5, and 2, respectively. However, the crystallographic data for the metal-metal bond lengths showed them to be invariant in **41** and **44**, while such information was not available for **42**.

In an effort to explain the inconsistency between bond length and bond order for the cobalt complexes, Hoffmann undertook a molecular orbital examination of these species,³⁵ but his calculations predicted a significant lengthening of the Co-Co bond upon reduction of the bond order, and no explanation for the discrepancy was offered. Later, Schore investigated a series of dimeric cobalt carbonyl monoanions with substituted

cyclopentadienyl ligands.³⁶ The ESR studies were inconclusive, however, because the unpaired electron could not be assigned to a specific molecular orbital, thus rendering uncertain the effect this electron would have on the metal-metal bond. Dahl studied the Cp* analog of 41 and the corresponding neutral compound,³⁷ and x-ray crystallography indicated a decrease in the Co-Co bond length upon removal of an electron from the monoanion, which was consistent with an increase in bond order. The change was significantly smaller than predicted by Hoffmann's calculations, but this discrepancy was explained by the fact that the Co-CO bonds lengthened upon oxidation of the anion, thereby opposing the change in metal-metal bond length. Dahl was also able to assign the unpaired electron in the monoanion to a π^*_{yz} molecular orbital, which was strongly antibonding between the metal atoms. This series of investigations indicates the significant structural, in addition to electronic, effects that bridging ligands can exert in dinuclear complexes.

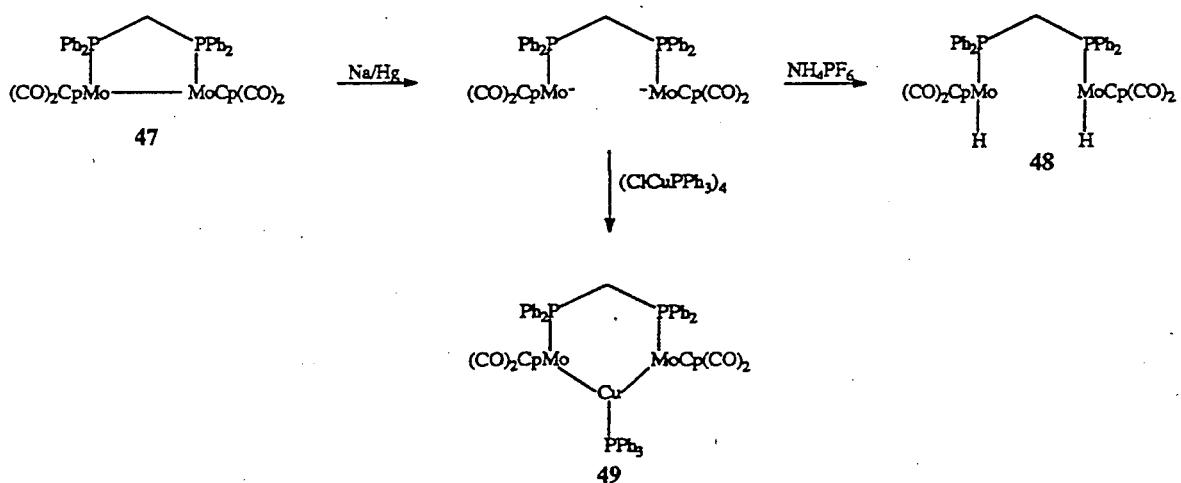
While the preceding example illustrated how bridging groups cause structural changes in bimetallic compounds, these ligands are more commonly employed as a means of maintaining the molecular framework of dinuclear complexes in the event of scission of the metal-metal bond. Since metal-metal bond cleavage is a common reaction of bimetallic species upon reduction, bridging ligands have played an important role in examining the redox behavior of these compounds. This approach can provide information about structural reorganization upon electron transfer which would not be available if the starting complex fragmented into mononuclear species. Dessy provided some of the earliest electrochemical investigations of these bridged bimetallic complexes,³⁸ and his studies again led to some generalizations. Dessy found that there was a good correlation between the presence of a metal-metal bond and the ability of a compound to undergo reduction to a stable radical anion. For example, the nickel complex 45 was found to undergo two one-electron reductions, the first of which produced a radical anion which could be examined by ESR spectroscopy (Scheme 2.6).

Scheme 2.6



The utility of bridging ligands in the redox chemistry of metal-metal bonded bimetallic compounds has recently been illustrated for the molybdenum complex 47.³⁹ In this case, the bidentate diphenylphosphinomethane ligand served to hold both metal centers in place after cleavage of the metal-metal bond by reduction with Na/Hg amalgam (Scheme 2.7). The reactivity of the resulting dimolybdenum dianion was then explored, allowing the production of the dihydride by protonation as well as providing access to trinuclear species upon treatment with $(\text{ClCuPPh}_3)_4$. However, the basicity of the anionic molybdenum centers, which was enhanced by the bridging phosphine ligand, frustrated attempts to prepare other trimetallic compounds, as electron transfer from the dianion was observed exclusively.

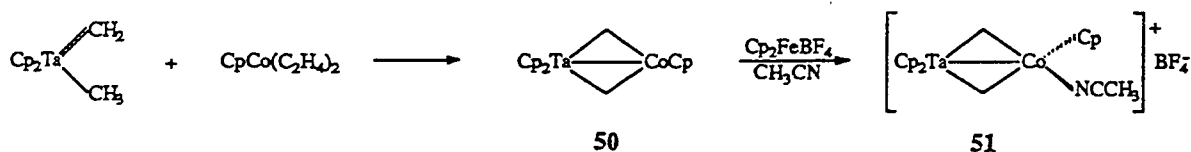
Scheme 2.7



Bridging ligands have also found widespread application with heterobimetallic complexes. Bergman has investigated the Ta-Co compound 50,⁴⁰ which is structurally

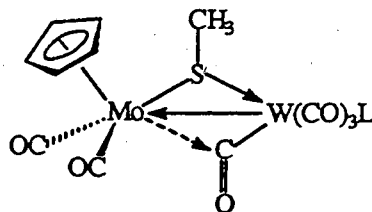
similar to the dicobalt complexes which were previously studied in his group. Complex 50 could be readily oxidized to the corresponding cation by $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ (Scheme 2.8), although reduction to the anion was not reported. Perhaps the most interesting aspect of 50 was its electronic structure. The neutral species is a radical, and in this case it was found that the unpaired electron was localized on one metal center. Based on the EPR data, it was concluded that the complex existed as a Co(II)/Ta(V) species, thereby placing the unpaired electron on the cobalt center.

Scheme 2.8



An intriguing example of the redox behavior of heterobimetallic complexes has been provided by Talarmin,⁴¹ who studied the W-Mo compounds 52 and 53. Both complexes showed two successive one-electron reductions, and the reduction was proposed to occur by an EC-disp.-type mechanism,⁴² signifying that the second electron transfer was homogeneous. These results were interpreted as evidence that the metal-metal bond in each compound was a donor-acceptor $\text{W} \rightarrow \text{Mo}$ bond. Thus, both electron transfer steps occurred at the molybdenum center, representing the reduction from Mo(II) to Mo(0) while the oxidation state of tungsten remained unchanged. Furthermore, the substitution of P(OMe)_3 for CO was found to have a dramatic effect on the redox behavior, as the electronic influence was transmitted through the polar metal-metal bond. The phosphite-substituted complex 53 was more difficult to reduce, and both the mono- and dianion were more stable than for the parent compound 52. These electronic effects provide a good illustration of how redox properties can be modified by ligand substitution.

One of the more unusual choices of a bridging ligand has been provided by Heck,⁴³ who complexed two metal centers on the same face of a cyclooctatetraene ring to give



52, L = CO

53, L = P(OMe)₃

compounds with metal-metal multiple bonds. In addition, linked cyclopentadienyl rings were utilized to provide another bridge between the metals (Figure 2.1). Both the homo- and heterobimetallic compounds showed similar redox behavior, as all the complexes except 54 showed two electrochemically reversible redox pairs (-1/0;0/+1) corresponding to one-electron transfers. The dichromium compounds also provided access to the (+1/+2) redox couple, making this system one of the most flexible known in terms of redox properties. For the homobimetallic species, the radical ions containing 29 or 31 valence electrons were sufficiently stable to be studied by ESR spectroscopy, and again the unpaired electron was found to be delocalized over both metal centers. While this delocalization provided good evidence of electronic communication between the metals, the results were different for the heterobimetallic example 62, as the unpaired electron was localized on the vanadium center. This result was interpreted as signifying that there was only a weak δ interaction of the metal-metal bond.

This introduction has provided examples of the redox behavior of bimetallic complexes containing metal-metal bonds, illustrating the wide variety of compounds which have been studied by electrochemical methods as well as some of the primary concerns in these electrochemical studies. For this class of compounds, one of the most important considerations is electronic communication between the metal centers, which can lead to delocalization of unpaired electrons. These compounds have also raised interesting questions about molecular structure, and bridging ligands have been employed extensively as a means of maintaining the integrity of the molecular framework in the event of metal-

metal bond cleavage. The next section will describe the electrochemical studies of fulvalene complexes.

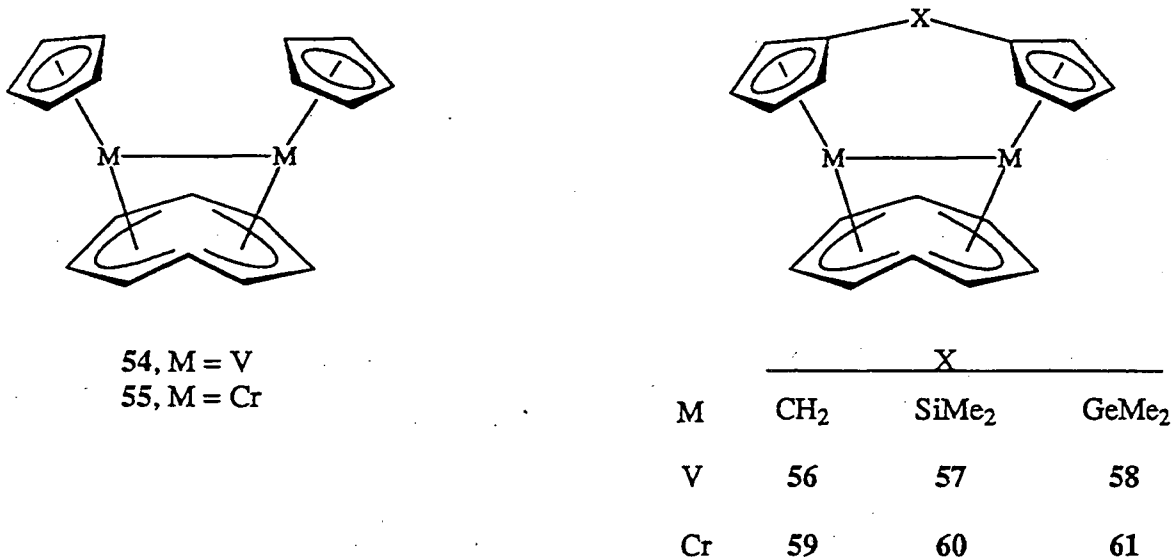
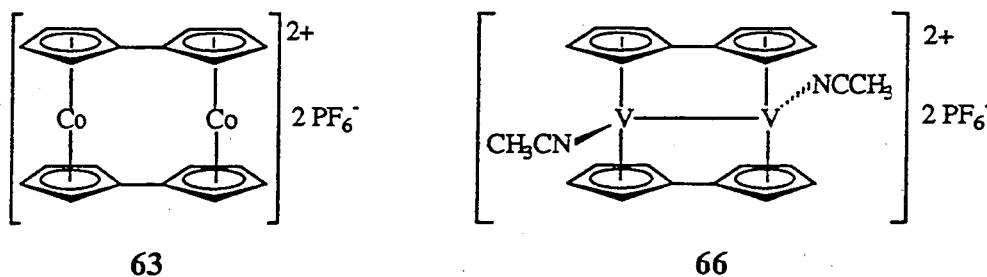


Figure 2.1. Bimetallic complexes utilizing a single cyclooctatetraene ring. For the divanadium species, the metal-metal bond order is 3, while it is 2 for the dichromium analogs.

2.2. Redox Properties of Fulvalene Complexes

One of the most widely studied aspects of dinuclear fulvalene compounds is their electrochemical behavior. As noted in Chapter 1, the fulvalene ligand allows electronic communication between the metal centers, and this property has led to extensive investigations of the mixed-valence nature of these compounds. Most of these studies have utilized bis(fulvalene) or bimetalloocene complexes because of their relative ease of preparation. This section will summarize the findings for a variety of homobimetallic as well as the few known heterobimetallic fulvalene compounds.

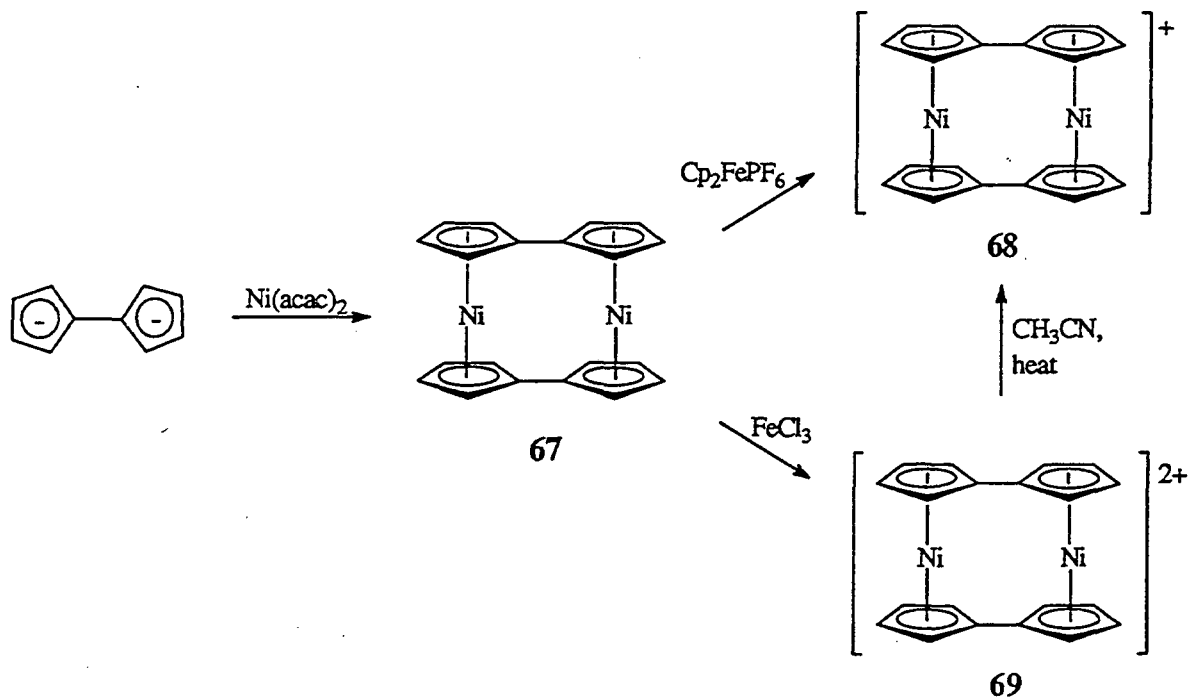
One of the earliest reports on the redox properties of bimetallic fulvalene complexes was provided by Davison,⁴⁴ who prepared the bis(fulvalene)dnicobalt dication **63** by oxidation of the neutral complex **64** with HCl and oxygen. It was found that both **63** and the bimetalloocene analog **65** were more easily reduced than the corresponding mononuclear species $[\text{Cp}_2\text{Co}][\text{PF}_6]$. Additionally, both fulvalene compounds showed two reversible one-electron reduction waves, indicating that the metal centers could be reduced selectively to generate mixed-valence species. Later, Smart prepared the analogous bis(fulvalene)divanadium dication, which was isolated as the bis(acetonitrile) adduct, by oxidation of the neutral compound with ferrocenium hexafluorophosphate.⁴⁵



The remarkable redox flexibility exhibited by dinuclear fulvalene compounds was also illustrated by Smart in the preparation of bis(fulvalene)dinickel in three oxidation states.⁴⁶ The neutral parent complex **67** was obtained by treating a solution of fulvalene dianion with nickel acetylacetonate (Scheme 2.9). Compound **67** could then be oxidized to the radical cation **68** by treatment with one equivalent of $[\text{Cp}_2\text{Fe}][\text{PF}_6]$. This behavior

contrasts with that shown by the divanadium complex, which would not undergo a one-electron oxidation. By using ferric chloride as the oxidizing agent, the dication **69** could be obtained. It was also possible to reduce **69** by one electron to **68** by warming the compound in acetonitrile, indicating that **69** was unstable in the absence of an oxidant. By examining the magnetic susceptibility data for the diiron (*vide infra*), dicobalt, and dinickel complexes, Smart concluded that complete magnetic coupling existed for bis(fulvalene)dimetal systems containing 34 to 40 valence electrons, although it was not determined whether this coupling resulted from direct metal-metal exchange or through the bridging ligands.

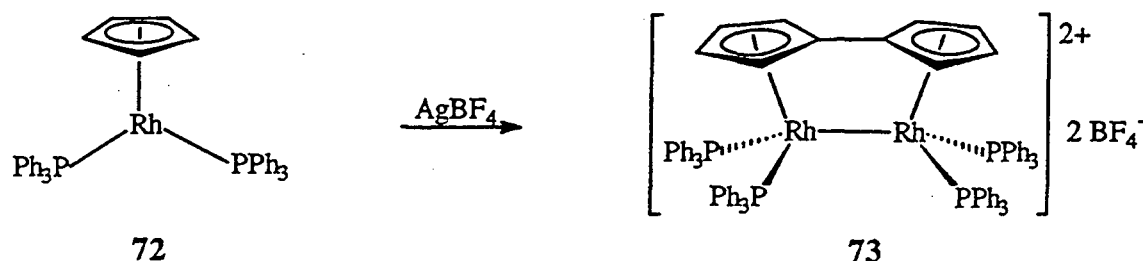
Scheme 2.9



An interesting variation on bis(fulvalene)dimetal compounds has recently been provided by Obendorf,⁴⁷ who examined the redox chemistry of the Co-Fe (**70**) and Co-Ru (**71**) heterobimetallic complexes by cyclic voltammetry. Compound **70** displayed a rich redox chemistry, as it showed two reversible one-electron reduction waves and a reversible one-electron oxidation, thereby giving access to four oxidation states (Equation 2.1). The waves were assigned to a specific metal center based on comparison with the

$[\text{Cp}_2\text{Fe}][\text{PF}_6]$.⁵¹ Interestingly, oxidation of the mononuclear analog, $\text{CpRh}(\text{CO})_2$, results in unidentifiable products. This difference in redox behavior was attributed to the rapid formation of the metal-metal bond for the fulvalene complex, which then prevented any radical decomposition pathway.

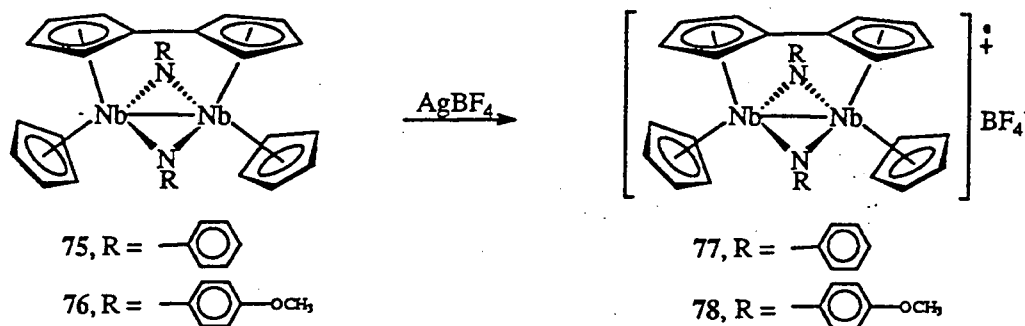
Scheme 2.10



Although the majority of the electrochemical studies of fulvalene compounds have focused on the late transition metals, some investigations have been devoted to the early metals. The oxidation of the dinickel complexes **75** and **76** has been reported by Lemenovskii, and the crystal structures for both **77** and **78** were obtained.⁵² The oxidation with AgBF_4 was a one-electron process, producing a radical cation (Scheme 2.11). The ESR spectrum of **77** indicated that the unpaired electron was delocalized over the two metal centers, which would be expected for a homobimetallic compound with both bridging ligands and a metal-metal bond. The crystal structures revealed that the molecular framework remained virtually intact upon oxidation, although the metal-metal bond in **78** was elongated by 0.1 Å. Additionally, the Nb_2N_2 moiety was nonplanar in the cation, but it was unclear whether this result was due to electronic or steric effects.

While the redox properties for a variety of dinuclear bis(fulvalene) and fulvalene complexes have been examined, the most intensively studied compounds are the diiron species, and the emphasis has been placed on the mixed-valence behavior. It was found that bis(fulvalene)diiron (biferrocenylene) **79** could be oxidized selectively to the monocation **80** or to the dication **81**, which decomposed in solution in the absence of an

Scheme 2.11



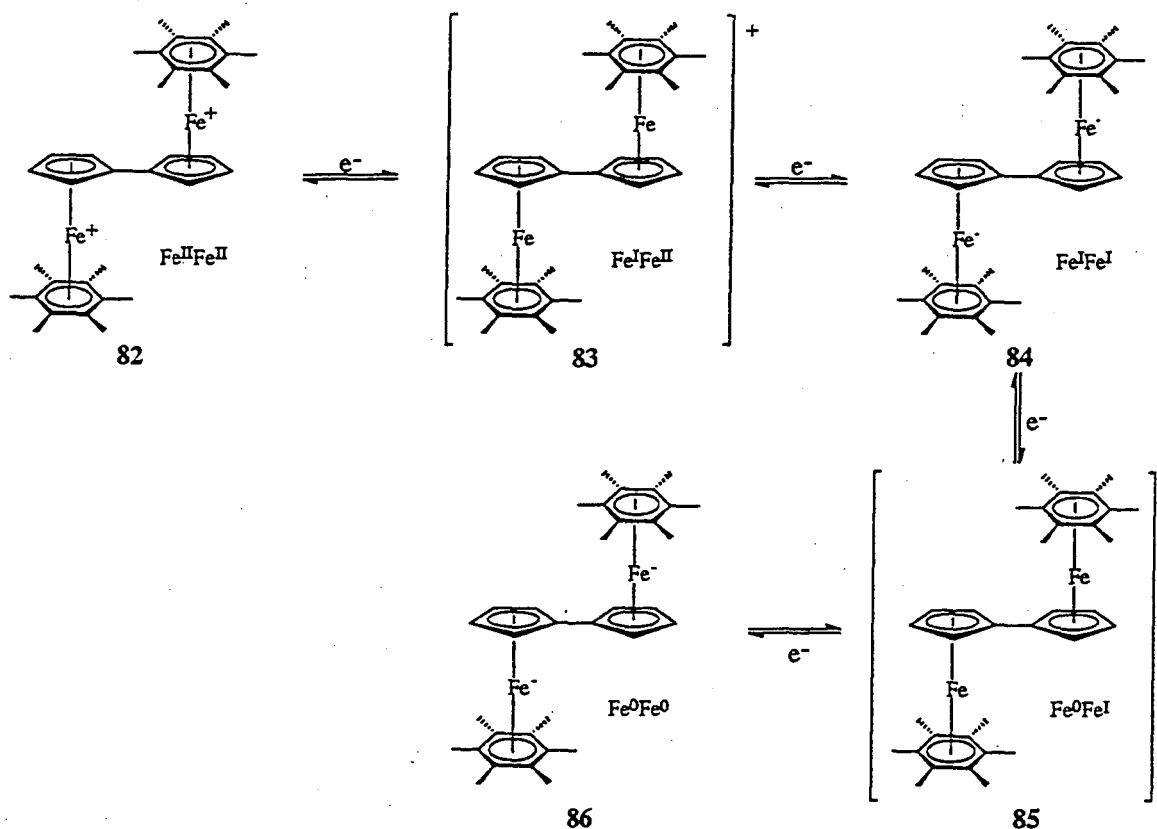
oxidizing agent.⁵³ The radical cation was originally thought to be a class II⁵⁴ mixed-valence compound,⁵⁵ indicating that the two iron centers were in different oxidation states, but later studies showed that the system was fully delocalized so that the metal centers were equivalent.^{17c} Interestingly, molecular orbital calculations showed that the one-electron oxidation removed an electron from the metal d orbitals rather than the highest occupied molecular orbital (HOMO).⁵⁶ This finding was attributed to stabilization resulting from d-electron relaxation effects; however, the dication was found to result from the removal of two electrons from the delocalized π HOMO. The electronic properties of **79** have led recently to the use of this material in electrode films.⁵⁷

In contrast to bis(fulvalene)diiron, biferrocene has been shown to exhibit mixed-valence behavior upon one-electron oxidation.^{16,58} This behavior has led to extensive investigations of these complexes, and numerous derivatives have been prepared with substituents on the cyclopentadienyl rings¹⁶ and even on the fulvalene ligand itself.⁵⁹ Several complexes which employ a bridge between the 2,2'-positions of the fulvalene ligand have been synthesized,⁶⁰ but only one has given rise to a mixed-valence salt upon oxidation.^{60b} It has been shown that the tilt of the cyclopentadienyl rings can have a significant effect on the rate of intramolecular electron transfer, as larger tilt angles gave rise to faster electron transfer.⁶¹ The mixed-valence properties of this group of compounds have also been reviewed.¹⁶

The electrochemical behavior of another series of fulvalene diiron complexes has been studied extensively by Astruc.¹⁵ The (fulvalene)diiron sandwich complexes 82-86 proved to be readily accessible electron reservoirs, affording species with 36 to 40 valence electrons (Scheme 2.12). Analogous complexes with different arene rings (benzene, toluene, ethylbenzene, and mesitylene) were also prepared and found to display similar electrochemistry, although the reversibility of the reduction waves did increase with the number of methyl groups on the arene.^{15b} The radical cation 83 was found to be a delocalized, or class III, mixed-valence compound, which contrasts with the behavior usually observed for biferrocenes. Localized, or class I, mixed-valence species were obtained by preparing mixed biferrocenes containing one ancillary Cp ring and one hexamethylbenzene ligand.⁶² For these compounds, both the $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ complexes exhibited localized mixed-valence behavior. The analogous decamethylbiferrocene series⁶³ showed localized behavior for the $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ state and was classified as a class II mixed-valence species. Interestingly, the permethylation of the ancillary ligands was found to increase the delocalization in the hexamethylbenzene compounds ($\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$) while having the opposite effect in the Cp^* complex.⁶⁴ This behavior was attributed to the fact that different molecular orbitals are involved in the different oxidation states, as the Fe^{I} species involves an orbital with more ligand character which facilitates the superexchange mechanism invoked to account for the delocalization in these compounds.

Astruc also reported on the effects which a salt can have on the nature of electron transfer in fulvalene complexes.⁶⁵ The fulvalene compound 87, which possesses two 19-electron iron centers, was found to undergo facile reactions with external ligands such as CO and PMe_3 (Scheme 2.13). When CO was used, initial displacement of one arene ring was observed, and in the absence of NaPF_6 , this species would undergo further substitution to yield the hexacarbonyl complex 88. In the presence of NaPF_6 , however, intramolecular electron transfer occurred, eventually leading to decomplexation of one of

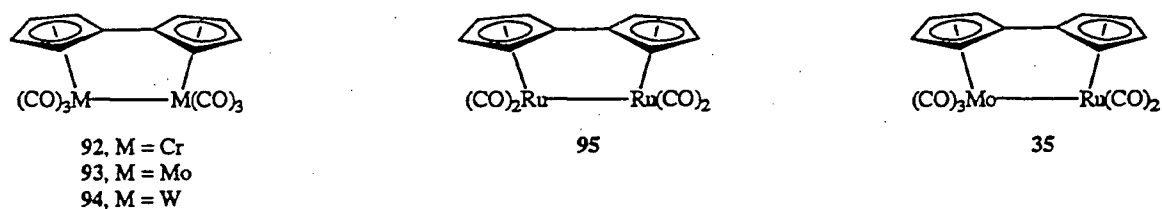
Scheme 2.12



the fulvalene rings and isolation of the $\text{Fe}(\text{II})$ species **89**. In contrast to this reactivity, the mononuclear $\text{CpFe}(\text{C}_6\text{H}_6)$ was found to undergo benzene displacement to give $[\text{CpFe}(\text{CO})_2]_2$ regardless of whether NaPF_6 was present.⁶⁶ With PMe_3 compound **87** showed the same reactivity as for CO in the absence of NaPF_6 . When NaPF_6 was present, intermolecular electron transfer occurred between **87** and the intermediate trimethylphosphine complex to produce **91**, in which both iron centers have been oxidized to $\text{Fe}(\text{II})$. These reactions again emphasize the remarkable versatility of fulvalene complexes, as well as showing how their electronic properties can be modulated.

As the preceding discussion indicates, the vast majority of the fulvalene complexes which have been subjected to electrochemical investigations have been sandwich-type compounds, primarily because of the relative ease of preparation of these species. However, a detailed study of the redox properties of several (fulvalene)dimetal carbonyl complexes (Figure 2.2) has recently been provided.⁶⁷ Cyclic voltammetry revealed that all

These compounds also behaved similarly upon reduction, as all five showed a reversible two-electron wave, but the potentials did vary significantly with the metal centers. The data were consistent with an ECE mechanism, where the chemical reaction was taken to be elongation of the metal-metal bond resulting from the addition of one electron to a metal-metal antibonding orbital. This molecular relaxation was postulated to facilitate the second electron transfer so that the radical anion was more easily reduced than the starting material, giving the dianion with cleavage of the metal-metal bond. Surprisingly, the heterobimetallic complex 35 showed only a single reduction wave despite the large potential difference for the reduction of the homobimetallic analogs 93 and 95. It was also shown that dihalide products could be prepared by treatment of 92, 93, or 95 with Br_2 or I_2 , and the reduction of these dihalides resulted in the liberation of halogen and reformation of the starting complexes when the metal-halide bond was weak, as for $(\text{fulvalene})\text{Cr}_2(\text{CO})_6\text{I}_2$ and $(\text{fulvalene})\text{Ru}_2(\text{CO})_4\text{Br}_2$.



Compound	E_{pa}		E_{pc}	
	$\text{M}_2 \rightarrow \text{M}_2^{2+}$		$\text{M}_2 \rightarrow \text{M}_2^{2-}$	
92	1.02		-0.43	
93	1.08		-0.77	
94	1.02		-0.82	
95	1.05		-1.65	
35	1.03		-1.25	

Figure 2.2. Bimetallic fulvalene carbonyl complexes studied by cyclic voltammetry. The table gives the oxidation and reduction potentials in volts vs. NHE.

The electrochemical investigations of dinuclear fulvalene compounds have illustrated the remarkable redox flexibility available in these systems and that the fulvalene ligand maintains the molecular framework upon oxidation and reduction. This property, coupled

with the electronic communication between the metal centers, makes fulvalene compounds attractive subjects for further electrochemical studies. The remainder of this chapter will describe the redox behavior of two heterobimetallic fulvalene complexes.

2.3 Electrochemistry of (Fulvalene)WFe(CO)₅ 30

The findings of Bard for the redox properties of bimetallic fulvalene complexes failed to show any distinctions between the two metal centers. As all the compounds were reduced or oxidized in two-electron processes, their behavior was not very different from that of the analogous cyclopentadienylmetal dimers. In particular, the unexceptional reactivity of the heterobimetallic complex 35 was surprising, since it would have been expected that the two different metal centers would have exhibited selective metal reduction or oxidation. Despite these early results, the potential of heterodinuclear fulvalene compounds to display metal-specific redox reactivity remained an attractive goal, and the W-Fe complex 30 was selected for further study.

Cyclic voltammetry revealed that 30 showed two oxidation waves (E_{pa}), the first at 0.965 V vs SCE and the second at 1.255 V at a scan rate (v) of 0.4 V/s. A prewave to the oxidation was observed on the first scan but was absent on successive scans. A similar result was reported by Bard and was attributed to the formation of an adsorption product of the oxidized species on the electrode.⁶⁷ However, the presence of two oxidation waves contrasts with the previous results, and the proposal that the oxidation removes electrons from an orbital that is primarily ligand based⁶⁷ is inconsistent with their observance. In this case, it is more likely that the electrons are removed from metal-based orbitals, as oxidation of the first metal center renders the second oxidation more difficult, thereby giving rise to the two waves. The oxidation processes were irreversible, a finding ascribed to reactions of the oxidized species with the solvent. Unfortunately, electrode passivation proved to be a problem, so the oxidation studies were not pursued further.

Reduction of compound 30 proved to be more interesting, as the cyclic voltammogram (CV) showed two well-spaced one-electron reduction waves (E_{pc}) at potentials of -1.130 and -1.710 V vs SCE at a scan rate of 0.4 V/s (Figure 2.3). The fact that each wave represented the transfer of only one electron was confirmed by comparison

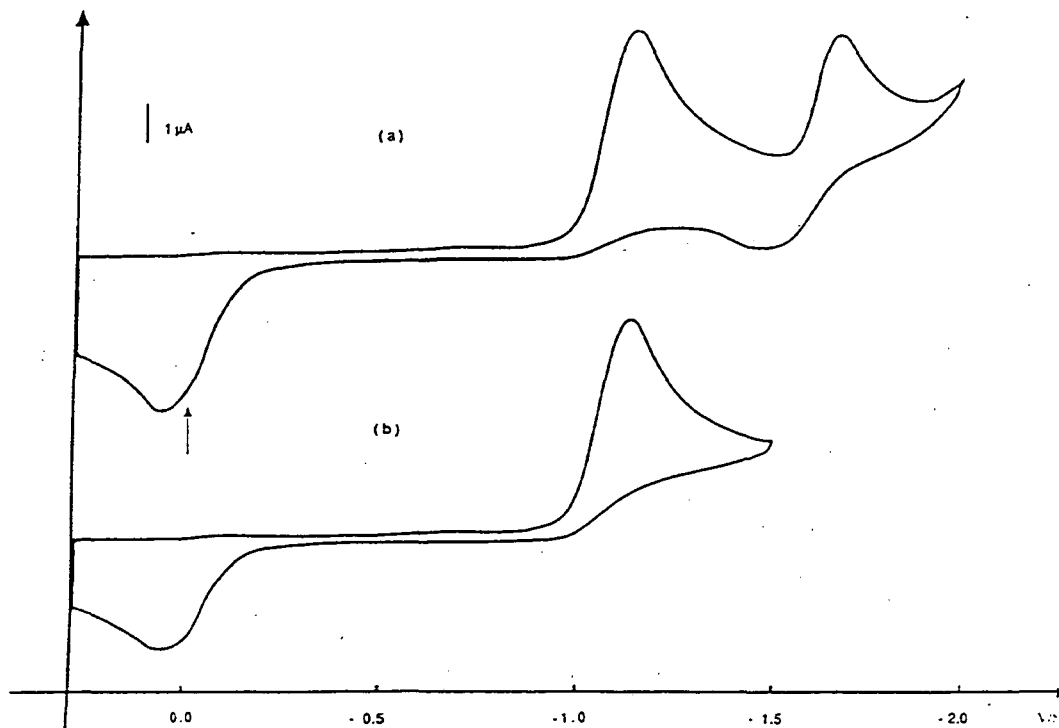


Figure 2.3. Cyclic voltammogram of 30. (a) Scan between 0.3 and -2.0 V showing two waves. (b) Switching potential applied between the two waves at -1.5 V.

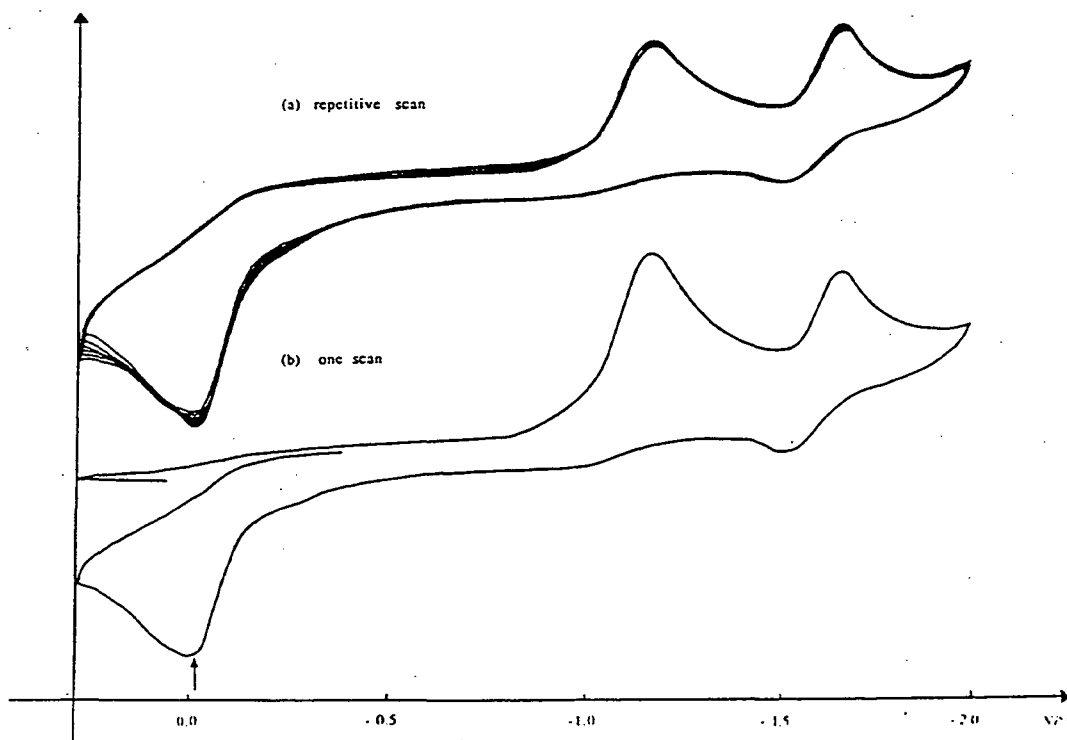


Figure 2.4. Cyclic voltammogram of 30 showing the evolution of the oxidation wave with time.

with the CV for complex 31 and by chemical studies (*vide infra*). Thus, compound 30 provided the first example in which the two metal centers of a heterobimetallic fulvalene complex displayed distinct redox behavior. Table 2.1 shows the electrochemical data collected at scan rates from 20 to 800 mV/s.

Table 2.1. Electrochemical data for 30, showing the peak currents (i_p) and potentials for both reduction and reoxidation waves.

v (mV/s)	i_{pc1} (μ A)	i_{pc2} (μ A)	i_{pa} (μ A)	E_{pc1} (V)	E_{pc2} (V)	E_{pa1} (V)	i_{pa}/i_{pc1}
20	1.45	1.26	0.25	-1.070	-1.670	-0.070	0.17
40	1.90	1.65	0.90	-1.080	-1.670	-0.035	0.47
60	2.25	1.95	1.15	-1.090	-1.680	0.000	0.45
80	2.55	2.21	1.40	-1.095	-1.700	0.010	0.55
200	4.05	3.52	2.30	-1.110	-1.700	0.045	0.57
400	5.70	4.90	2.40	-1.130	-1.710	0.050	0.54
600	6.70	5.80	2.50	-1.150	-1.700	0.040	0.65
800	7.90	6.87	2.80	-1.165	-1.700	0.055	0.64

The reoxidation wave displayed in the CV's of compound 30 was examined closely, and a shoulder, indicated by the arrows in Figures 2.3 and 2.4, was observed on its right side. This shoulder was absent when a switching potential was applied before the second reduction wave or when the CV was recorded at $-30\text{ }^\circ\text{C}$. Furthermore, the small oxidation wave at -1.45 V appeared when the entire region from 0 to -2.0 V was scanned but not when the second reduction wave was isolated by limiting the scan region from -1.3 to -2.0 V . Both reduction processes were shown to be electrochemically irreversible by the application of several criteria.

The data in Table 2.1 indicated that the first reduction potential (E_{pc1}) and the associated oxidation (E_{pa1}) varied systematically with the scan rate. Thus, plots of peak

potentials vs $\log v$ were linear for values of v from 20 to 800 mV/s, and good correlation coefficients were obtained (Figure 2.5). It has been shown that the slopes of these plots can be used to determine the relative rates of heterogeneous electron transfers,⁶⁸ and the magnitude of these slopes provide the basis for one of the primary tests for electrochemical reversibility.⁶⁹ Slopes between 0 and 30 mV at 298 K indicate reversible electron transfer while values greater than 30 mV are characteristic of irreversible waves based on Equation 2.4:

$$E_p = 2.3 RT \log v / 2\alpha n_a F + \text{constant} \quad (\text{Eqn. 2.4})$$

where α is the electron transfer coefficient, n_a is the number of electrons transferred in the rate-limiting step, and F is the faraday. Equation 2.4 was derived by Delahay⁷⁰ and Nicholson and Shain^{69a} and later extended by Savéant⁷¹ to linear sweep voltammetry, and it also applies for the half-peak potential $E_{p/2}$. Thus, the first reduction wave is electrochemically irreversible, as the plot of E_{pc1} vs $\log v$ gives a slope of 56.9 mV. The situation is more complicated for the second reduction wave, E_{pc2} . The slope of 22.2 mV is indicative of fast heterogeneous electron transfer followed by a fast and irreversible chemical step. Other phenomena probably occur as well, since no oxidation wave was observed when E_{pc2} was isolated (*vide supra*).

The constancy of the electron transfer coefficient α was also examined. According to Equation 2.4, a plot of E_p vs $\log v$ will have a slope of $(2.3 RT)/(2\alpha n_a F)$. This method gave a value for α of 0.53 for E_{pc1} and 0.63 for $E_{pc1/2}$. Furthermore, it has been shown that for an irreversible wave, the width depends only on α as indicated by Equation 2.5:^{69a}

$$E_p - E_{p/2} = 1.857 (RT/\alpha n_a F) \quad (\text{Eqn. 2.5})$$

In addition, the relationship between peak potential and peak current for an irreversible wave is described by Equation 2.6:

$$E_p = 2.3 (RT/\alpha n F) \log i_p + \text{constant} \quad (\text{Eqn. 2.6})$$

which was originally derived by Gokhshtein⁷² and later by Nicholson and Shain.^{69a} The values of α obtained by these four methods are shown in Table 2.2, and they display

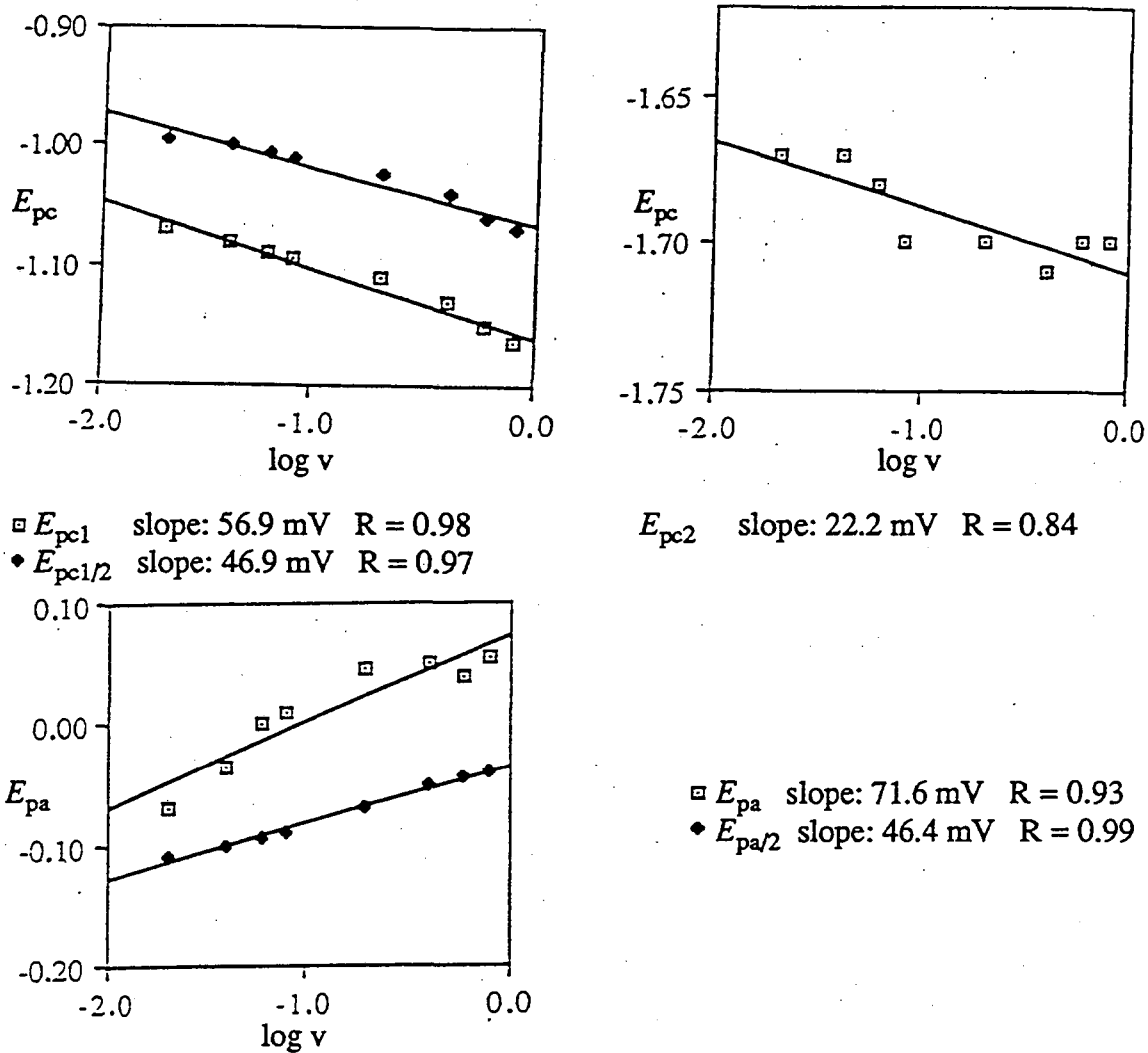


Figure 2.5. Plots of peak potentials vs $\log v$ for 30, with respective slopes and correlation coefficients.

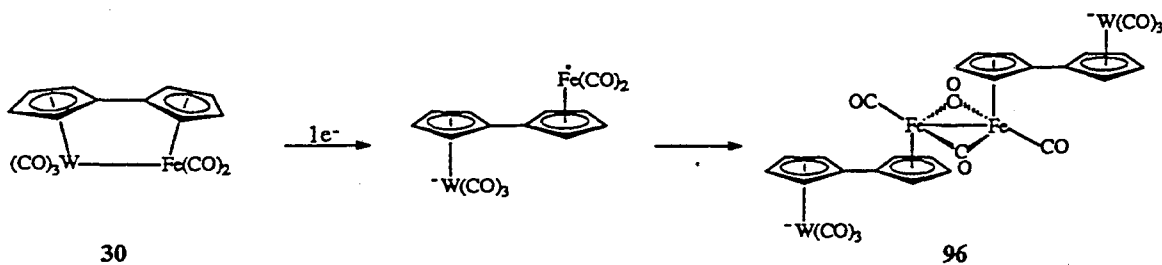
Table 2.2. Charge transfer coefficients for 30 determined by various methods.

Method	$\alpha (E_{pc1})$	$1 - \alpha (E_{pa})$
E_p vs $\log v$	0.53	0.42
$E_{p/2}$ vs $\log v$	0.63	0.64
$E_p - E_{p/2}$	0.56	0.55
E_p vs $\log i$	0.48	0.55
Average	0.55 (± 0.08)	0.55 (± 0.12)

good internal consistency. Thus, the electron transfer coefficients provide additional evidence that E_{pc1} represents an irreversible electron transfer step.

The fact that the CV of compound **30** showed two reduction waves suggested that one metal center could be selectively reduced by using a reducing agent with a potential between -1.130 and -1.710 V. Of the two metal centers in **30**, it was felt that the tungsten would be more easily reduced than iron, which is in agreement with Bard's results for the analogous ditungsten complex **94** and the diruthenium compound **95**. The reduction potential for (fulvalene)tetracarbonyldiiron has not been reported, but the trend illustrated by Bard for the Group 6 metals was assumed to hold for the Group 8 metals as well, in which case the iron center would be significantly more difficult to reduce than the tungsten one. The one-electron reduction of **30** held the promise of leading to novel reactivity through cleavage of the tungsten-iron bond, as illustrated in Scheme 2.14. In order to test this hypothesis, chemical studies were undertaken.

Scheme 2.14

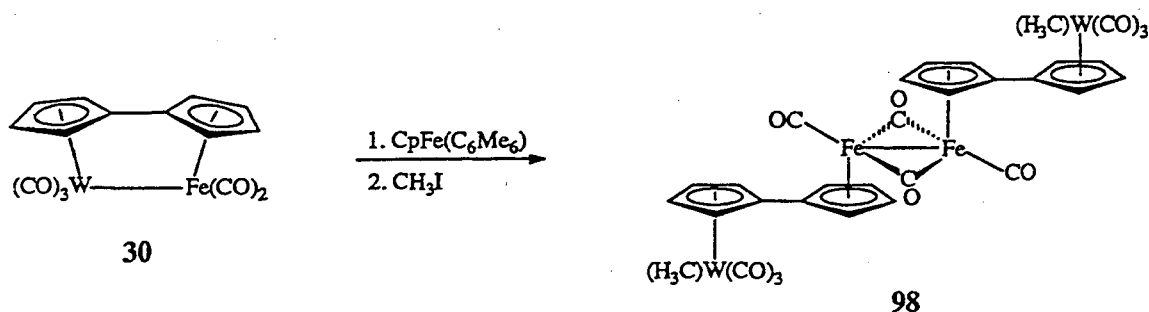


2.4 Reduction Chemistry of (Fulvalene)WFe(CO)₅ 30

Although the CV studies of compound **30** provided good evidence for the selective reduction of the two metal centers, synthetic investigations were necessary to corroborate these results. The most important consideration was finding an appropriate reducing agent which would allow reduction of only one metal center. The first choice was the 19-electron species CpFe(C₆Me₆) **97**, which has been shown to be a very effective reductant.⁷³ The reduction potential, -1.55 V vs. SCE, is ideally situated between the two reduction waves for **30**, thereby ensuring that only one electron would be transferred. This compound was particularly appealing because it is readily generated by reduction of the 18-electron [CpFe(C₆Me₆)]PF₆ with Na/Hg amalgam in dimethoxyethane (DME).

The application of **97** in the anticipated manner proved to be straightforward. A solution of **30** in tetrahydrofuran (THF) was treated with one equivalent of **97** in DME. The reduction was presumed to yield the dianion **96**, which was quenched with CH₃I to give the corresponding dimethyl complex (Scheme 2.15). After removal of the solvent, the crude mixture was dissolved in a minimal amount of THF and filtered through a plug of silica gel to remove [CpFe(C₆Me₆)]⁺, and the red powder obtained upon removal of solvent was analytically pure.

Scheme 2.15



The structure and empirical formula of **98** were readily confirmed by spectroscopic methods and elemental analysis, respectively. The tetranuclear structure was indicated by the mass spectrum, which showed diagnostic peaks at 878 ($M^+ - 6\text{CO}$), 834 ($M^+ - 7\text{CO} -$

CH_4), 806 ($M^+ - 8\text{CO} - \text{CH}_4$), 762 ($M^+ - 9\text{CO} - 2\text{CH}_4$), and 523 ($M^+/2$). Unfortunately, the peak for the molecular ion was not detected. Further support for the tetranuclear structure was provided by the infrared spectrum, which showed a band at 1740 cm^{-1} . This band was in the region typical for bridging carbonyl groups, and the presence of these moieties is consistent with the formulation of **98** as a tetranuclear analog of the well-known $[\text{CpFe}(\text{CO})_2]_2$. The ^1H NMR spectrum showed four triplets in the fulvalene region, which is typical for symmetrical heterobimetallic fulvalene compounds. Additionally, a singlet at δ 0.26 ppm was indicative of the methyl groups on tungsten, and satellites due to coupling to the ^{183}W nucleus confirmed that the methyl groups were not bonded to the iron center. The ^{13}C NMR spectrum provided further evidence for the W- CH_3 groups, as a peak was observed at δ -29.2 ppm. Efforts to confirm the structure of **98** by x-ray crystallography were unsuccessful, as attempted recrystallization gave the starting complex **30** instead.

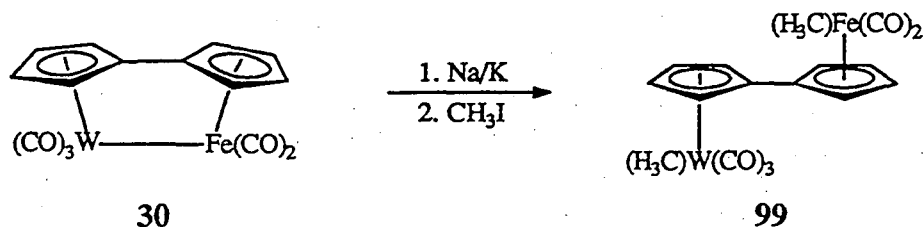
The formation of **98** is entirely consistent with the electrochemistry of **30**. The transfer of only one electron would lead to a radical anion, a species which could then readily undergo cleavage of the W-Fe bond. Scission of the metal-metal linkage would result in the formation of an anionic metal center and a metal radical. In accordance with Dessy's findings for heterodinuclear complexes, reduction (anion formation) occurs at the metal center which is more easily reduced in the corresponding homobimetallic analogs. In this case, the studies by Bard indicate that the tungsten center should be easier to reduce, and the presence of the W- CH_3 groups in **98** confirms that the tungsten center exists as an anion in the intermediate **96** (Scheme 2.14). The formation of the tetranuclear species is consistent with the dimerization of an iron-centered radical. Thus, the combination of CV studies and synthetic chemistry provides the first example of selective reduction of one metal center in a heterobimetallic fulvalene complex.

The problems encountered in the attempted recrystallization of **98** merit further discussion. The remarkable solubility of **98** made recrystallization difficult, and time

periods of several days were necessary for crystal formation. The fact that the resulting crystals were of **30** instead of **98** indicates that solutions of **98** are unstable over time. Although the recrystallization was carried out in a glovebox, trace amounts of oxygen could have catalyzed the decomposition of **98** to **30** by an electron transfer chain mechanism. Loss of the methyl groups as methane or ethane would provide a driving force for the reaction, as would the crystallization of the relatively insoluble **30**. However, no efforts were made to study this decomposition pathway.

After the one-electron reduction of **30** was achieved, the two-electron process to the dianion was investigated. Although the reduction potentials of **97** and **30** suggest that the second electron transfer would be endergonic, this is actually not the case due to the coulombic factor.⁷⁴ Thus, addition of two equivalents of **97** to a solution of **30** generated the desired dianion. In practice, it was found that the stronger reducing agent Na/K alloy⁷⁵ provided more convenient access to this species. Thus, treatment of a THF solution of **30** with an excess of Na/K alloy yielded clean solutions of the product after removal of the remaining alloy by filtration. The dianion was converted to the dimethyl complex **99** by addition of CH₃I (Scheme 2.16). Compound **99** was readily purified by filtration through silica gel and isolated as a yellow powder. The color change from the reddish-black **30** to the yellow **99** is typical for reactions of fulvalene compounds which involve metal-metal bond cleavage.

Scheme 2.16



The elemental composition of **99** was confirmed by combustion analysis, and the spectroscopic data were entirely consistent with the proposed structure. The mass

spectrum showed a peak at 538 for the molecular ion. The ^1H NMR spectrum showed four triplets for the fulvalene ligand, as well as two singlets for the methyl groups, one of which displayed the expected coupling to the ^{183}W nucleus. The ^{13}C NMR spectrum also exhibited peaks for the two methyl groups at δ -18.49 (Fe-CH₃) and -28.93 ppm (W-CH₃). The IR spectrum contained only bands for terminal carbonyl groups. The extreme solubility of **99** prevented crystallization of the material.

Thus, all of hypotheses based on the CV studies of **30** were confirmed by preparative scale experiments. The novel reduction chemistry of **30** suggested that further synthetic chemistry would be possible, and the results of those investigations are presented in Chapter 3. Additionally, the redox properties of **30** provided an impetus for the investigation of the ruthenium analog **31**.

2.5 Electrochemistry of (Fulvalene)WRu(CO)₅ 31

Because the redox chemistry of compound **30** proved to be novel, similar studies were conducted for the ruthenium analog **31**. Unlike **30**, compound **31** showed only one oxidation wave, which is analogous to the results of Bard. Once again, however, the oxidation behavior was not amenable to detailed study, so attention was focused on the reduction of **31**. In this case, unique behavior was again observed, as indicated by the cyclic voltammogram (Figure 2.6). The CV of **31** indicates a two-electron reduction process at a potential of -1.565 V vs SCE at a scan rate of 0.4 V/s, which is similar to Bard's findings for the molybdenum-ruthenium complex **35**. However, the oxidation of the reduced species shows two one-electron waves at -0.66 and -0.01 V vs SCE. The fact that the two anodic waves were connected to the reduced species was confirmed by the application of a switching potential at -1.2 V, in which case no anodic processes were observed (Figure 2.6). The peak current for the reduction wave (i_{pc}) was larger than the sum of the anodic peak currents ($i_{pa1} + i_{pa2}$), and this difference was attributed to the diffusion of the reduced species away from the electrode surface during scanning of the region between E_{pc} and E_{pa2} . The data for **31** are summarized in Table 2.3.

Table 2.3. Electrochemical data for **31**. Units are the same as those in Table 2.1.

v	i_{pc}	i_{pa1}	i_{pa2}	E_{pc}	E_{pa1}	E_{pa2}	E_{pc2}	i_{pa1}/i_{pc}	i_{pa2}/i_{pc}
20	3.80	0.00	0.00	-1.482	---	---	-1.395	0.00	0.00
40	5.10	0.40	0.40	-1.495	-0.060	-0.730	-1.405	0.08	0.08
60	6.20	1.20	1.10	-1.505	-0.050	-0.710	-1.410	0.16	0.18
80	7.20	1.40	1.50	-1.515	-0.045	-0.705	-1.415	0.19	0.21
200	11.40	2.50	3.00	-1.545	-0.030	-0.680	-1.435	0.20	0.26
400	15.60	3.20	4.60	-1.565	-0.010	-0.660	-1.455	0.22	0.30
600	19.40	4.20	5.90	-1.585	0.000	-0.655	-1.470	0.22	0.30
800	23.00	4.90	7.00	-1.610	0.020	-0.650	-1.490	0.22	0.30

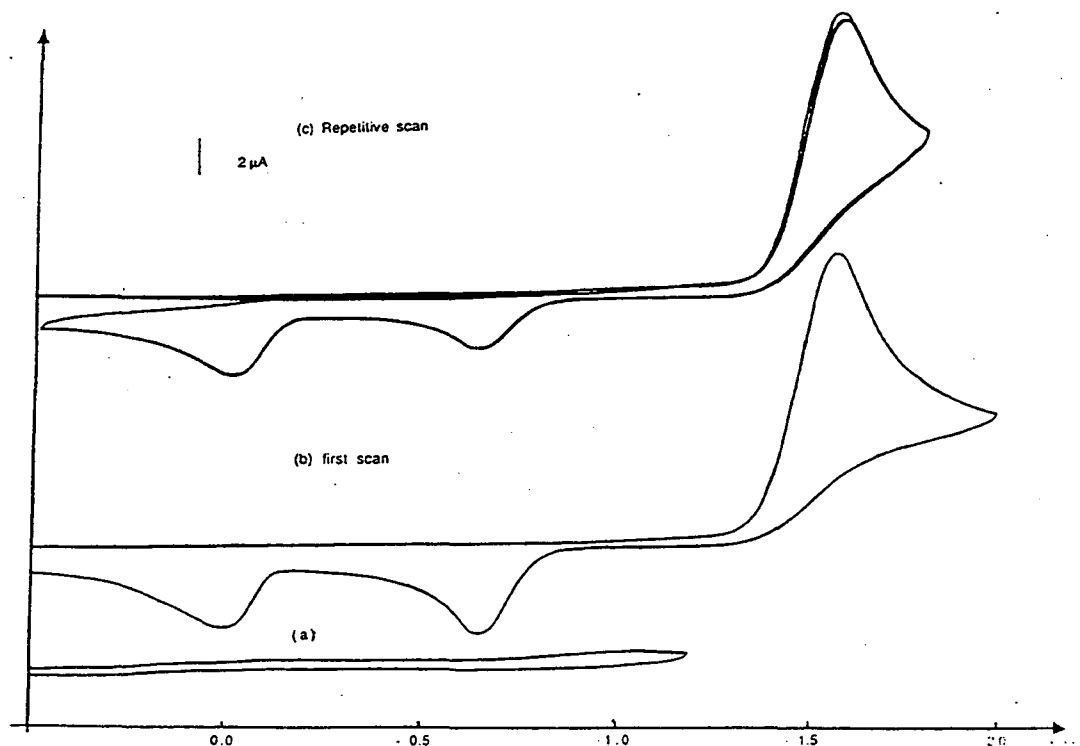


Figure 2.6. Cyclic voltammogram of **31**. (a) Switching potential applied at -1.2 V, before the reduction wave. (b) Switching potential applied at -2.0 V, beyond the reduction wave. (c) Continuous scan with switching potential applied at -1.8 V.

The tests for electrochemical irreversibility detailed for **30** were applied to **31**. The plot of E_{pc} vs $\log v$ gave a slope of 77 mV, while the plots for E_{pa1} and E_{pa2} gave slopes of 56 and 60 mV, respectively (Figure 2.7). The electron-transfer coefficient for E_{pc} was found to be 0.42 for the average of the four methods of determination (Table 2.4). All of these results are consistent with slow heterogeneous electron transfer (electrochemical irreversibility) for each wave. The reduction was postulated to be an ECE process in analogy with the results of Bard, while the two reoxidations were EC processes in which the electron transfer was rate limiting.

The results for **31** were quite different from those for **30**, but a distinction between the metal centers was observed in each case. It was felt that one metal center in **31** could be selectively oxidized after initial reduction to the dianion. On the basis of Bard's findings,

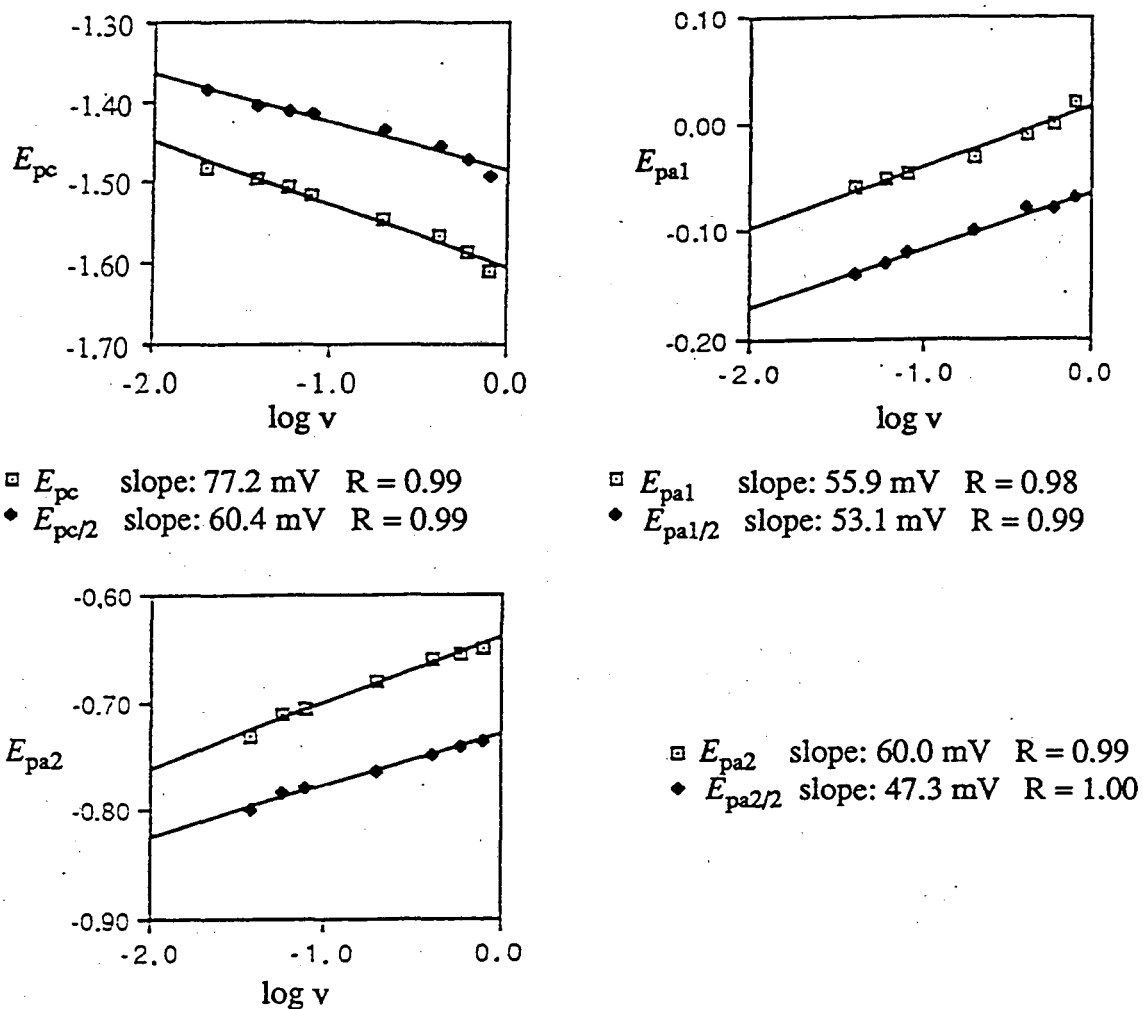


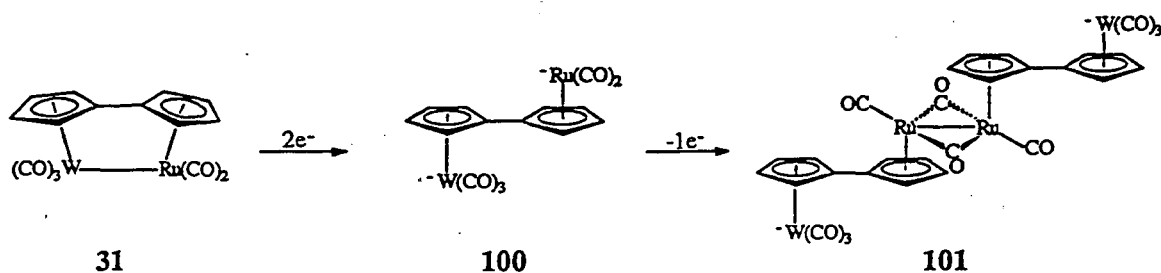
Figure 2.7. Plots of peak potentials vs $\log v$ for 31, with respective slopes and correlation coefficients.

Table 2.4. Charge transfer coefficients for 31 determined by various methods.

Method	$\alpha (E_{pc})$	$1 - \alpha (E_{pa1})$	$1 - \alpha (E_{pa2})$
E_p vs $\log v$	0.38	0.53	0.50
$E_{p/2}$ vs $\log v$	0.48	0.55	0.62
$E_p - E_{p/2}$	0.45	0.60	0.59
E_p vs $\log i$	0.38	0.56	0.75
Average	0.42 (± 0.06)	0.56 (± 0.04)	0.60 (± 0.08)

it was felt that the ruthenium center would be more easily oxidized than the tungsten one. Thus, the two-electron reduction of **31** followed by a one-electron reoxidation offered the possibility of the formation of the tetranuclear species **101** (Scheme 2.17). In order to test this hypothesis, chemical studies were conducted on **31**.

Scheme 2.17



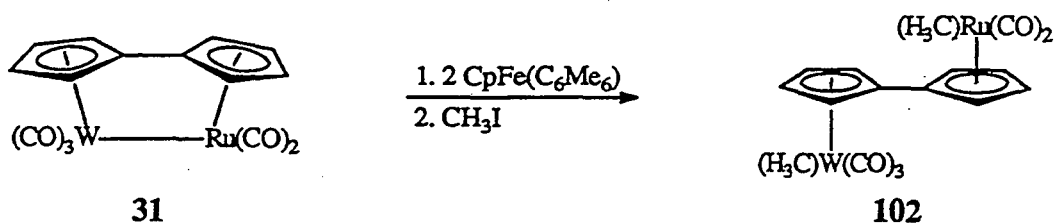
2.6 Redox Chemistry of (Fulvalene)WRu(CO)₅ 31

The first test of the electrochemistry of **31** was the two-electron reduction to confirm that the dianion was indeed formed. Since Na/K alloy had proven to be an excellent reducing agent for **30**, it was the first choice for use with **31**. In this case, however, substantial decomposition occurred upon stirring a solution of **31** with excess Na/K, even when the alloy was removed after only a few minutes. Two other common reducing agents, Na/Hg amalgam and K/benzophenone, were also tried, but only decomposition of **31** was observed. These results were somewhat surprising, as Na/Hg amalgam had been used for the reduction of the analogous ditungsten compound **94**,⁷⁶ while K/benzophenone ketyl had been successfully employed with diruthenium systems.⁷⁷

Because the reduction potential of **31** was less negative than that of **30**, it was felt that CpFe(C₆Me₆) could be utilized as an alternative reducing agent. Thus, treatment of an orange THF solution of **31** with two equivalents of CpFe(C₆Me₆) in DME rapidly gave a yellow solution, and the dimethyl complex **102** was isolated after addition of CH₃I (Scheme 2.18). The observed color changes provided a convenient means of following the progress of the reduction. Since the desired product was yellow and the solution of CpFe(C₆Me₆) was dark green, complete reduction was ensured by the addition of the CpFe(C₆Me₆) solution until a pale green color persisted, indicating a slight excess of the reducing agent. Thus, it was essentially possible to titrate a solution of **31** with CpFe(C₆Me₆), and good yields of the corresponding dimethyl complex were obtained. Addition of only one equivalent of CpFe(C₆Me₆) followed by quenching with CH₃I resulted in the isolation of approximately equal amounts of **102** and **31**, as expected for a two-electron reduction process.

The physical properties of **102** were very similar to those of **99**, and again the spectroscopic characterization readily revealed the structure. The mass spectrum showed a peak for the molecular ion at 584. The presence of two singlets at δ 0.30 and 0.25 ppm in the ¹H NMR spectrum was indicative of the two methyl groups, and the ¹³C NMR

Scheme 2.18

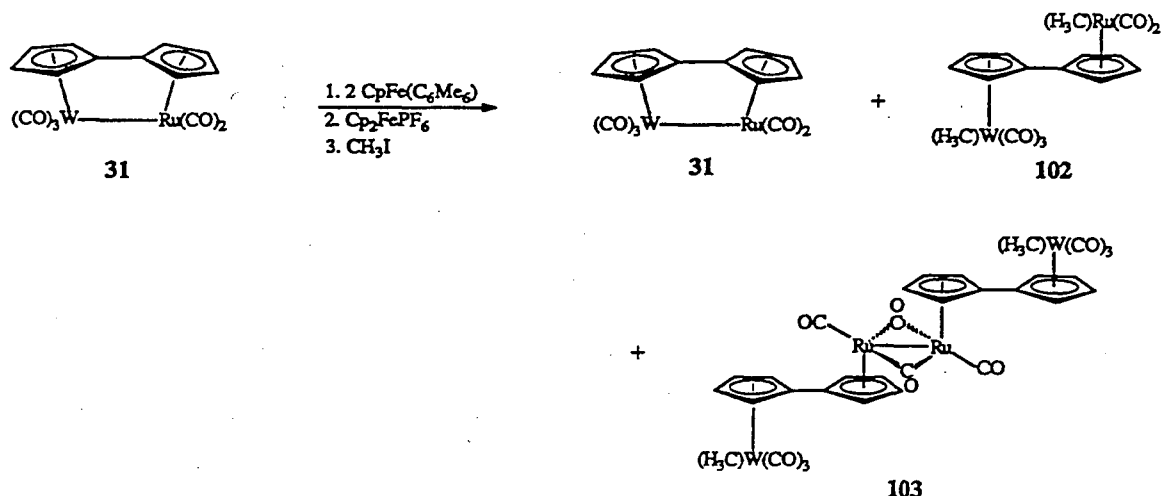


spectrum also showed two peaks at -24.79 (Ru-CH₃) and -28.55 ppm (W-CH₃). As was the case for **99**, the IR spectrum showed absorbances only for terminal carbonyl groups.

Once an efficient preparation of the dianion **100** was established, attempts were made to achieve the selective reoxidation of the ruthenium center. Unfortunately, this process was not straightforward. Treatment of a solution of **100** with one equivalent of [Cp₂Fe][PF₆] followed by quenching with CH₃I gave a mixture of products (Scheme 2.19). Two of the compounds were identified as **31** and **102** by comparison of the ¹H NMR data, while the third compound was formulated as the desired tetranuclear complex **103**. It was not possible to separate the components of the mixture by chromatography or crystallization, making it impossible to obtain all the necessary data for **103**. However, the ¹H NMR spectrum was very similar to that for **98**, as it showed four fulvalene triplets and a singlet at δ 0.26 ppm with the satellites expected for a W-CH₃ group. The IR spectrum indicated the presence of bridging carbonyl groups, and the mass spectrum showed a peak for the molecular ion at 1136. Thus, it appeared that the desired compound **103** was formed in the reaction, but it was only a minor product. In an effort to improve the yield of **103**, several variations of the oxidation step were tried. Addition of the oxidant at -45 °C did not significantly affect the product distribution, but oxidation at -78 °C gave **103** as approximately 20% of the product mixture as estimated by integration of the ¹H NMR spectrum. Substitution of acetone for THF as the solvent had no effect on the reaction.

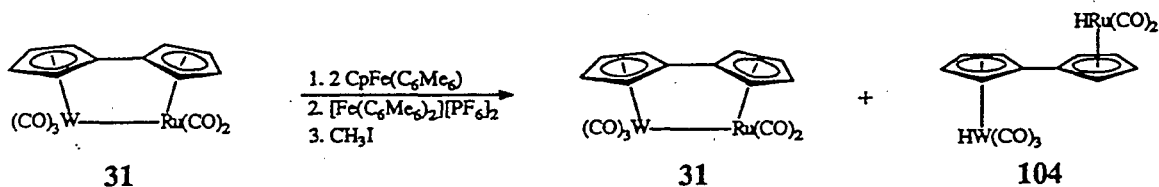
Since the formation of the dianion had already been firmly established, it was thought that **31** was being formed in the reaction due to the oxidation of both metal centers. The redox potential of ferrocenium is 0.4 V vs SCE in dimethylformamide,

Scheme 2.19



indicating that oxidation of the tungsten center could be achieved. As a result, an oxidant with a potential between the two reoxidation waves was tried, in analogy with the selective reduction of **30**. Since the dication [Fe(C₆Me₆)₂][PF₆]₂ has a first reduction potential of -0.55 V vs SCE, it was felt that it would be ideal for this situation. However, use of this oxidant at room temperature gave none of the desired compound. Instead, a mixture of **31** and the dihydride **104** was isolated (Scheme 2.20). The identity of the dihydride was established by its independent preparation by treatment of the dianion **100** with acetic acid. The formation of the dihydride was not surprising, as the methyl groups in [Fe(C₆Me₆)₂][PF₆]₂ are relatively acidic. This reaction could be prevented by performing the oxidation at low temperature, in which case the same product mixture was obtained as when ferrocenium was used as the oxidant. Thus, it proved to be impossible to find reaction conditions which gave a significant yield of **103**.

Scheme 2.20



The inability to prepare **103** efficiently was disappointing, and the failure of the reoxidation reaction may be attributed to competing electron transfer reactions. For example, it is possible that **103** is formed in substantial amounts in the reaction but then decomposes to **31** by an electrocatalytic pathway in which the oxidant serves as the catalyst. This explanation is analogous to that proposed for the decomposition of **98** to **30** during attempted crystallization, but in this case the reaction is much more rapid due to the presence of a high concentration of oxidant. Consumption of the oxidant in this decomposition reaction would also account for the presence of the dimethyl complex **102** in the reaction mixture. However, no direct evidence for this reaction was obtained.

The chemistry of the tungsten-ruthenium system, then, proved to be more complicated than for the tungsten-iron complex. Although the dianions could be generated efficiently in each case, the reoxidation of **100** failed to give an effective preparation of the tetranuclear species **103**, apparently due to competing reactions. Thus, specific metal recognition was possible for both **30** and **31**, as indicated by cyclic voltammetry, but the distinction between the two metal centers was exploited synthetically only for **30**.

Chapter Three

Electrocatalytic Ligand Substitution in Fulvalene Complexes

3.1 Introduction

The success of the electrochemical investigations of complex **30** prompted further studies of the reactivity of this compound. Since it had been clearly established that the tungsten center could be selectively reduced in **30**, it was felt that this distinction between the metals could be exploited synthetically through metal-specific ligand substitution. This hypothesis led to the investigation of electron-transfer-chain (ETC) catalysis of CO substitution in **30**, and this chapter will describe the results obtained for **30** as well as the extension of electrocatalysis to other bimetallic fulvalene compounds. The subject of ETC catalysis in transition metal complexes has been reviewed,⁷⁸ so this introduction will simply provide some background information on ETC processes.

The first example of an electrocatalyzed reaction was reported by Rich and Taube,⁷⁹ who observed chloride exchange in $[\text{AuCl}_4]^-$ initiated by the reducing agent $[\text{Fe}(\text{CN})_6]^{4-}$. Feldberg and coworkers later applied electrochemistry to establish the mechanism of this type of reaction,⁸⁰ which can be described as an ECE process. The first E denotes the initiation by electron transfer, C is the chemical propagation step, and the second E is the back electron transfer propagation step. This type of reaction has found widespread applications in transition metal chemistry,^{78a} but most of the focus has been on promoting ligand substitution reactions.

The primary reason for the interest in ETC reactions is the fact that dramatic rate increases can be achieved by this method. These rate increases are attributed to the intermediacy of odd-electron species due to electron transfer. For example, an 18-electron complex which is relatively inert can be oxidized to a 17-electron radical, and the greatly enhanced reactivity of such species is well known.⁸¹ In fact, the chemistry of 17-electron radicals has become a subject of intense interest, as these species have been found to play important roles in numerous stoichiometric and catalytic reactions.^{81, 82}

Although it was understood that 17-electron species were the key to greatly accelerated substitution rates, it remained unclear whether these intermediates reacted by a dissociative mechanism to give 15-electron species or through associative processes to give 19-electron species. The primary argument against the associative pathway was based on the assumption that 19-electron species were inherently unstable. However, confirmation of the associative mechanism was provided by Poë and coworkers,⁸³ who conducted kinetic studies on the competition between chlorine atom abstraction from CCl_4 and ligand substitution by tertiary phosphines in $\text{Re}(\text{CO})_5$. Further evidence for an associative pathway for substitution in $\text{Mn}(\text{CO})_5$ was reported by Herrinton and Brown,⁸⁴ and Basolo and coworkers provided findings consistent with the associative mechanism for substitution in $\text{V}(\text{CO})_6$.⁸⁵

The stability of 19-electron species, as well as the enhanced reactivity of the corresponding 17-electron species, can be understood on the basis of a simple qualitative molecular orbital diagram, which is illustrated in Figure 3.1 for the $\text{Mn}(\text{CO})_5$ fragment.⁸⁶ Assuming that the unpaired electron in $\text{Mn}(\text{CO})_5$ is in a pure d_{z^2} orbital, which is antibonding with respect to the apical CO ligand, the bond order for M-CO along the z-axis is 1/2. Interaction of this fragment with a two-electron ligand L then results in a bonding-antibonding pair of orbitals with the odd electron in the higher-energy antibonding orbital. Thus, the overall bond order along the z-axis is still only 1/2, but the competition for the d_{z^2} orbital between the apical CO and L results in a formal order of 1/4 for each bond. This reduction in bond order explains why substitution is much more rapid in 17-electron complexes. The assumption that the singly occupied orbital in $\text{Mn}(\text{CO})_5$ is purely d_{z^2} in character is an oversimplification, as this orbital also has some p_z and s components.⁸⁷ The mixing of these higher-energy orbitals with the antibonding orbital in the 19-electron species results in an overall stabilization, and the bond order along the z axis is actually greater than 1/2. This stabilization is the driving force for the formation of the 19-electron complex. The degree of stabilization varies with both the metal and the

entering ligand, and pi backbonding to the other ligands further lowers the energy of the 19-electron species.

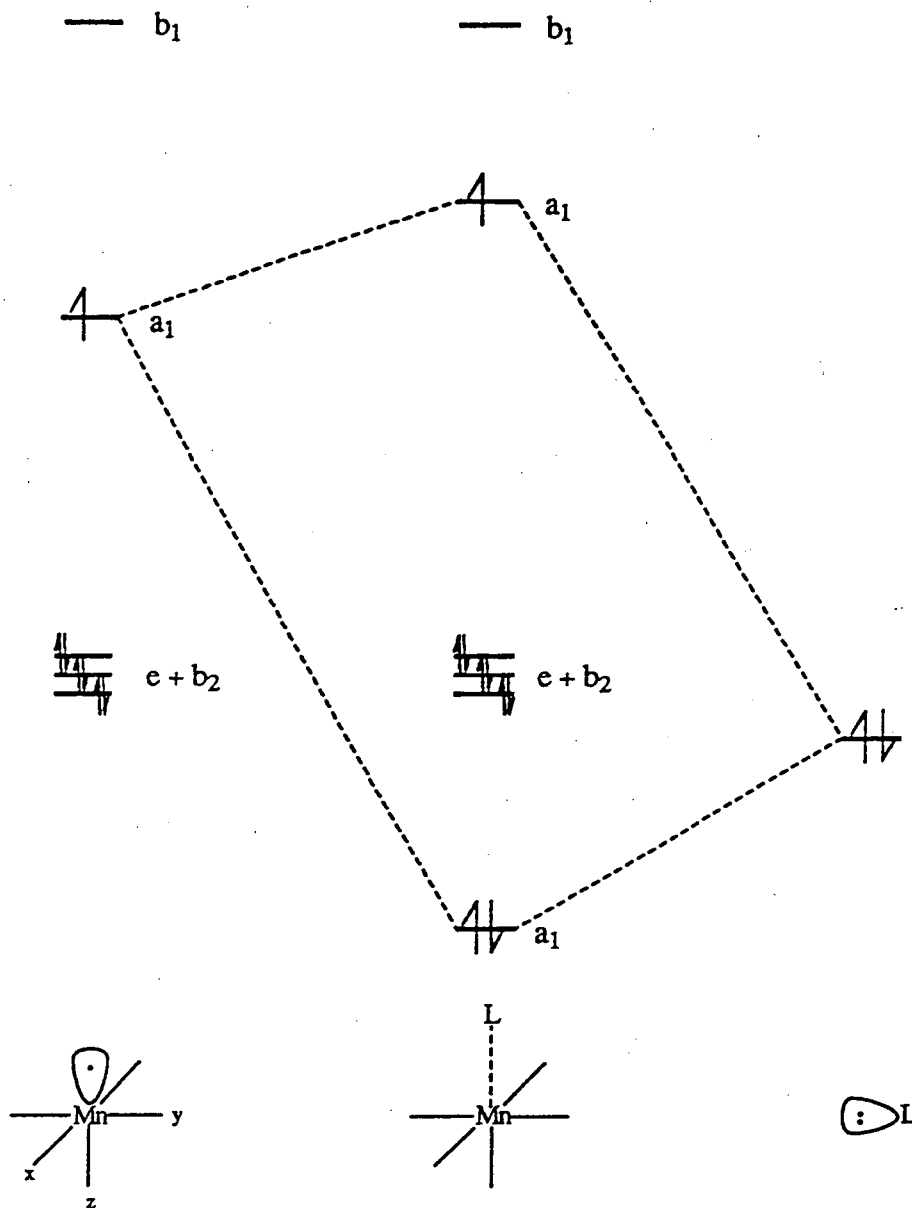


Figure 3.1. Molecular orbital scheme showing the interaction between an $\text{Mn}(\text{CO})_5$ fragment with a two-electron ligand L .

Although the preceding discussion shows that odd-electron species should be more reactive toward substitution, this rule is not without exception. Poli *et al.* have reported ETC catalyzed substitution of iodide by chloride in $\text{CpMoI}_2(\text{PMe}_3)_2$ to give

$\text{CpMoCl}_2(\text{PMe}_3)_2$.⁸⁸ The starting complex is a 17-electron species, and the substitution was catalyzed by oxidation to give the 16-electron cation. The rate acceleration observed for the latter was attributed to the fact that the steric crowding precluded an associative mechanism to give a 19-electron intermediate from the starting 17-electron complex. The high energy HOMO in the starting compound also disfavored associative substitution and facilitated the oxidation to give the stable 16-electron species.⁸⁹

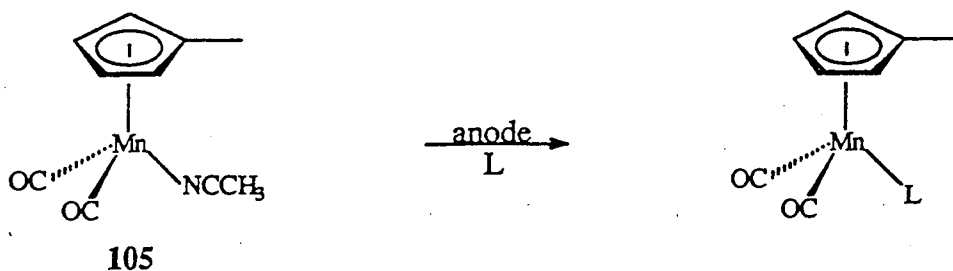
The fact that virtually all electrocatalytic reactions proceed through odd-electron species points to an important consideration in the design of the catalytic cycle. Organometallic radicals, whether 17- or 19-electron, are highly reactive species which are prone to a variety of side reactions, such as dimerization, atom abstraction, and disproportionation. In order to minimize these side reactions in an electrocatalytic process, both of the propagation steps should be very fast. Since the chemical reaction which is the first propagation step will usually be fast in the absence of steric constraints, the primary concern is the second propagation step, or back electron transfer. Thus, an exergonic electron transfer will usually provide the driving force for the propagation, although an irreversible chemical propagation step can accomplish the same.^{78a}

Since the reversibility of the first propagation step is usually not known in advance, it is better to rely on the back electron transfer to provide efficient catalysis. This consideration will determine the type of initiation, either oxidative or reductive, to be used. For a substitution reaction, then, the primary concern is the electron donating ability of the entering ligand vs. that of the departing ligand. If the entering ligand is more electron rich, the final product will be more difficult to reduce than the starting material, so a favorable back electron transfer can be obtained through the use of reductive initiation. Similarly, oxidative initiation will provide a favorable electron transfer when the entering ligand is less electron rich than the displaced ligand, as the product will be more difficult to oxidize than the starting material.

Although the favorable nature of the back electron transfer step is important, it should be noted that this condition alone does not guarantee an efficient electrocatalytic cycle, as side reactions can still pose a problem. For example, electrocatalysis of CO substitution in mononuclear species has rarely been reported, as dimerization of the 17-electron species usually predominates. Rieger *et al.* showed that only small amounts of substituted products were obtained in treating $\text{Fe}(\text{CO})_5$ with phosphines or phosphites under reducing conditions,⁹⁰ and this difficulty can be attributed to the rapid dimerization of the 17-electron radical anion $\text{Fe}(\text{CO})_4^-$. Similar problems are encountered with dinuclear compounds which lack bridging ligands, as cleavage of the metal-metal bonds produces mononuclear radicals which are subject to rapid dimerization (see Chapter 2). Thus, most of the successful cases of ETC catalyzed CO substitution have been reported for clusters or dinuclear complexes with one or more bridging ligands.^{78a}

While catalytic processes are usually evaluated in terms of the number of turnovers achieved, the effectiveness of an electrocatalytic reaction is measured by the coulombic efficiency. This criterion is determined by the number of molecules of product obtained per electron transferred by the initiator. For example, if an electrocatalytic process requires ten mole percent of ferrocenium to give a yield of 90%, there are nine molecules of product formed per electron, so the coulombic efficiency is nine. Much higher numbers are often obtained; Kochi and coworkers reported coulombic efficiencies greater than 1000 for the ligand exchange reaction illustrated in Scheme 3.1.⁹¹

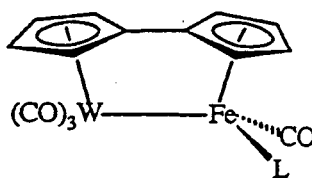
Scheme 3.1



The successful application to a variety of organometallic, inorganic, and organic reactions has illustrated the remarkable versatility of this process. It is particularly useful in transition metal chemistry, since transition metals undergo facile changes in oxidation states and the reactivity of odd-electron (17- or 19-electron) species is greatly enhanced compared to the corresponding 18-electron complexes. Additionally, the fact that electrocatalytic reactions are usually complete in a few minutes at room temperature makes this process an attractive alternative to thermal reactions. The remainder of this chapter will describe the application of electrocatalysis to CO substitution in bimetallic fulvalene compounds.

3.2 Electrocatalysis of Ligand Substitution in (Fulvalene)WFe(CO)₅ 30

The electrochemical investigations of compound **30** indicated that it was possible to reduce the tungsten center selectively, leaving the iron nucleus as a 17-electron radical. This result suggested the possibility of performing ligand substitution exclusively at the iron center by taking advantage of its enhanced reactivity (*vide supra*). Thus, it was felt that electrocatalysis could provide complexes of the type **106**, where L is a two-electron ligand such as a phosphine. This section will present the results of these ligand substitution studies.



106

Since the one-electron reduction of **30** gave good isolated yields of the dimer **98** (Section 2.4), it seemed unlikely that the intermediate 17-electron species was prone to significant side reactions. As a result, the only reaction expected to compete with the desired CO substitution was this dimerization. However, the fact that only catalytic amounts of the reducing agent were to be used ensured that the concentration of the 17-electron radical would always be low, thereby minimizing the chance of dimerization. In order to favor formation of the desired products, then, it was necessary to use a reducing agent whose concentration could be carefully controlled. Once again, the ideal choice was CpFe(C₆Me₆) (**97**). The first ligand chosen to test was trimethylphosphite, P(OMe)₃, since its small cone angle (107°)⁹² guaranteed that steric problems would be minimal.

Although electrocatalysis was achieved with this system, the product was not that expected. When a THF solution containing **30** and excess P(OMe)₃ was treated with a catalytic amount (0.10 eq.) of CpFe(C₆Me₆) in DME, a precipitate began to form after a few minutes. Analysis of the reaction mixture by thin layer chromatography (TLC) after 15 minutes indicated that **30** was no longer present. Curiously, there was no compound

which moved above the baseline. The TLC behavior and insolubility of the product seemed inconsistent with a complex of the type **106**, which would be expected to be more soluble than **30**.

Although the product was found to be insoluble in ethereal solvents, it was slightly soluble in acetone and quite so in acetonitrile (CH_3CN). Thus, the product was purified simply by removal of the reaction solvents, dissolution in CH_3CN , and filtration through a short column of Celite. Crystallization from CH_3CN at low temperature resulted in deep red crystals which gave an elemental analysis consistent with a fulvalene tungsten-iron complex containing four CO and two $\text{P}(\text{OMe})_3$ ligands. In support of this assignment, the mass spectrum showed a molecular ion of 632. The ^1H NMR spectrum displayed the four triplets expected for a symmetrical fulvalene ligand as well as a pseudotriplet (arising from virtual coupling with the two phosphorus atoms) integrating for 18 hydrogens, which is consistent with two $\text{P}(\text{OMe})_3$ ligands bound to the same metal center. The ^{31}P NMR spectrum showed only one singlet, indicating that the two P atoms were equivalent. Since no coupling to the ^{183}W nucleus was observed, it was concluded that both phosphite ligands were on the iron center.

The spectral data, as well as the solubility properties, were consistent with the formulation of the product as a zwitterion in which one of the CO ligands of **30** had been replaced by two $\text{P}(\text{OMe})_3$ ligands. In order to confirm this hypothesis, an x-ray diffraction study was undertaken. Suitable crystals were grown by slow cooling of a saturated CH_3CN solution, and the ORTEP drawing is shown in Figure 3.2. The x-ray structure confirmed the proposed formulation of the product and showed a trans orientation of the metal centers with respect to the fulvalene ligand, an arrangement which is always observed in complexes lacking a metal-metal bond.

This electrocatalytic reaction, depicted in Scheme 3.2, resulted in the displacement of one CO group from the iron center and addition of two phosphite ligands. The presence of three two-electron ligands on iron requires that this center have a positive

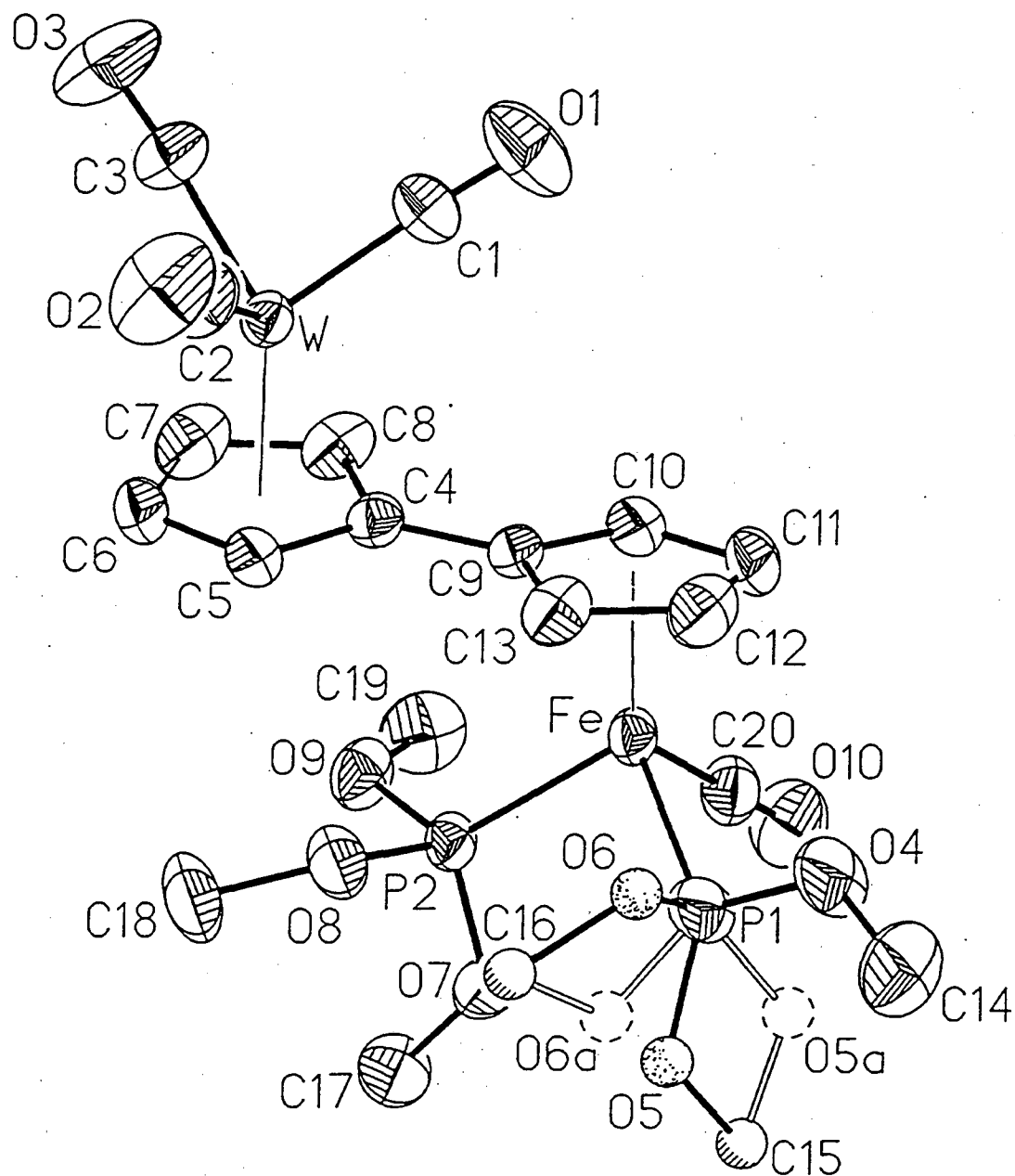


Figure 3.2. ORTEP drawing of the zwitterion 107.

Table 3.1. Bond angles (°) for 107.

C(1)-W-C(2)	89.5(2)	C(1)-W-C(3)	90.0(2)
C(2)-W-C(3)	89.9(2)	C(1)-W-C(4)	99.2(2)
C(2)-W-C(4)	120.9(2)	C(3)-W-C(4)	147.5(2)
C(1)-W-C(5)	126.1(2)	C(2)-W-C(5)	95.5(2)
C(3)-W-C(5)	143.4(2)	C(4)-W-C(5)	34.7(2)
C(1)-W-C(6)	158.0(2)	C(2)-W-C(6)	102.0(3)
C(3)-W-C(6)	108.5(2)	C(4)-W-C(6)	58.2(2)
C(5)-W-C(6)	35.1(1)	C(1)-W-C(7)	135.9(2)
C(2)-W-C(7)	134.4(2)	C(3)-W-C(7)	93.3(2)
C(4)-W-C(7)	58.4(1)	C(5)-W-C(7)	58.0(2)
C(6)-W-C(7)	34.7(2)	C(1)-W-C(8)	104.1(2)
C(2)-W-C(8)	153.9(2)	C(3)-W-C(8)	112.0(2)
C(4)-W-C(8)	35.6(1)	C(5)-W-C(8)	58.5(2)
C(6)-W-C(8)	58.5(2)	C(7)-W-C(8)	35.2(2)
P(1)-Fe-P(2)	93.1(1)	P(1)-Fe-C(9)	140.0(1)
P(2)-Fe-C(9)	90.4(1)	P(1)-Fe-C(10)	153.2(1)
P(2)-Fe-C(10)	112.6(1)	C(9)-Fe-C(10)	38.4(2)
P(1)-Fe-C(11)	114.1(2)	P(2)-Fe-C(11)	152.2(1)
C(9)-Fe-C(11)	65.2(2)	C(10)-Fe-C(11)	39.6(2)
P(1)-Fe-C(12)	89.2(1)	P(2)-Fe-C(12)	141.5(2)
C(9)-Fe-C(12)	64.8(1)	C(10)-Fe-C(12)	66.2(2)
C(11)-Fe-C(12)	40.1(3)	P(1)-Fe-C(13)	101.8(1)
P(2)-Fe-C(13)	103.0(1)	C(9)-Fe-C(13)	39.0(1)
C(10)-Fe-C(13)	66.3(2)	C(11)-Fe-C(13)	67.1(2)
C(12)-Fe-C(13)	39.5(2)	P(1)-Fe-C(20)	89.9(1)
P(2)-Fe-C(20)	92.0(2)	C(9)-Fe-C(20)	129.7(2)
C(13)-Fe-C(20)	96.3(2)	C(11)-Fe-C(20)	93.7(3)
C(12)-Fe-C(20)	126.4(2)	C(13)-Fe-C(20)	160.3(2)
Fe-P(1)-O(4)	112.0(2)	Fe-P(1)-O(5)	129.6(3)
O(4)-P(1)-O(5)	115.7(3)	Fe-P(1)-O(5A)	109.4(2)
O(4)-P(1)-O(5A)	90.8(3)	Fe-P(1)-O(6)	107.5(4)
O(4)-P(1)-O(6)	73.3(5)	O(5)-P(1)-O(6)	97.2(5)
O(5A)-P(1)-O(6)	142.9(5)	Fe-P(1)-O(6A)	124.3(2)
O(4)-P(1)-O(6A)	115.6(3)	O(5A)-P(1)-O(6A)	97.3(3)
Fe-P(2)-O(7)	111.6(1)	Fe-P(2)-O(8)	112.6(1)
O(7)-P(2)-O(8)	108.2(2)	Fe-P(2)-O(9)	119.1(1)
O(7)-P(2)-O(9)	103.6(2)	O(8)-P(2)-O(9)	100.7(2)
P(1)-O(4)-C(14)	125.6(5)	P(1)-O(5)-C(15)	120.1(6)
P(1)-O(5A)-C(15)	122.0(6)	P(1)-O(6)-C(16)	116.1(8)
P(1)-O(6A)-C(16)	118.2(5)	P(2)-O(7)-C(17)	124.9(3)
P(2)-O(8)-C(18)	126.8(4)	P(2)-O(9)-C(19)	120.7(3)
W-C(1)-O(1)	175.2(4)	W-C(2)-O(2)	173.8(5)
W-C(3)-O(3)	176.4(5)	W-C(4)-C(5)	71.8(2)
W-C(4)-C(8)	72.3(2)	C(5)-C(4)-C(8)	107.7(3)
W-C(4)-C(9)	122.9(2)	C(5)-C(4)-C(9)	127.4(3)
C(8)-C(4)-C(9)	124.8(4)	W-C(5)-C(4)	73.5(2)
W-C(5)-C(6)	72.5(2)	C(4)-C(5)-C(6)	109.0(4)
W-C(5)-C(5)	72.4(3)	W-C(6)-C(7)	72.2(3)

Table 3.1. Bond angles (°) for 107.

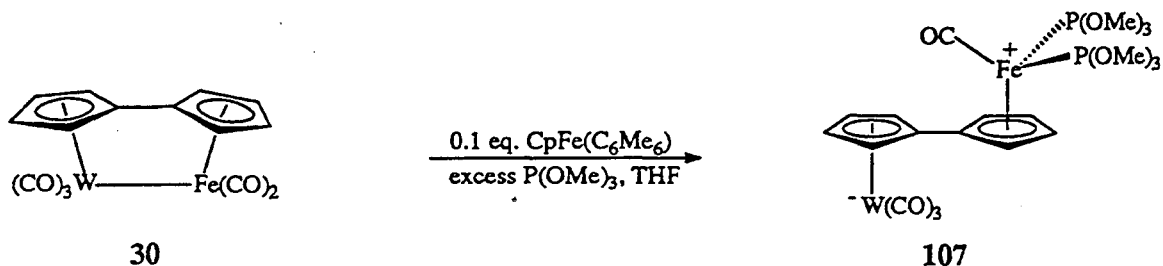
C(5)-C(6)-C(7)	107.6(5)	W-C(7)-C(6)	73.1(3)
W-C(7)-C(8)	73.7(2)	C(6)-C(7)-C(8)	109.7(4)
W-C(8)-C(4)	72.1(2)	W-C(8)-C(7)	71.1(3)
C(4)-C(8)-C(7)	106.0(4)	Fe-C(9)-C(4)	130.8(2)
Fe-C(9)-C(10)	68.8(2)	C(4)-C(9)-C(10)	126.2(3)
Fe-C(9)-C(13)	67.8(2)	C(4)-C(9)-C(13)	125.0(4)
C(10)-C(9)-C(13)	108.7(3)	Fe-C(10)-C(9)	72.8(3)
Fe-C(10)-C(11)	68.7(3)	C(9)-C(10)-C(11)	108.0(5)
Fe-C(11)-C(10)	71.7(3)	Fe-C(11)-C(12)	69.7(3)
C(10)-C(11)-C(12)	107.1(6)	Fe-C(12)-C(11)	70.2(3)
Fe-C(12)-C(13)	71.4(2)	C(11)-C(12)-C(13)	109.3(4)
Fe-C(13)-C(9)	73.2(2)	Fe-C(13)-C(12)	69.2(3)
C(9)-C(13)-C(12)	106.7(5)	Fe-C(20)-O(10)	178.7(4)

Table 3.2. Bond lengths (Å) for 107.

W-C(1)	1.926 (5)	W-C(2)	1.927 (5)
W-C(3)	1.936 (4)	W-C(4)	2.369 (3)
W-C(5)	2.347 (4)	W-C(6)	2.348 (5)
W-C(7)	2.337 (4)	W-C(8)	2.370 (4)
Fe-P(1)	2.159 (1)	Fe-P(2)	2.154 (1)
Fe-C(9)	2.187 (3)	Fe-C(10)	2.134 (5)
Fe-C(11)	2.093 (6)	Fe-C(12)	2.087 (4)
Fe-C(13)	2.116 (4)	Fe-C(20)	1.762 (5)
P(1)-O(4)	1.537 (4)	P(1)-O(5)	1.553 (7)
P(1)-O(5A)	1.680 (6)	P(1)-O(6)	1.662 (11)
P(1)-O(6A)	1.512 (7)	P(2)-O(7)	1.586 (3)
P(2)-O(8)	1.593 (4)	P(2)-O(9)	1.590 (3)
O(1)-C(1)	1.160 (8)	O(2)-C(2)	1.173 (7)
O(3)-C(3)	1.158 (7)	O(4)-C(14)	1.416 (7)
O(5)-C(15)	1.573 (11)	O(5A)-C(15)	1.414 (9)
O(6)-C(16)	1.487 (18)	O(6A)-C(16)	1.604 (11)
O(7)-C(17)	1.422 (5)	O(8)-C(18)	1.442 (8)
O(9)-C(19)	1.435 (8)	O(10)-C(20)	1.131 (7)
C(4)-C(5)	1.405 (7)	C(4)-C(8)	1.449 (5)
C(4)-C(9)	1.454 (5)	C(5)-C(6)	1.414 (6)
C(6)-C(7)	1.398 (9)	C(7)-C(8)	1.424 (7)
C(9)-C(10)	1.420 (7)	C(9)-C(13)	1.438 (5)
C(10)-C(11)	1.433 (7)	C(11)-C(12)	1.432 (11)
C(12)-C(13)	1.419 (7)		

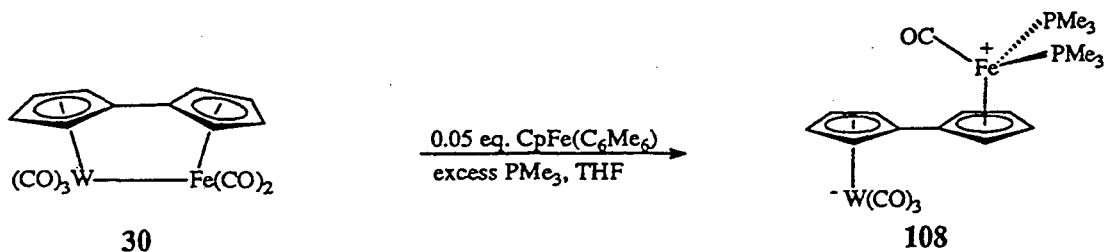
charge, while the tungsten center retains the negative charge imparted by the initial reduction. Since no monosubstituted product was obtained, it was felt that the disubstitution may have resulted from the excess of $\text{P}(\text{OMe})_3$ in the reaction mixture. However, when only one equivalent of $\text{P}(\text{OMe})_3$ was used, the disubstituted complex **107** was still the only product, and unreacted **30** was recovered.

Scheme 3.2



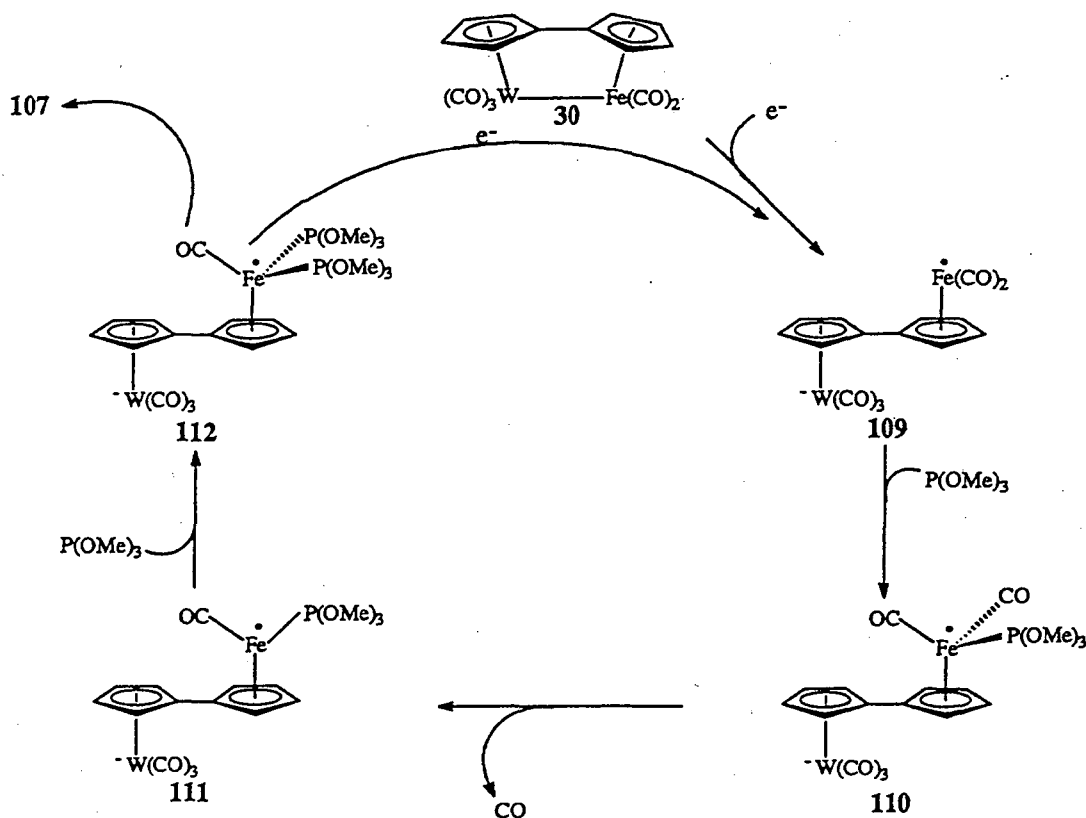
Since it was clearly established that only disubstitution could be achieved, it was reasoned that the reaction would be limited by steric constraints. As a result, a series of phosphine ligands were tested to determine how large a cone angle (θ) could be tolerated in the reaction. Not surprisingly, trimethylphosphine ($\theta = 118^\circ$) proved to work extremely well, as only 5 mole percent of $\text{CpFe}(\text{C}_6\text{Me}_6)$ was necessary to give a 79% yield of the zwitterion **108** (Scheme 3.3). Again, the spectroscopic and analytical data confirmed that disubstitution had occurred. Attempts with other phosphines proved to be unsuccessful. Using triethylphosphine ($\theta = 132^\circ$), a reaction occurred which led to uncharacterizable, oily products, while no reaction took place with triphenylphosphine ($\theta = 145^\circ$). Chelating phosphines, such as diphenylphosphinoethane (dppe) and dimethylphosphinomethane (dmpm), also gave uncharacterizable products.

Scheme 3.3



Based on the observed products and the known reactivity of 17- and 19-electron species, a simple mechanism for the electrocatalytic process can be developed (Scheme 3.4). The initiation step is the reduction of **30** to give the radical anion **109**. The 17-electron iron center then undergoes associative substitution to give the 19-electron **110**. Assuming that intermediate **110** is not sufficiently electron rich to reduce **30** (that is, the back electron transfer is endergonic for **110**), loss of CO gives the 17-electron radical **111**, which undergoes associative addition of a second $\text{P}(\text{OMe})_3$ to produce the 19-electron **112**. Since two $\text{P}(\text{OMe})_3$ ligands have been added, **112** is capable of reducing **30** to close the catalytic cycle. The back electron transfer results in a cationic iron center, while the anionic tungsten center remains unchanged throughout the propagation steps.

Scheme 3.4



In order to gain more insight into the mechanism of this reaction, CV studies were performed on **30** in the presence of $\text{P}(\text{OMe})_3$, and the resulting voltammogram is shown in Figure 3.3. The peak labeled R1 corresponds to the reduction of the tungsten center

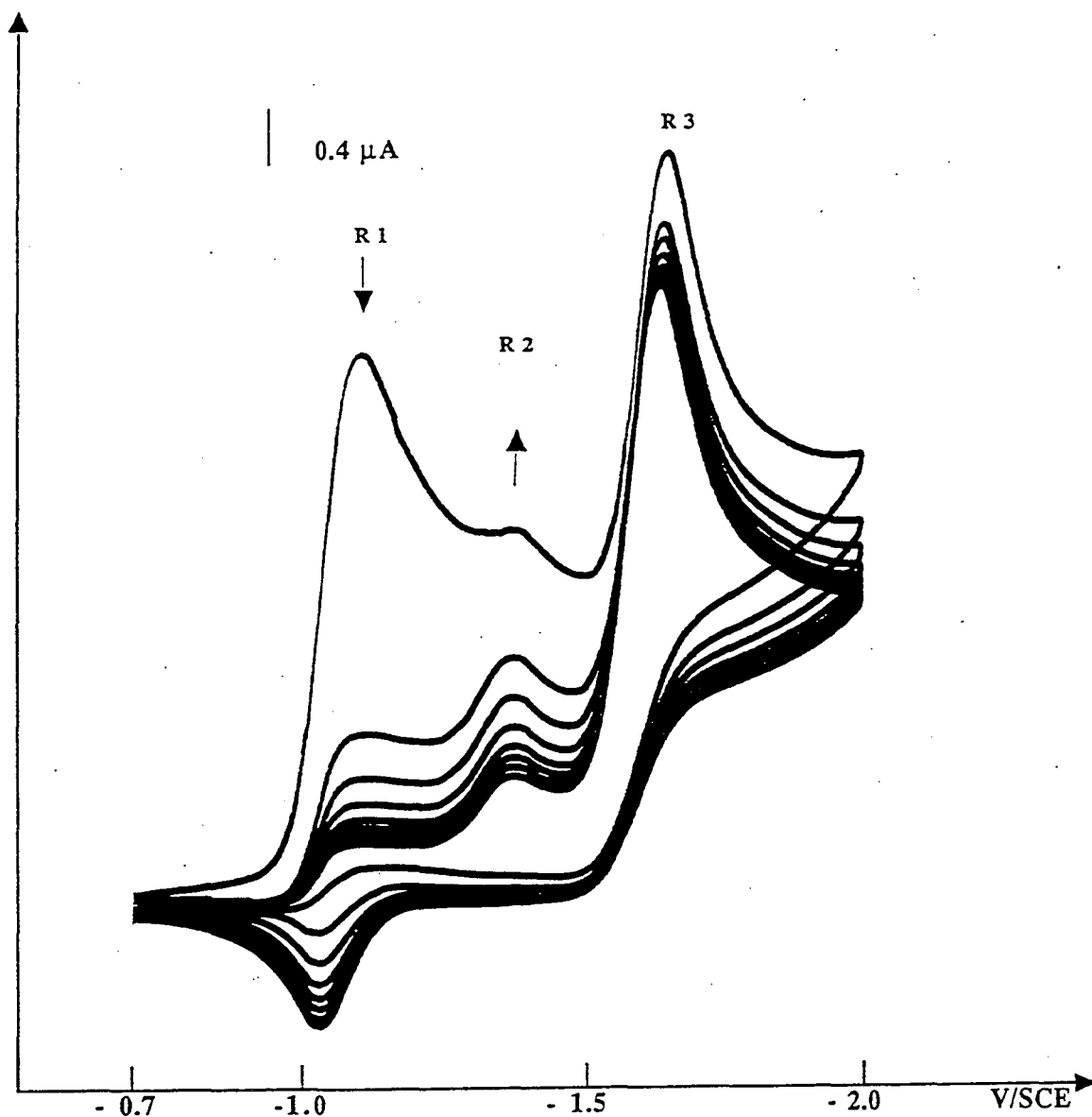


Figure 3.3. Cyclic voltammogram of complex 30 in the presence of $P(OMe)_3$.

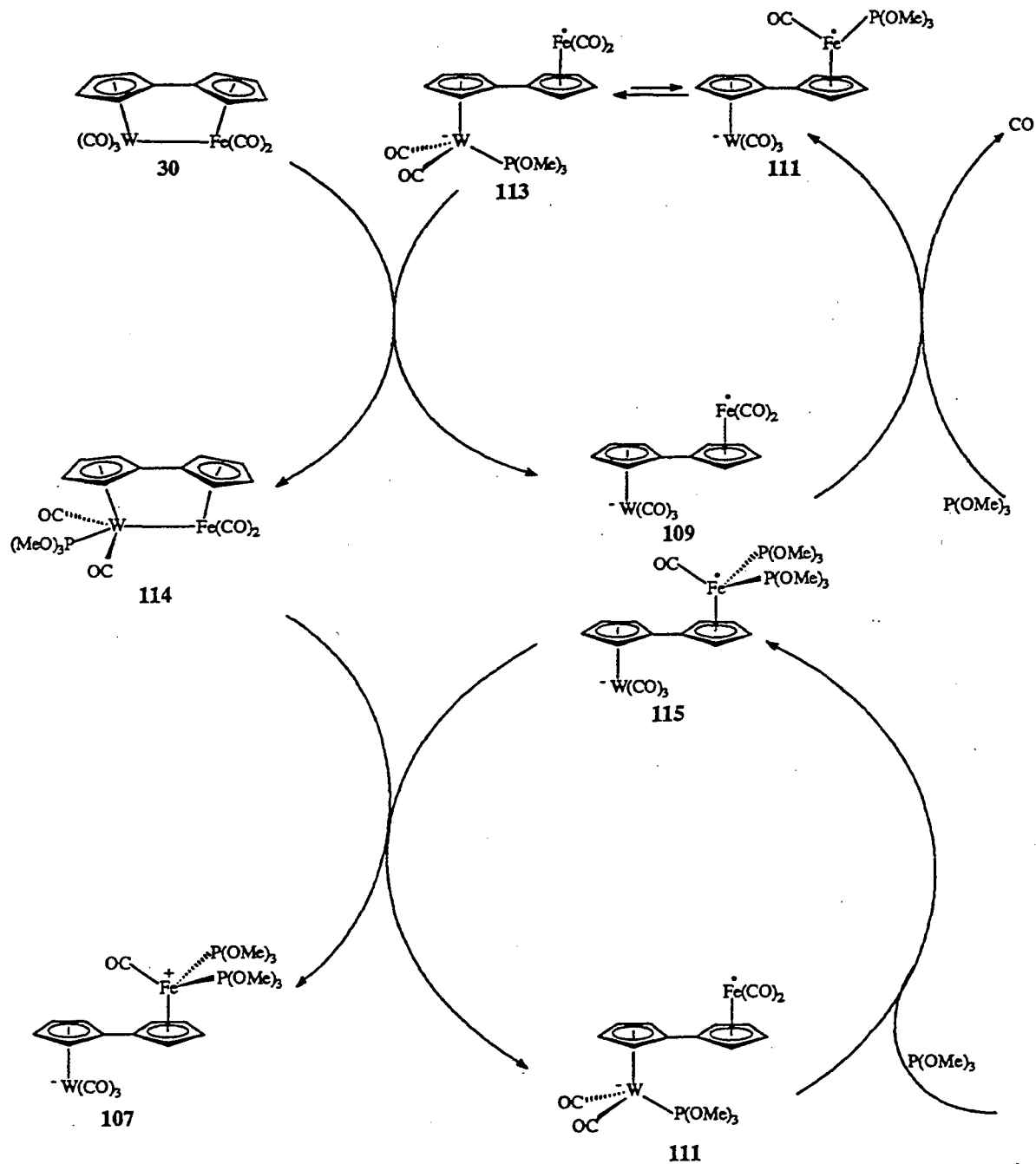
(Section 2.3), and this wave rapidly decays with repetitive scans. This consumption of the starting material is a typical indication of an electrocatalytic process. A small wave R2 begins to grow in but never becomes very intense. The third wave R3 initially indicates reduction of the iron center, but this wave does not decrease over time, although it does seem to shift to a slightly less negative potential. Thus, this wave must correspond to the

main product in the reaction, since it remains intense while R1 diminishes. To confirm these assignments for R1, R2, and R3, the CV of **107** was also recorded. Surprisingly, it was found that R2 corresponds to the zwitterion, indicating that R3 must be due to some intermediate which shows only one reduction wave.

The CV studies indicated that the mechanism proposed in Scheme 3.4 was incorrect, since it fails to describe a stable intermediate which would explain the reduction wave R3. As a result, a new mechanistic proposal was developed based on a double electrocatalytic cycle (Scheme 3.5). The first cycle converts **30** into the potential intermediate indicated by R3 while the second cycle produces the zwitterion from the intermediate. This scheme invokes intramolecular ligand rearrangements for the radical anions, a phenomenon which has been observed for di- and polynuclear metal carbonyl compounds.⁹³ The ligand rearrangement, in which P(OMe)₃ is transferred from iron to tungsten, gives rise to the potential intermediate **114**. In this case, the replacement of a carbonyl ligand by P(OMe)₃ renders the anionic tungsten center more electron-rich, thereby causing the back electron transfer to be exergonic. Electron transfer from the radical anion **113** would give a diradical which would be expected to undergo rapid intramolecular metal-metal bond formation to produce **114**. Once **30** has been completely consumed, the remaining radical anion **113** may proceed to give the zwitterion **107**, since electron transfer from **113** would no longer be available. This reaction would again involve ligand rearrangement to place both P(OMe)₃ ligands on iron in the radical anion **115**. The 19-electron iron center can then reduce **114** to close the second catalytic cycle. In the CV experiment this second cycle does not proceed to a significant extent, while in the preparative-scale experiment it goes to completion. This difference may be attributed to the precipitation of the zwitterion in the preparative reactions, which were typically run at concentrations an order of magnitude greater than in the CV studies.

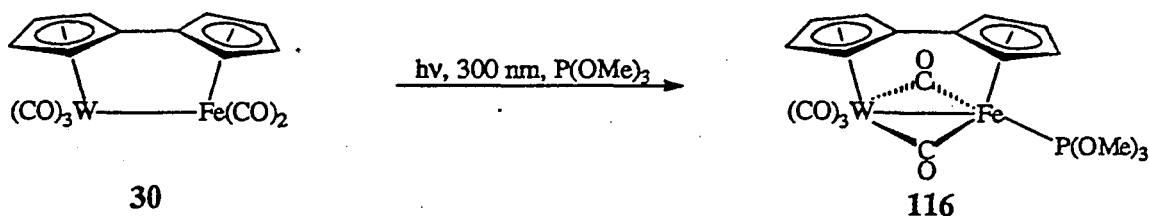
Although it seemed likely that the intramolecular transfer of P(OMe)₃ would occur to give an exergonic back electron transfer step in the first electrocatalytic cycle, the

Scheme 3.5



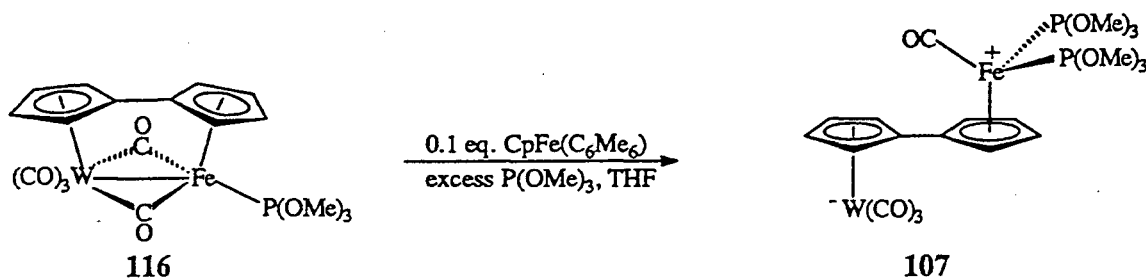
possibility of electron transfer from the unsubstituted tungsten anion could not be excluded. In this case the product (intermediate) would have one P(OMe)₃ ligand on the iron center. To eliminate this possibility, the monosubstituted complex 116 was prepared by photolysis at 300 nm of a THF solution of 30 containing P(OMe)₃ (Scheme 3.6). The product was easily purified by chromatography followed by recrystallization. The mass

Scheme 3.6



spectrum failed to show the molecular ion, but fragmentation showing successive losses of CO groups was observed, and the elemental analysis proved that only one $\text{P}(\text{OMe})_3$ ligand had been added. The ^{31}P NMR spectrum confirmed that the phosphite ligand was on the iron center, as no coupling to the ^{183}W nucleus was observed. The ^1H NMR spectrum showed a doublet at 3.61 ppm integrating to nine hydrogens for the $\text{P}(\text{OMe})_3$ ligand and four peaks for the fulvalene ligand. This symmetrical fulvalene pattern is consistent with the proposed structure of **116**. The presence of absorptions at 1880 and 1866 cm^{-1} in the IR spectrum confirmed that bridging carbonyl groups were present. It is interesting to note that monosubstitution of (fulvalene)tetracarbonyldiruthenium (**95**) with phosphines did not give rise to structures containing bridging carbonyl ligands.⁹⁴ The CV of **116** showed reduction waves at -1.305 and -1.420 V vs SCE, neither of which matched R3. Thus, compound **116** was ruled out as the observed intermediate. However, electrocatalysis did occur with **116**, as the zwitterion **107** was produced in nearly quantitative yield based on integration of the ^1H NMR spectrum (Scheme 3.7).

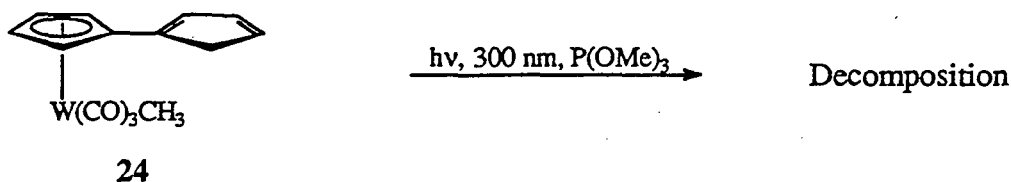
Scheme 3.7



Since the monosubstituted compound **116** proved not to be the desired intermediate, attention was focused on synthesizing **114**. This problem was much more difficult, since

substitution in **30** occurred at the iron center. As a result, attempts were made to introduce the P(OMe)_3 ligand before the iron center was present. Unfortunately, irradiation of the diene **24** in the presence of P(OMe)_3 led only to decomposition (Scheme 3.8). The limited thermal stability of **24** and the relative inertness of the tungsten center precluded heating **24** at a temperature sufficient to induce substitution. Use of trimethylamine-*N*-oxide (Me_3NO) failed to give any reaction at room temperature and caused decomposition upon heating of the reaction mixture. These failures frustrated further attempts to gain insight into the mechanism of the electrocatalytic process.

Scheme 3.8



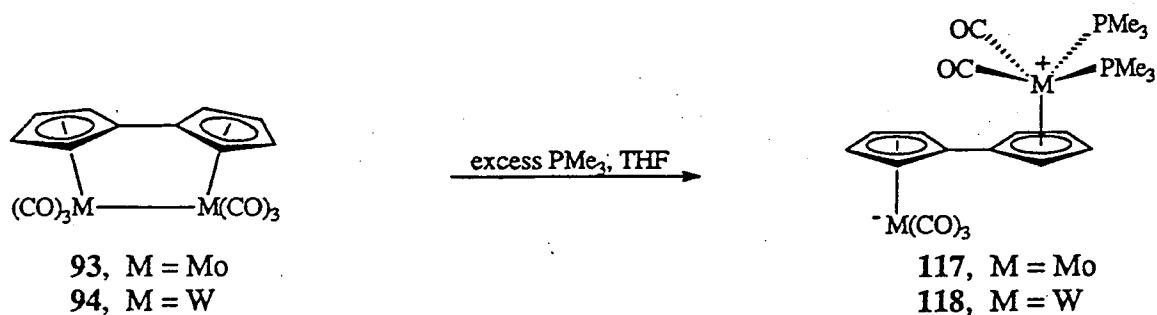
Electrocatalysis of CO substitution in the fulvalene complex **30** was accomplished using phosphorus ligands with small cone angles, and the success of this reaction can be attributed to the ability of the fulvalene ligand to serve as an electron sink,^{78a, 95} thereby preventing side reactions of the intermediate radical species. Cyclic voltammetric studies suggested that the reaction proceeds by a double electrocatalytic cycle, but efforts to substantiate this hypothesis by preparation of the key intermediate **114** were unsuccessful. Nevertheless, these results encouraged further investigations into the use of electrocatalysis to effect ligand substitution in fulvalene compounds.

3.3 Zwitterions in Fulvalene Chemistry

The zwitterions **107** and **108** isolated from the electrocatalytic reactions of **30** were not unique among fulvalene complexes. In fact, several analogs had been prepared for both homo- and heterobimetallic fulvalene compounds.^{19a,96} The existence of these species, which were all prepared by uncatalyzed substitution reactions, suggested that electrocatalysis might be applicable to a number of bimetallic fulvalene compounds. This section will review these other preparations of fulvalene zwitterions.

The first examples were encountered on treatment of (fulvalene)hexacarbonyldimolybdenum (**93**) and -ditungsten (**94**) with PMe_3 , which resulted in the formation of the disubstituted zwitterions **117** and **118**, respectively (Scheme 3.9).^{96a} Use of dmpm instead of PMe_3 led to the corresponding chelated derivatives. The chemistry of the dimolybdenum system was developed extensively, and charge-localized behavior was displayed by each metal, as the cationic center reacted with electrophiles and the anionic center reacted with nucleophiles. In addition, it was shown that formation of the zwitterion did not proceed through the monosubstituted complex containing a metal-metal bond, as this compound did not react with PMe_3 under the same conditions that produced **117**.

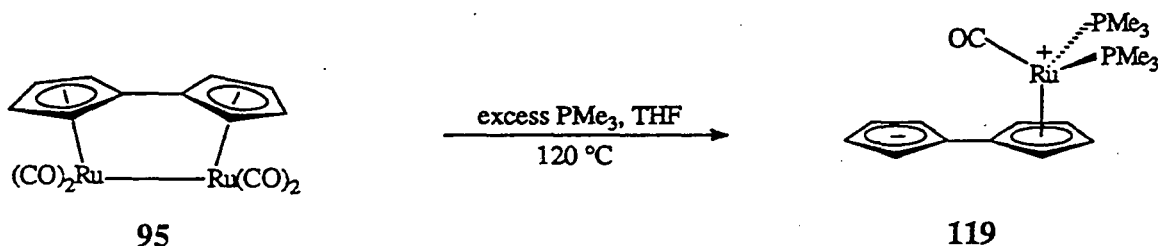
Scheme 3.9



A similar type of reactivity was later found for (fulvalene)tetracarbonyldiruthenium (**95**), which underwent reaction with excess PMe_3 at $120\text{ }^\circ\text{C}$ to give the mononuclear zwitterion **119** (Scheme 3.10).^{96b} In this case, decomplexation of one metal center

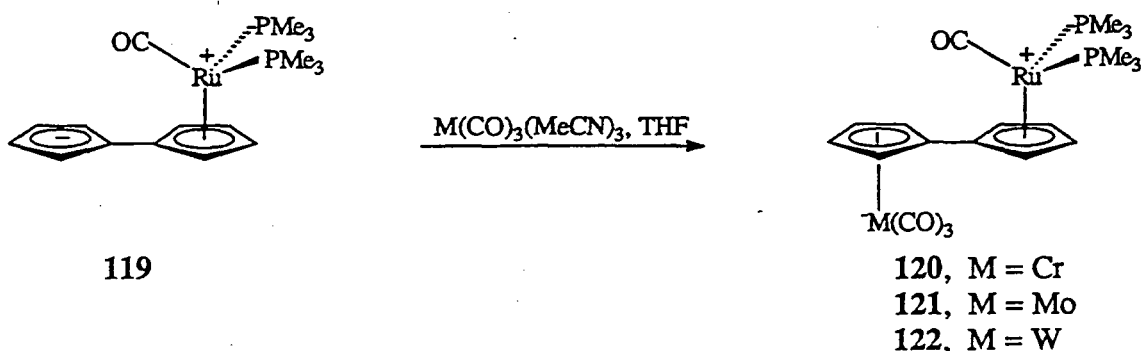
occurred, a process also observed for **93** at higher temperatures.^{96a} Interestingly, no evidence was obtained for the bimetallic zwitterion of **95** even when the reaction with PMe_3 was monitored by NMR spectroscopy. It was also shown that the monosubstituted derivative of **95** did react with PMe_3 to give the zwitterion **119**, but at a much lower rate of conversion than the parent complex.

Scheme 3.10



The fact that decomplexation could be achieved in these reactions led to a new preparation of heterobimetallic complexes.^{19a} For example, treatment of **119** with various metal reagents produced the bimetallic zwitterions **120-122** (Scheme 3.11). Thus, these precursors provided access to a number of heterobimetallic complexes, but the methodology had limited appeal due to the fact that one metal center had to be decomplexed in the starting homobimetallic species. However, the existence of this general class of zwitterions suggested that electrocatalysis could be used to obtain the same compounds, and these investigations will be detailed in the next section.

Scheme 3.11



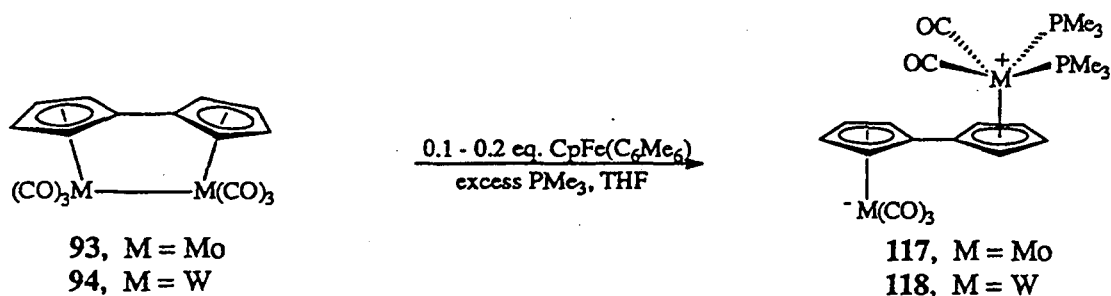
3.4 Generality of the Electrocatalytic Process

The success of the electrocatalysis experiments with **30** and the large number of known bimetallic fulvalene zwitterions encouraged the exploration of electron transfer catalyzed ligand substitution with other fulvalene complexes. The fact that the uncatalyzed reactions involved extended reaction periods in almost every case also contributed to the appeal of an alternative route to the same compounds. Furthermore, the electrochemistry of the starting materials was already known.⁶⁷

While the CV of **30** showed a distinction between the metal centers upon reduction, making it easy to substitute selectively at iron, all the other compounds of interest were reduced in two-electron processes. However, since the reductions followed an ECE mechanism, it was hoped that the radical anions could be intercepted before the second electron transfer occurred, thereby giving the desired substitution products. The fact that there was no distinction between the two metal centers for any of the compounds also raised an intriguing question of selectivity in the heterobimetallic cases. It was felt that substitution to give the zwitterions would also be favored over reduction to the dianions by the fact that electrocatalytic conditions would be used, meaning that the concentration of reductant would always be low. In order to favor substitution further, PMe_3 was chosen as the entering ligand for all the reactions, since it had given the best results with **30**, and it was always used in large excess (10 eq.). The reducing agent of choice was again $\text{CpFe}(\text{C}_6\text{Me}_6)$, as its potential was sufficient to effect electron transfer in almost every case.

The homobimetallic dimolybdenum, **93**, ditungsten, **94**, and diruthenium, **95**, complexes were chosen for the first tests, since in these cases there would be no complications of selectivity for one metal center. Indeed, both **93** and **94** gave good results in the electrocatalytic process, affording the desired zwitterions in 60% and 70% yields, respectively (Scheme 3.12). Both compounds were readily identified by comparison of their spectral data to those previously reported.^{76, 96a} Complex **94** did

Scheme 3.12



require an even larger excess (20 eq.) of PMe₃ to give efficient conversion, as the use of lower PMe₃ concentrations resulted in the need for larger amounts of reducing agent, which in turn resulted in the formation of some dianion. Once again, only disubstituted products were obtained.

Although these first results were encouraging, significant difficulties were encountered with compound 95. This complex displayed an extremely negative reduction potential (-2.0 V vs SCE),⁹⁷ and both CpFe(C₆Me₆) ($E_p = -1.55$ V) and Cp*Fe(C₆Me₆) ($E_p = -1.85$ V) produced no reaction. Even the use of stronger reducing agents such as Na/K alloy failed to give any substitution products. The CV of 95 in the presence of PMe₃ revealed a slow electrocatalytic process,⁹⁸ and it is likely that no electrocatalysis was observed in the preparative experiments due to side reactions of the radical species. It is interesting to note that the desired bimetallic zwitterion was also not observed during the uncatalyzed substitution reaction (*vide supra*).

Despite the failure to achieve electrocatalysis with 95, it was felt that the heterobimetallic molybdenum-ruthenium (35) and tungsten-ruthenium (31) complexes offered excellent potential for the desired reactivity. Compound 35 displayed electrocatalytic substitution to give the zwitterion 121 in 60% yield, and the product was readily identified by comparison of the spectral data with that known for 121.^{19a} The fact that substitution had occurred exclusively at the ruthenium center was easily confirmed as well by this comparison. Thus, the electrocatalytic pathway provided a viable alternative to the previous synthesis of 121.

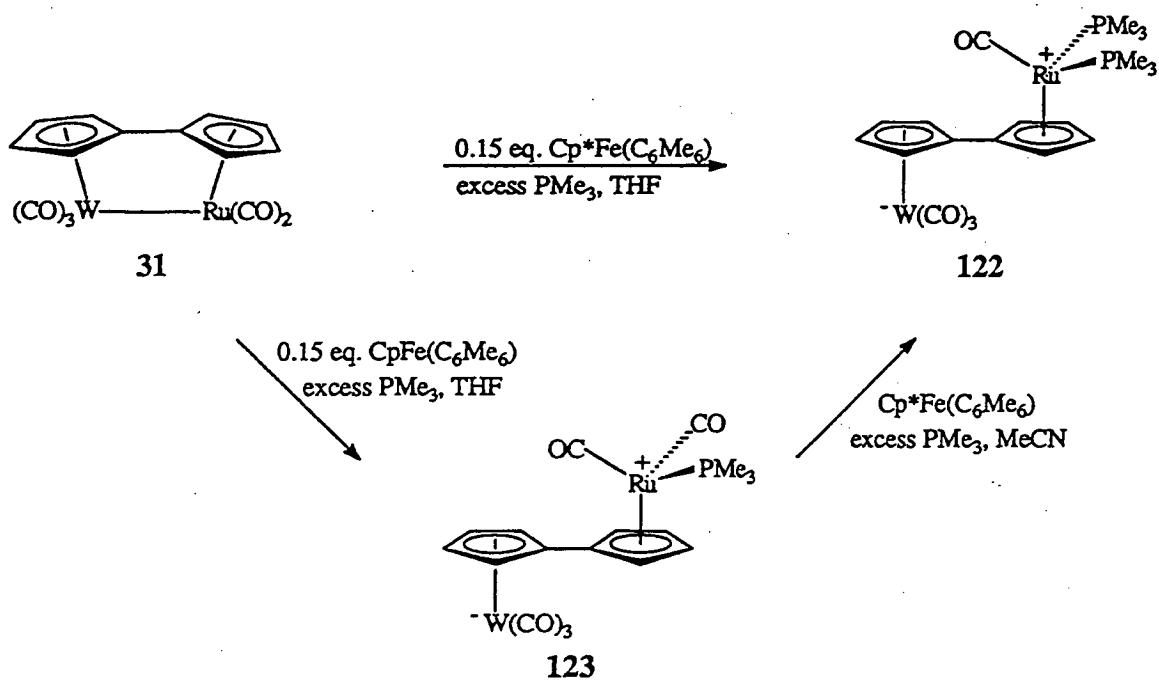
The behavior of complex **31** proved to be more complicated. Treatment of a THF solution of **31** with a catalytic amount of $\text{CpFe}(\text{C}_6\text{Me}_6)$ in the presence of PMe_3 resulted in the rapid formation of a precipitate which was isolated and purified in the usual way. Although this complex was expected to be the known zwitterion **122**, the spectral data revealed that it was a new complex. The ^1H NMR spectrum showed a doublet at 1.68 ppm which integrated to nine hydrogens, indicating that only one PMe_3 ligand was present. The absence of coupling to the ^{183}W nucleus in the ^{31}P NMR spectrum confirmed that the phosphine was bonded to ruthenium. The complex proved to be extremely insoluble, which prevented recrystallization to give analytically pure material. However, the formulation of the complex as a zwitterion with one PMe_3 and two CO ligands on the ruthenium center was confirmed by high-resolution mass spectroscopy. This compound, then, represented the only case in which monosubstitution was achieved through electrocatalysis.

The formation of the monosubstituted zwitterion **123** was unexpected, and it was postulated that this product reflected a dependence of the reaction on the potential of the reducing agent. To test this hypothesis, the reaction was carried out with $\text{Cp}^*\text{Fe}(\text{C}_6\text{Me}_6)$ as the reductant, and in this case the zwitterion **122** was obtained. Furthermore, it was possible to convert **123** into **122** by treating **123** with $\text{Cp}^*\text{Fe}(\text{C}_6\text{Me}_6)$ in the presence of PMe_3 . The electrocatalytic behavior of **31** is summarized in Scheme 3.13. This dependence on the nature of the reducing agent was not general, as treatment of **30** with $\text{CpFe}(\text{C}_6\text{H}_6)$ ($E_p = -1.25$ V) in the presence of $\text{P}(\text{OMe})_3$ gave only **107**.

Electron transfer catalyzed ligand substitution was found to be a general reaction for bimetallic fulvalene complexes. The reaction proceeds to give zwitterionic products in all cases, and only one example of monosubstitution was found. All of the reactions are extremely fast, reaching completion after only a few minutes at room temperature. This fact, coupled with the relatively facile isolation of the products, makes the electrocatalytic process an attractive alternative to the uncatalyzed substitution reactions. Furthermore,

remarkable selectivity is observed, as substitution always occurs exclusively at one metal center. Although the exact mechanism of the process remains unclear, it nonetheless provides a convenient pathway to selectively substituted bimetallic zwitterions.

Scheme 3.13



Chapter Four

Oligocyclopentadienyl Complexes

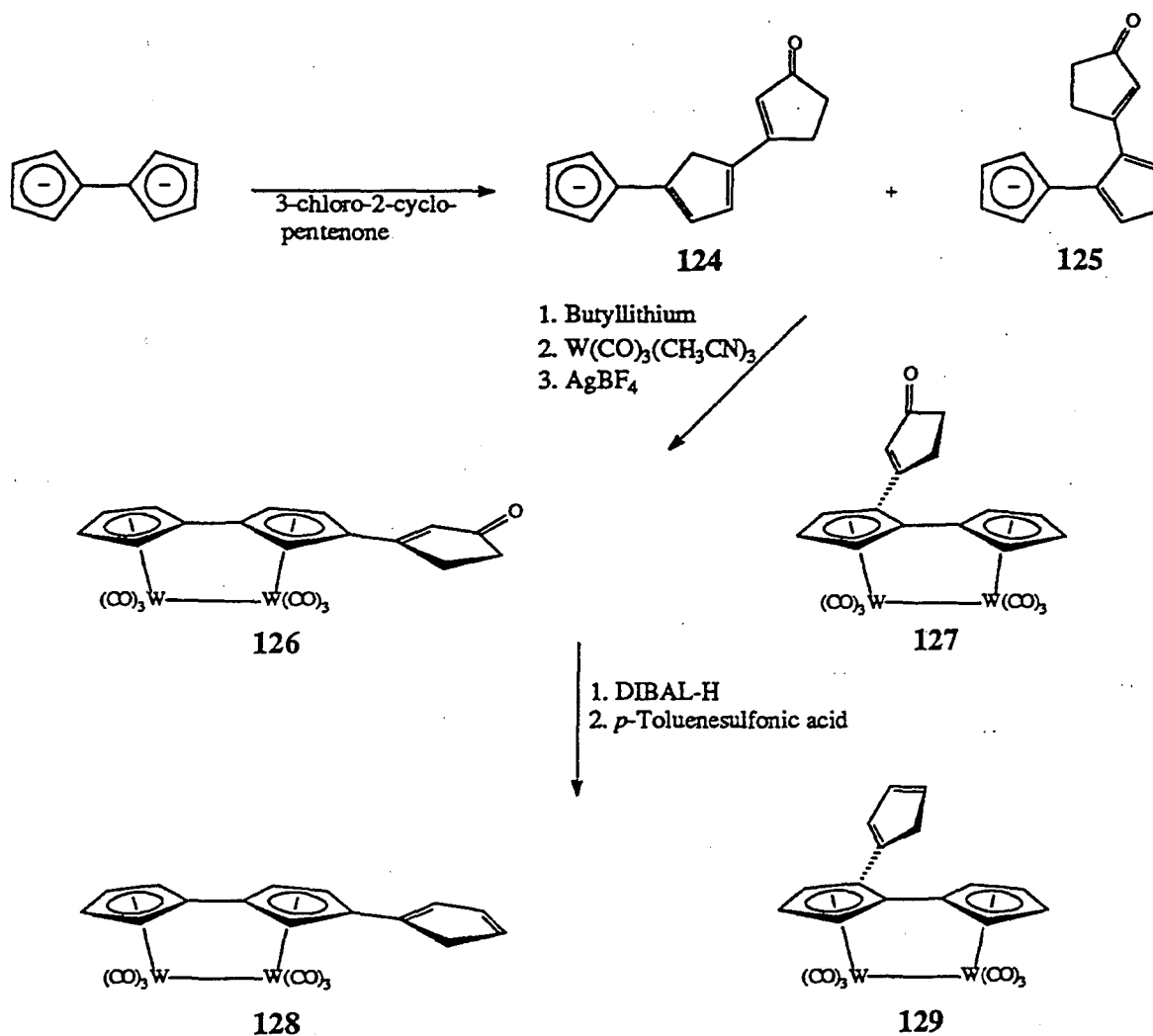
4.1 Introduction

Investigations into the chemistry of bimetallic fulvalene complexes confirmed the hypothesis that this class of compounds would display unique reactivity compared to the mononuclear analogs. This success encouraged the preparation of systems containing three, four, or more linked cyclopentadienyl rings, as these oligocyclopentadienyl ligands offered the possibility of combining multiple metal centers within a single molecule. Such complexes would be expected to exhibit novel reactivity as well, and preliminary studies have provided evidence to support this hypothesis. This chapter will describe efforts to devise efficient synthetic routes to quatercyclopentadienyl complexes, and the introduction will detail the previous investigations of these systems.

The methodology developed for the preparation of heterobimetallic fulvalene complexes (Chapter 1) was applied to the synthesis of tercyclopentadienyl compounds.⁹⁹ This approach involved treatment of fulvalene dianion with 3-chloro-2-cyclopentenone, producing the regioisomers **124** and **125**, which were not isolated (Scheme 4.1). Instead, butyllithium was added to the mixture to deprotonate the cyclopentenone-substituted rings, thereby generating fulvalene dianion moieties which were metallated using $W(CO)_3(CH_3CN)_3$. The resulting metal anions were then oxidized with $AgBF_4$ to provide the metal-metal bonded complexes **126** and **127** in an overall yield of 46% for the two isomers. The cyclopentenone moieties were converted to cyclopentadienyl rings by reduction with diisobutyl aluminum hydride (DIBAL-H) followed by acid-catalyzed dehydration with *p*-toluenesulfonic acid, and the resulting rings were then metallated. This pathway allowed the preparation of homo- and diheterotrimetallic tercyclopentadienyl complexes, while a modification led to the first triheterotrimetallic analog.

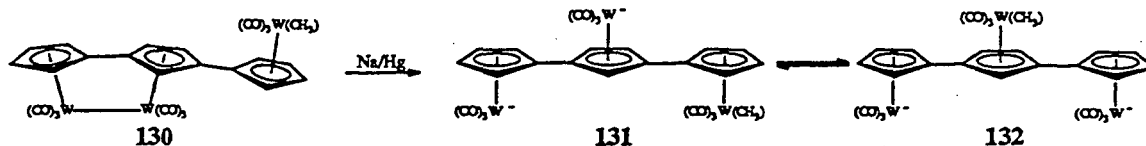
As expected, the reactivity of these tercyclopentadienyl systems proved to be different from that observed for the fulvalene complexes. For example, the presence of

Scheme 4.1

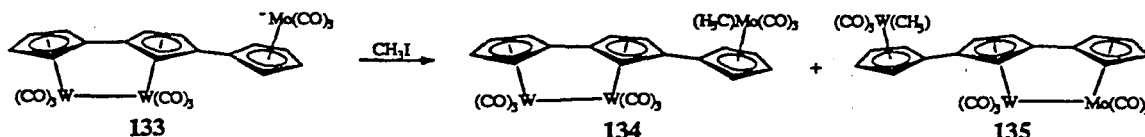


three metal centers gave rise to intriguing ligand transfer reactions. This process is illustrated in Scheme 4.2 for the dianion **131**, which was generated by reduction of the corresponding metal-metal bonded complex **130**. It was found that migration of the terminal methyl group to the central tungsten atom was favored by a 6:1 ratio, and the driving force was reasoned to be the separation of charge in **132**.¹⁰⁰ Additionally, rearrangements of the metal-metal bonds, as illustrated for complex **133** (Scheme 4.3), have been found to be a general process in these systems. For **133**, the rearranged product **135** was formed in a 3:2 ratio with **134**, indicating that formation of the molybdenum-tungsten bond was favored for this isomer.¹⁰¹

Scheme 4.2

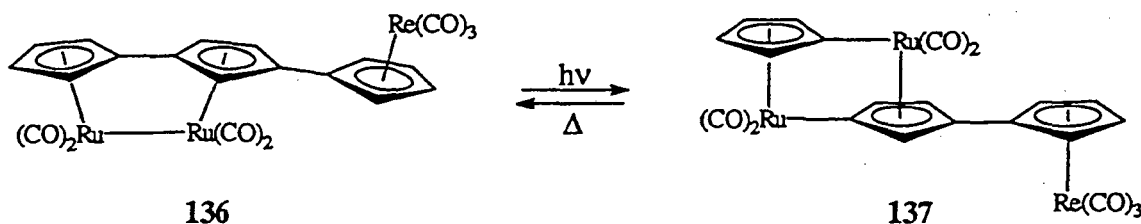


Scheme 4.3



Although the tercyclopentadienyl compounds showed distinct reactivity, some processes observed in fulvalene complexes could be carried over to the trimetallic analogs. The photoisomerization of (fulvalene)tetracarbonyldiruthenium was one of the most intensely studied fulvalene reactions,^{94,102} and this transformation was applied to the tercyclopentadienyl complex 136, which contains the (fulvalene)diruthenium unit of interest.⁷⁷ Indeed, the photoisomerization and corresponding thermal reversion were found to be possible in this trimetallic system (Scheme 4.4), illustrating that the rich chemistry of fulvalene complexes could be extended to tercyclopentadienyl compounds.

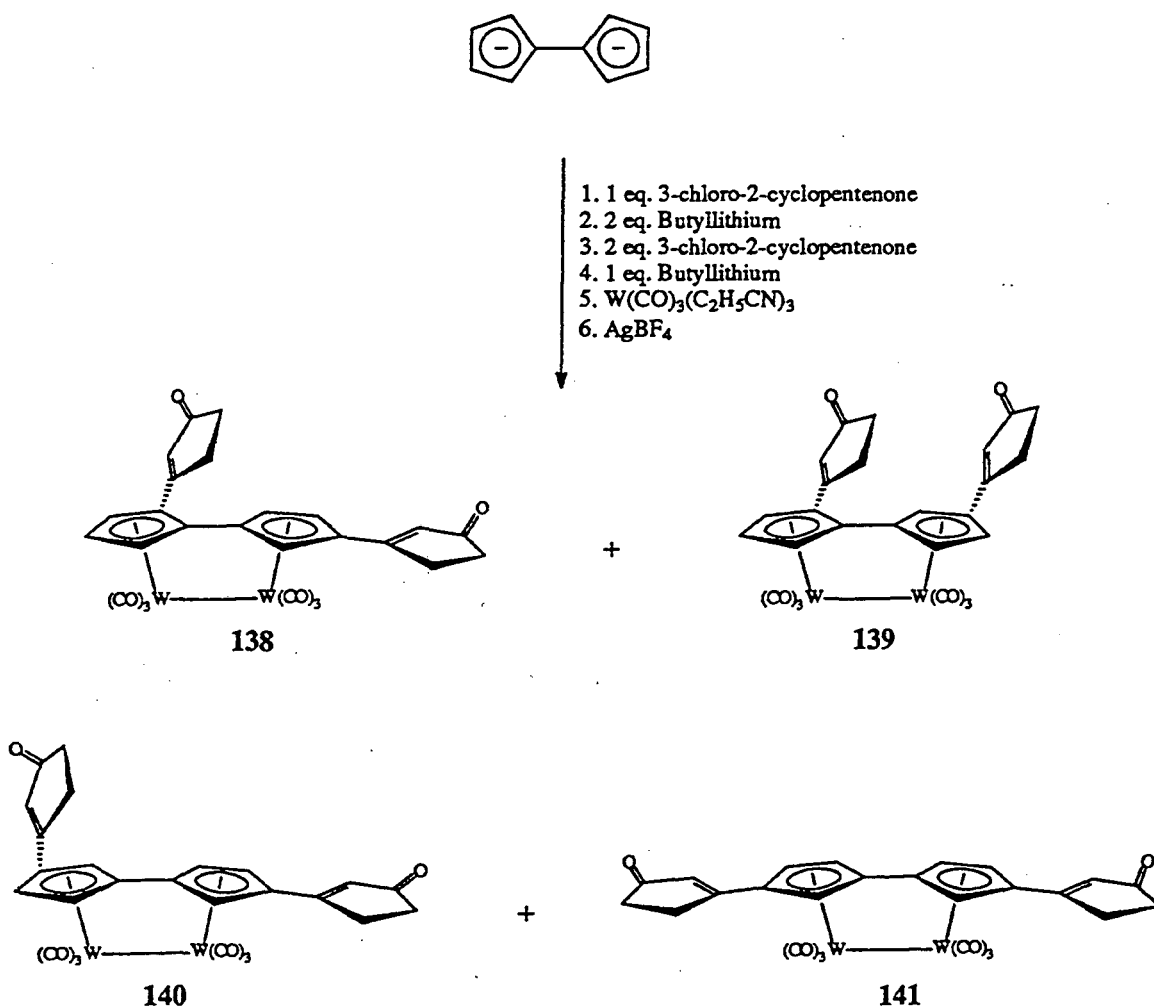
Scheme 4.4



Given the success of the investigations of the tercyclopentadienyl species, efforts were directed toward the synthesis of the next higher homologs, the quatercyclopentadienyl complexes.¹⁰⁰ By a modification of the synthetic strategy presented in Scheme 4.1, it was possible to prepare the corresponding quatercyclopentadienyl precursors 138-141 in an overall yield of 70% (Scheme 4.5).¹⁰³ Unfortunately, this route gave rise to four isomers, which were difficult to separate.

Additionally, it was found that the corresponding diene complexes decomposed rapidly at room temperature upon isolation. The preparation of the tetrametallic species was further complicated by rearrangements of the metal-metal bonds, as was observed for the tercyclopentadienyl complexes. As a result of these difficulties, it was not possible to isolate sufficient quantities of the tetrametallic compounds to investigate their chemistry. Also, the poor overall yields limited the synthesis to the homotetrametallic complexes of tungsten.

Scheme 4.5



The problems encountered in the preparation of the quatercyclopentadienyl complexes indicated the need for an alternative synthesis, as the iterative introduction of the rings seemed to be limited to the fulvalene and tercyclopentadienyl systems. It was

hoped that a more convergent route could be found which would allow for the introduction of a variety of metal centers and could be extended to the preparation of higher homologs, such as the sexicyclopentadienyls. The remainder of this chapter will describe efforts directed toward the development of an efficient synthetic approach to the quatercyclopentadienyl compounds.

4.2 Fulvalene Complexes from Cyclopentadienyl Precursors

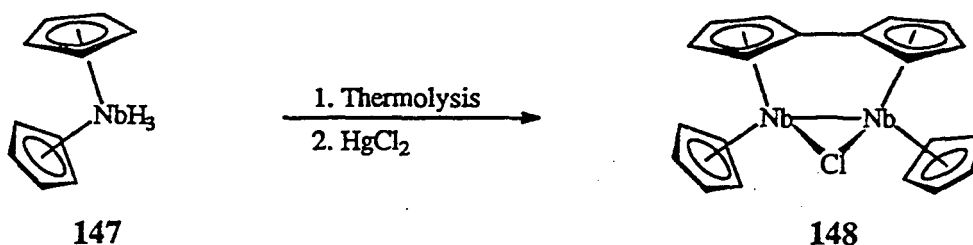
In the effort to find a more viable synthetic route to oligocyclopentadienyl complexes, it was felt that it would be advantageous to utilize heterobimetallic fulvalene precursors, since these compounds could be prepared in good yields for most metals^{19b} (Chapter 1). There have been numerous reports in the literature of reactions which involve the dimerization or coupling of cyclopentadienyl complexes to give fulvalene products. Thus, it was felt that by incorporating the appropriate metal fragments into fulvalene compounds it would be possible to employ similar reactions to effect coupling of the fulvalene ligands, thereby generating quatercyclopentadienyl complexes. Application of the same methodology using tercyclopentadienyl precursors would give the corresponding sexicyclopentadienyls. This section will summarize the various reactions which converted cyclopentadienyl compounds into fulvalene species and will present the results of the extension of some of these reactions to the preparation of quatercyclopentadienyl complexes.

Of the numerous cyclopentadienyl coupling reactions, some examples were presented in Section 2.2 for $\text{CpRh}(\text{CO})(\text{PPh}_3)^{50}$ and $\text{CpRh}(\text{PPh}_3)_2$.⁴⁹ In both cases oxidation of the Cp compounds resulted in the formation of the corresponding dicationic fulvalene complexes with Rh-Rh bonds (Scheme 4.6). It was also noted by Connelly and coworkers⁵⁰ that the use of AgPF_6 as the oxidizing agent resulted in the incorporation of silver in the products. Since the dication **143** could then be reduced to the neutral complex, it was felt that this oxidative coupling could be employed in the preparation of quatercyclopentadienyl compounds.

A variety of related reactions have been reported for the coupling of $\text{CpMn}(\text{CO})_3$ to give (fulvalene)hexacarbonyldimanganese **145**. Rausch and coworkers described four routes to **145**, each of which involved the intermediacy of mercury derivatives of **144**.¹⁰⁴ However, the yields for the various reactions were somewhat low (< 35%) even in the best cases. An improved synthesis was provided by Nesmeyanov *et al.*¹⁰⁵ It was found

example, thermolysis of Cp_2NbH_3 was found to give a complex with two bridging $\eta^1:\eta^5$ - C_5H_4 ligands,¹⁰⁷ and this compound underwent reaction with HgCl_2 to give the fulvalene product **148**¹⁰⁸ (Scheme 4.9), while treatment with aryl diazenes gave the nitrene-bridged fulvalenes **75** and **76**⁵² (Section 2.2). Further reports described the preparation of fulvalene complexes by treatment of niobocene dichloride with potassium or NaH .¹⁰⁹

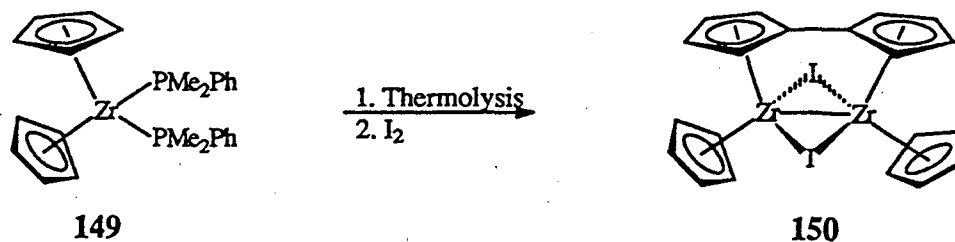
Scheme 4.9



The intermediacy of $\eta^1:\eta^5$ - C_5H_4 units in the formation of fulvalene complexes is somewhat general for the early transition metals. This type of intermediate was proposed as the product of the thermolysis of the phosphine-substituted zirconocene **149**, and the structural assignment was based on ^{13}C NMR data.¹¹⁰ Treatment of this species with I_2 resulted in the formation of the fulvalene complex **150** (Scheme 4.10), in which bridging iodides were invoked in analogy to previously characterized titanium complexes. This structure was later confirmed by x-ray crystallography, but it was reasoned that the distance of 3.472 Å between the zirconium atoms precluded the existence of a metal-metal bond.¹¹¹ Gambarotta and coworkers later exploited this type of methodology for the preparation of several (fulvalene)dizirconium complexes.¹¹² NMR spectroscopy was also used to characterize a similar $\eta^1:\eta^5$ - C_5H_4 species resulting from the thermolysis of $(\text{Cp}_2\text{ZrCl})_2$,¹¹³ which was obtained from the reduction of zirconocene dichloride with Na/Hg amalgam.¹¹⁴

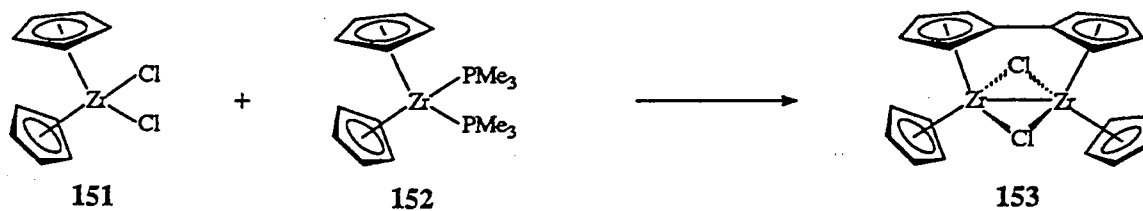
Another route to fulvalene species was provided by Gambarotta and Chiang,¹¹⁵ who utilized a comproportionation reaction instead of oxidation or reduction. The reaction of zirconocene dichloride with $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$ resulted in the formation of **153** (Scheme 4.11), and the structure was confirmed by x-ray crystallography. Complex **153**

Scheme 4.10



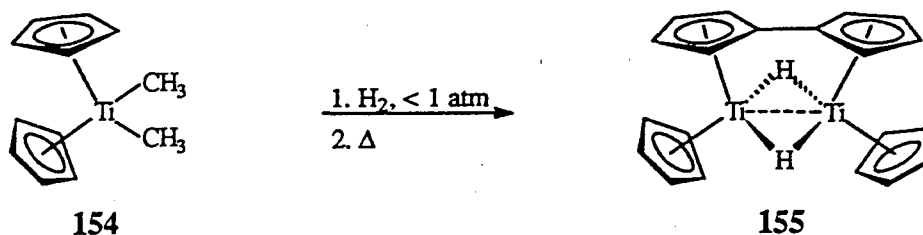
represented the first structurally characterized example of a dinuclear organometallic Zr(III) species. The distance between the zirconium atoms was found to be 3.233 Å, which was deemed to be consistent with the existence of a metal-metal bond.

Scheme 4.11



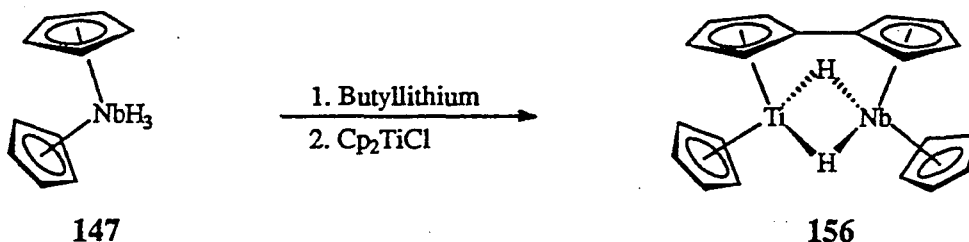
Although reduction of titanocene dichloride was reported to give the corresponding fulvalene complex,¹¹⁶ an alternative pathway was developed by Brintzinger and Bercaw.¹¹⁷ Hydrogenolysis of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ generated a hydride species which eliminated H_2 and rearranged to the fulvalene complex 155 upon heating (Scheme 4.12). The proposed structure was confirmed by x-ray crystallography of several derivatives.¹¹⁸ The x-ray structure of the parent complex has recently been obtained, and the Ti-Ti distance of 2.989 Å suggests the presence of a metal-metal bond.¹¹⁹ The mechanism for this novel reaction remains unclear, and it appears to be unique to titanium, as no comparable example with a different metal has been reported.

Scheme 4.12



The coupling of Cp-metal complexes has even been utilized for the preparation of a heterobimetallic fulvalene compound.¹²⁰ Treatment of Cp_2NbH_3 with butyllithium followed by the addition of Cp_2TiCl gave the heterobimetallic species **156** in greater than 90% yield (Scheme 4.13). The paramagnetic **156** was characterized only by mass and ESR spectroscopy. The ESR spectrum showed a 21-line pattern, and the small splitting by the niobium nucleus was interpreted as indicating that the unpaired electron was primarily localized on titanium.

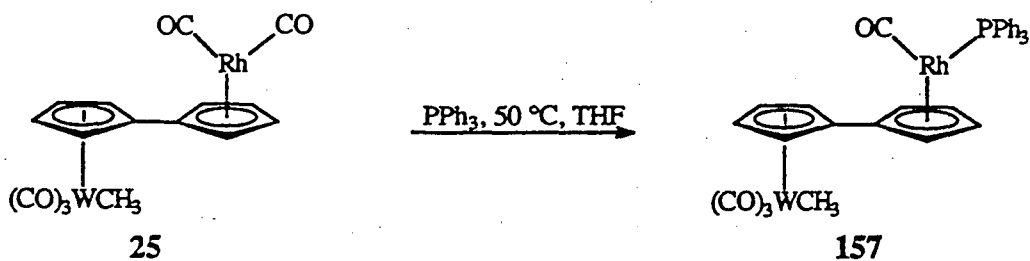
Scheme 4.13



Since a wide variety of reactions which produce fulvalene compounds from Cp-metal precursors had been reported, it was felt that utilizing such reactions could give rise to numerous quatercyclopentadienyl complexes with various metals. The primary consideration in this approach was the preparation of the necessary bimetallic fulvalene starting materials which would mimic the behavior of the corresponding cyclopentadienyl compounds. Thus, attention was first focused on the most easily accessible fulvalene complexes.

Of the heterobimetallic fulvalene complexes which had been previously reported, the highest yield was obtained for the tungsten-rhodium compound **25**. As a result, this species was a particularly attractive starting material, and it was reasoned that substitution of a carbonyl ligand on rhodium by triphenylphosphine would give the necessary moiety to utilize the oxidative coupling reported by Connelly *et al.*⁵⁰ In fact, this substitution reaction proved to be facile, as heating of a THF solution of **25** at 50 °C for four hours in the presence of two equivalents of PPh_3 gave a 74% yield of **157** (Scheme 4.14). No evidence of disubstitution was found. Complex **157** was easily purified by column

Scheme 4.14

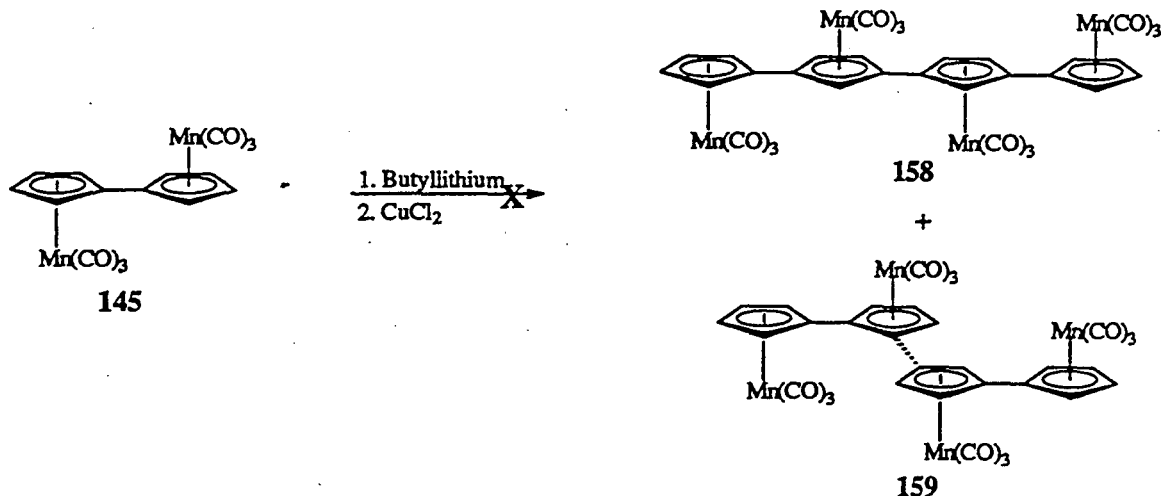


chromatography followed by recrystallization, and the elemental analysis confirmed the molecular composition. The ^1H NMR spectrum showed the four signals expected for the fulvalene, as well as multiplets for the PPh_3 ligand. The ^{31}P NMR displayed a doublet due to coupling of the ^{103}Rh nucleus, thereby confirming that the substitution had occurred at rhodium.

With the desired precursor **157** available, the next step was to attempt the oxidation. Treatment of a THF solution of **157** with ferrocenium gave no reaction, indicating that the reduction potential of the oxidant was not sufficiently positive. Since the use of AgPF_6 in the oxidation of $\text{CpRh}(\text{CO})(\text{PPh}_3)$ had resulted in the incorporation of silver in the product,⁵⁰ it was felt that another oxidant with a similar potential should be used. Thus, **157** was oxidized with tris(4-bromophenyl)aminium hexafluoroantimonate ($E_p = 1.2$ V vs SCE) to give a brown powder which was insoluble in organic solvents and water. This result was unexpected, and the CV of **157** was recorded in an effort to gain insight into the oxidation process. The CV revealed that **157** undergoes a two-electron oxidation,⁹⁸ indicating that there is no distinction between the two metal centers. It is likely, then, that the oxidation produced the dication of **157** rather than the desired quatercyclopentadienyl product. Because of this difficulty, this approach was not pursued further.

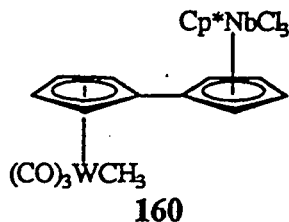
After the failure of the oxidation of **157**, attention was focused on coupling (fulvalene)hexacarbonyldimanganese to give the corresponding homometallic quatercyclopentadienyl complexes. In this case, it was hoped that deprotonation of **145** with butyllithium followed by oxidative coupling with CuCl_2 would give the desired products

Scheme 4.15



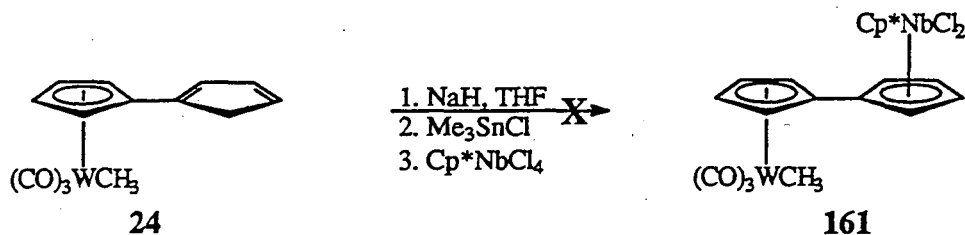
(Scheme 4.15). Unfortunately, it was not possible to generate the intermediate lithiated species, as **145** gave no reaction with butyllithium or a combination of butyllithium and potassium *t*-butoxide. While this result was disappointing, the methodology, if successful, was deemed to be of limited scope, making the route impractical for most complexes. Specifically, this approach was limited to homobimetallic species, which could give only two ring-lithiated products. The use of a heterobimetallic complex would give the possibility of four ring-lithiated species which could couple to give numerous quatercyclopentadienyl products.

The lack of success with these first attempts to prepare quatercyclopentadienyl complexes suggested that efforts should be focused on the use of the early transition metals, since a greater number of possible coupling reactions had been reported for these elements. As a result, the next precursor target was the tungsten-niobium species **160**, which would hopefully mimic the behavior of the mononuclear niobium metallocenes. The Cp* ligand on the niobium center was chosen to prevent any dimerization through this ancillary ring, thereby guaranteeing that any coupling would have to occur at the fulvalene ligand. The synthesis of **160** was attempted by deprotonation of the diene **24** with NaH followed by treatment of the resulting anion with Cp*NbCl₄. Unfortunately, this route failed to give any characterizable products.

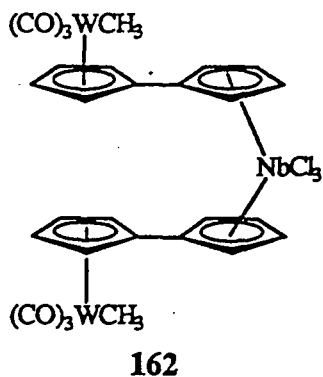


Since it had been reported that treatment of niobocene dichloride with NaH resulted in the formation of a fulvalene complex,¹⁰⁹ efforts were next directed toward the incorporation of a Cp*NbCl₂ moiety into a fulvalene compound. Green and Jousseume found that addition of CpNbCl₄ to (cyclopentadienyl)tributyltin resulted in the formation of niobocene dichloride in good yield,¹²¹ and attempts were made to adapt this approach to the synthesis of 161. Previous investigations had revealed that it was not possible to prepare the tributyltin derivative of 24 cleanly but that the trimethyltin compound could be obtained quantitatively by treatment of the anion of 24 with Me₃SnCl.²⁰ Thus, the trimethyltin complex was prepared *in situ*, and a solution of Cp*NbCl₄ was added (Scheme 4.16), but only decomposition occurred.

Scheme 4.16

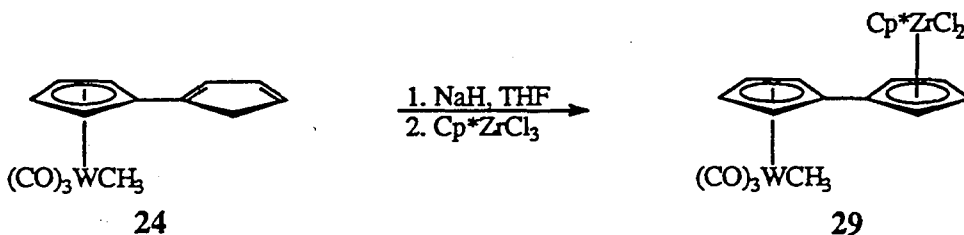


As no success was obtained using Cp*NbCl₄ as the source of niobium, it was felt that the situation could be simplified by eliminating the Cp* ligand. The next precursor target, then, was the bis(fulvalene) complex 162. This molecule appeared to represent the greatest potential to give the desired coupling reaction, since the presence of two fulvalene units on niobium guaranteed that any coupling product would contain a quater-cyclopentadienyl ligand. The synthesis of 162 was attempted by treatment of the anion of 24 with NbCl₅, but once again only decomposition occurred. The problem in this case may be due to the strong Lewis acidity of NbCl₅.



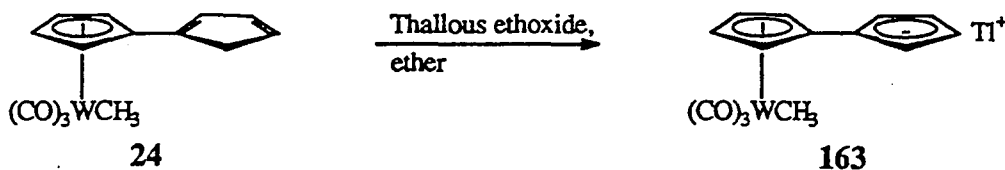
The results from the attempted preparations of various precursors with niobium forced these investigations to be abandoned, and emphasis was next placed on the group 4 metals. The desired zirconium precursor **29** had been synthesized previously, but the yield was a disappointing 20%.^{19b} Efforts were made to improve this procedure, but addition of Cp*ZrCl₃ to a solution of the anion of **24** under various conditions gave only a 27% optimized yield (Scheme 4.17). Due to the low yield of **29**, it was decided that this complex could not be used in a practical synthesis of quatercyclopentadienyl compounds. As a result, attention was focused on the preparation of the titanium analog.

Scheme 4.17



Since the attempts to prepare heterobimetallic complexes with the early transition metals using the sodium salt of **24** had given disappointing results, it was reasoned that the problem may have been with this sodium salt. Thallium cyclopentadienide has been utilized to synthesize a number of Cp-metal complexes, including the "mixed" metallocene CpCp*TiCl₂.¹²² Thus, efforts were directed toward the preparation of the thallium salt **163** in the hope that it would give better results. It was found that **163** could be conveniently prepared by addition of thallos ethoxide to an ether solution of **24** (Scheme 4.18), and the resulting salt precipitated from the reaction mixture. The salt was isolated

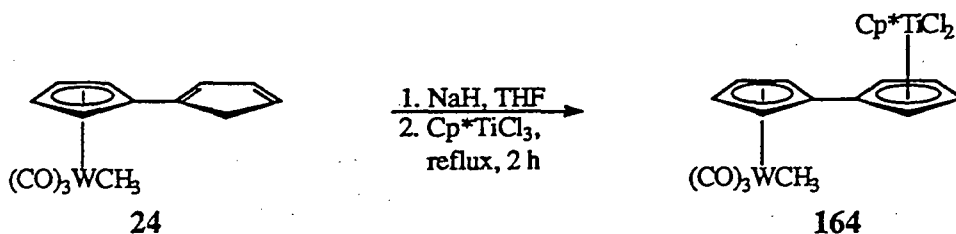
Scheme 4.18



by removal of the solvent and washing with ether to remove unreacted thallos ethoxide, and the ^1H NMR spectrum showed the four triplets expected for **163** along with the methyl group on tungsten. Unfortunately, **163** did not display the desired reactivity, as it gave no reaction with Cp^*TiCl_3 even after heating above $100\text{ }^\circ\text{C}$. However, decomposition and the formation of an uncharacterizable precipitate were observed when the reaction mixture was allowed to stand at room temperature for several hours. Due to these findings, it was clear that the sodium salt would have to be used.

Unlike the experiments with zirconium and niobium reagents, the sodium salt of **24** was found to give good results with Cp^*TiCl_3 . Thus, deprotonation of **24** with NaH followed by the addition of a THF solution of Cp^*TiCl_3 and heating at reflux for two hours gave **164** in 61% yield (Scheme 4.19). Complex **164** was isolated simply by removal of the solvent followed by recrystallization. The mass spectral and analytical data confirmed the molecular composition of **164**. The ^1H NMR spectrum revealed the four triplets of the fulvalene ligand along with singlets for the Cp^* ligand and W-CH_3 group.

Scheme 4.19



The success encountered in the synthesis of **164** encouraged the preparation of the analogous hafnium complex **165**. Once again, good results were obtained by heating a THF solution of the anion of **24** and Cp^*HfCl_3 at reflux, although the reaction time had to be extended to fifteen hours. Compound **165** was isolated in 71% yield after

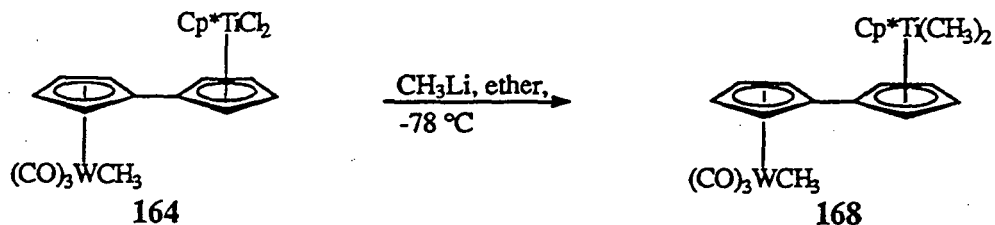
recrystallization. The mass spectral and analytical data were consistent with the formulation of 165, and the structure was confirmed by the ^1H NMR spectrum, which showed the same peak pattern as that for 164.

With the desired precursor 164 now readily available, the next step was to choose the coupling reaction to use. Since the route reported by Brintzinger and Bercaw avoided the use of strong reducing agents,¹¹⁷ which may have caused overreduction of 164, it was chosen as the method to pursue. However, it was unclear what effect the Cp* ligand might have on the reaction, since "tucking in" of one of the ring methyl groups was observed when the reaction sequence was conducted with $\text{Cp}^*_2\text{TiCl}_2$ instead of Cp_2TiCl_2 .¹²³ Because of this potential complication, it was decided that the reactivity of the model complex $\text{CpCp}^*\text{TiCl}_2$ 166 should be explored first.

The mixed metallocene 166 was prepared according to the literature procedure,¹²² and treatment of this compound with CH_3Li at low temperature resulted in the formation of the yellow dimethyl complex 167. Attempts were then made to conduct the hydrogenolysis reaction. It was found that a hexane solution of 167 gave no reaction with hydrogen gas at pressures up to ten atmospheres. However, when solid 167 was exposed to hydrogen gas, a rapid color change to brownish-purple occurred. This compound was not characterized, but the ^1H NMR spectrum clearly indicated the presence of paramagnetic materials, which is similar to the result reported for the hydrogenolysis of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$.¹¹⁷ Heating of this material did not produce any change, and there was no evidence for the formation of a fulvalene product.

While the results of the model study were inconclusive due to the unknown nature of the hydrogenolysis product, it was decided to attempt the same sequence with 164. The first step was conversion to the dimethyl complex 168, which was produced cleanly by addition of CH_3Li to an ether solution of 164 at low temperature (Scheme 4.20). The yellow product was isolated by removal of the solvent followed by extraction of the residue with hexane. The NMR spectra clearly revealed the presence of the two methyl

Scheme 4.20

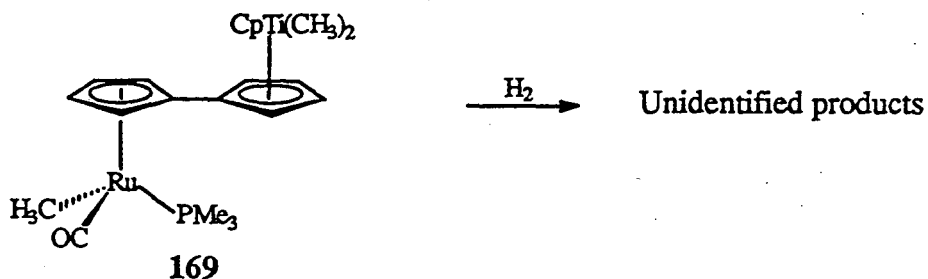


groups on titanium. Unlike the model compound **167**, the fulvalene species proved to be unreactive toward hydrogen gas, as exposure of solid **168** to high pressures (90 atmospheres) of hydrogen resulted in no change. The reason for this lack of reactivity is unclear.

The failure of the hydrogenolysis reaction with **168** was surprising, and an alternative approach was pursued. It had been reported that reduction of titanocene dichloride with magnesium turnings in the presence of PMe_3 resulted in quantitative conversion to the bis(trimethylphosphine) complex, which reacted with a variety of substrates, including hydrogen.¹²⁴ Unfortunately, no reaction occurred when **164** was exposed to either magnesium turnings or powder in the presence of PMe_3 . This result suggested that **164** was an inadequate precursor for the formation of quater-cyclopentadienyl species.

Since **164** did not display the desired reactivity, it was thought that the Cp^* ligand may have been the source of the problem. As a result, attempts were made to prepare other potential precursors with titanium. The analogous complex with an ancillary Cp instead of Cp^* ligand proved to be inaccessible, as treatment of the anion of **24** with CpTiCl_3 gave only an insoluble purple material which could not be characterized. It is noteworthy that a heterobimetallic fulvalene complex incorporating a $\text{CpTi}(\text{CH}_3)_2$ unit has been prepared, but hydrogenolysis of this compound led to the formation of numerous uncharacterizable products⁹⁴ (Scheme 4.21). Attempts to prepare the bis(fulvalene) complex analogous to **162** by treatment of the anion of **24** with $\text{TiCl}_4(\text{THF})_2$ were also unsuccessful, as only decomposition was observed. In this case it again is likely that the

Scheme 4.21



strong Lewis acidity of the metal chloride was the cause of the decomposition, suggesting that metallocenes of this type are inaccessible.

After these disappointing results with the titanium system, it was decided that an alternative approach to the quatercyclopentadienyl complexes was needed. In cases where the desired fulvalene precursors were prepared, their reactivity proved to be significantly different from that of the mononuclear analogs, while in other cases the precursors themselves were inaccessible. An additional problem of this route was its lack of generality, as specific reactions were required for each different metal system. As a result, efforts were directed toward the development of a more general pathway to quatercyclopentadienyl compounds, and the results of these investigations are presented in the next section.

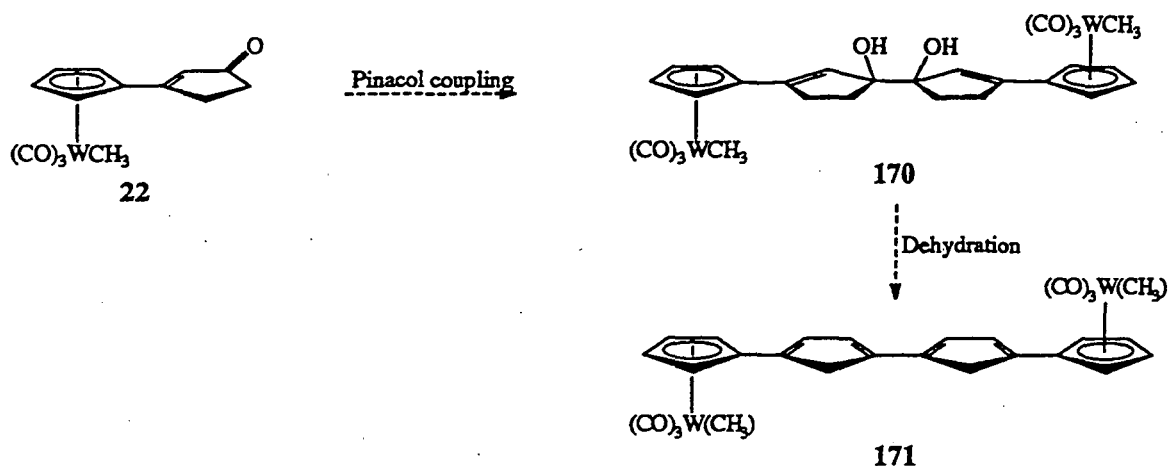
4.3 Pinacol Formation as an Entry into Quatercyclopentadienyl Complexes

With the failure of the Cp-coupling route, a new approach to oligocyclopentadienyl ligands was sought. Since the goal was to develop a general synthetic pathway which would allow the preparation of a variety of complexes incorporating different metal centers, it was desirable to obtain precursors which contained uncomplexed cyclopentadienyl rings. In this way, it was felt that many different metal centers could then be introduced, in analogy with the synthesis of heterobimetallic fulvalene complexes. This section will describe the results obtained from one such approach to the preparation of quatercyclopentadienyl compounds.

The coupling of aldehydes and ketones to give pinacol products is a well-established reaction in organic synthesis. This transformation is usually accomplished by the use of low-valent transition metals, and a variety of such reagents has been reported.¹²⁵ Perhaps the best-known system is that developed by McMurry and coworkers, which utilizes a low-valent titanium species generated *in situ* through the reduction of $\text{TiCl}_3(\text{DME})_{1.5}$ by a Zn-Cu couple.¹²⁶ The McMurry reaction is known to tolerate a number of other functional groups, making it a versatile synthetic tool which usually gives high yields of the coupled products.^{125b} Thus, efforts were made to apply this reaction to the coupling of the enone **22** (Scheme 4.22), which was readily available as the precursor to the diene **24**. Dehydration of the resulting diol **170** would then give **171**, which could be trapped with various metal reagents to give diheterotetrametallic quatercyclopentadienyl complexes. This route was particularly appealing due to the fact that only one isomer could arise from the coupling reaction.

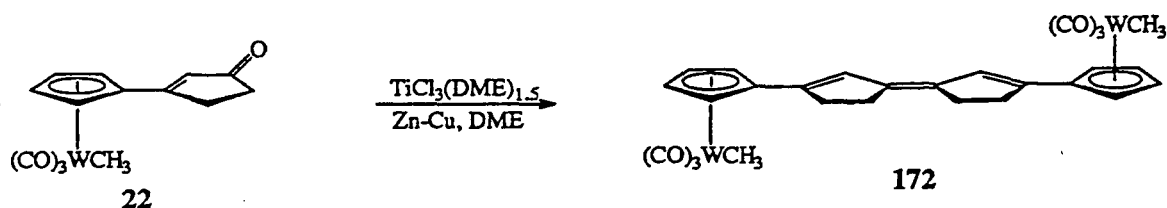
One potential problem with the McMurry system was the fact that the reaction typically did not stop at the pinacol stage but proceeded to give alkene products through deoxygenation of the intermediate species.^{125b} It was hoped that the use of mild conditions would allow the isolation of the pinacol product, but this was not the case. It was found that addition of a solution of **22** to the $\text{TiCl}_3(\text{DME})_{1.5}/\text{Zn-Cu}$ mixture

Scheme 4.22



proceeded to give the conjugated triene **172** even when the reaction was conducted at low temperature¹²⁷ (Scheme 4.23). It was felt that there was no efficient means of converting **172** into **171**, so an alternative procedure was sought which would allow the isolation of pinacol **170**.

Scheme 4.23

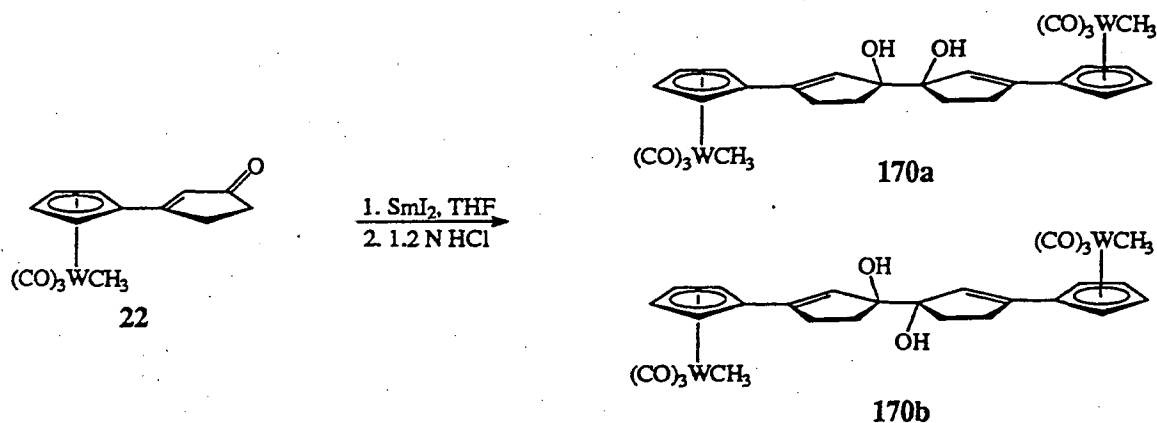


Another reagent which has been reported to give good results in pinacol coupling reactions is SmI_2 .¹²⁸ This strong electron donor was found to give high yields of pinacol products with aromatic aldehydes and ketones, and the diols were isolated in each case. Additionally, no reduction of the carbonyl groups to the corresponding alcohols was observed. The conditions employed were extremely mild, and in many cases the reactions were complete in less than one minute at room temperature. Due to all of these factors, SmI_2 was selected as the next reagent to test with **22**.

Gratifyingly, excellent results were obtained with this reagent. It was found that addition of a 0.1 N solution of SmI_2 in THF to a THF solution of **22** gave complete reaction after only a few minutes, and the desired pinacols were isolated in quantitative

yield after quenching with 1.2 N HCl and extraction with ether (Scheme 4.24). This reaction was easily monitored by the disappearance of the characteristic deep blue-green color of Sm^{2+} , and the reactions were judged to be complete when this color persisted. As expected,¹²⁸ the reaction gave rise to diastereomers (**170a** and **b**) in approximately equal amounts. It was possible to separate these diastereomers on a small scale by preparative thin-layer chromatography, but the complexes proved to be unstable on silica gel, and significant decomposition was observed during the separation. Due to this limitation, the products were not separated except to facilitate their characterization, as both diastereomers would give **171** upon dehydration. The proposed structures of **170a** and **b** were consistent with the NMR data, and the molecular composition was confirmed by elemental analysis. The mass spectrum of each diastereomer showed the molecular ion at 858.

Scheme 4.24



Since an efficient method for producing the diols **170a** and **b** had been developed, the next step was to find a means of accomplishing the desired dehydration. This reaction presented several potential problems. First, the expected product **171** contains a dihydrofulvalene moiety, which would be anticipated to be extremely prone to acid-catalyzed polymerization. Additionally, the use of acid to accomplish the dehydration also presented the possibility that **170a** and **b** would undergo pinacol rearrangements to give spiroketone products¹²⁹ instead of **171**. Despite these concerns, the acid-catalyzed

dehydration using *p*-toluenesulfonic acid was attempted, but no reaction occurred even in refluxing toluene. The surprising stability of **170a** and **b** was further evidenced by their failure to react with phosphoric, trifluoroacetic, and sulfuric acid at room temperature. However, heating a solution of the diols in the presence of phosphoric or sulfuric acid resulted in decomposition. While the most common method for the dehydration of 1,2-diols involves the use of concentrated acids at high temperatures, several alternative routes have been reported.¹³⁰ One such approach utilized phosphorus oxychloride in pyridine, which gave dehydration to the corresponding diene without any rearrangements.¹³¹ Unfortunately, this reagent gave no reaction with **170a** and **b**, even when the mixture was heated to reflux.

After these failures, efforts were directed toward converting the hydroxyl functionalities into good leaving groups so that elimination with base would provide **171**. An additional advantage of this route was that excess base could be used to deprotonate **171**, thereby allowing metallation of the central rings without the need to isolate **171**. Unfortunately, attempted conversion of **170a** and **b** to the corresponding ditosylates or ditriflates was unsuccessful. A reaction did occur with mesyl chloride in dichloromethane in the presence of triethylamine at 0 °C, but the resulting products were difficult to characterize. A mixture of diastereomers was expected, but only one spot was observed on thin-layer chromatography. The ¹H NMR spectrum indicated that the hydroxyl protons of **170a** and **b** were no longer present, but the mass spectrum indicated that only one mesyl group had been incorporated. The same result was obtained even when a large excess (10 eq.) of mesyl chloride and higher temperatures were used.

Since the efforts to prepare derivatives of **170a** and **b** which would give elimination upon treatment with base were unsuccessful, another approach was attempted. Dehydration of alcohols was accomplished under mild conditions by converting the hydroxyl groups to the corresponding selenides followed by oxidation to the unstable selenoxides, which then underwent elimination.¹³² However, treatment of a solution of

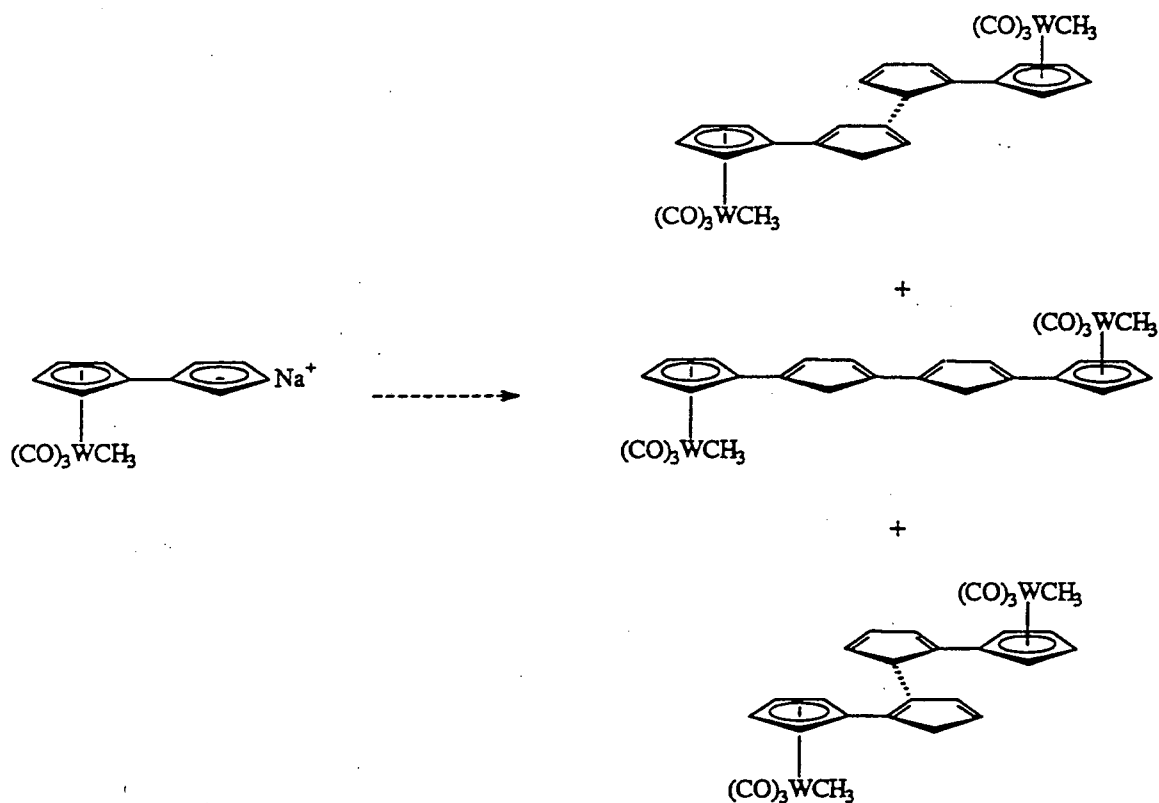
170a and b with *o*-nitrophenylselenocyanate in the presence of tributylphosphine gave an unknown product. Once again, the ^1H NMR spectrum revealed that the hydroxyl protons were no longer present, but the mass spectrum showed a species with mass 861, which is only three units higher than that of the diols. Attempted oxidation of this unknown compound with hydrogen peroxide gave only decomposition.

After the failure of this last attempt, the pinacol route to quatercyclopentadienyl compounds was abandoned. Although the diols 170a and b could be prepared in excellent yield, their lack of reactivity frustrated efforts to obtain 171. One possible explanation for these difficulties is that steric crowding around the hydroxyl groups prevented their further functionalization, although the stability of the diols in the presence of acids remains surprising. Nevertheless, it was felt that another approach was needed, and the results for this final attempted route are presented in the next section.

4.4 Cyclopentadienyl Anion Coupling

Although the pinacol route to quatercyclopentadienyl species was unsuccessful, it was felt that **171** was still an attractive precursor for these compounds. Thus, another potential route to **171** was sought. Since **171** contains a dihydrofulvalene moiety, it was decided to attempt the preparation of **171** by applying the synthesis of dihydrofulvalene to the anion of **24** (Scheme 4.25). The primary drawback of this pathway was the fact that it could give rise to several isomers. This section will describe the results of these investigations into this third alternative approach to the preparation of quatercyclopentadienyl complexes.

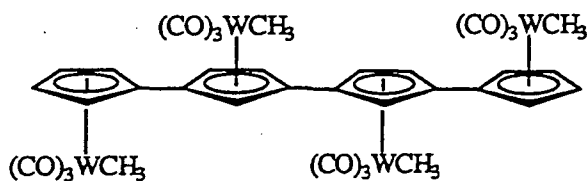
Scheme 4.25



There have been two basic routes to dihydrofulvalene through the coupling of sodium cyclopentadienide (NaCp) reported. The first approach involves treatment of a solution of NaCp with I_2 followed by work-up with sodium thiosulfate and extraction of the resulting dihydrofulvalene into heptane.¹⁰² Dilute solutions of dihydrofulvalene

prepared in this manner were found to be stable at low temperature. The second synthesis of dihydrofulvalene utilized CuCl_2 in an oxidative coupling of NaCp ,¹³³ and the product was isolated by low-temperature chromatography. This second route was chosen for application to the coupling of the anion of **24** due to the simpler manipulation of the product.

In order to attempt the coupling reaction, the anion of **24** was first prepared by treating **24** with excess NaH in THF. The resulting solution was cooled to $-35\text{ }^\circ\text{C}$ and added to a suspension of CuCl_2 in THF. The mixture was filtered at $-78\text{ }^\circ\text{C}$ to remove the copper salts, and excess lithium bis(trimethylsilyl)amide was added. Finally, $\text{W}(\text{CO})_3(\text{C}_2\text{H}_5\text{CN})_3$ was added, followed by CH_3I . The entire sequence was carried out in one flask to avoid the isolation of any unstable species. Only one product was isolated from the reaction, and comparison of its ^1H NMR spectrum with those obtained by Newman¹⁰⁰ for various quatercyclopentadienyl compounds revealed that the product was **173**. Unfortunately, only trace amounts of this compound were obtained, and it was not possible to purify the complex. It is unclear why only one of three expected isomers was isolated, but it is possible that the other isomers were simply formed in amounts too small to be detected. Nevertheless, it was quite clear that most of the starting material was lost to decomposition.



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This final approach to quatercyclopentadienyl complexes also gave disappointing results. While the coupling was not attempted using I_2 , it is unlikely that this modification would result in a significant improvement. Since this route also can give rise to several isomers, it does not offer a clear advantage over the previous synthesis. As a result, there is still only one synthetic pathway to the quatercyclopentadienyl complexes, and it is

unclear whether this route can be improved to allow the isolation of significant quantities of the tetrametallic species.

Chapter Five

Experimental Section

General. Unless specifically stated otherwise, all manipulations (column chromatography, recrystallizations, etc.) were performed under an atmosphere of purified argon or nitrogen, either in a Vacuum Atmospheres or Braun glovebox or using standard Schlenk and vacuum line techniques. Diethyl ether (Et_2O), dimethoxyethane (DME), tetrahydrofuran (THF), $\text{THF-}d_8$, and toluene were distilled under nitrogen from sodium or potassium benzophenone ketyl before use. Acetonitrile (CH_3CN), CD_3CN , and hexanes were distilled from CaH_2 . Acetone and acetone- d_6 were distilled from K_2CO_3 and degassed by three freeze-pump-thaw cycles. The compounds $\text{CpFe}(\text{C}_6\text{Me}_6)\text{PF}_6$,¹³⁴ $\text{CpFe}(\text{C}_6\text{H}_6)\text{PF}_6$,¹³⁵ $(\text{C}_6\text{Me}_6)_2\text{Fe}(\text{PF}_6)_2$,¹³⁶ Cp^*TiCl_3 ,¹³⁷ (fulvalene) $\text{WFe}(\text{CO})_5$ (30),^{19b} (fulvalene) $\text{WRu}(\text{CO})_5$ (31),^{19b} (fulvalene) $\text{Mo}_2(\text{CO})_6$ (93),¹⁰² (fulvalene) $\text{W}_2(\text{CO})_6$ (94),¹⁰² (fulvalene) $\text{MoRu}(\text{CO})_5$ (35),²² (fulvalene) $[\text{W}(\text{CO})_3\text{Me}][\text{Rh}(\text{CO})_2]$ (25),^{19b} (cyclopentadienyl)cyclopentadienyltungsten tricarbonyl methyl (24),^{19b} and (3-oxo-1-cyclopentenyl)cyclopentadienyltungsten tricarbonyl methyl (22)^{19b} were prepared according to literature procedures. $\text{Cp}^*\text{Fe}(\text{C}_6\text{Me}_6)\text{PF}_6$ was generously provided by Dr. Marie-Hélène Delville. All other reagents were obtained from commercial suppliers and used without further purification.

^1H NMR spectra were recorded on a U.C. Berkeley 300 MHz instrument equipped with a Nicolet Model 1280 data collection system and a Cryomagnets, Inc. magnet or on Bruker AMX-300 or AMX-400 instruments. ^1H NMR spectra are reported as follows: chemical shift in ppm downfield of tetramethylsilane using the residual proton resonances of the deuterated solvent as an internal standard (multiplicity, coupling constant in Hertz, number of protons). The AA'XX' patterns of symmetrical fulvalene ligands are reported as triplets with a coupling constant equal to half the frequency difference between the outer two lines. Satellites due to coupling to the ^{183}W nucleus (14% natural abundance)

are reported as $^2J_{\text{WH}}$. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on the Bruker AMX-400 instrument operating at 100 MHz. $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts are reported relative to tetramethylsilane using the deuterated solvent resonances as internal standards. The resonances due to the carbons in $\text{Fe}(\text{P}(\text{OMe})_3)_2$ and $\text{Fe}(\text{PMe}_3)_2$ fragments are reported as triplets with coupling constants equal to the frequency difference between the outer two lines representing the sum of $^1J_{\text{PC}}$ and $^3J_{\text{PC}}$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on the U.C. Berkeley 300 MHz instrument operating at 121.5 MHz. ^{31}P NMR chemical shifts are reported relative to an external standard of 85% H_3PO_4 in CD_3CN or $\text{THF-}d_8$. Infrared spectra were recorded on a Perkin-Elmer Model 681 spectrophotometer equipped with a 580 B data station or on a Perkin-Elmer System 2000 FTIR spectrophotometer; only the most intense peaks in the spectra are reported. Mass spectra were acquired by the U.C. Berkeley Mass Spectrometry Laboratory on AEI-MS12, Finnigan 4000, or Kratos MS50 instruments. The natural isotopic distribution of the transition metals produced broad peak envelopes; only the most intense peak of each fragment is reported. Elemental analyses were performed by the U.C. Berkeley Microanalytical Laboratory. Melting points were measured on a Büchi melting point or Thomas Hoover Unimelt apparatus in glass capillary tubes sealed under argon and are uncorrected.

(Fulvalene)[$\text{W}(\text{CO})_3\text{CH}_3$][$\text{Fe}(\text{CO})_2$] Dimer (98). In the glovebox a Schlenk flask was charged with $\text{CpFe}(\text{C}_6\text{Me}_6)\text{PF}_6$ (43 mg, 0.10 mmol), 0.7% Na/Hg (3.0 g, 21 mg Na, 0.91 mmol), and DME (5 mL). The flask was removed from the glovebox and the mixture stirred at room temperature for 1.5 h. The resulting green solution was transferred *via* cannula to a Schlenk flask containing (fulvalene) $\text{WFe}(\text{CO})_5$ (30) (51 mg, 0.10 mmol) in THF (5 mL). After 10 min CH_3I (100 μL , 1.6 mmol) was added *via* syringe and the mixture stirred for 20 min. The solvent was removed under vacuum and the flask taken into the glovebox. The residue was dissolved in THF and filtered through a plug (6 x 50 mm) of silica gel using hexanes as eluent. The solvent was removed under vacuum to give the dimer as a reddish-black powder (40 mg, 76%): mp > 270 °C; ^1H

NMR (400 MHz, THF- d_8) δ 5.95 (t, $J = 2.3$ Hz, 4H), 5.57 (t, $J = 2.3$ Hz, 4H), 5.14 (t, $J = 2.2$ Hz, 4H), 4.77 (t, $J = 2.2$ Hz, 4H), 0.26 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF- d_8) δ 230.46, 217.70, 106.74, 98.07, 90.81, 90.48, 90.37, 90.14, 89.64, 86.02, 84.75, 84.47, -29.20; IR (THF) 2007, 1994, 1918, 1784 cm^{-1} ; MS, m/z (rel intensity) 878 ($\text{M}^+ - 6\text{CO}$, 4.6), 834 ($\text{M}^+ - 7\text{CO} - \text{CH}_4$, 1.9), 806 ($\text{M}^+ - 8\text{CO} - \text{CH}_4$, 3.9), 762 ($\text{M}^+ - 9\text{CO} - 2\text{CH}_4$, 6.0), 523 ($1/2 \text{M}^+$, 8.3), 147 (base); Anal. Calcd for $\text{C}_{32}\text{H}_{22}\text{Fe}_2\text{O}_{10}\text{W}_2$: C, 36.74; H, 2.12. Found C, 36.64; H, 2.09.

(Fulvalene)[W(CO) $_3$ CH $_3$][Fe(CO) $_2$ CH $_3$] (99). In the glovebox a round-bottom flask was charged with (fulvalene)WFe(CO) $_5$ (30) (51 mg, 0.10 mmol) and THF (8 mL). Na/K alloy (0.50 mL) was added and the mixture stirred for 1.5 h. The mixture was filtered through a medium frit to give an orange-red solution which was removed from the glovebox. CH $_3$ I (200 μL , 3.2 mmol) was added *via* syringe and the mixture quickly became yellow with the formation of a precipitate. The mixture was stirred for 20 min and the solvent removed under vacuum. The residue was taken into the glovebox, dissolved in toluene, and filtered through a plug (6 x 50 mm) of silica gel using hexanes as eluent. The solvent was removed under vacuum to give the product as a yellow powder (45 mg, 83%): mp 146-148 $^\circ\text{C}$; ^1H NMR (300 MHz, THF- d_8) δ 5.84 (t, $J = 2.3$ Hz, 2H), 5.51 (t, $J = 2.3$ Hz, 2H), 5.13 (t, $J = 2.2$ Hz, 2H), 4.93 (t, $J = 2.2$ Hz), 0.29 (s, $^2J_{\text{WH}} = 1.7$ Hz, 3H), 0.13 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF- d_8) δ 217.94, 217.54, 107.46, 101.77, 90.31, 90.11, 84.76, 84.45, -18.49, -28.93; IR (THF) 2004, 1951, 1919 cm^{-1} ; MS, m/z (rel intensity) 538 (M^+ , 3.6), 510 ($\text{M}^+ - \text{CO}$, 2.3), 482 ($\text{M}^+ - 2\text{CO}$, 20.2), 452 ($\text{M}^+ - 2\text{CO} - 2\text{CH}_3$, 45.2), 424 ($\text{M}^+ - 3\text{CO} - 2\text{CH}_3$, 86.8), 380 (base). Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{FeO}_5\text{W}$: C, 37.95; H, 2.63. Found: C, 37.97; H, 2.74.

(Fulvalene)[W(CO) $_3$ CH $_3$][Ru(CO) $_2$ CH $_3$] (102). In the glovebox a Schlenk flask was charged with CpFe(C $_6$ Me $_6$)PF $_6$ (42 mg, 0.10 mmol), 0.7% Na/Hg amalgam (2.0 g, 14 mg Na, 0.61 mmol), and DME (5 mL). The flask was removed from the glovebox and the mixture stirred for 1 h. The resulting green solution was transferred *via* cannula to a

Schlenk flask containing (fulvalene)WRu(CO)₅ (30) (25 mg, 0.045 mmol) in THF (5 mL). The reaction mixture became pale green and a precipitate formed. After 5 min CH₃I (100 μL, 1.6 mmol) was added *via* syringe and the mixture became yellow. The mixture was stirred 25 min and the solvent removed under vacuum. The residue was taken into the glovebox, dissolved in THF, and filtered through a plug (6 x 50 mm) of silica gel using hexanes as eluent. The solvent was removed under vacuum to give the product as an orange-yellow powder (16 mg, 61%): mp 162-163 °C; ¹H NMR (300 MHz, THF-*d*₆) δ 5.79 (t, *J* = 2.2 Hz, 2H), 5.59 (t, *J* = 2.1 Hz, 2H), 5.47 (t, *J* = 2.2 Hz, 2H), 5.44 (t, *J* = 2.1 Hz, 2H), 0.30 (s, 3H), 0.25 (s, 3H); ¹³C{¹H} NMR (100 MHz, THF-*d*₆) 217.53, 202.68, 107.25, 103.67, 90.02, 89.89, 88.57, 85.57, -24.79, -28.55; IR (THF) 2007, 1955, 1919 cm⁻¹; MS, *m/z* (rel intensity) 584 (M⁺, 8.7), 500 (M⁺ - 3CO, 16.5), 412 (M⁺ - Ru - 2CO - CH₃, 47.6), 425 (base). Anal. Calcd for C₁₇H₁₄O₅RuW: C, 35.01; H, 2.42. Found: C, 35.37; H, 2.50.

(Fulvalene)[W(CO)₃CH₃][Ru(CO)₂] Dimer (103). Method A: In the glovebox a Schlenk flask was charged with CpFe(C₆Me₆)PF₆ (41 mg, 0.095 mmol), 0.7% Na/Hg amalgam (2.0 g, 14 mg Na, 0.61 mmol), and DME (5 mL). The flask was removed from the glovebox and the mixture stirred for 1 h. The resulting green solution was transferred *via* cannula to a Schlenk flask containing (fulvalene)WRu(CO)₅ (31) (25 mg, 0.045 mmol) in THF (5 mL). The yellow-brown mixture was stirred for 0.5 h then transferred *via* cannula to a Schlenk flask containing a slurry of Cp₂FePF₆ (15 mg, 0.045 mmol) in THF (3 mL). After 5 min CH₃I (100 μL, 1.6 mmol) was added and the mixture stirred for 0.5 h, during which time it became yellow-orange. The solvent was removed under vacuum. ¹H NMR of the crude product showed (fulvalene)WRu(CO)₅ (31) and (fulvalene)-WRu(CO)₅Me₂ (102) in approximately equal amounts while the dimer 103 was only a minor product. Data for 103: ¹H NMR (300 MHz, acetone-*d*₆) δ 6.03 (t, *J* = 2.1 Hz, 4H), 5.83 (t, *J* = 2.1 Hz, 4H), 5.67 (t, *J* = 2.2 Hz, 4H), 5.49 (t, *J* = 2.1 Hz, 4H), 0.26 (s, ²*J*_{WH}

= 1.4 Hz, 6H); IR (THF) 2010, 1959, 1921, 1788 cm^{-1} ; MS, m/z (rel intensity) 1136 (M^+ , 0.1), 349 (base).

Method B: In the glovebox a Schlenk flask was charged with $\text{CpFe}(\text{C}_6\text{Me}_6)\text{PF}_6$ (41 mg, 0.095 mmol), 0.7% Na/Hg amalgam (2.0 g, 14 mg Na, 0.61 mmol), and DME (5 mL). The flask was removed from the glovebox and the mixture stirred for 1 h. The resulting green solution was transferred *via* cannula to a Schlenk flask containing (fulvalene) $\text{WRu}(\text{CO})_5$ (**31**) (25 mg, 0.045 mmol) in THF (5 mL). The mixture was cooled to $-78\text{ }^\circ\text{C}$ and a slurry of Cp_2FePF_6 (15 mg, 0.045 mmol) in THF (5 mL) was added in small portions over a 10 min period. The resulting yellow-brown mixture was stirred at $-78\text{ }^\circ\text{C}$ for 20 min then CH_3I (100 μL , 1.6 mmol) was added *via* syringe. The mixture was allowed to warm to room temperature and the solvent removed under vacuum. The ^1H NMR spectrum of the crude product showed the same mixture of compounds as before except that the dimer now composed about 20% of the mixture.

Method C: In the glovebox a Schlenk flask was charged with $\text{CpFe}(\text{C}_6\text{Me}_6)\text{PF}_6$ (41 mg, 0.095 mmol), 0.7% Na/Hg amalgam (2.0 g, 14 mg Na, 0.61 mmol), and DME (5 mL). The flask was removed from the glovebox and the mixture stirred for 1 h. The resulting green solution was transferred *via* cannula to a Schlenk flask containing (fulvalene) $\text{WRu}(\text{CO})_5$ (**31**) (25 mg, 0.045 mmol) in acetone (5 mL), and the mixture became yellow-green. After 5 min a solution of $(\text{C}_6\text{Me}_6)_2\text{Fe}(\text{PF}_6)_2$ (60 mg, 0.090 mmol) in acetone (4 mL) was added *via* cannula, and the mixture became greenish-brown. The mixture was stirred for 0.5 h, during which time it became greenish-yellow. CH_3I (100 μL , 1.6 mmol) was added *via* syringe and the mixture stirred for 25 min. The solvent was removed under vacuum. The ^1H NMR spectrum of the crude mixture showed approximately equal amounts of (fulvalene) $\text{WRu}(\text{CO})_5$ (**31**) and (fulvalene)- $\text{WRu}(\text{CO})_5(\text{H})_2$ (**104**). Data for **104**: ^1H NMR (300 MHz, acetone- d_6) δ 6.21 (s, 2H), 5.94 (t, $J = 1.5$ Hz, 2H), 5.68 (s, 2H), 5.44 (t, $J = 1.5$ Hz, 2H), -7.01 (s, 1H) [W-H], -10.90 (s, 1H) [Ru-H]; MS, m/z (rel intensity) 554 ($\text{M}^+ - \text{H}_2$, 24.7), 412 (base).

Method D: In the glovebox a Schlenk flask was charged with $\text{CpFe}(\text{C}_6\text{Me}_6)\text{PF}_6$ (41 mg, 0.095 mmol), 0.7% Na/Hg amalgam (2.0 g, 14 mg Na, 0.61 mmol), and DME (5 mL). The flask was removed from the glovebox and the mixture stirred for 1 h. The resulting green solution was transferred *via* cannula to a Schlenk flask containing (fulvalene)WRu(CO)₅ (31) (25 mg, 0.045 mmol) in acetone (5 mL), and the mixture became yellow-green. The mixture was stirred at room temperature for 5 min then cooled to -78 °C. A solution of $(\text{C}_6\text{Me}_6)_2\text{Fe}(\text{PF}_6)_2$ (30 mg, 0.045 mmol) in acetone (3 mL) was added in small portions, and the mixture became dark brown. The mixture was stirred at -78 °C for 0.5 h, then CH_3I (100 μL , 1.6 mmol) was added *via* syringe. The mixture was stirred at -78 °C for 0.5 h then allowed to warm to room temperature. The solvent was removed under vacuum. The ¹H NMR spectrum of the crude mixture showed (fulvalene)WRu(CO)₅ (31), (fulvalene)WRu(CO)₅Me₂ (102), and the dimer 103 in an approximately 3:2:1 ratio.

Preparation of the standard $\text{CpFeC}_6\text{Me}_6$ (97) solution. In the glovebox a Schlenk flask was charged with $\text{CpFe}(\text{C}_6\text{Me}_6)\text{PF}_6$ (43 mg, 0.10 mmol) and DME (5 mL). Na/Hg amalgam (0.7%, 1.5 g) was added and the mixture stirred for 1 h, during which time it became dark green. The reduction was assumed to be quantitative, and aliquots of solutions prepared in this manner were used in the electrocatalysis experiments.

(Fulvalene)[W(CO)₃]⁻[Fe(CO)(P(OMe)₃)₂]⁺ (107). **Method A:** In the glovebox a Schlenk flask was charged with (fulvalene)WFe(CO)₅ (30) (51 mg, 0.10 mmol) and THF (10 mL). P(OMe)₃ (100 μL , 0.80 mmol) was added *via* syringe, followed by a solution of $\text{CpFe}(\text{C}_6\text{Me}_6)$ (0.01 mmol) in DME. The reaction mixture became reddish-purple, and a precipitate began to form within 5 min. After 15 min TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the glovebox, dissolved in CH_3CN , and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum and the residue recrystallized from acetone/hexanes at -78 °C to give a red powder (51 mg,

70%): mp 128-129 °C; ^1H NMR (400 MHz, CD_3CN) δ 5.63 (t, $J = 2.4$ Hz, 2H), 5.14 (t, $J = 2.4$ Hz, 2H), 5.12 (m, 2H), 4.96 (t, $J = 1.9$ Hz, 2H), 3.68 (m, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3CN) δ 225.86, 90.75, 86.55, 86.32, 83.92, 79.48, 54.45 (t, $J_{\text{PC}} = 3.7$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_3CN) δ 167.97; IR (CH_3CN) 1985, 1895, 1783 cm^{-1} ; MS, m/z (rel intensity) 700 ($\text{M}^+ - \text{CO}$, 10), 672 ($\text{M}^+ - 2\text{CO}$, 26.2), 616 ($\text{M}^+ - 4\text{CO}$, 36.8), 520 ($\text{M}^+ - \text{P}(\text{OMe})_3 - 3\text{CO}$, 18.1), 492 ($\text{M}^+ - \text{P}(\text{OMe})_3 - 4\text{CO}$, 34.4). Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{FeO}_{10}\text{P}_2\text{W}$: C, 32.99; H, 3.61. Found: C, 33.07; H, 3.59.

Method B: In the glovebox a Schlenk flask was charged with (fulvalene)- $\text{WFe}(\text{CO})_5$ (**30**) (51 mg, 0.10 mmol) and THF (10 mL). A second flask was charged with $\text{CpFe}(\text{C}_6\text{H}_6)\text{PF}_6$ (33 mg, 0.10 mmol) and DME (5 mL). To this flask was added 0.7% Na/Hg amalgam (1.5 g), and the mixture stirred for 1 h at -20 °C. To the first flask was added $\text{P}(\text{OMe})_3$ (100 μL , 0.80 mmol), followed by an aliquot of the $\text{CpFe}(\text{C}_6\text{H}_6)$ solution (0.01 mmol). The reaction mixture quickly became dark red, and a precipitate formed. After 15 min TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the glovebox, dissolved in CH_3CN , and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum and the residue recrystallized from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ at -30 °C in the glovebox to give red crystals (52 mg, 72%). ^1H NMR confirmed that the product was **107**.

X-Ray Diffraction Analysis of 107.¹³⁸ X-ray quality crystals were grown by slow cooling of a solution of **107** in CH_3CN . Crystal size 0.39 x 0.31 x 0.23 mm, space group $P\bar{1}$, $a = 9.766$ (1) Å, $b = 10.973$ (1) Å, $c = 12.536$ (2) Å, $\alpha = 77.60$ (1), $\beta = 73.43$ (1), $\gamma = 81.13$ (1), $V = 1242.5$ (3) Å³, $Z = 2$, $d_{\text{cal}} = 1.720$ g/cm³, $\mu = 5.33$ mm⁻¹, radiation: Mo- $\text{K}\alpha$, data collection of 9062 unique intensities ($2\theta_{\text{max}} = 45^\circ$), 8250 observed ($F \geq 4\sigma(F)$), empirical absorption correction: min/max transmission 0.36/0.91, R_{merg} before/after correction: 0.169/0.0228, structure solution with direct methods and refinement with full matrix least squares (299 parameters) (riding groups for hydrogen atoms; common

isotropic U-values for each group) and isotropic U-values for the disordered atoms O5, O6, and C15, $R = 0.0393$, $R_w = 0.0426$, $w^{-1} = \sigma^2(F) + 0.0015 \cdot F^2$. Atomic coordinates, H-atom coordinates, and anisotropic displacement coefficients are listed in Tables 5.1, 5.2, and 5.3, respectively.

(Fulvalene)[W(CO)₃]⁻[Fe(CO)(PMe₃)₂]⁺ (108). In the glovebox a Schlenk flask was charged with (fulvalene)WFe(CO)₅ (30) (51 mg, 0.10 mmol) and THF (10 mL). PMe₃ (105 μ L, 1.0 mmol) was added, followed by a solution of CpFe(C₆Me₆) (0.005 mmol) in DME. The reaction mixture immediately became orange and a precipitate began to form. After 10 min TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the glovebox, dissolved in CH₃CN, and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum. The residue was recrystallized from CH₃CN/Et₂O at -30 °C in the glovebox to give orange-red crystals (50 mg, 79%); mp > 250 °C (decomposes without melting); ¹H NMR (400 MHz, CD₃CN) δ 5.57 (t, $J = 2.3$ Hz, 2H), 5.12 (t, $J = 2.3$ Hz, 2H), 4.87 (t, $J = 2.0$ Hz, 2H), 4.81 (t, $J = 2.3$ Hz, 2H), 1.48 (m, 18H); ¹³C{¹H} NMR (100 MHz, CD₃CN) δ 226.16, 86.26, 85.87, 84.93, 78.27, 21.28 (t, $J_{PC} = 16.2$ Hz); ³¹P{¹H} NMR (121.5 MHz, CD₃CN) δ 25.33; IR (CH₃CN) 1958, 1895, 1785 cm⁻¹; FAB-MS (nitrobenzyl alcohol), m/z 632 (M⁺). Anal. Calcd for C₂₀H₂₆FeO₄P₂W: C, 37.99; H, 4.15. Found: C, 37.69; H, 4.12.

(Fulvalene)WFe(CO)₄(P(OMe)₃) (116). In the glovebox a Schlenk flask was charged with (fulvalene)WFe(CO)₅ (30) (102 mg, 0.20 mmol). THF (25 mL) was added, followed by P(OMe)₃ (100 μ L, 0.80 mmol). The mixture was irradiated at 300 nm for 40 min, and the solvent removed under vacuum. The residue was dissolved in THF (4 mL) and transferred *via* cannula to a Schlenk column containing silica gel (230-400 mesh, 2 x 15 cm). Elution with Et₂O/hexanes (1:1) gave a brownish-black band which was collected and the solvent removed under vacuum. The residue was taken into the glovebox and recrystallized from THF/hexanes at -30 °C to give purple-black crystals (80 mg, 66%); mp

Table 5.1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$).

	x	y	z	U(eq)
W	1268(1)	4600(1)	2106(1)	30(1)+
Fe	-4067(1)	7281(1)	2381(1)	32(1)+
P(1)	-5823(1)	7994(1)	3654(1)	56(1)+
P(2)	-2840(1)	8831(1)	2161(1)	33(1)+
O(1)	-332(6)	2369(4)	2151(5)	87(2)+
O(2)	1747(6)	3362(6)	4455(4)	96(2)+
O(3)	4214(5)	3355(6)	924(5)	93(2)+
O(4)	-6993(4)	7088(4)	4151(4)	72(2)+
O(5)	-6275(8)	9358(6)	3872(6)	46(2)
O(5A)	-6933(6)	9034(5)	3023(5)	58(1)
O(6)	-5523(15)	7368(11)	4907(9)	90(4)
O(6A)	-5662(6)	8793(5)	4446(5)	52(1)
O(7)	-3784(3)	10136(3)	2003(3)	49(1)*
O(8)	-2174(4)	8761(3)	3196(3)	48(1)*
O(9)	-1449(3)	9005(3)	1128(3)	45(1)*
O(10)	-5439(5)	8585(4)	636(4)	73(2)*
C(1)	326(5)	3179(4)	2114(4)	46(1)*
C(2)	1578(6)	3821(5)	3561(4)	53(2)*
C(3)	3091(5)	3785(5)	1371(4)	50(1)*
C(4)	-611(4)	6219(3)	1951(3)	33(1)*
C(5)	137(4)	6496(4)	2660(4)	42(1)*
C(6)	1558(5)	6706(4)	2027(5)	56(2)*
C(7)	1699(5)	6538(4)	925(5)	56(2)*
C(8)	371(4)	6241(4)	837(3)	43(1)*
C(9)	-2111(4)	5984(3)	2243(3)	33(1)*
C(10)	-2883(5)	5844(4)	1480(4)	47(1)*
C(11)	-4277(5)	5500(4)	2131(7)	68(3)*
C(12)	-4349(5)	5468(4)	3294(6)	59(2)*
C(13)	-3045(5)	5815(4)	3370(4)	44(1)*
C(14)	-8256(6)	7269(7)	5024(6)	75(2)*
C(15)	-7130(9)	10316(6)	3107(7)	85(2)
C(16)	-4839(9)	8155(8)	5398(8)	92(2)
C(17)	-3234(6)	11325(4)	1636(6)	59(2)*
C(18)	-1044(7)	9455(5)	3213(7)	71(3)*
C(19)	-1527(7)	9075(6)	-9(5)	67(2)*
C(20)	-4917(5)	8072(4)	1326(4)	45(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 5.2. H-atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$).

	x	y	z	U
H(5)	-287	6615	3427	89(7)
H(6)	2275	7008	2264	89(7)
H(7)	2523	6668	290	89(7)
H(8)	135	6147	168	89(7)
H(10)	-2512	5921	675	89(7)
H(11)	-5015	5293	1851	89(7)
H(12)	-5157	5239	3917	89(7)
H(13)	-2810	5848	4057	89(7)
H(14A)	-8830	6587	5165	89(7)
H(14B)	-7978	7288	5695	89(7)
H(14C)	-8803	8045	4817	105(9)
H(17A)	-3994	11988	1594	105(9)
H(17B)	-2743	11438	2166	105(9)
H(17C)	-2571	11343	903	105(9)
H(18A)	-874	9229	3951	105(9)
H(18B)	-183	9244	2656	105(9)
H(18C)	-1317	10340	3057	105(9)
H(19A)	-594	9181	-520	105(9)
H(19B)	-1849	8316	-70	105(9)
H(19C)	-2189	9776	-198	105(9)

Table 5.3. Anisotropic displacement coefficients ($\text{\AA}^2 \times 10^3$).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	28(1)	31(1)	33(1)	-3(1)	-10(1)	-4(1)
Fe	26(1)	28(1)	41(1)	-7(1)	-10(1)	-2(1)
P(1)	39(1)	50(1)	75(1)	-18(1)	10(1)	-27(1)
P(2)	28(1)	27(1)	42(1)	-8(1)	-9(1)	1(1)
O(1)	111(4)	65(2)	92(4)	-52(3)	-14(3)	-17(2)
O(2)	93(4)	137(5)	49(2)	12(3)	-34(2)	3(3)
O(3)	64(3)	119(4)	83(3)	36(3)	-10(2)	-31(3)
O(4)	49(2)	73(2)	89(3)	-32(2)	20(2)	-35(2)
O(7)	35(1)	30(1)	74(2)	-5(1)	-9(1)	3(1)
O(8)	50(2)	44(1)	57(2)	-13(1)	-23(1)	-7(1)
O(9)	33(1)	45(1)	49(2)	-11(1)	-4(1)	2(1)
O(10)	79(3)	71(2)	83(3)	3(2)	-54(2)	-6(2)
C(1)	58(2)	37(2)	45(2)	-14(2)	-14(2)	-5(1)
C(2)	52(2)	69(3)	41(2)	3(2)	-21(2)	-9(2)
C(3)	44(2)	54(2)	48(2)	8(2)	-14(2)	-9(2)
C(4)	32(1)	28(1)	37(2)	-1(1)	-11(1)	-3(1)
C(5)	41(2)	39(2)	55(2)	-3(1)	-20(2)	-17(2)
C(6)	40(2)	38(2)	97(4)	-9(2)	-25(2)	-16(2)
C(7)	40(2)	40(2)	72(3)	-10(2)	0(2)	14(2)
C(8)	41(2)	41(2)	37(2)	-1(1)	-6(1)	5(1)
C(9)	30(1)	29(1)	42(2)	-1(1)	-12(1)	-7(1)
C(10)	42(2)	45(2)	66(3)	1(2)	-23(2)	-25(2)
C(11)	44(2)	36(2)	135(6)	-11(2)	-33(3)	-22(3)
C(12)	40(2)	32(2)	92(4)	-13(1)	-6(2)	12(2)
C(13)	40(2)	38(2)	45(2)	-3(1)	-9(2)	10(1)
C(14)	50(3)	90(4)	69(4)	-22(3)	12(3)	-8(3)
C(17)	56(3)	30(2)	87(4)	-10(2)	-23(3)	7(2)
C(18)	74(3)	52(3)	107(5)	-22(2)	-54(4)	-7(3)
C(19)	66(3)	69(3)	54(3)	-9(3)	-3(2)	-6(2)
C(20)	42(2)	42(2)	56(2)	-7(1)	-21(2)	-4(2)

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 (h^2 a^2 U_{11} + \dots + 2hka^*b^*U_{12})$$

141-142 °C; ^1H NMR (400 MHz, CD_3CN) δ 5.29 (t, $J = 2.3$ Hz, 2H), 4.84 (t, $J = 2.3$ Hz, 2H), 4.67 (q, $J = 2.4$ Hz, 2H), 3.95 (q, $J = 2.1$ Hz, 2H), 3.61 (d, $J = 5.6$ Hz, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{THF-}d_8$) δ 220.08, 218.39, 217.63, 91.44, 86.87, 84.88, 84.04, 82.26, 72.50, 52.94 (d, $J_{\text{PC}} = 5.40$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_3CN) δ 194.83; IR (THF) 1971, 1921, 1880, 1866 cm^{-1} ; MS, m/z , (rel intensity) 604 (M^+ , 100), 576 ($\text{M}^+ - \text{CO}$, 10.4), 548 ($\text{M}^+ - 2\text{CO}$, 5.3), 480 ($\text{M}^+ - \text{P}(\text{OMe})_3$, 9.5), 452 ($\text{M}^+ - \text{P}(\text{OMe})_3 - \text{CO}$, 29.9), 424 ($\text{M}^+ - \text{P}(\text{OMe})_3 - 2\text{CO}$, 38.6), 396 ($\text{M}^+ - \text{P}(\text{OMe})_3 - 3\text{CO}$, 30.9), 368 ($\text{M}^+ - \text{P}(\text{OMe})_3 - 4\text{CO}$, 49.8). Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{FeO}_7\text{PW}$: C, 33.80; H, 2.84. Found: C, 33.65; H, 3.17.

Preparation of 107 from 116. In the glovebox a Schlenk flask was charged with **8** (32 mg, 0.053 mmol) and THF (10 mL). $\text{P}(\text{OMe})_3$ (50 μL , 0.40 mmol) was added, followed by a solution of $\text{CpFe}(\text{C}_6\text{Me}_6)$ (0.01 mmol) in DME. The reaction mixture immediately became deep red. After 10 min TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the glovebox, dissolved in CH_3CN , and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum. The ^1H NMR spectrum showed only **107**, and the yield was 35 mg (91%).

(Fulvalene)[Mo(CO) $_3$] $^-$ [Mo(CO) $_2$ (PMe $_3$) $_2$] $^+$ (**117**). In the glovebox a Schlenk flask was charged with (fulvalene) $\text{Mo}_2(\text{CO})_6$ (**93**) (48 mg, 0.10 mmol) and THF (15 mL). PMe_3 (105 μL , 1.0 mmol) was added, followed by a solution of $\text{CpFe}(\text{C}_6\text{Me}_6)$ (0.015 mmol) in DME. The purple reaction mixture quickly became orange-yellow, and a precipitate began to form within a few minutes. After 15 min TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. Et_2O (30 mL) was added to complete the precipitation, and the solvent was removed *via* cannula. The precipitate was dried under vacuum, taken into the glovebox, dissolved in CH_3CN , and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum. The residue was recrystallized from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ at -30 °C in the glovebox to give a yellow powder (**37**

mg, 60%); mp 248-250 °C; $^1\text{H NMR}$ (400 MHz, CD_3CN) δ 5.54 (m, 2H), 5.50 (t, $J = 2.4$ Hz, 2H), 5.22 (m, 2H), 5.06 (t, $J = 2.4$ Hz, 2H), 1.64 (d, $J = 10.3$ Hz, 18H). Lit.:^{96a} mp 242-244 °C; $^1\text{H NMR}$ (300 MHz, CD_3CN) δ 5.53 (m, 2H), 5.50 (t, $J = 2.4$ Hz, 2H), 5.22 (m, 2H), 5.06 (t, $J = 2.4$ Hz, 2H), 1.64 (d, $J = 10.3$ Hz, 18H).

(Fulvalene)[$\text{W}(\text{CO})_3^-$][$\text{W}(\text{CO})_2(\text{PMe}_3)_2^+$] (118). In the glovebox a Schlenk flask was charged with (fulvalene) $\text{W}_2(\text{CO})_6$ (94) (66 mg, 0.10 mmol) and THF (15 mL). PMe_3 (210 μL , 2.0 mmol) was added, followed by a solution of $\text{CpFe}(\text{C}_6\text{Me}_6)$ (0.020 mmol) in DME. The purple reaction mixture quickly became yellow, and a precipitate began to form within a few minutes. After 15 min TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. Et_2O (30 mL) was added to complete the precipitation, and the solvent was removed *via* cannula. The precipitate was dried under vacuum, taken into the glovebox, dissolved in CH_3CN , and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum. The residue was recrystallized from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ at -30 °C in the glovebox to give a yellow powder (55 mg, 70%); mp > 300 °C; $^1\text{H NMR}$ (300 MHz, CD_3CN) δ 5.59 (m, 2H), 5.48 (t, $J = 2.3$ Hz, 2H), 5.33 (m, 2H), 5.08 (t, $J = 2.2$ Hz, 2H), 1.76 (d, $J = 10.2$ Hz, 18H). Lit.:^{96a} mp > 300 °C; $^1\text{H NMR}$ (300 MHz, CD_3CN) δ 5.60 (m, 2H), 5.48 (t, $J = 2.2$ Hz, 2H), 5.33 (m, 2H), 5.08 (t, $J = 2.2$ Hz, 2H), 1.76 (d, $J = 10.4$ Hz, 18H).

(Fulvalene)[$\text{Mo}(\text{CO})_3^-$][$\text{Ru}(\text{CO})(\text{PMe}_3)_2^+$] (121). In the glovebox a Schlenk flask was charged with (fulvalene) $\text{MoRu}(\text{CO})_5$ (35) (47 mg, 0.10 mmol) and THF (10 mL). PMe_3 (105 μL , 1.0 mmol) was added, followed by a solution of $\text{CpFe}(\text{C}_6\text{Me}_6)$ (0.010 mmol) in DME. The reaction mixture quickly became dark red. After 10 min the reaction mixture had turned orange and a precipitate had begun to form. After 0.5 h TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the glovebox, dissolved in CH_3CN , and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum. The residue was recrystallized from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ at -30 °C in the glovebox to give a

yellow powder (35 mg, 60%); mp 284-287 °C; $^1\text{H NMR}$ (400 MHz, CD_3CN) δ 5.56 (t, $J = 2.4$ Hz, 2H), 5.36 (t, $J = 2.1$ Hz, 2H), 5.17 (t, $J = 2.1$ Hz, 2H), 5.09 (t, $J = 2.4$ Hz, 2H), 1.53 (d, $J = 10.1$ Hz, 18H). Lit.:^{19a} mp 280-282 °C; $^1\text{H NMR}$ (300 MHz, CD_3CN) δ 5.55 (t, $J = 2.3$ Hz, 2H), 5.36 (t, $J = 2.3$ Hz, 2H), 5.17 (t, $J = 2.0$ Hz, 2H), 5.08 (t, $J = 2.3$ Hz, 2H), 1.52 (d, $J = 10.1$ Hz, 18H).

(Fulvalene)[W(CO)₃]⁻[Ru(CO)(PMe₃)₂]⁺ (122). In the glovebox a Schlenk flask was charged with (fulvalene)WRu(CO)₅ (31) (55 mg, 0.10 mmol) and THF (10 mL). A second flask was charged with Cp*Fe(C₆Me₆)PF₆ (48 mg, 0.10 mmol) and DME (5 mL). To this flask was added 0.7% Na/Hg amalgam (2.0 g) and the resulting mixture stirred for 1.5 h to generate Cp*Fe(C₆Me₆). PMe₃ (105 μL , 1.0 mmol) was added to the solution of (fulvalene)WRu(CO)₅, followed by an aliquot of the solution of Cp*Fe(C₆Me₆) (0.020 mmol). The reaction mixture immediately became deep red. After 10 min the mixture had become orange and a precipitate had formed. After 0.5 h TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the glovebox, dissolved in CH₃CN, and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum and the crude product recrystallized from CH₃CN/Et₂O at -30 °C in the glovebox to give orange-yellow crystals (37 mg, 54%); mp 295-298 °C (dec); $^1\text{H NMR}$ (400 MHz, CD_3CN) δ 5.53 (t, $J = 2.3$ Hz, 2H), 5.38 (t, $J = 2.1$ Hz, 2H), 5.18 (t, $J = 2.1$ Hz, 2H), 5.09 (t, $J = 2.3$ Hz, 2H), 1.54 (d, $J = 10.2$ Hz, 18H). Lit.:^{19a} mp 297-299 °C; $^1\text{H NMR}$ (300 MHz, CD_3CN) δ 5.53 (t, $J = 2.3$ Hz, 2H), 5.38 (t, $J = 2.1$ Hz, 2H), 5.18 (t, $J = 2.1$ Hz, 2H), 5.09 (t, $J = 2.3$ Hz, 2H), 1.54 (d, $J = 10.1$ Hz, 18H).

(Fulvalene)[W(CO)₃]⁻[Ru(CO)₂(PMe₃)₂]⁺ (123). In the glovebox a Schlenk flask was charged with (fulvalene)WRu(CO)₅ (31) (55 mg, 0.10 mmol) and THF (10 mL). PMe₃ (105 μL , 1.0 mmol) was added, followed by a solution of CpFe(C₆Me₆) (0.020 mmol) in DME. The reaction mixture immediately turned dark red but quickly became orange, and a precipitate formed. After 15 min TLC analysis (silica gel, 1:1 THF/hexanes)

indicated that no starting material remained. Et₂O (35 mL) was added to complete the precipitation. The solvent was removed *via* cannula and the precipitate dried under vacuum. The precipitate was taken into the glovebox, dissolved in CH₃CN, and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum and the residue recrystallized from CH₃CN/Et₂O at -30 °C in the glovebox to give a yellow powder (45 mg, 71%); mp > 300 °C (dec); ¹H NMR (400 MHz, CD₃CN) δ 5.69 (t, *J* = 2.1 Hz, 2H), 5.62 (t, *J* = 2.4 Hz, 2H), 5.57 (t, *J* = 2.1 Hz, 2H), 5.14 (t, *J* = 2.4 Hz, 2H), 1.68 (d, *J* = 11.5 Hz, 9H); ¹³C{¹H} NMR (100 MHz, CD₃CN) δ 245.82, 225.54, 110.44, 89.13, 86.84, 86.24, 85.63, 81.61, 20.76 (d, *J*_{PC} = 36.7 Hz); ³¹P{¹H} NMR (121.5 MHz, CD₃CN) δ 6.62; IR (CH₃CN) 2003, 1899 cm⁻¹; HRMS (FAB, nitrobenzyl alcohol) Calcd for C₁₈H₁₈O₅P⁹⁹Ru¹⁸²W (MH⁺): 625.9433. Found: 625.9431.

Conversion of 123 to 122. In the glovebox a Schlenk flask was charged with zwitterion **123** (25 mg, 0.040 mmol) and CH₃CN (15 mL). PMe₃ (210 μL, 2.0 mmol) was added followed by a solution of Cp*Fe(C₆Me₆) (0.030 mmol). The green color of the reducing agent gradually faded, and the reaction mixture changed from orange to yellow. The mixture was stirred for 1.5 h and the solvent removed under vacuum. The residue was taken into the glovebox, dissolved in CH₃CN, and filtered through a plug of Celite (1 x 4 cm). The solvent was removed under vacuum. The ¹H NMR spectrum of the resulting crude product showed **122** as the only fulvalene compound present.

(Fulvalene)[W(CO)₃Me][Rh(CO)(PPh₃)] (157). In the glovebox a Schlenk flask was charged with (fulvalene)[W(CO)₃Me][Rh(CO)₂] (**25**) (300 mg, 0.526 mmol) and THF (10 mL). PPh₃ (136 mg, 1.05 mmol) was added against a flow of argon and the reaction mixture warmed to 50 °C. After 6 h, TLC (silica; pentane) indicated that no **25** remained. The solvent was removed under vacuum and the residue dissolved in THF-hexanes (2:3) and applied in air to a silica gel column. The column was eluted with pentane to remove unreacted PPh₃. Elution with Et₂O-hexanes (1:1) gave an orange band which afforded **157** after removal of solvent by rotary evaporation and vacuum.

Recrystallization from toluene-hexanes at $-78\text{ }^{\circ}\text{C}$ gave **157** (317 mg, 74%): orange crystals, mp $153\text{-}154\text{ }^{\circ}\text{C}$; ^1H NMR (300 MHz, THF- d_8) δ 7.53 (m, 6H), 7.37 (m, 9H), 5.44 (t, $J = 2.5\text{ Hz}$, 2H), 5.31 (t, $J = 1.9\text{ Hz}$, 2H), 5.24 (t, $J = 2.0\text{ Hz}$, 2H), 5.22 (m, 2H), 0.16 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF- d_8) δ 231.34, 218.26, 195 (d, $J_{\text{RhC}} = 23.8\text{ Hz}$), 137.60 (d, $J_{\text{PC}} = 47.4\text{ Hz}$), 134.61 (d, $J_{\text{PC}} = 12.7\text{ Hz}$), 130.71 (d, $J_{\text{PC}} = 2.2\text{ Hz}$), 128.88 (d, $J_{\text{PC}} = 10.5\text{ Hz}$), 100.44, 89.03 (d, $J_{\text{RhC}} = 3.5\text{ Hz}$), 87.26 (d, $J_{\text{RhC}} = 19.1\text{ Hz}$), 86.53, 86.50, 86.47, -25.42; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, THF- d_8) δ 49.66 (d, $J_{\text{RhP}} = 199\text{ Hz}$); IR (THF) 2006, 1954, 1917 cm^{-1} ; MS, m/z (rel intensity) 804 (M^+ , 9.76), 776 ($\text{M}^+ - \text{CO}$, 3.55), 748 ($\text{M}^+ - 2\text{CO}$, 6.93), 720 ($\text{M}^+ - 3\text{CO}$, 6.36), 692 ($\text{M}^+ - 4\text{CO}$, 17.34), 262 (base). Anal. Calcd for $\text{C}_{33}\text{H}_{26}\text{O}_4\text{PRhW}$: C, 49.28; H, 3.26. Found: C, 49.59; H, 2.98.

(Fulvalene)[W(CO) $_3$ Me][Cp*ZrCl $_2$] (**29**). In the glovebox a standard anion solution was prepared from **24** (30 mg, 0.073 mmol) with excess NaH in THF (5 mL) according to the method of Kahn.^{19b} The anion solution was filtered through a plug of glass wool into a Schlenk flask containing a solution of Cp*ZrCl $_3$ (24 mg, 0.073 mmol) in THF (5 mL). The flask was removed from the box, and the yellow reaction mixture was heated at reflux for 12 h. The contents of the flask were allowed to cool, and the solvent was removed under vacuum. The crude product was recrystallized by diffusion of hexane vapors into a saturated THF solution to give **29** as a light yellow powder (14 mg, 27%), mp $200\text{ }^{\circ}\text{C}$ dec; ^1H NMR (400 MHz, THF- d_8) δ 6.38 (t, $J = 2.8\text{ Hz}$, 2H), 6.10 (t, $J = 2.8\text{ Hz}$, 2H), 5.90 (t, $J = 2.3\text{ Hz}$, 2H), 5.44 (t, $J = 2.3\text{ Hz}$, 2H), 2.01 (s, 15H), 0.20 (s, 3H); IR (THF) 2008, 1918 cm^{-1} . Lit.:^{19b} mp $200\text{ }^{\circ}\text{C}$ dec; ^1H NMR (300 MHz, THF- d_8) δ 6.39 (t, $J = 2.8\text{ Hz}$, 2H), 6.12 (t, $J = 2.8\text{ Hz}$, 2H), 5.91 (t, $J = 2.3\text{ Hz}$, 2H), 5.44 (t, $J = 2.3\text{ Hz}$, 2H), 2.02 (s, 15H), 0.20 (s, 3H); IR (THF) 2008, 1918 cm^{-1} .

(Fulvalene)[W(CO) $_3$ Me][Cp*TiCl $_2$] (**164**). In the glovebox a standard anion solution was prepared from **24** (100 mg, 0.24 mmol) with excess NaH in THF (5 mL) according to the method of Kahn.^{19b} The anion solution was filtered through a plug of glass wool into a Schlenk flask containing a solution of Cp*TiCl $_3$ (47 mg, 0.16 mmol) in

THF (5 mL). The flask was removed from the box, and the dark red reaction mixture was heated at reflux for 2 h. The contents of the flask were allowed to cool, and the solvent was removed under vacuum. The crude product was recrystallized by diffusion of hexane vapors into a saturated THF solution to produce analytically pure **164** (65 mg, 61%) as reddish-black needles, mp 200 °C dec: ^1H NMR (400 MHz, THF- d_6) δ 6.33 (t, J = 2.8 Hz, 2H), 6.11 (t, J = 2.8 Hz, 2H), 5.94 (t, J = 2.3 Hz, 2H), 5.45 (t, J = 2.3 Hz, 2H), 2.03 (s, 15H), 0.24 (s, $^2J_{\text{WH}}$ = 2.6 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF- d_6) δ 218.35, 130.26, 126.92, 121.40, 114.76, 91.63, 89.89, 13.45, -30.11; IR (THF) 2012, 1972, 1919 cm^{-1} ; MS, m/z (rel intensity) 637 (M^+ - CO, 1.3), 609 (M^+ - 2CO, 22.3), 581 (M^+ - 3CO, 41.7), 135 (base). Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{O}_3\text{TiW}$: C, 43.33; H, 3.95. Found: C, 43.55; H, 3.91.

(Fulvalene)[W(CO) $_3$ Me][Cp*HfCl $_2$] (**165**). In the glovebox a standard anion solution was prepared from **24** (100 mg, 0.24 mmol) with excess NaH in THF (5 mL) according to the method of Kahn.^{19b} The anion solution was filtered through a plug of glass wool into a Schlenk flask containing a solution of Cp*HfCl $_3$ (100 mg, 0.24 mmol) in THF (5 mL). The flask was removed from the box, and the light yellow reaction mixture was heated at reflux for 15 h. The contents of the flask were allowed to cool, and the solvent was removed under vacuum. The crude product was recrystallized by diffusion of hexane vapors into a saturated THF solution, affording **165** (136 mg, 71%) as a light yellow powder, mp 210 °C dec: ^1H NMR (400 MHz, THF- d_6) δ 6.32 (t, J = 2.8 Hz, 2H), 6.06 (t, J = 2.8 Hz, 2H), 5.91 (t, J = 2.3 Hz, 2H), 5.44 (t, J = 2.3 Hz, 2H), 2.07 (s, 15H), 0.20 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF- d_6) δ 231.05, 218.25, 123.40, 122.93, 115.12, 111.67, 108.90, 90.67, 89.30, 12.18, -28.9; IR (THF) 2012, 1918 cm^{-1} ; MS, m/z (rel intensity) 780 (M^+ - CH $_3$, 3.2), 767 (M^+ - CO, 1.3), 739 (M^+ - 2CO, 21.8), 711 (M^+ - 3CO, 19.9), 119 (base). Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{HfO}_3\text{W}$: C, 36.22; H, 3.30. Found: C, 36.21; H, 3.30.

(η^5 : η^5 -1,1':3',1'':3'',1''''-(3',1''-Dihydroxytetrahydroquatercyclopentadienyl)- $[\text{W}(\text{CO})_3\text{CH}_3]_2$ (170a,b). In the glovebox a Schlenk flask was charged with enone 22 (100 mg, 0.23 mmol) and THF (15 mL). A solution of SmI_2 (0.1 N in THF) was added slowly *via* cannula until the blue-green color of SmI_2 persisted. The reaction was quenched with 0.1 N HCl (10 mL) and the mixture extracted with Et_2O (25 mL). The organic layer was dried over K_2CO_3 and the solvent removed by rotary evaporation. The residue was dissolved in a minimal amount of THF and filtered through a short column (5 cm) of alumina II using Et_2O as eluent. The solvent was removed by rotary evaporation and vacuum to give 170a,b (98 mg, 100%) as a yellow oil. An analytical sample was prepared by recrystallization by diffusion of hexanes vapors into a THF solution of 170a,b. The diastereomers were separated by preparative TLC (silica) using ethyl acetate-hexanes (1:1) as eluent. First diastereomer: $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{THF-}d_8$) δ 231.11, 230.94, 218.32, 217.74, 217.28, 216.93, 117.85, 117.75, 97.31, 94.69, 94.36, 92.70, 92.62, 91.54, 90.94, 89.54, 82.52, 62.33, 55.70, 53.48, 48.43, 38.48, 36.63, 34.57, 33.11, 30.36, -33.42, -33.88; Second diastereomer: $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{THF-}d_8$) δ 231.19, 230.39, 218.04, 217.95, 217.31, 217.17, 215.68, 125.78, 118.53, 95.56, 94.39, 94.32, 92.69, 92.55, 92.47, 89.78, 89.19, 82.18, 65.86, 57.99, 55.75, 53.24, 49.72, 40.44, 34.17, 32.96, 31.76, 31.40, 30.35, 29.96, -33.53, -33.64; IR (THF) 2007, 1954, 1919 cm^{-1} ; MS, m/z (rel intensity) 858 (M^+ , 15.73). Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{O}_8\text{W}_2$: C, 39.18; H, 3.06. Found: C, 39.57; H, 2.96.

(η^5 : η^5 : η^5 : η^5 -1,1':3',1'':3'',1''''-Quatercyclopentadienyl) $[\text{W}(\text{CO})_3\text{CH}_3]_4$ (173). In the glovebox a standard anion solution was prepared from 24 (68 mg, 0.17 mmol) with excess NaH in THF (3 mL) according to the method of Kahn.^{19b} The resulting solution was loaded in a syringe. A Schlenk flask was charged with CuCl_2 (30 mg, 0.20 mmol) and THF (5 mL) and the slurry cooled to -35 °C. The anion solution was added by syringe pump over 0.75 h and the reaction mixture stirred an additional 0.5 h at -35 °C. Pentane (15 mL), which had been cooled to -78 °C, was added and the reaction mixture

filtered at $-78\text{ }^{\circ}\text{C}$ to give a cloudy yellow solution. A 1.0 M solution of $\text{LiN}(\text{SiMe}_3)_2$ (180 μL , 0.18 mmol) was added, causing the reaction to turn dark purple. This mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 0.5 h then $\text{W}(\text{CO})_3(\text{C}_2\text{H}_5\text{CN})_3$ (80 mg, 0.20 mmol) was added against an argon purge. THF (5 mL) was added and the reaction mixture allowed to warm to room temperature. After 1.5 h CH_3I (100 μL , 17 mmol) was added and the mixture stirred for an additional 0.5 h. The reaction mixture was filtered through a plug of silica gel using Et_2O -hexanes (1:1) as eluent and the solvent removed by rotary evaporation and vacuum. The residue was dissolved in THF and applied to a silica column. Elution with Et_2O -hexanes (1:1) gave a yellow band which was collected and the solvent removed by rotary evaporation and vacuum. The ^1H NMR spectrum of the residue indicated that it was 173, but the complex could not be sufficiently purified to allow full characterization.

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720

