

To the Graduate Council:

I am submitting herewith a thesis written by Michelle Royster Dial entitled "Synthesis, Characterization, and Reactivity of Novel Trinuclear Organometallic Cluster Complexes of Iridium, Rhodium, and Cobalt." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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SYNTHESIS, CHARACTERIZATION AND REACTIVITY
OF NOVEL TRINUCLEAR ORGANOMETALLIC
CLUSTER COMPLEXES OF
IRIDIUM, RHODIUM, AND COBALT

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Michelle Royster Dial

March 1988

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1988

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DEDICATION

To my parents:

the advice was theirs;
the decision was mine.

ACKNOWLEDGMENT

The author would like to thank Dr. Craig E. Barnes without whose guidance, enthusiasm, encouragement and friendship, none of this would have been possible.

Acknowledgement is made of the Petroleum Research Fund and Research Corporation for partial financial support of this research.

Appreciation is also given to Professor Arnold Rheingold and Donna Staley for their contribution of the X-ray crystal structures included in this work, to Karl Sienerth for the use of his personal computer, and to Steven Pawel and his family for their unfailing support.

ABSTRACT

Reported herein is a description of the synthesis, spectroscopic characterization, and X-ray structural analyses for five novel trinuclear organometallic cluster complexes of iridium, rhodium, and cobalt. These complexes are 46 electron clusters which contain carbonyl ligands and both cyclopentadienide and pentamethylcyclopentadienide ligands. Results of temperature dependent ^1H NMR studies are presented as well as an interpretation of the data as it applies to the ground states of these complexes. Reactivity studies involving two electron donor ligands and olefin-like exchange processes are described.

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CHAPTER I

INTRODUCTION

The properties of organometallic cluster complexes are of considerable interest because of the recognition of the important role played by transition metals as catalysts in organic chemistry. An organometallic cluster complex may be described as a complex which contains more than one transition metal atom and organic ligands. Hoffmann[1] has built a bridge between transition metal cluster fragments and organic moieties. This bridge is merely a comparison of the frontier orbitals, the HOMO and LUMO, of a cluster fragment and an organic fragment, resulting in the development of an isolobal analogy. Two fragments are said to be "isolobal if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar -- not identical, but similar"[1]. This bridge has come to be known as the Isolobal Theory. Stone [2-10] and others[11-27] have employed this theory of isolobal relationships as a guide to the synthesis of a wide variety of homo- and hetero-metallic clusters for the study of catalysts in olefin metathesis[28-29], C-H and C-C bond activation[30], and insertion reactions[31-32]. Various types of reactivity of transition metal clusters have also been studied as models for reactions observed at metal surfaces[33-40]. Herrmann[41-

50] and others[51-54] have done considerable research involving the reaction of transition metal clusters with diazoalkanes to produce transition metal methylene groups in an attempt to model a reaction which takes place at a metal surface.

One area of transition metal mediated catalysis has involved the study of polynuclear metal clusters of the Group 9 metals, cobalt, rhodium, and iridium. An important consideration with regard to the stability of transition metal clusters is the number of valence electrons present in a complex. In order to quickly and accurately determine the number of valence electrons in a cluster, an electron counting formalism has been developed. If a cluster contains three metal centers which all obey the 18 electron rule, then it is described as a 54 electron complex, i.e., $3 \times 18 = 54$. Clusters containing metal-metal bonds contain $2n$ fewer electrons ($n = \#$ of metal-metal bonds) than a cluster containing no metal-metal bonds. Thus, for a trinuclear cluster complex containing three metal-metal bonds, an electron count of 48 indicates compliance with the 18 electron rule.

Common oxidation states of the Group 9 metals are +2 and +3 for cobalt, +1 and +3 for rhodium, and +1 and +3 for iridium. Common ligands in organometallic cluster complexes are the cyclopentadienide ligand (Cp), pentamethylcyclopentadienide ligand (Cp*) and carbon monoxide. Carbon

monoxide is normally considered to be a neutral ligand which donates two electrons to the valence electron count of the cluster. The oxidation states of the metals in a cluster containing only cyclopentadienide and carbonyl ligands depend upon the counting formalism applied to the cyclopentadienide ligands. If the Cp ligand is considered to be a neutral five electron donor, then the metal to which the Cp ligand is bonded has no charge. If the Cp ligand is considered to be a negatively charged, six electron donor, then the metal to which the Cp ligand is bonded has an oxidation state of +1.

The research described in this thesis involves the synthesis, characterization and reactivity of a series of trinuclear cluster complexes of the Group 9 metals containing carbonyl ligands and both cyclopentadienide (Cp) and pentamethylcyclopentadienide (Cp*) ligands. In 1983, Herrmann *et al.* [47] reported the synthesis of a 46 electron trinuclear cluster complex of iridium and cobalt which contained two carbonyl ligands and both cyclopentadienide and pentamethylcyclopentadienide ligands, $(\text{Cp}^*\text{Ir})(\mu_3\text{-CO})_2(\text{CoCp})_2$. One goal of this research was to determine if the synthetic scheme described by Herrmann might be generally applied to other Group 9 metal clusters. Presented herein is a description of five new clusters which, together with Herrmann's trinuclear cluster, form a series of six clusters. These complexes can be divided into

two types. The Type 1 clusters contain two CpCo fragments, and the Type 2 clusters contain one CpCo fragment as illustrated in Figure 1.

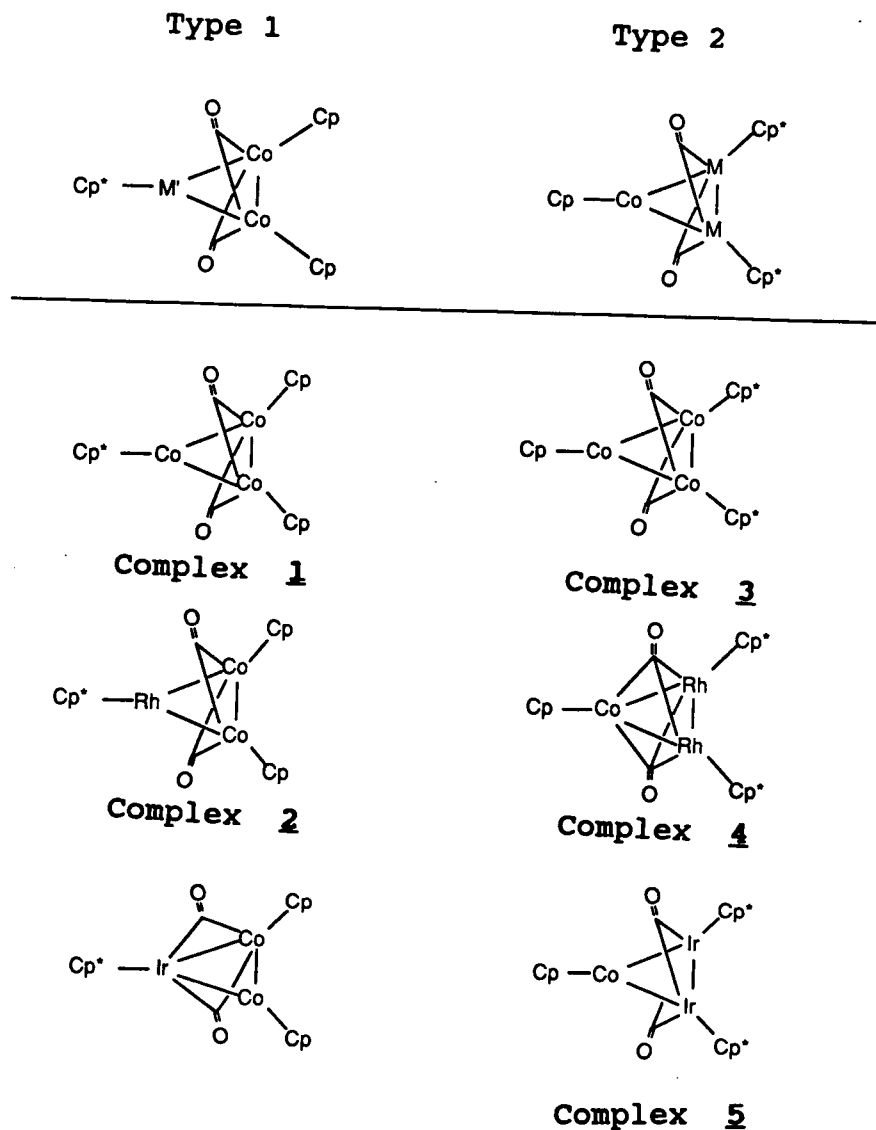


Figure 1. A series of organometallic cluster complexes of Co, Rh, and Ir.

Based on the electron counting formalisms described above, these clusters are 46 electron complexes, two electrons shy of the desired 48 valence electrons, and therefore are expected to be somewhat unstable. Having electron deficient clusters opens the door for studies involving reactivity with a wide variety of electron donating substituents such as carbon monoxide, nitric oxide, olefins, phosphines, and diazoalkanes. The reaction of these clusters with carbon monoxide is expected to result in the formation of tricarbonyl species since the clusters are deficient by two electrons. Based on the results of previous studies of the reactions of transition metal complexes with diazoalkanes, the reaction of these clusters with diazoalkanes is expected to give bridging alkylidene species upon the liberation of nitrogen. The results of the reaction of these complexes with CO and a specific diazoalkane are discussed in Chapter IV.

Using the isolobal analogies developed by Hoffmann and the results of solid state X-ray structure determinations, most of these cluster complexes appear to contain a dinuclear transition metal fragment, which is isolobal with ethylene, interacting with a unique CpM-like fragment. With this model in mind, the question arises as to whether or not these cluster complexes will undergo olefin-like exchange of the dinuclear fragment with other dinuclear complexes. The observation of an olefin-like exchange reaction provides the

basis for detailed dynamic and thermodynamic studies which may lead to a broader understanding of the fundamental processes involved in cluster formation and degradation. A brief investigation into this area is described in Chapter V.

CHAPTER II

EXPERIMENTAL PROCEDURES

Introduction.

All solvents were reagent grade or had been distilled under nitrogen from Na/K alloy or calcium hydride to insure anaerobic and anhydrous conditions. Reactions which were run under nitrogen were done using Schlenk techniques and a vacuum/nitrogen manifold. Special glassware was designed for the air sensitive experimental procedures and is shown in Appendix A. Much of the air sensitive work was carried out in an inert atmosphere (argon) dry box. The oxygen content was monitored using an MBRAUN O₂-Analyzer (serial number 152-011) which operates on the basis of a silver electrode and a lead electrode filled with KOH (5N). The presence of oxygen produces hydroxyl ions and the lead is oxidized to Pb(OH)₂. An oxygen content of less than 10ppm was maintained. Chromatographic separations were carried out under anaerobic and anhydrous conditions using jacketed flash chromatography columns. The separation medium was silica gel which had been placed under vacuum and refilled with nitrogen several times over two days. Columns were prepared in hexane and the solvent polarity increased as the constituents were eluted. Air sensitive compounds which did not need refrigeration were stored in an inert atmosphere

dry box. Air sensitive compounds requiring refrigeration were stored in Schlenk vessels under nitrogen at 2°C or -25°C. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL FX90Q (¹H, 90MHz) Fourier transform instrument, Varian T60 (¹H, 60MHz) instrument, or a Nicolet NT-200 (¹H, 200MHz) Fourier transform instrument. Chemical shifts were referenced to the residual proton signal of the deuterated solvent: δ (C₆D₅H) 7.15ppm, δ (C₇D₇H) 2.09ppm (methyl quintet), δ (THF-d₇) 3.58ppm or 1.73ppm, δ (CHCl₃) 7.26ppm. Because of the existence of two sign conventions, it should be noted that proton shifts at high field (above TMS) are negative. Infrared (IR) spectra were recorded on either a Perkin-Elmer 1330 Spectrophotometer or a Digilab FTS-20E FTIR Spectrometer. Infrared spectra were referenced to polystyrene, 1601.4 cm⁻¹. Elemental analyses were done by Desert Analytics - Organic Microanalysis of Tucson, Arizona. Solvents were removed using a double trapped oil pump vacuum (0.1torr) unless otherwise specified.

Synthetic Procedures.

1,2,3,4,5-Pentamethylcyclopentadiene, Cp^{*}-H, [55].

In a three-necked round bottom flask, 32g (4.6moles) lithium metal (Li⁰) was stirred in 1000mL diethyl ether under argon (See NOTE) as 46mL (d = 1.327g/mL, 0.24moles) 2-bromo-2-butene was added dropwise over 45 minutes using a pressure equalizing addition funnel. A mixture of 162mL (1.6moles)

2-bromo-2-butene and 92mL ethyl acetate was added dropwise to the reaction mixture at a rate sufficient to maintain reflux. After the addition was complete, ethyl acetate was added dropwise until the refluxing ceased (30 min.). The reaction mixture was cooled to room temperature and 600mL of a saturated ammonium chloride solution was added dropwise to hydrolyze the excess Li^0 . The aqueous layer was extracted three times with 100mL portions of diethyl ether. The ether extracts were combined and concentrated on the rotary evaporator. A slurry of 18g (0.095moles) p-toluene sulfonic acid monohydrate in diethyl ether was added to the ether solution by pipet as the ether solution refluxed. When the refluxing had stopped, the reaction mixture was slowly poured into a saturated sodium bicarbonate solution. The ether solution was removed and the aqueous layer was extracted three times with 100mL portions of diethyl ether. The ether portions were combined and dried over magnesium sulfate and concentrated to 150mL. Vacuum (0.1torr) distillation yielded three fractions. The second fraction was the major fraction and distilled at 28 to 32°C to yield 95mL (59.4%) of a pale yellow transparent liquid identified by ^1H NMR to be $\text{Cp}^*\text{-H}$. ^1H NMR (60MHz, CDCl_3/TMS , 25°C) δ 2.4 (m, 1 H), 1.75 (s, 12 H), 1.0 (d, 3 H).

NOTE: *Use of nitrogen causes a nitride coating to form on the lithium surface.*

Di- μ -chloro-bis(pentamethylcyclopentadiene)-
diiridium(II) chloride, $[\text{Cp}^*\text{IrCl}]_2\text{Cl}_2$, [56]. In a 250mL
Schlenk vessel, 1.0g (2.8mmoles) $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ was dissolved in
25mL degassed methanol and heated to reflux. $\text{Cp}^*\text{-H}$ (0.7mL,
 $d = 0.87\text{g/mL}$, 0.58g, 4.3mmoles) was added. The reaction
mixture went through several changes during the reaction.
The solution was initially green. Within an hour, the
solution had turned dark reddish brown. After 18 hours, the
solution was reddish orange and an orange precipitate had
formed. The reaction was stopped and cooled at 2°C for
several hours. The orange precipitate was collected by
suction filtration and washed twice with ice cold degassed
methanol. The crude product was dissolved in methylene
chloride (10mL) and hexane was added until the solution
became cloudy (50mL). The methylene chloride was removed on
the rotary evaporator. The hexane solution was virtually
clear and there was a crystalline orange precipitate
present. The orange crystals were collected by suction
filtration and washed once with cold degassed hexane. The
yield was 0.688g (61%) orange crystalline product identified
by ^1H NMR to be $[\text{Cp}^*\text{IrCl}]_2\text{Cl}_2$. ^1H NMR (CDCl_3 , 25°C) δ 1.595
(s).

Di- μ -chloro-bis(pentamethylcyclopentadiene)-
dirhodium(II) chloride, $[\text{Cp}^*\text{RhCl}]_2\text{Cl}_2$, [57]. A stirred
solution of 1.03g (4mmoles) rhodium trichloride trihydrate
($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) in 35mL degassed methanol was heated to reflux

under nitrogen. A small excess of $\text{Cp}^*\text{-H}$ (0.8mL, $d=0.87$, 0.7g, 5mmoles) was added and the reaction mixture refluxed for three hours. The methanol was removed and the residue dissolved in methylene chloride. Hexane was added until the mixture became cloudy (1:1). The methylene chloride was removed on the rotary evaporator and a dark red-orange precipitate formed. The crystalline precipitate was collected by suction filtration and washed with cold hexane until the washes were clear. The filtrate was taken to dryness and the residue dissolved in methylene chloride. Hexane was added until the mixture became cloudy. The methylene chloride was removed slowly and the remaining hexane solution was filtered. The total amount of dark red-orange crystalline product collected was 1.02g (2mmoles, 84%). ^1H NMR (CDCl_3 , 25°C) δ 1.623(s).

Di- μ -chloro-bis(1,5-cyclooctadiene)diiridium(I), $[\text{Ir}(\text{COD})\text{Cl}]_2$, [58]. In a 100mL Schlenk vessel 20mL 95% ethanol, 10mL distilled water, 2mL ($d = 0.882$, 16mmoles) 1,5-cyclooctadiene (COD) and 0.5g (1.4 moles) iridium tri-chloride trihydrate ($\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$) were combined and refluxed under nitrogen for 24 hours. Cyclooctadiene, being insoluble in ethanol, was broken up into little droplets by vigorous stirring. During the reaction, the droplets took on a red brick color as the product formed and dissolved in them. As the droplets became more solid, they clumped together and then were broken apart by the stirring into an

orange powder. The reaction mixture was cooled to room temperature and the precipitate was collected by suction filtration. The orange precipitate was washed with ice cold degassed methanol and dried under vacuum to yield 0.36g (91%) of an air stable orange powder which was soluble in chloroform.

Di- μ -chloro-bis[bis(cyclooctene)iridium], $[\text{Ir}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$, [59]. Method A. In a 250mL Schlenk vessel, 2.65g (4.7mmoles) sodium chloroiridate hexahydrate ($\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$) and 12mL ($d = 0.846\text{g/mL}$, 10.2g, 92mmoles) cyclooctene were stirred in a mixture of 30mL reagent grade isopropanol and 90mL distilled water. The reaction mixture was refluxed under nitrogen at an oil bath temperature of 85°C for four hours. Several changes took place in the reaction mixture as the reaction progressed. Initially the mixture was yellow-brown. After 1.5 hours, the solution took on a yellow-orange color. The organic layer continued to darken as the aqueous layer grew lighter in color. After four hours, the aqueous layer was light yellow and the organic layer was dark orange. The stirring was stopped and the reaction mixture was cooled to room temperature. A significant amount of oily orange residue settled to the bottom of the reaction vessel. The aqueous layer was separated from the organic layer by pipet and extracted with methylene chloride. The methylene chloride extracts were taken to dryness to yield a small amount of yellow residue.

The solvents were removed from the organic layer under vacuum to yield an oily residue. The residue was dissolved in warm degassed ethanol and cooled in an ice water/salt bath for approximately two hours. The solution was filtered and the precipitate washed with ice cold degassed ethanol and dried overnight in a vacuum desiccator. The ethanol filtrate was taken to dryness to yield a small amount of yellow residue. The combined yield was 1.79g (2.0mmoles, 84%) of a yellow-orange powder.

Method B. Iridium trichloride trihydrate (3.5g, 9.9mmoles) was added to a mixture of cyclooctene (6mL, 5.1g, 46mmoles), reagent grade isopropanol (45mL) and distilled water (10mL). The reaction mixture was heated at reflux for four hours. During the course of the reaction the solution color changed from red-brown to yellow-orange, and an orange precipitate formed. The heating was stopped and the reaction mixture was cooled to room temperature under nitrogen. The precipitate was collected via suction filtration, washed with cold degassed methanol and dried under vacuum for several hours. The yield was 0.90g of an orange powder. The filtrate solvent was removed under vacuum and the residue taken up in a 1:1 mixture of degassed isopropanol and distilled water. The solution was filtered and the precipitate was washed with cold degassed methanol and dried under vacuum. The second crop was 2.43g of orange powder. The total yield was 3.33g (3.7mmoles, 75%) of an orange powder.

Preparation of Cyclopentadiene, Cp-H. Cyclopentadiene undergoes a Diels-Alder reaction with itself at room temperature (25°C). This reaction is thermally reversible. Distillation of dicyclopentadiene (Diels-Alder product) reverses this reaction and is the general way of obtaining Cp-H.

Dicyclopentadiene (400mL) was placed in a 500mL round bottom flask equipped with an insulated vigreux column and distillation finger. The solution was refluxed at 130°C for an hour before the Cp-H was collected at -78°C. The cyclopentadiene was stored under nitrogen at -78°C until used. Cyclopentadiene is stable at -78°C for several weeks.

Thallium cyclopentadiene, [60]. In a hood, 450mL of 1.8M potassium hydroxide was added to 30g (59mmoles) thallium sulfate with vigorous stirring in a large Schlenk vessel. Freshly cracked cyclopentadiene (15mL, d = 0.802g/ml, 182mmoles) was added slowly and the solution was stirred vigorously for 15 minutes (See NOTE). After about two minutes, a fluffy white/beige precipitate formed. Upon completion of the reaction, the solution was suction filtered. The precipitate was rinsed with distilled water, washed twice with ethanol and dried under vacuum overnight. The yield was 23.8g of crude product. The crude product was sublimed (0.1torr) at 75°C onto a -10°C cold finger for several hours to yield 23.6g (88mmoles, 83%) of a beige light-sensitive powder.

NOTE: *The product is sensitive to light and the reaction vessel should be covered with aluminum foil.*

Sodium or Potassium metal sand, Na^0 or K^0 . Large chunks of the metal which had been stored in mineral oil were cut into smaller pieces and rinsed with toluene. The pieces were placed in 750mL toluene in a 2000mL round bottom flask with a nitrogen inlet. The flask was equipped with a mercury bubbler and heated with a hot air gun until the metal melted. The magnetic stirrer was turned on and the liquified metal was broken up into small beads. The stirrer was turned off and the metal beads were allowed to cool undisturbed. After the beads had cooled, the toluene was decanted and the metal sand was dried under vacuum. Both metals react with air and moisture and, therefore, were stored in an inert atmosphere dry box until used.

Sodium Cyclopentadiene, NaCp , [61]. CAUTION: *This reaction generates hydrogen gas and should be run in a well ventilated hood.* In a 750mL Schlenk vessel under nitrogen, 107g (4.6moles) of sodium metal (Na^0) was stirred in freshly distilled THF (200mL) as 350mL (281g, 4.3moles) freshly cracked cyclopentadiene was added portionwise. Each addition caused a vigorous exothermic reaction in which hydrogen gas was produced. The temperature was kept near room temperature by cooling with an ice bath. When the additions were complete and the temperature was stable, the reaction was stirred overnight. The following morning the

reaction vessel was flushed with nitrogen for five minutes to remove any H_2 remaining in the flask and the excess sodium metal was removed from the peach colored solution. The solvent was removed under vacuum and the beige powder was dried further by heating to $80^\circ C$ under diffusion pump vacuum (10^{-5} torr) overnight. The beige powder is highly air sensitive and should be handled and stored under nitrogen or in an inert atmosphere box. The yield was 258g (2.9moles, 69%).

Hexaamminecobalt(II) chloride, $[Co(NH_3)_6]Cl_2$, [62].

Method A. Cobalt chloride hexahydrate (100g, 0.42moles) was ground into a fine powder using a mortar and pestle and placed in a 500mL Schlenk vessel. Aqueous ammonia (350mL) was added until the slurry would just stir. An ammonia purge was started and the reaction mixture was heated gently (warm to touch) for several hours during which the reaction mixture went through several color changes. The final color change was from dark blue to pink. When no further change in the pink color was observed, the reaction was stopped and the reaction vessel was closed off and allowed to sit undisturbed overnight. The following morning the solution was decanted away from the peach precipitate which had formed. The precipitate was washed with an ice cold ammonia saturated ethanol solution until the washes were clear. Each time the residue was well stirred, allowed to settle, and the ethanol decanted. The precipitate was then washed

three times with cold ammonia saturated diethyl ether solution. Each time the residue was well stirred and allowed to settle between washes. As much of the ether as possible was decanted and the rest was removed under vacuum (See NOTE). The peach powder is air stable but moisture sensitive, and therefore, it is stored in an inert atmosphere dry box.

NOTE: *The flask should not be warmed. Warming causes a loss of ammonia and the product begins to turn blue (pentaamminecobalt(II)chloride).*

Method B. In a 500mL Schlenk vessel concentrated aqueous ammonia (180mL) was added to 30g (0.01moles) finely crushed $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The solution was stirred under NH_3 with gentle heating until the solid was dissolved (overnight). More aqueous ammonia was added (20mL portions) as needed until the solid just dissolved. The resulting solution was red. The following morning a 1.5 molar excess of potassium chloride was added in 5g portions over 15 minutes, causing a pink solid to precipitate. The precipitate was collected under nitrogen in a jacketed, fritted column by filtration and washed several times with reagent grade methanol to remove the potassium nitrate. The pink crystals were dried under nitrogen purge (See NOTE). The hexaamminecobalt(II) chloride is not air sensitive, but does react with water to form aquo complexes and, thus, it should be stored in an inert atmosphere dry box. The yield was 80-90% with a small

amount of KCl contaminant which does not interfere in any subsequent reactions.

NOTE: *Vacuum causes the product to decompose due to the loss of NH₃.*

Bis-cyclopentadiene cobalt(II), Cobaltacene, Cp₂Co,
[63]. In an inert atmosphere dry box, 1.03g (4.5mmoles) [Co(NH₃)₆]Cl₂ and 0.8g (9mmoles) NaCp were mixed in a 250mL Schlenk vessel. The Schlenk vessel was removed from the dry box and to the solid mixture was added 100mL freshly distilled THF. Immediate gas (NH₃) evolution was observed. The reaction mixture was heated to reflux for 1.5 hours before the solvent was removed under vacuum. The residue was taken into an inert atmosphere dry box and scraped into a sublimation bottom. The residue was sublimed under vacuum (10⁻³ - 10⁻⁵torr) overnight at 100°C into a -5°C jacketed column. The yield was 0.76g (4.2mmoles, 91%) dark purple crystals. This reaction was repeated on a 50g scale of [Co(NH₃)₆]Cl₂ and gave an 80% yield after a second sublimation. Cobaltacene is air and moisture sensitive and should be stored in an inert atmosphere dry box.

NOTE: *When preparing cobaltacene on a large scale, trying to sublime the product too quickly causes the powder to be carried into the jacketed sublimation column and a second sublimation is necessary to obtain pure cobaltacene.*

Cyclopentadiene cobalt bis-ethylene, $\text{CpCo}(\text{C}_2\text{H}_4)_2$,

[64]. **CAUTION:** This reaction involves the use of ethylene gas which is toxic and flammable and should be attempted only in a well ventilated hood. In an inert atmosphere dry box, a 500mL jacketed Schlenk vessel was loaded with 2.8g (15mmoles) of freshly sublimed (see NOTE) and finely crushed cobaltacene and 250mL distilled diethyl ether. The reaction vessel was removed from the dry box and connected to an ethylene gas line. The solution was cooled to -8°C and saturated with ethylene. Potassium metal (0.8g, 21mmoles), which had been chopped up in order to expose as much clean metal surface as possible, was added. The reaction was stirred for 14.5 hours, at which time another addition of potassium metal was made. The reaction was stirred under an ethylene atmosphere overnight. The solution was initially deep red. Upon completion the solution was burnt orange (the color of the desired product) and a grey precipitate (KCp) had formed. Stirring was stopped and the precipitate (KCp) was allowed to settle. The solution was cannulated into a Schlenk vessel under nitrogen at -78°C . All of the solution was cannulated such that a rinse of the precipitate was unnecessary. The solvent was removed under vacuum keeping the solution temperature under 40°C . The orange residue was sublimed at room temperature onto a -10°C cold finger to yield 1.5g (8.3mmoles, 56%) crystalline orange product. The product is temperature sensitive and unstable

in the absence of ethylene due to the lability of the ethylene ligands. It can, however, be stored cold (2°C), under ethylene for several months. ^1H NMR (C_6D_6 , 25°C) δ 4.286 (s, 5 H), 2.53 (m, 4 H), 0.65 (m, 4 H). NOTE: It is important that the cobaltacene is freshly sublimed to avoid side reactions due to impurities which hinder the formation of the bis-ethylene complex.

Pentamethylcyclopentadiene iridium dicarbonyl, $\text{Cp}^*\text{Ir}(\text{CO})_2$, [56,65]. CAUTION: This synthesis involves the use of toxic chemicals ($\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$) and evolves carbon monoxide and should be carried out in a well ventilated fume hood.

Method A. In a 100mL Schlenk vessel in a hood, 0.1g (0.1mmoles) $[\text{Cp}^*\text{IrCl}]_2\text{Cl}_2$, 0.457g (1.2mmoles) diiron nonacarbonyl ($\text{Fe}_2(\text{CO})_9$), and 0.05g (0.5mmoles) of anhydrous sodium carbonate were stirred together in 30mL absolute ethanol. Carbon monoxide was introduced and the dark orange solution was heated to 70°C under a CO atmosphere. The reaction solution color remained dark orange for several hours, but after about 19 hours, the solution had become deep red. The ethanol was removed under vacuum and the residue was sublimed (0.1torr) at 50°C onto a -15°C cold finger to yield 0.059g (0.15mmoles, 62%) of a bright yellow solid.

Method B. A solution of 1.0g (1.2mmoles) $[\text{Cp}^*\text{IrCl}]_2\text{Cl}_2$ and 1g (2mmoles) of triiron dodecacarbonyl ($\text{Fe}_3(\text{CO})_{12}$) in degassed benzene (250mL) was heated to reflux with vigorous stirring in a 500mL Schlenk vessel. After 22 hours, heating was discontinued and the precipitate (decomposed excess $\text{Fe}_3(\text{CO})_{12}$) was removed by suction filtration. The filtrate was a dark yellow color. The solvent was removed from the filtrate under vacuum with loss of some product to the collection reservoir (See NOTE). The residue was sublimed under vacuum (0.1torr) at 52°C onto a -12°C cold finger to yield 0.725g (1.9mmoles, 75%) yellow product. ^1H NMR (C_6D_6 , 25°C) δ 1.779 (s, 15 H); ^1H NMR (CDCl_3 , 25°C) δ 2.186 (s, 15 H); ^1H NMR (THF-d_8 , 25°C) δ 2.169 (s, 15 H); IR (CH_2Cl_2) $\nu(\text{CO})$ 2000 (s), 1925 (s) cm^{-1} ; IR (Hexane) $\nu(\text{CO})$ 2020 (s), 1954 (s) cm^{-1} .

NOTE: The addition of hexane to the benzene solution before solvent removal may prevent the co-distillation of the product with the solvent.

Pentamethylcyclopentadiene cobalt dicarbonyl,
 $\text{Cp}^*\text{Co}(\text{CO})_2$, [66]. **CAUTION:** This reaction evolves carbon monoxide and should be attempted only in a well ventilated fume hood. Dicobalt octacarbonyl (7g, 20mmoles) was dissolved in 250mL freshly distilled methylene chloride in a 500mL Schlenk vessel. The solution was stirred under a nitrogen purge as 6.4mL ($d = 0.87\text{g/mL}$, 5.56g, 41mmoles) of pentamethylcyclopentadiene was added. The deep red-orange solu-

tion was heated to reflux. After six hours the solution was a dark green and there appeared to be no further change in the next 36 hours of heating. The reaction was stopped and the solvent was removed under vacuum. The residue was dissolved in hexane and chromatographed on an anaerobic and anhydrous column (water cooled) to separate the product from the starting material. Two bands were collected. The first orange band was eluted with pure hexane. The second deep green band was eluted with a mixture (1:1) of hexane and methylene chloride. The solvents were removed from both fractions. The residue from the second fraction was recrystallized from hot hexane to give the dinuclear cobalt species, $(\text{Cp}^*\text{Co})_2(\mu\text{-CO})_2$. The residue from the first fraction was sublimed at 40°C onto a -10°C cold finger. The yield of orange crystals $(\text{Cp}^*\text{Co}(\text{CO})_2)$ was 7.25g (70%). The product is air and light sensitive and was stored in a dark container in the dry box. ^1H NMR (C_6D_6 , 25°C) δ 1.908 (s, 15 H); ^1H NMR (CDCl_3 , 25°C) δ 1.591 (s, 15 H); IR (KBr) $\nu(\text{CO})$ 1925 (s), 1990 (s) cm^{-1} ; IR (Hexane) $\nu(\text{CO})$ 1950 (s), 2010 (s) cm^{-1} .

Pentamethylcyclopentadiene rhodium dicarbonyl, $\text{Cp}^*\text{Rh}(\text{CO})_2$, [67]. *CAUTION: This reaction evolves carbon monoxide and should be attempted only in a well ventilated fume hood.* In a hood 1.0g (1.6mmoles) $[\text{Cp}^*\text{RhCl}]_2\text{Cl}_2$ was stirred in 30mL degassed methanol in a 100mL Schlenk vessel under CO until the solution was saturated. The solution was

then heated to reflux for 10 hours during which 0.70g (11mmoles) reagent grade zinc mesh was added in 0.1g portions. The reaction was cooled and the solution was extracted with hexane. The hexane extracts were combined and the hexane removed under vacuum. The residue was sublimed (0.1torr) at 50°C onto a cold finger at -10°C for nine hours to yield 0.775g (2.6mmoles, 81.4%) orange product which was air sensitive and stored in a dry box. ^1H NMR (CDCl_3 , 25°C) δ 2.051 (s, 15 H); ^1H NMR (THF-d_8 , 25°C) δ 2.047 (s, 15 H); IR (KBr) $\nu(\text{CO})$ 2000 (s), 1930 (s) cm^{-1} ; IR (Hexane) $\nu(\text{CO})$ 2022 (s), 1963 (s) cm^{-1} .

Pentamethylcyclopentadienyliridium- μ -dicarbonyl-cyclopentadienylcobalt, $\text{Cp}^*\text{Ir}(\mu\text{-CO})_2\text{CoCp}$, [47]. In an inert atmosphere dry box, 1.02g (2.6mmoles) $\text{Cp}^*\text{Ir}(\text{CO})_2$ was dissolved in THF. The solution was stirred as a solution of 0.23g (1.2mmoles) $\text{CpCo}(\text{C}_2\text{H}_4)_2$ dissolved in THF was added portion-wise. After each addition a slight vacuum was pulled in order to remove ethylene being released in the reaction. The reaction was stirred for ten minutes between additions. Upon completion of the reaction, the THF was removed under vacuum. The reaction vessel was removed from the dry box and the residue was placed on the head of an anaerobic column in methylene chloride. Three bands were collected. The first yellow band was eluted with a mixture (1:1) of hexane and methylene chloride. The solvent was removed under vacuum and the residue was sublimed to give 0.605g

$\text{Cp}^*\text{Ir}(\text{CO})_2$. The second band was eluted with straight methylene chloride and was deep red-violet in color. The solvent was removed under vacuum. The residue was dissolved in hot hexane and cooled slowly to -78°C . The solution was decanted and the crystalline precipitate, which was the desired product, was dried under vacuum. ^1H NMR (C_6D_6 , 25°C) δ 4.67 (s, 5 H), 1.57 (s, 15 H); ^1H NMR (CDCl_3 , 25°C) δ 4.78 (s, 5 H), 1.89 (s, 15 H); ^1H NMR (THF-d_8 , 25°C) δ 4.639 (s, 5 H), 1.879 (s, 15 H); IR (KBr) $\nu(\text{CO})$ 1717 (s) cm^{-1} ; IR (CH_2Cl_2) $\nu(\text{CO})$ 1725 (s) cm^{-1} . The third band was eluted with methylene chloride and ether (99:1). It contained a small amount of polynuclear clusters and was not characterized further.

Di- μ -carbonyl-bis(pentamethylcyclopentadiene)-dicobalt, $(\text{Cp}^*\text{Co})_2(\mu\text{-CO})_2$, [68]. *CAUTION: This reaction evolves carbon monoxide and should be attempted only in a well ventilated fume hood.* In a hood, 5.0g (20mmoles) $\text{Cp}^*\text{Co}(\text{CO})_2$ were dissolved in 300mL freshly distilled toluene and refluxed under nitrogen. The initial solution was dark orange. After four hours the solution had taken on a green color, but not quite that of the expected dinuclear complex, and the Schlenk vessel was coated with metal (mirror-like coating). The reaction mixture was heated for two days, after which the solvent was removed under vacuum and the residue was added to the head of an anaerobic water cooled column in a mixture of hexane and methylene chloride. Two

bands were collected. The first band was orange and was eluted with a mixture (1:1) of hexane and methylene chloride. The solvent was removed and the residue was sublimed to give 2g (8mmoles) $\text{Cp}^*\text{Co}(\text{CO})_2$. The second band was deep green and was eluted with straight methylene chloride. The solvent was removed to yield lavender crystals which were taken into a dry box, dissolved in hot hexane and filtered through a glass frit to remove impurities. The solution was cooled slowly to -26°C . Dark green, almost black, crystals were collected by decanting the solution. The yield was 2.0g (4.5mmoles, 75% based on recovered starting material). ^1H NMR (C_6D_6 , 25°C) δ 1.414 (s); ^1H NMR (Toluene- d_8 , 25°C) δ 1.415 (s); ^1H NMR (THF- d_8 , 25°C) δ 1.444 (s); IR (Hexane) $\nu(\text{CO})$ 1750 cm^{-1} ; IR (Benzene) $\nu(\text{CO})$ 1742 (s) cm^{-1} ; IR (CH_2Cl_2) $\nu(\text{CO})$ 1740 (s) cm^{-1} ; IR (KBr) $\nu(\text{CO})$ 1750 (s) cm^{-1} .

Di- μ -carbonyl-bis(pentamethylcyclopentadiene)-dirhodium, $(\text{Cp}^*\text{Rh})_2(\mu\text{-CO})_2$, [69]. *CAUTION: This reaction evolves carbon monoxide and should be attempted only in a well ventilated fume hood.* In a hood 1.032g (3.5mmoles) $\text{Cp}^*\text{Rh}(\text{CO})_2$ were dissolved in 50mL degassed reagent grade acetone to give a bright orange solution. Solid trimethylamine-N-oxide dihydrate ($(\text{CH}_3)_3\text{NO} \cdot 2\text{H}_2\text{O}$) was added and the reaction was heated to reflux under nitrogen with vigorous stirring. After two hours, the heat was removed and the reaction was cooled. The solvent was removed under vacuum

and the residue was added to the head of an anaerobic column in a mixture of hexane and methylene chloride. Two bands were collected. The first fraction was orange and was eluted with hexane. The solvent was removed and the residue sublimed to give 0.3g (1mmole) $\text{Cp}^*\text{Rh}(\text{CO})_2$. The second band was intense blue and was eluted with a mixture (1:1) of hexane and methylene chloride. The solvent was removed and the microcrystalline residue was recrystallized to give 0.525g (0.9mmoles, 79%) of the desired product. ^1H NMR (C_6D_6 , 25°C) δ 1.509 (s); ^1H NMR (toluene- d_8 , 25°C) δ 1.517 (s); ^1H NMR (THF- d_8 , 25°C) δ 1.638 (s); IR (KBr) $\nu(\text{CO})$ 1717 (s) cm^{-1} ; IR (CH_2Cl_2) $\nu(\text{CO})$ 1717 (s) cm^{-1} ; IR (benzene) $\nu(\text{CO})$ 1732 (s) cm^{-1} . Two other bands were present which were not identified, but their chromatography characteristics indicated that they were probably polynuclear cluster complexes.

Di- μ -carbonyl-bis(pentamethylcyclopentadiene)-diiridium, $(\text{Cp}^*\text{Ir})_2(\mu\text{-CO})_2$, [70]. *CAUTION: This reaction evolves carbon monoxide and should be attempted only in a well ventilated fume hood.* In a hood in a minimum of n-butanol (2mL), 0.15g (0.4mmoles) $\text{Cp}^*\text{Ir}(\text{CO})_2$ was heated to 150°C under nitrogen with vigorous stirring. The oil bath was kept above solvent level so that the desired product would crust out above the solvent and not be washed down by refluxing solvent. The refluxing solvent was yellow due to the $\text{Cp}^*\text{Ir}(\text{CO})_2$. After about three days, the refluxing

solvent was no longer yellow. The reaction was allowed to proceed for another day. When the reaction mixture became clear, the reaction was stopped and the solvent was removed under vacuum. The residue was rinsed with hot hexane to yield 0.028g of the desired product. The hot hexane was filtered through glass wool and cooled to -25°C . The solution was decanted from the crystalline material and the precipitate (0.032g) was rinsed with cold distilled hexane and dried under vacuum. The total yield was 0.06g (0.8mmoles, 43%) dark orange microcrystalline powder. ^1H NMR (C_6D_6 , 25°C) δ 1.578 (s); ^1H NMR (Toluene- d_8 , 25°C) δ 1.599 (s); ^1H NMR (THF- d_8) δ 1.740 (s); IR (KBr) $\nu(\text{CO})$ 1685 (s) cm^{-1} ; IR (FTIR-Toluene) $\nu(\text{CO})$ 1688 (s) cm^{-1} ; IR (CH_2Cl_2) $\nu(\text{CO})$ 1672 (s) cm^{-1} ; IR (Benzene) $\nu(\text{CO})$ 1685 (s) cm^{-1} ; IR (FTIR-Hexane) $\nu(\text{CO})$ 1701 (s) cm^{-1} ; IR (FTIR-THF) $\nu(\text{CO})$ 1692 (s) cm^{-1} .

Di- μ -carbonyl-bis(cyclopentadiene)-dicobalt-pentamethylcyclopentadiene-iridium, $(\eta^5\text{-C}_{10}\text{H}_{15})\text{Ir}(\mu\text{-CO})_2\text{Co}_2(\eta^5\text{-C}_5\text{H}_5)_2$, [47]. Method A. In an inert atmosphere dry box, 0.15g (0.29mmoles) $\text{Cp}^*\text{Ir}(\mu\text{-CO})_2\text{CoCp}$ was dissolved in a mixture (60:20) of distilled ether and hexane to give a deep red-violet solution. An excess (0.098g, 0.54mmoles) of $\text{CpCo}(\text{C}_2\text{H}_4)_2$ was dissolved in 10mL hexane and added in small portions to the solution of the dinuclear complex. After each addition, a slight vacuum was pulled to remove the ethylene released in the reaction. The reaction was stirred

five minutes between additions. The final solution color was burnt orange. After the reaction was complete, the solvent volume was reduced to about 40mL. A microcrystalline precipitate formed. The stirring bar was removed and the solution was decanted. The precipitate was rinsed with a small amount of hexane and dried under vacuum. The total yield was 0.175g (0.27mmoles, 94%) dark orange microcrystalline product.

Method B. In an inert atmosphere dry box, 0.699g (1.8mmoles) $\text{Cp}^*\text{Ir}(\text{CO})_2$ was dissolved in 30mL hexane and 5mL ether and stirred as a solution of 0.65g (3.6mmoles) $\text{CpCo}(\text{C}_2\text{H}_4)_2$ in 10mL hexane was added portionwise. A slight vacuum was pulled between additions to remove ethylene being liberated in the reaction. After the additions were complete, the solvent was concentrated to 30mL. A microcrystalline precipitate formed. The solvent was decanted from the precipitate. The precipitate was rinsed with hexane and dried under vacuum to yield 0.949g (83%) of the desired product. The decantate and precipitate rinse were combined, concentrated to 20mL, and cooled to -25°C overnight. A microcrystalline precipitate formed and was collected by decanting the solvent and drying under vacuum. The second precipitate was slightly impure based on its analysis by ^1H NMR. ^1H NMR (THF-d_8 , 25°C) δ -22.94 (s, 15 H), -45.34 (s, 10 H); IR (KBr) $\nu(\text{CO})$ 1688 (s) cm^{-1} ; IR (Benzene) $\nu(\text{CO})$ 1710 (s) cm^{-1} .

Di- μ -carbonyl-bis(cyclopentadienide)-dicobalt-penta-methylcyclopentadienide-cobalt, $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\mu\text{-CO})_2\text{Co}_2(\eta^5\text{-C}_5\text{H}_5)_2$, Complex 1. In an inert atmosphere dry box, 0.313g (1.7mmoles) $\text{CpCo}(\text{C}_2\text{H}_4)_2$ was dissolved in a mixture of 30mL hexane and 10mL ether. This orange solution was stirred vigorously as a solution of 0.215g (0.86mmoles) $\text{Cp}^*\text{Co}(\text{CO})_2$ in 5mL hexane was added portionwise. A slight vacuum was pulled after each addition to remove ethylene liberated in the reaction. The reaction was stirred 15 minutes following the addition of the final portion. The resulting dark orange solution was concentrated to 25mL. The stirring was stopped and a microcrystalline precipitate settled. The solution was decanted away from the precipitate and the precipitate was dried under vacuum. The product was identified as $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\mu\text{-CO})_2\text{Co}_2(\eta^5\text{-C}_5\text{H}_5)_2$ and was pure based on its analysis by ^1H NMR. The yield was 0.400g (94%) microcrystalline precipitate. In order to get single crystals for a solid state X-ray crystal structure, the microcrystalline product was dissolved in hot hexane and cooled to room temperature over several hours. The recrystallization solution was then placed in the refrigerator (2°C) overnight and then in the deep freezer (-25°C) over a second night. Single crystals were recovered by decanting the solution away from the crystals and drying them under vacuum. Separate samples for X-ray and elemental analysis were sealed under vacuum in Pyrex ampules. ^1H NMR

(C₆D₆, 24°C) δ -2.24 (s, 15 H), -11.25 (s, 10 H); ¹H NMR (Toluene-d₈, 23°C) δ -2.14 (s, 15 H), -11.051 (s, 10 H); ¹H NMR (THF-d₈, 24°C) δ -2.108 (s, 15 H), -11.443 (s, 10 H); IR (FTIR-KBr) ν (CO) 1699 (s) cm⁻¹; IR (THF) ν (CO) 1707 (s) cm⁻¹; IR (Hexane) ν (CO) 1695 (s) cm⁻¹; IR (CH₂Cl₂) ν (CO) 1688 (s) cm⁻¹; IR (Benzene) ν (CO) 1702 (s) cm⁻¹. Elemental analysis calculated for C₂₂H₂₅Co₃O₂ (498.24): C, 53.05, H, 5.06. Found: C, 52.99, H, 5.06.

Di- μ -carbonyl-bis(cyclopentadiene)-dicobalt-pentamethylcyclopentadiene-rhodium, (η^5 -C₅Me₅)Rh(μ -CO)₂Co₂(η^5 -C₅H₅)₂, Complex 2. In an inert atmosphere box, 0.338g (1.88mmoles) CpCo(C₂H₄)₂ was dissolved in a mixture of 40mL hexane and 5mL ether. To this orange solution was added 0.305g (1.04mmoles) Cp^{*}Rh(CO)₂ in 5mL hexane. After each addition a slight vacuum was pulled to remove the ethylene being released in the reaction. The reaction mixture turned olive green. When the reaction was complete, the solvent volume was reduced to 30mL. The stirring bar was removed and the microcrystalline precipitate settled. The solution was decanted and the precipitate was dried under vacuum. The yield was 0.520g (93%) product identified by ¹H NMR as (η^5 -C₅Me₅)Rh(μ -CO)₂Co₂(η^5 -C₅H₅)₂. ¹H NMR (C₆D₆, 24°C) δ 3.61 (s, 10 H), 0.309 (s, 15 H); ¹H NMR (Toluene-d₈, 23°C) δ 3.704 (s, 10 H), 0.434 (s, 15 H); ¹H NMR (THF-d₈, 25°C) δ 3.673 (s, 10 H), 0.757 (s, 15 H); IR (FTIR-KBr) ν (CO) 1701 (s) cm⁻¹; IR (THF) ν (CO) 1705 (s) cm⁻¹; IR (CH₂Cl₂) ν (CO)

1675 (s) cm^{-1} ; IR (Benzene) $\nu(\text{CO})$ 1702 (s) cm^{-1} . Elemental analysis calculated for $\text{C}_{22}\text{H}_{25}\text{Co}_2\text{O}_2\text{Rh}$ (542.21): C, 48.73, H, 4.65. Found: C, 48.73, H, 4.77.

Di- μ -carbonyl-bis(pentamethylcyclopentadiene)-dicobalt-cyclopentadiene-cobalt, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Co}_2(\mu\text{-CO})_2\text{Co}(\eta^5\text{-C}_5\text{H}_5)$, Complex 3. In an inert atmosphere dry box, 0.20g (0.45mmoles) $(\text{Cp}^*\text{Co})_2(\mu\text{-CO})_2$ was dissolved in a mixture of 25mL hexane and 5mL ether to give a deep green solution. A solution of two equivalents (0.162g, 0.9mmoles) $\text{CpCo}(\text{C}_2\text{H}_4)_2$ in 5mL hexane was added portionwise until there was no sign of the dinuclear starting material remaining. A slight vacuum was pulled following each addition to remove the ethylene being liberated during the reaction. The reaction mixture was yellow-brown. The solvent was removed under vacuum and a ^1H NMR was taken which indicated that the desired product was slightly impure. The reaction residue was dissolved in hot hexane and filtered to remove any insoluble impurities. The recrystallization solution was then cooled to room temperature in the dry box. After several hours at room temperature, the solution was cooled to 2°C overnight. The following morning there were a few crystals present and the solution was cooled to -25°C overnight. The solution was decanted and the crystals were dried under vacuum. Separate samples for X-ray and elemental analysis were sealed under vacuum in Pyrex ampules. The yield was 0.240g (94%) $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Co}_2(\mu\text{-$

CO)₂Co(η^5 -C₅H₅). ¹H NMR (C₆D₆, 24°C) δ -7.179 (s, 30 H), -55.42 (s, 5 H); ¹H NMR (Toluene-d₈, 22°C) δ -7.28 (s, 30 H), -56.12 (s, 5 H); ¹H NMR (THF-d₈, 25°C) δ -6.998 (s, 30 H), -55.596 (s, 5 H); IR (FTIR-KBr) ν (CO) 1703 (w), 1686 (s) cm⁻¹; IR (THF) ν (CO) 1698 (s) cm⁻¹; IR (CH₂Cl₂) ν (CO) 1690 (s) cm⁻¹. Elemental analysis calculated for C₂₇H₃₅Co₃O₂ (568.37): C, 57.06, H, 6.21. Found: C, 56.83, H, 6.33.

Di- μ -carbonyl-bis(pentamethylcyclopentadiene)-dirhodium-cyclopentadiene-cobalt, (η^5 -C₅Me₅)₂Rh₂(μ -CO)₂-Co(η^5 -C₅H₅), Complex 4. In an inert atmosphere dry box, 0.30g (0.56mmoles) (Cp^{*}Rh)₂(μ -CO)₂ was dissolved in 20mL ether to give a deep blue solution. An orange solution of 0.10g (0.56mmoles) CpCo(C₂H₄)₂ in 10mL hexane was added portionwise. After each addition, a slight vacuum was pulled to remove the ethylene being liberated in the reaction. When the reaction was complete, the black cherry red solution was concentrated to 10mL. A microcrystalline precipitate formed. The solution was decanted and the precipitate was washed with a small amount of hexane and dried under vacuum. The yield was 0.28g (0.42mmoles, 76%) (η^5 -C₅Me₅)₂Rh₂(μ -CO)₂Co(η^5 -C₅H₅). The precipitate was slightly impure and was recrystallized from hexane (See NOTE). Separate samples for X-ray and elemental analysis were sealed under vacuum in Pyrex ampules. ¹H NMR (C₆D₆, 24°C) δ -10.825 (s, 30 H), -41.932 (s, 5 H); ¹H NMR (Toluene-d₈, 23°C) δ -11.343 (s, 30 H), -44.067 (s, 5 H); ¹H

NMR (THF- d_8 , 25°C) δ -10.89 (s, 30 H), -42.71 (s, 5 H); IR (FTIR-KBr) ν (CO) 1690 (s) cm^{-1} ; IR (THF) ν (CO) 1692 (s) cm^{-1} ; IR (CH_2Cl_2) ν (CO) 1680 (s) cm^{-1} ; IR (Benzene) ν (CO) 1688 (s) cm^{-1} . Elemental analysis calculated for $\text{C}_{27}\text{H}_{35}\text{CoO}_2\text{Rh}_2$ (656.32): C, 49.41, H, 5.37. Found: C, 49.13, H, 5.41.

NOTE: Heating may cause decomposition.

Di- μ -carbonyl-bis(pentamethylcyclopentadiene)-diiridium-cyclopentadiene-cobalt, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2(\mu\text{-CO})_2\text{-Co}(\eta^5\text{-C}_5\text{H}_5)$, Complex 5. In an inert atmosphere dry box, 0.06g (0.08mmoles) $(\text{Cp}^*\text{Ir})_2(\mu\text{-CO})_2$ was dissolved in 10mL ether to give a dark rust colored solution. A solution of 0.032g (0.2mmoles) $\text{CpCo}(\text{C}_2\text{H}_4)_2$ in 10mL hexane was added portionwise. A slight vacuum was pulled after each addition to remove the ethylene being liberated in the reaction. The resulting solution was dark yellow-brown. The solvent was concentrated to 10mL, but no precipitate formed. All of the solvent was removed and a ^1H NMR spectrum was taken of the residue which indicated that the desired product was in hand but was contaminated with excess $\text{CpCo}(\text{C}_2\text{H}_4)_2$. The residue was dissolved in a minimum of hexane (5mL) and cooled to -25°C overnight. The solution was decanted and the crystalline precipitate was dried under vacuum. The product was identified as $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2(\mu\text{-CO})_2\text{Co}(\eta^5\text{-C}_5\text{H}_5)$. ^1H NMR (C_6D_6 , 23°C) δ -23.023 (s, 30 H), -72.491 (s, 5 H); ^1H NMR (Toluene- d_8 , 24°C) δ -23.986 (s, 30 H), -72.701 (s, 5 H);

^1H NMR (THF- d_8 , 22°C) δ -24.086 (s, 30 H), -73.121 (s, 5 H); IR (KBr) $\nu(\text{CO})$ 1900 (m), 1685 (s) cm^{-1} ; IR (CH_2Cl_2) $\nu(\text{CO})$ 1665 (s) cm^{-1} ; IR (FTIR-Toluene, 25°C) $\nu(\text{CO})$ 1902 (s), 1686 (s) cm^{-1} ; IR (FTIR-Toluene, -78°C) $\nu(\text{CO})$ 1902 (s), 1686 (s) cm^{-1} ; IR (FTIR-THF) $\nu(\text{CO})$ 1900 (s), 1680 (s) cm^{-1} ; IR (FTIR-Hexane) $\nu(\text{CO})$ 1910 (s), 1690 (s) cm^{-1} . Elemental analysis calculated for $\text{C}_{27}\text{H}_{35}\text{CoIr}_2\text{O}_2$ (834.94): C, 38.84, H, 4.22. Found: C, 39.12, H, 4.35.

Reaction of Complex 1 with CO. *CAUTION: This reaction involves the use of carbon monoxide and should be attempted only in a well ventilated fume hood.* In a hood in a 150mL Schlenk vessel, Complex 1 was dissolved in THF (75mL) to give a dark yellow-brown solution. A slight vacuum was pulled and the solution was cooled to -78°C (dry ice/acetone bath) before carbon monoxide (5psi) was introduced. The reaction was stirred for 10 minutes at -78°C under CO and then warmed to room temperature under a CO atmosphere. There was no noticeable change in the reaction mixture. The solvent was removed and an anaerobic column was prepared in hexane. The major product was eluted with methylene chloride. The solvent was removed and the residue was recrystallized from hexane to give rhombic shaped platelets identified as the tricarbonyl Complex 6, $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\mu\text{-CO})_2(\mu_3\text{-CO})\text{Co}_2(\eta^5\text{-C}_5\text{H}_5)_2$. ^1H NMR (C_6D_6 , 25°C) δ 4.619 (s, 10 H), 1.390 (s, 15 H); IR (KBr) $\nu(\text{CO})$ 1800 (s), 1760 (m), 1650 (s) cm^{-1} ; IR (CH_2Cl_2) $\nu(\text{CO})$ 1828

(s), 1780 (m), 1670 (s) cm^{-1} . Elemental analysis calculated for $\text{C}_{23}\text{H}_{25}\text{Co}_3\text{O}_3$ (526.25): C, 52.49, H, 4.79. Found: C, 52.58, H, 4.72.

Reaction of Complex 2 with CO. CAUTION: *This reaction involves the use of carbon monoxide and should be attempted only in a well ventilated fume hood.* In a hood in a 100mL Schlenk vessel, Complex 2 (0.130g, 0.24mmoles) was dissolved in THF (30mL) under nitrogen to give an olive green solution. A slight vacuum was pulled and the temperature was lowered to -78°C (dry ice/acetone bath). Carbon monoxide (5psi) was introduced, and the mixture was stirred for 15 minutes. After 15 minutes the solution was yellow-brown. The dry ice/acetone bath was removed and the reaction was warmed to room temperature under a CO atmosphere. There was no further change in the reaction mixture. The solvent was removed. An anaerobic column was prepared in hexane. Two fractions were collected. The first fraction was blue and eluted with a 40/60 mixture of hexane and methylene chloride. The compound appeared to decompose upon removal of the solvent. The second fraction was the major fraction and was eluted with methylene chloride to give a dark yellow-brown solution. The solvent was removed. The residue was taken up in hexane and cooled to -25°C overnight. The crystals were collected by pouring off the mother liquor and drying under vacuum. The product was identified as the tricarbonyl Complex 7, $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-}$

$\text{CO})_2(\mu_3\text{-CO})\text{Co}_2(\eta^5\text{-C}_5\text{H}_5)_2$. ^1H NMR (C_6D_6) δ 4.619 (s, 10 H), 1.559 (s, 15 H); IR (KBr) $\nu(\text{CO})$ 1800 (s), 1760 (m), 1650 (s) cm^{-1} ; IR (CH_2Cl_2) $\nu(\text{CO})$ 1828 (s), 1780 (m), 1670 (s) cm^{-1} . Elemental analysis for $\text{C}_{23}\text{H}_{25}\text{Co}_2\text{O}_3\text{Rh}$ (570.22): C, 48.45, H, 4.42. Found: C, 48.69, H, 4.51.

Reaction of Complex 3 with CO. *CAUTION: This reaction involves the use of carbon monoxide and should be attempted only in a well ventilated fume hood.* In a hood in a 150mL Schlenk vessel, Complex 3 was dissolved in THF (100mL) to give a dark yellow-brown solution. A slight vacuum was pulled and the temperature was lowered to -78°C (dry ice/acetone bath). Carbon monoxide (5psi) was introduced and the reaction was stirred for 10 minutes. After just two minutes, the reaction mixture had taken on a greenish tint. After 10 minutes, the dry ice/acetone bath was removed and the reaction was warmed to room temperature under a CO atmosphere. The solvent was removed and an anaerobic column was prepared in hexane. Two fractions were collected. The first fraction was green and was eluted with a 50/50 mixture of hexane and methylene chloride. The product was identified by NMR as the dinuclear cobalt complex, $\text{Cp}^*\text{Co}(\mu\text{-CO})_2\text{CoCp}^*$. The second fraction was greenish yellow and was eluted with methylene chloride. The solvent was removed and the residue was recrystallized from hexane. The needle-like crystals were identified as the tricarbonyl Complex 8, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Co}_2(\mu\text{-CO})_2(\mu_3\text{-CO})\text{Co}(\eta^5\text{-$

C₅H₅). Elemental analysis calculated for C₂₈H₃₅Co₃O₃ (596.38): C, 56.39, H, 5.92. Found: C, 56.42, H, 5.76.

Reaction of Complex 4 with CO. CAUTION: *This reaction involves the use of carbon monoxide and should be attempted only in a well ventilated fume hood.* In a hood in a 100mL Schlenk vessel, Complex 4 (0.150g, 0.23mmoles) was dissolved in THF (30mL) to give a reddish brown solution. A slight vacuum was pulled and the temperature was lowered to -78°C (dry ice/acetone bath). Carbon monoxide (5psi) was introduced. The reaction mixture turned a dark yellow-brown almost immediately. The reaction was stirred for 15 minutes and then warmed to room temperature under a CO atmosphere. The solvent was removed and the residue was placed at the head of an anaerobic column prepared in hexane. Two fractions were collected. The first fraction was deep blue and was eluted with a 50/50 mixture of hexane and methylene chloride and was identified as the dinuclear rhodium complex, Cp^{*}Rh(μ-CO)₂RhCp^{*}. The second fraction was yellow-brown and was eluted with methylene chloride. The solvent was removed and the residue was recrystallized from warm hexane. The rhombic crystals were identified as the tricarbonyl Complex 9, (η⁵-C₅Me₅)₂Rh₂(μ-CO)₂(μ₃-CO)Co(η⁵-C₅H₅). Elemental analysis calculated for C₂₈H₃₅CoO₃Rh₂ (684.33): C, 49.14, H, 5.15. Found: C, 48.32, H, 5.16.

Reaction of Complex 5 with CO. *CAUTION: This reaction evolves carbon monoxide and should be attempted only in a well ventilated fume hood.* In a 100mL Schlenk vessel, Complex 5 (0.020g, 0.02mmoles) was dissolved in THF (30mL) to give a yellow-brown solution. A slight vacuum was pulled and the temperature was lowered to -78°C (dry ice/acetone bath). Carbon monoxide (5 psi) was introduced and the solution turned orange-brown. The reaction was stirred for 15 minutes and the dry ice/acetone bath was removed. The reaction was warmed to room temperature under a CO atmosphere. The solvent was removed and the residue was recrystallized from hexane. The product(s) has not yet been identified but spectroscopic data indicate a tricarbonyl complex, which at this time is labeled as Complex 10, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2(\mu\text{-CO})_2(\mu_3\text{-CO})\text{Co}(\eta^5\text{-C}_5\text{H}_5)$. Elemental analysis calculated for $\text{C}_{28}\text{H}_{35}\text{CoIr}_2\text{O}_3$ (862.95): C, 38.97, H, 4.09. Found: C, 39.60, H, 4.07.

Reaction of Complex 3 with 4,4'-dimethyldiazo-benzophenone. In a 100mL Schlenk vessel, Complex 3 (0.207g, 0.36mmoles) was dissolved in THF (30mL) to give a yellow-brown solution. The solution was cooled to -78°C under nitrogen and 0.090g (0.41mmoles) 4,4'-dimethyldiazobenzophenone was added in crystalline form. The reaction was stirred 15 minutes at -78°C . No apparent reaction occurred. The temperature was raised to 0°C . After five minutes, the solution had turned green. After 20 minutes, the reaction

was warmed to room temperature. The solvent was removed and the residue was placed on the head of an anaerobic column prepared in hexane. Two bands were collected. The first band was the major product. It was deep green and was eluted with a 50/50 mixture of hexane and methylene chloride. The product was identified as the dinuclear cobalt complex, $\text{Cp}^*\text{Co}(\mu\text{-CO})_2\text{CoCp}^*$. The second fraction was yellow-brown and was eluted with methylene chloride. The solvent was removed and a ^1H NMR was taken [(C_6D_6) δ 7.75 (d, 8 H), 6.88 (d, 8 H), 4.82 (s, 5 H), 4.26 (s, 20 H), 2.005 (s, 12 H), 1.447 (s, 15 H)]. Based on the NMR it was determined that three products were collected. The shifts at 7.75, 6.88, and 2.005ppm are due to the presence of bishydrazone. The signals at 4.82 and 1.447ppm are probably from the same product and the signal at 4.26ppm arises from a third product. Due to the lack of material, identification was not possible. These products were formed in less than five percent yield.

Reaction of Complex 4 with 4,4'-dimethyldiazobenzophenone. In the inert atmosphere box, Complex 4 (0.051g, 0.08mmoles) was dissolved in THF (40mL). 4,4'-dimethyldiazobenzophenone (0.020g, 0.09mmoles) was dissolved in THF (5mL). The solution of 4,4'-dimethyldiazobenzophenone was added to the deep black cherry red solution of the trinuclear complex. Upon introduction of vacuum, the solution turned deep blue. The reaction mixture was stirred

for five minutes at room temperature and the solvent was removed. An anaerobic column was prepared in hexane and the residue was placed on the head in hexane and a trace of methylene chloride. Two fractions were collected. The major fraction was deep blue and eluted with a 50/50 mixture of hexane and methylene chloride. It was identified as the dinuclear rhodium complex, $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$. The second fraction was very minor and could not be identified due to a lack of material.

Reaction of Complex 1 with 4,4'-dimethyldiazobenzophenone. In the inert atmosphere box, Complex 1 (0.302g, 0.61mmoles) was dissolved in THF (50mL) to give a yellow-brown solution. 4,4'-dimethyldiazobenzophenone (0.150g, 0.68mmoles) was crushed and added in solid form to the solution of the trinuclear complex. The solution immediately turned olive green. A slight vacuum was pulled, and the solution was stirred for 15 minutes. The solvent was removed and the residue was placed at the head of an anaerobic column prepared in hexane. Three major fractions were collected. The first was purple and eluted with a 75/25 mixture of hexane and methylene chloride. ^1H NMR (C_6D_6) δ 6.917 (d, AR-H), 6.618 (d, AR-H), 4.065 (s, Cp-H), 2.172 (s, AR- CH_3), 1.123 (s, $\text{Cp}^*\text{-H}$); IR (KBr) $\nu(\text{CO})$ 1780 (cm^{-1}). This product was identified as the dinuclear species $\text{Cp}^*\text{Co}(\mu\text{-CO})(\mu\text{-di-}p\text{-tolyl})\text{CoCp}$. Elemental analysis calculated for $\text{C}_{31}\text{H}_{34}\text{Co}_2\text{O}$ (540): C, 68.89, H, 6.34. Found:

C, 68.58, H, 6.36. The second major fraction was dark yellow-brown and was eluted with methylene chloride. The residue was recrystallized from hot hexane. Two crystalline products were separated. One was identified as bishydrazone. The other was collected in the form of rhombic platlets. ^1H NMR (C_6D_6) δ 4.616 (s, 10 H), 1.392 (s, 15 H); IR (KBr) $\nu(\text{CO})$ 1830 (s), 1782 (m), 1682 (b) cm^{-1} . Based on the spectroscopic data the product was identified as the carbonyl adduct of Complex 1. The third major fraction was yellow-brown and was eluted with a 99/1 mixture of hexane and THF. The solvent was removed and the product was recrystallized from hot hexane. ^1H NMR (C_6D_6) δ 8.01 (d, AR-H), 7.59 (d, AR-H), 7.024 (m, overlapping doublets, AR-H), 4.330 (s, Cp-H), 2.117 (s, AR- CH_3), 1.706 (s, Cp * -H); IR (KBr) $\nu(\text{CO})$ 1675 (b) cm^{-1} ; MS 692 parent ion. Based on the spectroscopic data this product was identified as a triply bridging diazoalkane trinuclear cluster complex. Elemental analysis calculated for $\text{C}_{36}\text{H}_{39}\text{Co}_3\text{N}_2\text{O}$ (692): C, 62.43, H, 5.60, N, 4.05. Found: C, 61.63, H, 5.60, N, 4.0.

Reaction of Complex 2 with 4,4'-dimethyldiazobenzophenone. In the inert atmosphere box, Complex 2 (0.349g, 0.64mmoles) was dissolved in THF (40mL) to give a yellow-green solution. 4,4'-dimethyldiazobenzophenone (0.158g, 0.71mmoles) was crushed and added as a solid to the solution of the trinuclear complex. There was a slight foaming action upon addition of the diazoalkane. A slight vacuum

was pulled and the reaction was stirred for 10 minutes. During the course of the reaction, the solution turned a dark green-brown color. The solvent was removed and the residue was placed on the head of an anaerobic column prepared in hexane. One minor and three major products were collected. The first fraction was minor. It was violet red in color and was eluted with a 50/50 mixture of hexane and methylene chloride. The solvent was removed. ^1H NMR (C_6D_6) δ 6.864 (d, AR-H), 6.690 (d, AR-H), 3.997 (s, Cp-H), 2.191 (s, AR- CH_3), 1.218 (s, $\text{Cp}^*\text{-H}$). Further identification was not possible due to a lack of material. The second fraction was intense blue and eluted with an increase in methylene chloride. The proton NMR showed four signals: 4.695, 4.25, 1.499, and 1.229ppm. The signal at 4.25ppm was due to $\text{CpCo}(\mu\text{-CO})_2\text{CoCp}$. The signal at 1.499ppm was due to $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$. Based on the relative integrations of the two remaining signals and the other products present, the signals at 4.695 and 1.229ppm were assigned to the dinuclear species $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{CoCp}$ which has not been described in the literature. All attempts to separate the three products resulted in the isolation of only the rhodium dimer. The third fraction was green-brown and eluted with methylene chloride. It was identified by NMR as unreacted trinuclear complex. The fourth fraction was green and streaked down the column. It was eluted with a 99/1 mixture of hexane and THF. The solvent was removed and the residue was

recrystallized from hot hexane. ^1H NMR (C_6D_6) δ 7.753 (d, AR-H), 7.418 (d, AR-H), 6.968 (d, AR-H), 6.883 (d, AR-H), 4.624 (s, Cp-H), 2.052 (s, AR- CH_3), 2.008 (s, AR- CH_3), 1.564 (s, Cp*-H). Further characterization and identification were not possible due to a lack of material.

Olefin-like exchange reactions. All reactions were conducted in flame sealed NMR tubes. Deuterated NMR solvents were vacuum transferred into the NMR tube. The solvents were dried over Na/K alloy. All reaction mixtures were kept frozen at -196°C (liquid nitrogen) until immediately before the NMR tube was placed into the Nicolet NT-200 FT-NMR spectrometer. The spectrometer had already been shimmed using a different NMR tube and sample which contained similar complexes. The parameters for the experiment were also already set. Qualitative kinetic studies were obtained using the KINET program. The first spectrum in each experiment was taken in less than 5 minutes after the solvent was thawed and the KINET program was initiated. All reactions were run at ambient temperature (22°C). No attempts were made to obtain quantitative data from these reaction.

CHAPTER III

SYNTHESIS, CHARACTERIZATION, AND STRUCTURE

Introduction

The synthesis, characterization and X-ray crystal structure of the first known trinuclear complex in this series, $(\eta^5\text{-C}_{10}\text{H}_{15})\text{Ir}(\mu\text{-CO})_2(\text{Co}(\eta^5\text{-C}_5\text{H}_5))_2$ denoted $^*\text{IrCo}_2$ [47,48], provides the starting point for the research involving two types of unsaturated trinuclear complexes. These complexes are denoted as Complexes 1-5 as defined below:

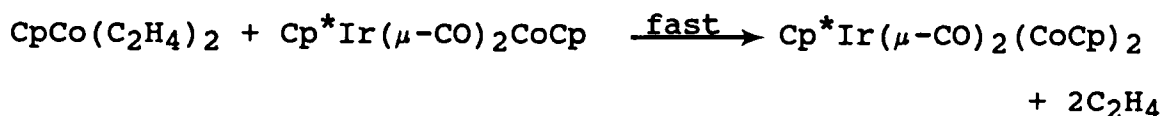
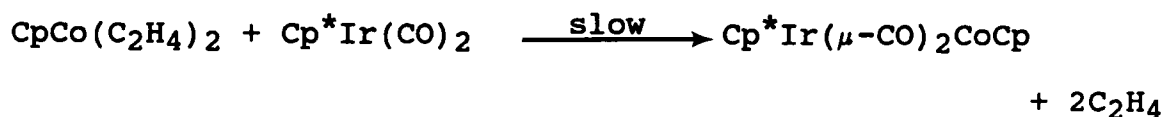
Complex <u>1</u>	$\text{Cp}^*\text{Co}(\mu_2\text{-CO})_2(\text{CoCp})_2$	$^*\text{CoCo}_2$
Complex <u>2</u>	$\text{Cp}^*\text{Rh}(\mu_2\text{-CO})_2(\text{CoCp})_2$	$^*\text{RhCo}_2$
Complex <u>3</u>	$(\text{Cp}^*\text{Co})_2(\mu_2\text{-CO})_2\text{CoCp}$	$^*\text{Co}_2\text{Co}$
Complex <u>4</u>	$(\text{Cp}^*\text{Rh})_2(\mu_3\text{-CO})_2\text{CoCp}$	$^*\text{Rh}_2\text{Co}$
Complex <u>5</u>	$(\text{Cp}^*\text{Ir})_2(\mu_2\text{-CO})_2\text{CoCp}$	$^*\text{Ir}_2\text{Co}$

Synthesis

An important building block to this series of complexes is cyclopentadienidecobalt bis-ethylene, $\text{CpCo}(\text{C}_2\text{H}_4)_2$ [64]. The lability of the ethylene ligands allows the bis-ethylene complex to function as a ready source of a "CpCo" fragment, essential to the synthesis of the trinuclear Complexes 1-5.

The first example within this series is the model $^*\text{IrCo}_2$, $^*\text{MCo}_2$. The synthesis of $^*\text{IrCo}_2$ may be broken down into two steps. First, the addition of a "CpCo" fragment to $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$ to form the dinuclear complex $^*\text{IrCo}$, which can be isolated in near quantitative yield, and second, the

addition of a second "CpCo" fragment to the dinuclear complex $^*\text{IrCo}$ to form the trinuclear complex $^*\text{IrCo}_2$ [47,48]. These steps are outlined below. $^*\text{IrCo}_2$ may also be synthesized directly by the addition of two equivalents of the bis-ethylene complex to the mononuclear dicarbonyl in one step.



This two-step mechanism should provide the basis for the synthesis of two new trinuclear species. The addition of the analogous cobalt and rhodium mononuclear dicarbonyl complexes to the bis-ethylene complex is expected to result in the formation of two new dinuclear species which, when reacted further with the bis-ethylene complex, will yield two new trinuclear clusters. However, the addition of the bis-ethylene complex to the $\text{Cp}^*\text{M}(\text{CO})_2$ ($\text{M} = \text{Rh}$ or Co) does not result in the isolation of the expected dinuclear complex $^*\text{MCo}$. Surprisingly, the dinuclear complex which is isolated is the homometal analogue, $(\text{Cp}^*\text{M})_2(\mu\text{-CO})_2$.

A possible explanation for these observations is that the "mixed" dinuclear species $^*MCo$ reacts with itself to form two different homodinuclear complexes, $(CpCo)_2(\mu-CO)_2$ [49] and $(Cp^*M)_2(\mu-CO)_2$ [68,69] as shown in Figure 2. This metathesis type reaction is the reverse of that described by Theopold and Bergman[71]. It should be noted, however, that Theopold and Bergman worked only with cobalt, not mixed metal systems, and also, that these workers used cyclopentadienide and methylcyclopentadienide ligands instead of the pentamethylcyclopentadiene ligand. This metathesis-type reaction does not appear to occur in systems containing only Cp^* ligands probably due to steric factors.

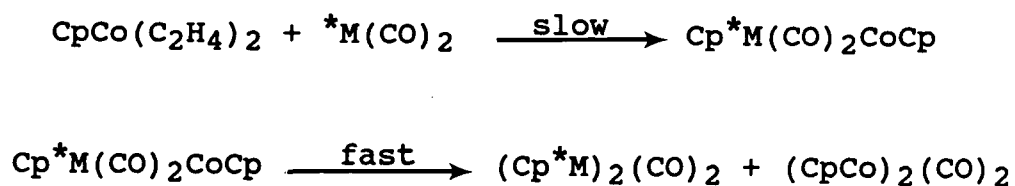


Figure 2. Mixed dinuclear formation and metathesis reactions.

The success of the two-step synthetic mechanism in yielding the trinuclear Complexes 1 and 2 relies on the relative rates of each step. In the synthetic scheme shown earlier, the addition of the bis-ethylene complex to the $^*M(CO)_2$ is relatively slow, whereas the addition of the bis-ethylene complex to the dinuclear species is fast. As shown in Figure 2, the reaction of the "mixed" dinuclear with

itself is also fast[47,48]. In order to minimize the metathesis-type reaction and favor the addition of the bis-ethylene complex to the dinuclear species, the two-step synthetic scheme is reduced to a one-step scheme in which the isolation of the dinuclear intermediate is circumvented by the inverse addition of the $^*M(CO)_2$ to at least two equivalents of the bis-ethylene complex in dilute solution. In this manner, the rhodium and cobalt trinuclear complexes, $^*MCo_2$, can be isolated in near quantitative yield. The fact that the desired trinuclear complexes are isolated is consistent with the formation of a $^*MCo$ intermediate which reacts further with the bis-ethylene complex before it can undergo a bimolecular metathesis reaction.

The second type of trinuclear complex in this series is formed by the addition of a "CpCo" fragment to a preformed $diCp^*$ -homodinuclear dicarbonyl complex, $(Cp^*M)_2(\mu-CO)_2$ ($M = Ir, Rh, \text{ or } Co$). The homonuclear dicarbonyl complexes are synthesized by decarbonylating the mononuclear dicarbonyl species[66-68]. The trinuclear Complex $^*Co_2Co$, 3 is isolated in near quantitative yield as a microcrystalline solid. The rhodium and iridium analogues, $^*Rh_2Co$, 4 and $^*Ir_2Co$, 5 are also produced quantitatively in the reaction, but lower yields of isolated material are obtained due to their solubility in the reaction and recrystallization solvents and the sensitivity of these complexes toward oxygen and moisture.

Characterization

These complexes have been characterized using IR and ^1H NMR spectroscopy.

Infrared Spectroscopy. The infrared spectra of these complexes are relatively featureless, showing only carbonyl ($\text{C}=\text{O}$) and aromatic and aliphatic $\text{C}-\text{H}$ stretching frequencies. Important information can be gained from the carbonyl stretching frequency alone. Metals with suitable $d-\pi$ orbitals back-bond to the carbonyl ligand, placing electron density into the CO antibonding orbital and reducing the CO bond order. Although these particular back-bonding interactions do not cause significant change in the CO bond length[72], there is a strong correlation of the carbonyl stretching frequency with the amount of $\text{M} (d-\pi)$ to $\text{L} (\pi^*)$ back-bonding. This correlation may be attributed to the following three factors which are illustrated by the transition metal complexes found in Table 1.

1) The greater the number of metals interacting with the carbonyl ligand, the greater the back-bonding and thus, the lower the carbonyl stretching frequency in the infrared. Typically, for metal complexes containing terminal carbonyl ligands (CO ligands which interact with only one metal atom), the CO stretching frequency is in the range of $2125\text{--}1850\text{ cm}^{-1}$. The stretching frequency for doubly bridging (μ_2 -) carbonyl ligands generally occur in the range of $1860\text{--}1700\text{ cm}^{-1}$. Finally, triply bridging (μ_3 -) carbonyl ligands

Table 1. Carbonyl stretching frequencies for selected transition metal carbonyl complexes illustrating back-bonding correlation to CO stretching frequencies.

Complex	$\nu(\text{CO})\text{ cm}^{-1}$	Complex	$\nu(\text{CO})\text{ cm}^{-1}$
<u>Terminal CO ligands^a</u>			
$\text{Cp}^*\text{Ir}(\text{CO})_2$	2020, 1954	$\text{CpIr}(\text{CO})_2$	2012, 1950
$\text{Cp}^*\text{Rh}(\text{CO})_2$	2022, 1963	$\text{CpRh}(\text{CO})_2$	2040, 1982
$\text{Cp}^*\text{Co}(\text{CO})_2$	2010, 1950	$\text{CpCo}(\text{CO})_2$	2022, 1970
<u>μ_2-CO ligands^b</u>			
$(\text{Cp}^*\text{Ir})_2(\mu\text{-CO})_2$	1692	$(\text{CpIr})_2(\mu\text{-CO})_2$	unknown
$(\text{Cp}^*\text{Rh})_2(\mu\text{-CO})_2$	1732	$(\text{CpRh})_2(\mu\text{-CO})_2$	unknown
$(\text{Cp}^*\text{Co})_2(\mu\text{-CO})_2$	1745	$(\text{CpCo})_2(\mu\text{-CO})_2$	1785
Complex	$\nu(\text{CO})\text{ cm}^{-1}$		
<u>μ_3-CO ligands</u>			
$(\text{Cp}^*\text{Co})_3(\mu_3\text{-CO})_2$	1675 ^c		
$(\text{Cp}^*\text{Co})_2(\mu\text{-CO})_2\text{CoCp}$	1698		
$\text{Cp}^*\text{Co}(\mu\text{-CO})_2(\text{CoCp})_2$	1707		
$(\text{CpCo})_3(\mu\text{-CO})_2$	1725 ^d		
$(\text{Cp}^*\text{Rh})_2(\mu_3\text{-CO})_2\text{CoCp}^*$	1677 ^c		
$(\text{Cp}^*\text{Rh})_2(\mu\text{-CO})_2\text{CoCp}$	1692		
$\text{Cp}^*\text{Rh}(\mu_3\text{-CO})_2(\text{CoCp}^*)_2$	1678 ^c		
$\text{Cp}^*\text{Rh}(\mu\text{-CO})_2(\text{CoCp})_2$	1705		
$(\text{Cp}^*\text{Ir})_2(\mu\text{-CO})_2\text{CoCp}$	1900, 1680		

^a in hexane, ^b in THF, ^c Bray et al., [38], ^d in KBr.

exhibit a carbonyl stretching frequency in the range of 1700-1600 cm^{-1} [72].

2) Metal to ligand back-bonding also depends on the transition metal involved. An increase in back-bonding ability from 1st to 2nd to 3rd row transition metals is observed for a wide variety of transition metal complexes [73]. For 3rd row transition metals, the valence 5d orbitals extend further from the metal nucleus than do the valence d orbitals of the 1st and 2nd row transition metals. The extended orbitals of the 3rd row transition metals allow for more efficient overlap with the CO π^* orbitals and as a result, the CO stretching frequencies are lowered.

3) The other ligands associated with the metal affect the interaction of the metal with the carbonyl ligand. When the metal is bonded to an electron donating ligand, there is an increase in the electron density on the metal. The metal d orbitals expand causing more efficient overlap with the CO π^* orbital and the carbonyl stretch is shifted to lower frequency. Both Cp and Cp* are good donor ligands which do not readily accept back-donation of electron density from the metal. The methyl groups on the Cp* ligand are electron donating substituents which cause the Cp* ligand to be a better donor than the Cp ligand. Thus, all other factors unchanged, the carbonyl ligands of a transition metal complex containing a Cp* ligand will generally exhibit lower CO stretching frequencies than a

transition metal complex containing a Cp ligand[56].

All six of these trinuclear dicarbonyl complexes exhibit CO stretching frequencies between 1710-1650 cm^{-1} (Table 2). In the cases where the dinuclear precursors are known, there is a significant decrease ($> 30 \text{ cm}^{-1}$) in the carbonyl stretching frequency from the dinuclear complex to the trinuclear complex. These data are consistent with the presence of triply bridging or semi-triply bridging character for the carbonyl ligands in these complexes. The solid state X-ray crystal structure data, which will be discussed later, support the structural description.

^1H NMR Spectroscopy. The normal diamagnetic shifts for Cp and Cp^* protons when present in a metal complex are approximately 5 and 2 ppm, respectively. Since these are the first trinuclear complexes which contain both Cp and Cp^* ligands, it is difficult to predict what should be expected for the ^1H NMR spectra of these complexes. The ^1H NMR spectra of Complexes 1-5 are shown in Figures 3-7. Each complex exhibits only two proton signals which in most cases are shifted dramatically upfield from the normal diamagnetic positions (Table 3). The larger signal is assigned by careful integration to the Cp^* methyl protons and the smaller signal to the Cp ring protons.

Type 1 clusters contain two Cp ligands and Type 2 clusters contain two Cp^* ligands. Depending on the positions of the carbonyl ligands, either one or two signals

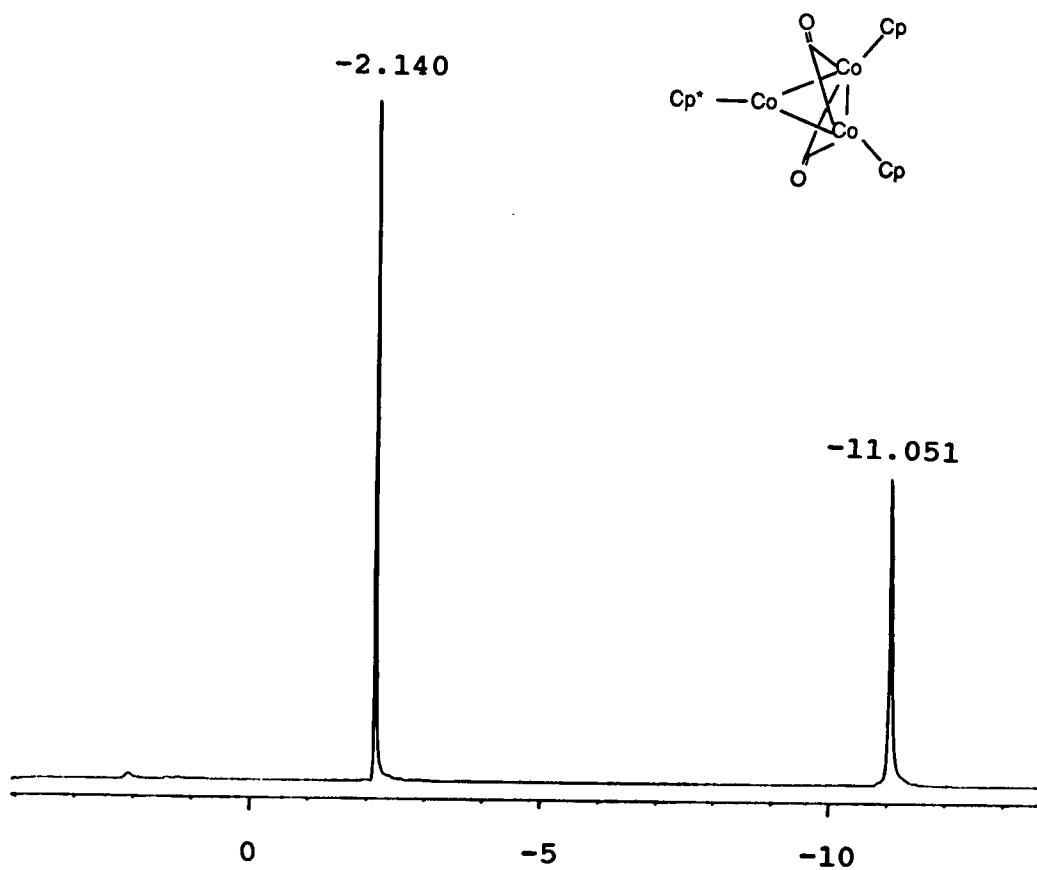


Figure 3. ^1H NMR spectrum of Complex 1, $^*\text{CoCo}_2$, in toluene- d_8 at 22°C .

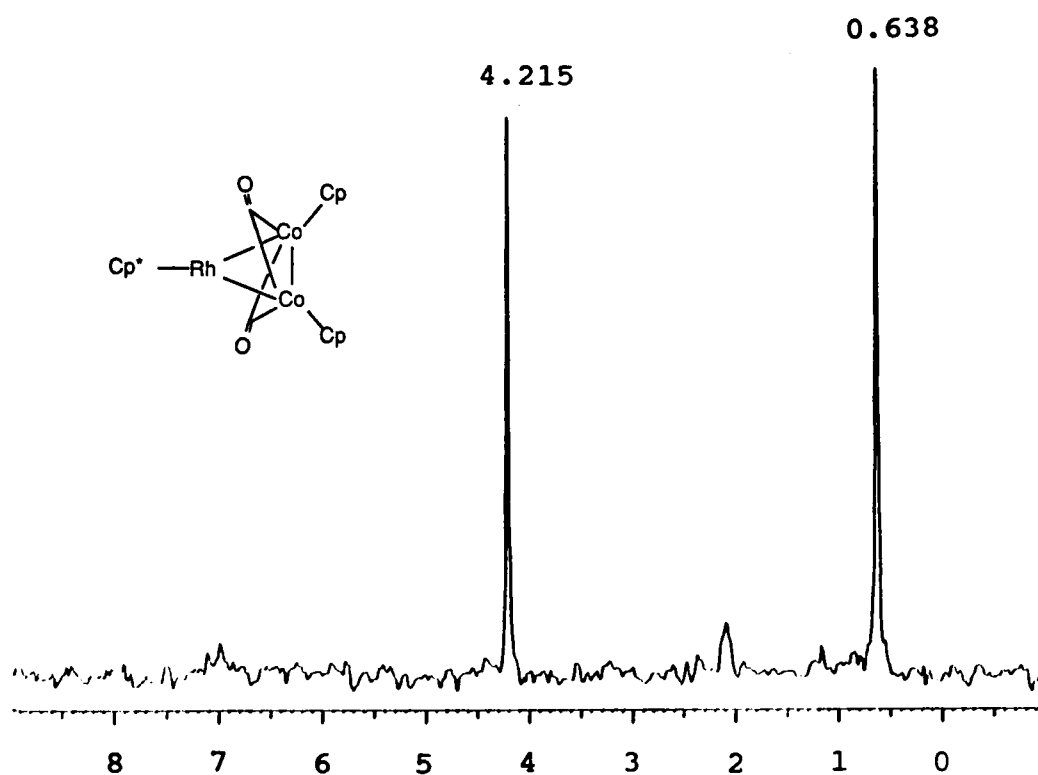


Figure 4. ^1H NMR spectrum of Complex 2, $^*\text{RhCo}_2$, in toluene- d_8 at 0.0°C .

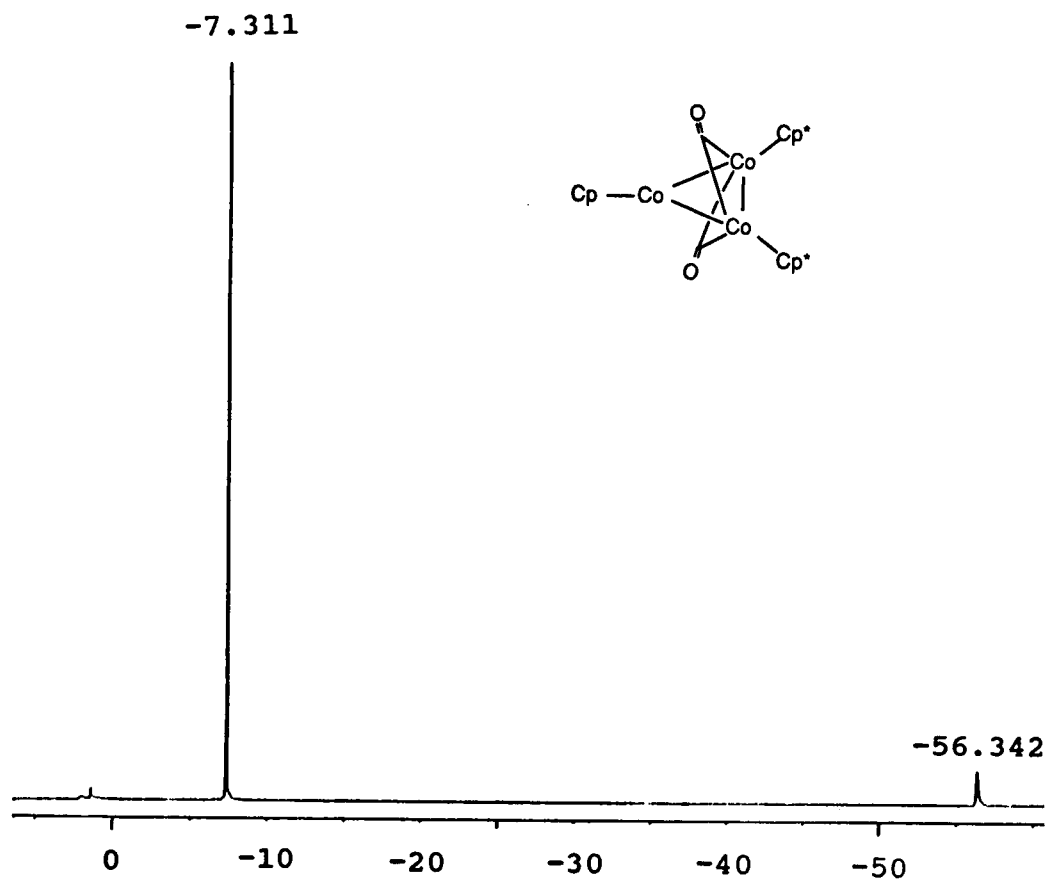


Figure 5. ^1H NMR spectrum of Complex 3, $^*\text{Co}_2\text{Co}$, in toluene- d_8 at 21.9°C .

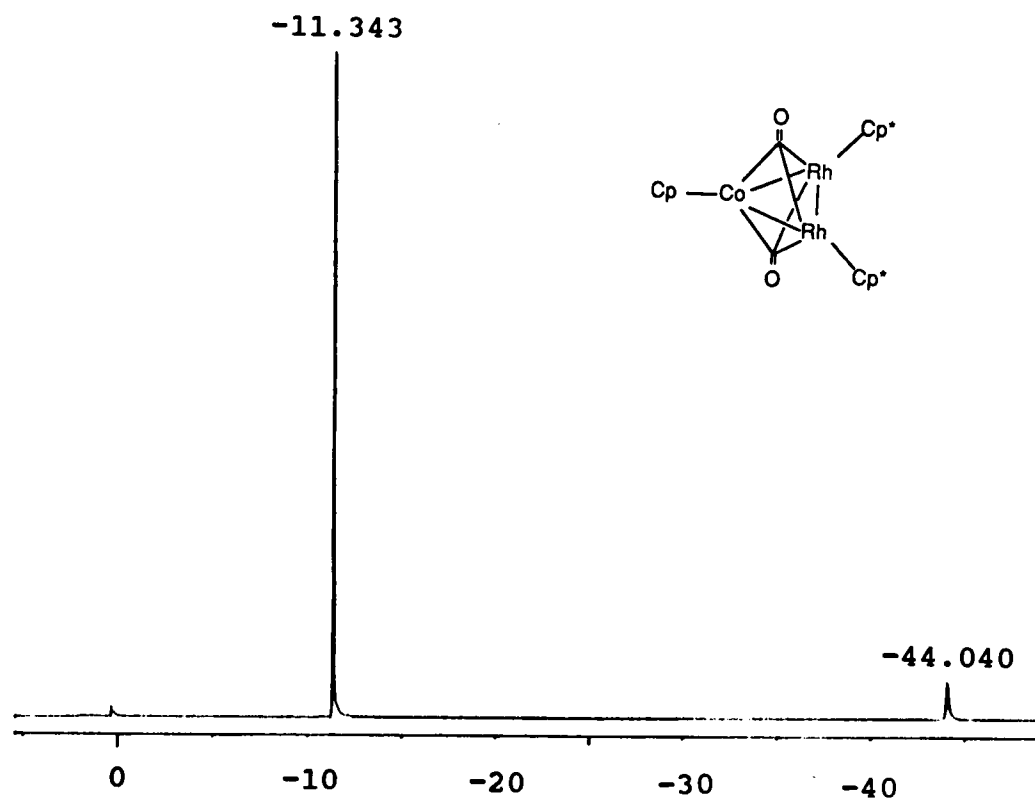


Figure 6. ^1H NMR spectrum of Complex 4, $^*\text{Rh}_2\text{Co}$, in toluene- d_8 at 21.9°C .

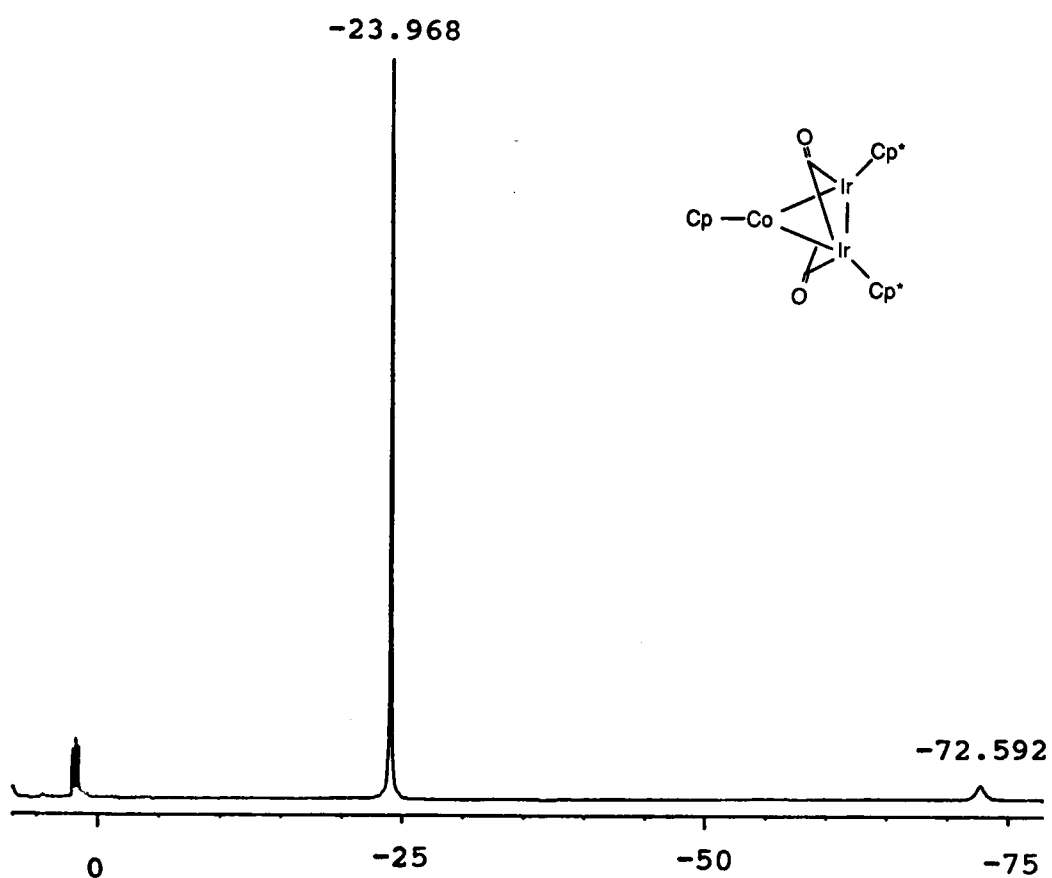


Figure 7. ^1H NMR spectrum of Complex 5, $^*\text{Ir}_2\text{Co}$, in toluene- d_8 at 23.7°C .

Table 2. Complete infrared spectroscopic data for Complexes 1-5.

SOLVENT	IR ν (CO) cm^{-1}				
	FT-KBr	HEXANE	CH_2Cl_2	THF	BENZENE
Complex <u>1</u>	1699	1695	1688	1707	1702
Complex <u>2</u>	1701		1675	1705	1702
Complex <u>3</u>	1703 1686	1710 1692	1690	1698	
Complex <u>4</u>	1690	1725	1680	1692	1688
Complex <u>5</u>	1900 1685	1910 1690	1665	1900 1680	

Table 3. Complete ^1H NMR spectroscopic data for Complexes 1-5.

SOLVENT	^1H NMR δ (Cp^*/Cp) ppm^a					
	C_6D_6		TOL-d_8		THF-d_8	
	Cp^*	Cp	Cp^*	Cp	Cp^*	Cp
Complex <u>1</u>	- 2.24	-11.25	- 2.14	-11.05	- 2.11	-11.44
Complex <u>2</u>	0.31	3.61	0.43	3.70	0.76	3.67
Complex <u>3</u>	- 7.18	-55.42	- 7.28	-56.12	- 7.33	-56.26
Complex <u>4</u>	-10.82	-41.93	-11.34	-44.07	-10.89	-42.71
Complex <u>5</u>	-23.02	-72.49	-24.02	-72.49	-24.09	-73.12

^a Spectra taken at 24°C.

might be expected for the Cp (Type 1) or Cp* (Type 2) ligand in these complexes. The fact that only one proton signal is observed for each suggests that Type 1 clusters must exist, in solution, in a geometry which renders the Cp ring protons equivalent, and that Type 2 clusters must exist, in solution, in a geometry which renders the Cp* methyl protons equivalent, i.e., there must be a plane of symmetry between the two ligands of the same type as illustrated in Figure 8. The carbonyl ligands, which are not shown in Figure 8, exist either in the mirror planes or symmetrically on both sides of these planes.

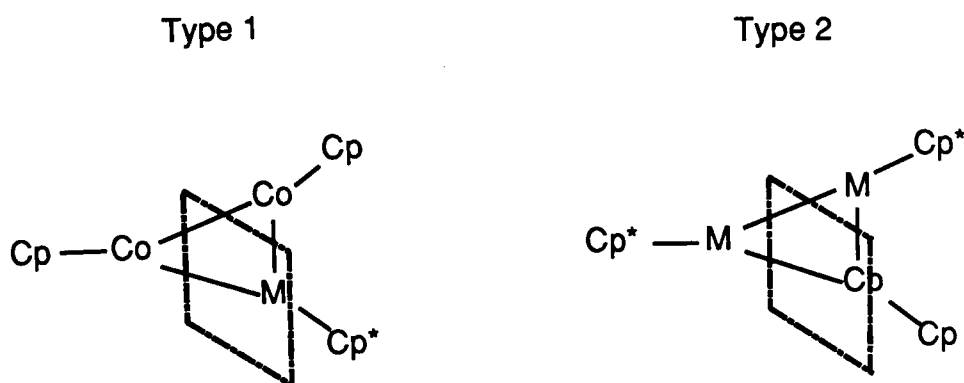


Figure 8. Type 1 and Type 2 clusters depicted with mirror plane.

The large upfield shifts from the diamagnetic norm indicate an unpaired spin, i.e., paramagnetism. Since these complexes are even electron complexes (46 electrons), the observed paramagnetism is attributed to the presence of two

unpaired spins and thus, a populated triplet state.

The temperature dependence of the ^1H NMR can be useful in characterizing the observed paramagnetism to determine if it is a result of 1) the ground state, i.e., ground state triplet, or 2) the population of a low lying, thermally available paramagnetic state from a ground state singlet. From the symmetry observed in the NMR spectra of these complexes in solution, Complexes 1-5 belong to the C_{2v} point group which does not contain any doubly degenerate (e) irreducible representations. Thus, it would seem that the ground states of these complexes must be singlet states. However, if the difference in energy (ΔE) between the HOMO and LUMO is less than the pairing energy of the electrons, then the electrons will occupy both orbitals rather than pair, giving rise to an accidental degeneracy, and a triplet ground state. Some of these complexes may exist as ground state singlets, and others may exist as ground state triplets due to accidental degeneracy. Olson *et al.* [74] attributed the temperature dependence of the paramagnetic shift behavior of $\text{Cp}^*_3\text{Co}_3(\mu_3\text{-CO})_2$ to a singlet-triplet spin equilibrium in solution. Magnetic susceptibility data are required to conclusively determine the actual ground state of these complexes and completely characterize the temperature dependence of the paramagnetic behavior. Tables 4-8 give the paramagnetically derived proton shift data, over the temperature range available to the NMR ($\pm 90^\circ\text{C}$),

Table 4. Temperature dependence of the paramagnetically derived shifts observed in the ^1H NMR spectrum for Complex **3**, $^*\text{Co}_2\text{Co}$, in toluene- d_8 .^{a, b}

Temperature K	Cp signal	Cp* signal
363	-52.55	- 7.57
348	-52.86	- 7.59
340	-53.88	- 7.86
333	-54.86	- 8.02
323	-56.42	- 8.35
315	-57.70	- 8.60
305	-59.42	- 8.92
295	-61.34	- 9.31
273	-65.84	-10.15
248	-71.82	-11.24
223	-78.98	-12.50
210	-83.26	-13.26

^aAll shifts referenced to tol- d_8 , $\delta(\text{CH}_3) = 2.09\text{ppm}$.

^bAll paramagnetically derived chemical shifts are calculated according to the equation: $\delta_{\text{obs}} = \delta_{\text{para}} + \delta_{\text{dia}}$. Diamagnetic reference shifts have been approximated as 2 and 5ppm for Cp* and Cp ligands, respectively.

Table 5. Temperature dependence of the paramagnetically derived shifts observed in the ^1H NMR spectrum for Complex 5, $^*\text{Ir}_2\text{Co}$, in toluene- d_8 .^{a, b}

Temp K	Cp signal	Cp [*] signal	New Cp	New Cp [*]
373	- 63.78	-20.78		
363	- 65.28	-21.33		
353	- 66.72	-21.89		
340	- 68.96	-22.72		
323	- 72.17	-23.86		
313	- 74.05	-24.59		
303	- 76.20	-25.39		
297	- 77.70	-25.99		
273	- 83.31	-28.22		
248	- 90.45	-31.16		
233	- 95.88	-33.04		
228	- 98.19	-33.50		
224	-100.84	-34.02		

Table 5 (continued)

Temp K	Cp signal	Cp* signal	New Cp	New Cp*
219	-102.57	-34.60	- 91.85	-40.86
214	-104.33	-35.44		
211	-105.48	-36.12	- 94.39	-43.28
203	-108.58	-37.95	- 97.25	-45.57
202	-108.75	-38.08	- 97.74	-45.41
193	-112.78	-40.78	-101.60	-48.19
183	-116.92	-43.94	-105.31	-51.14
172	-121.49	-47.76	-109.18	-54.46

^aAll shifts referenced to tol-d₈, $\delta(\text{CH}_3) = 2.09\text{ppm}$.

^bAll paramagnetically derived chemical shifts are calculated according to the equation: $\delta_{\text{obs}} = \delta_{\text{para}} + \delta_{\text{dia}}$. Diamagnetic reference shifts have been approximated as 2 and 5ppm for Cp* and Cp ligands, respectively.

Table 6. Temperature dependence of paramagnetically derived shifts observed in the ^1H NMR spectrum for Complex 1, $^*\text{CoCo}_2$, in toluene- d_8 .^{a, b}

Temperature K	Cp signal	Cp* signal
373	-20.57	- 4.28
363	-20.30	- 4.32
348	-19.83	- 4.41
323	-18.42	- 4.38
295	-16.05	- 4.14
273	-13.66	- 3.81
248	-10.37	- 3.24
223	- 6.85	- 2.55
213	- 5.53	- 2.26

^aAll shifts referenced to tol- d_8 , $\delta(\text{CH}_3) = 2.09\text{ppm}$.

^bAll paramagnetically derived chemical shifts are calculated according to the equation: $\delta_{\text{obs}} = \delta_{\text{para}} + \delta_{\text{dia}}$. Diamagnetic reference shifts have been approximated as 2 and 5ppm for Cp* and Cp ligands, respectively.

Table 7. Temperature dependence of the paramagnetically derived shifts observed in the ^1H NMR spectrum for Complex 4, $^*\text{Rh}_2\text{Co}$, in toluene- d_8 .^{a, b}

Temperature K	Cp signal	Cp [*] signal
363	-48.14	-12.58
348	-48.66	-12.80
340	-48.90	-12.93
333	-49.07	-13.04
323	-49.23	-13.15
315	-49.29	-13.23
305	-49.26	-13.32
295	-49.07	-13.34
273	-47.87	-13.26
248	-44.73	-12.69
223	-38.74	-11.35
210	-34.13	-10.24

^aAll shifts referenced to tol- d_8 , $\delta(\text{CH}_3) = 2.09\text{ppm}$.

^bAll paramagnetically derived chemical shifts are calculated according to the equation: $\delta_{\text{obs}} = \delta_{\text{para}} + \delta_{\text{dia}}$. Diamagnetic reference shifts have been approximated as 2 and 5ppm for Cp^{*} and Cp ligands, respectively.

Table 8. Temperature dependence of the paramagnetically derived shifts observed in the ^1H NMR spectrum for Complex **2**, $^*\text{RhCo}_2$, in toluene- d_8 .^{a, b}

Temperature K	Cp signal	Cp* signal
363	-4.07	-1.64
348	-3.48	-1.40
333	-2.91	-1.07
323	-2.38	-0.91
315	-2.07	-0.76
305	-1.74	-0.64
295	-1.38	-0.46
273	-0.86	-0.25
248	-0.50	-0.13
223	-0.24	-0.05
213	-0.15	-0.01
199	-0.06	0.00
188	0.00	0.00

^aAll shifts referenced to tol- d_8 , $\delta(\text{CH}_3) = 2.09\text{ppm}$.

^bAll paramagnetically derived chemical shifts are calculated according to the equation: $\delta_{\text{obs}} = \delta_{\text{para}} + \delta_{\text{dia}}$. Diamagnetic reference shifts have been approximated as 0.89 and 5.08ppm for Cp* and Cp ligands, respectively.

calculated according to the equation: $\delta_{obs} = \delta_{para} + \delta_{dia}$.

Figures 9-13 illustrate the change in the isotropic shift with inverse temperature. Surprisingly, three different types of shift versus inverse temperature behavior are observed. First, the known model $^*\text{IrCo}_2$ exhibits a linear dependence of the isotropic shift with inverse temperature over the temperature range studied[48]. As the temperature is lowered, there is an increase in the paramagnetically derived shift. Such behavior is also exhibited by Complex 3 as shown in Figure 9, and Complex 5 as shown in Figure 10, and is consistent with a single spin state (triplet) within this temperature range.

The temperature dependence observed for Complex 5 is slightly different than that observed for Complex 3. A linear dependence for the chemical shifts of the Cp and Cp* protons vs inverse temperature is observed but, as the temperature is lowered from 23°C to -100°C, the Cp and Cp* signals simultaneously broaden and then sharpen again as two new signals appear to move out from under the original signals. The linear dependence continues upon resolution of the two peaks as shown in Figure 10. One explanation for this coalescence behavior is that an equilibrium process is being frozen out. The infrared spectrum for Complex 5 indicates the presence of both terminal and triply bridging carbonyl ligands. An equilibrium between two trinuclear complexes, one containing terminal carbonyl ligands and the

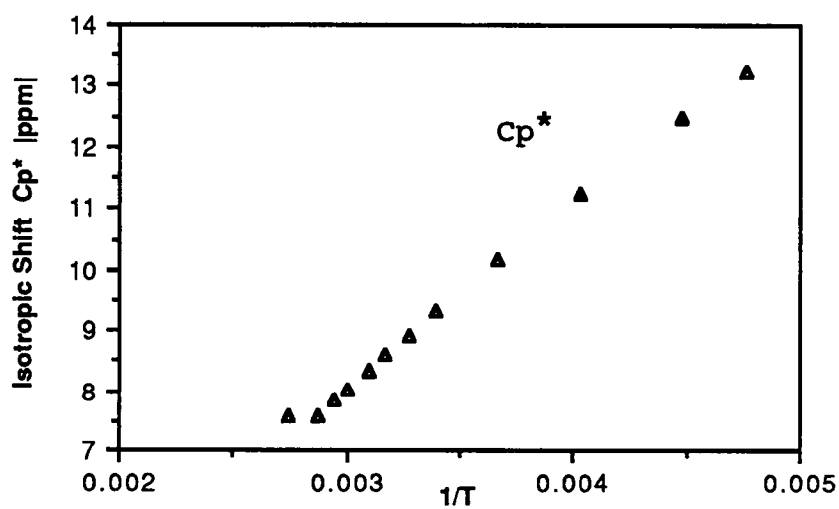
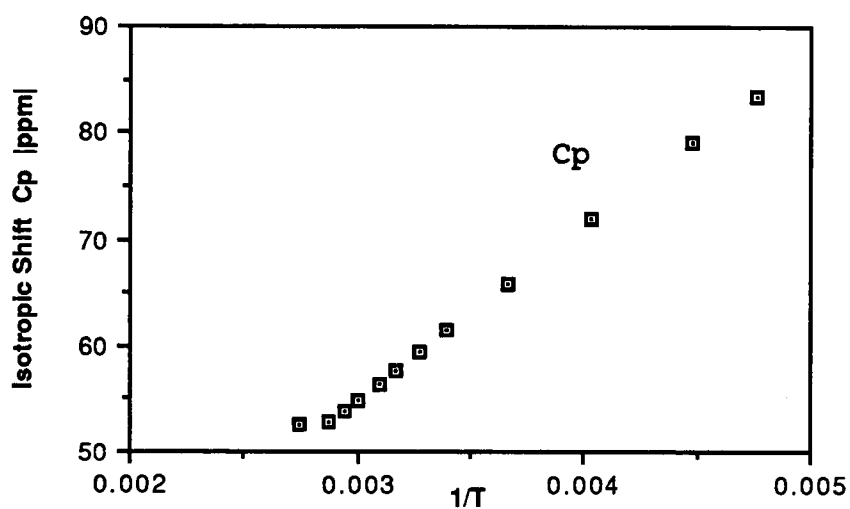


Figure 9. Plot illustrating paramagnetically derived isotropic shift vs $1/T$ for Complex 3, $^*\text{Co}_2\text{Co}$.

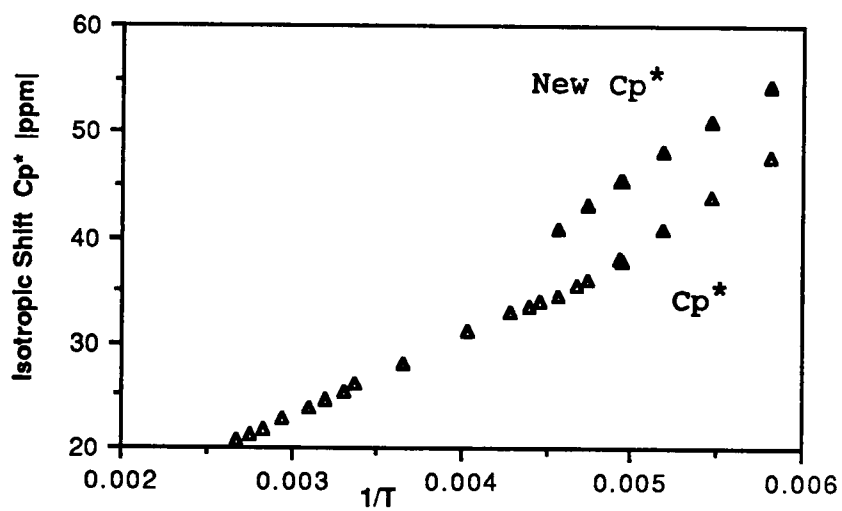
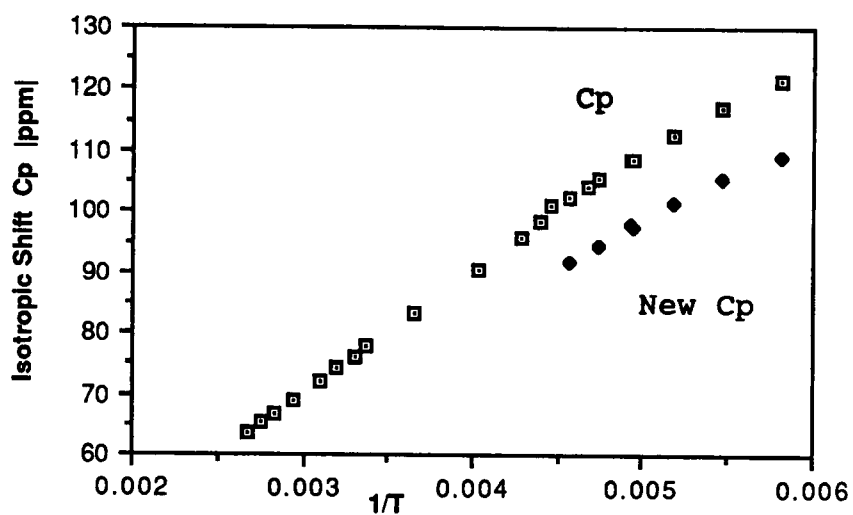


Figure 10. Plot illustrating paramagnetically derived isotropic shift vs $1/T$ for Complex 5, $^*\text{Ir}_2\text{Co}$.

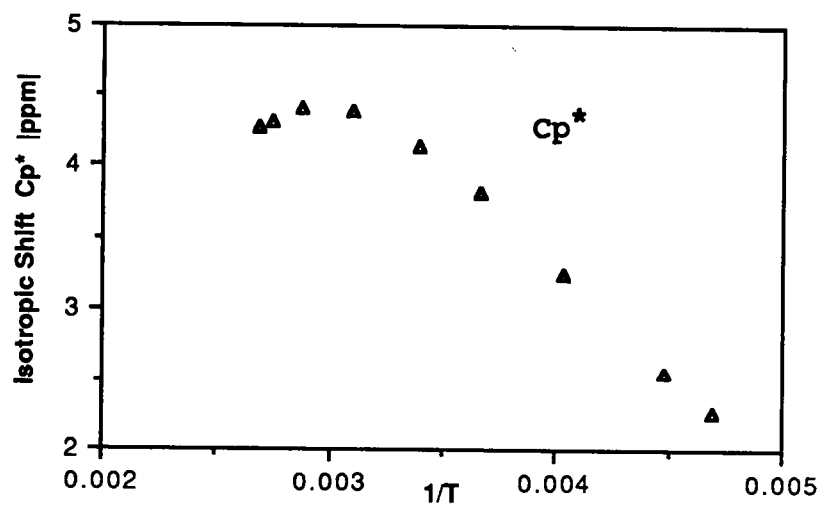
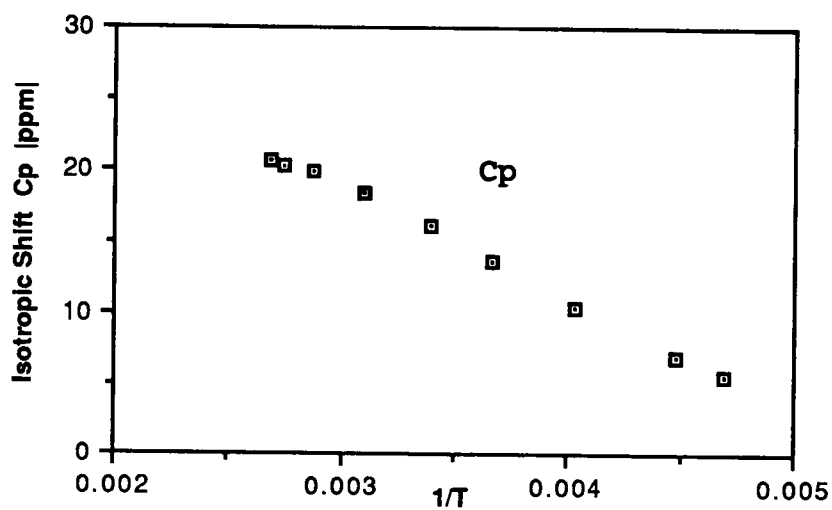


Figure 11. Plot illustrating paramagnetically derived isotropic shift vs $1/T$ for Complex 1, $^*\text{CoCo}_2$.

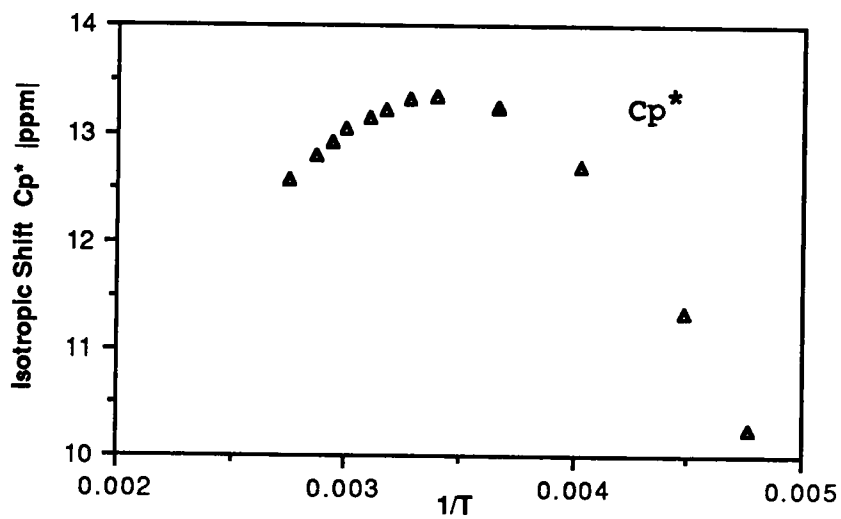
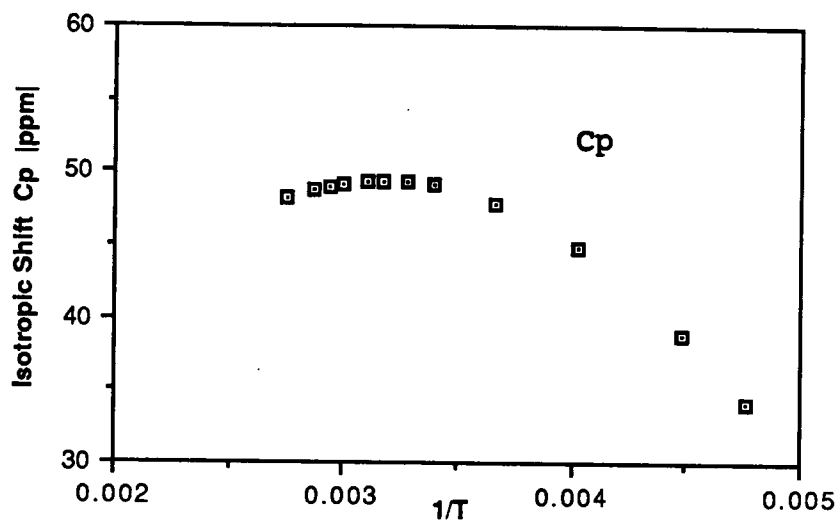


Figure 12. Plot illustrating paramagnetically derived isotropic shift vs $1/T$ for Complex 4, $^*Rh_2Co$.

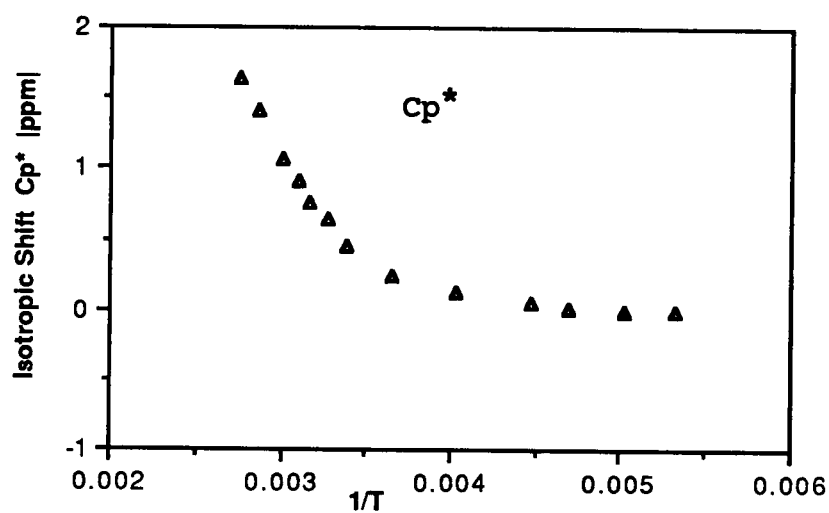
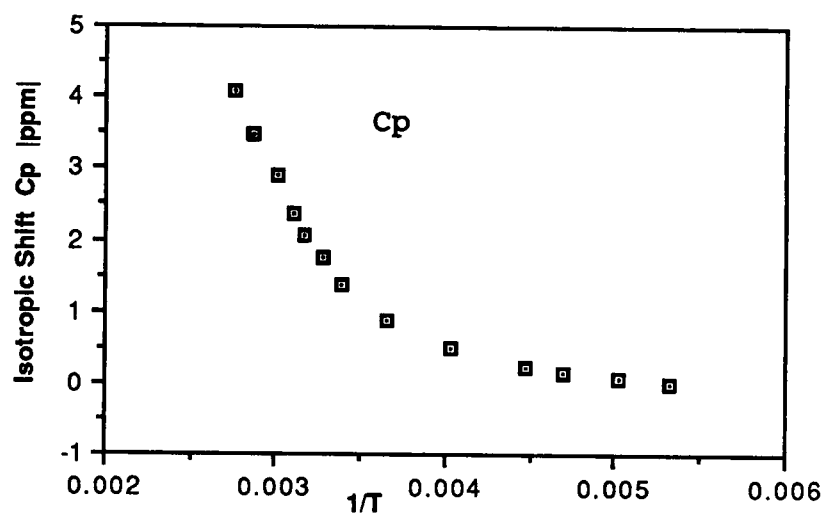


Figure 13. Plot illustrating paramagnetically derived isotropic shift vs $1/T$ for Complex 2, $^*\text{RhCo}_2$.

other containing bridging carbonyl ligands, is proposed to account for the ^1H NMR and IR data. Similar equilibria have been observed in other systems containing organometallic carbonyl complexes[75-78] as shown in Figure 14.

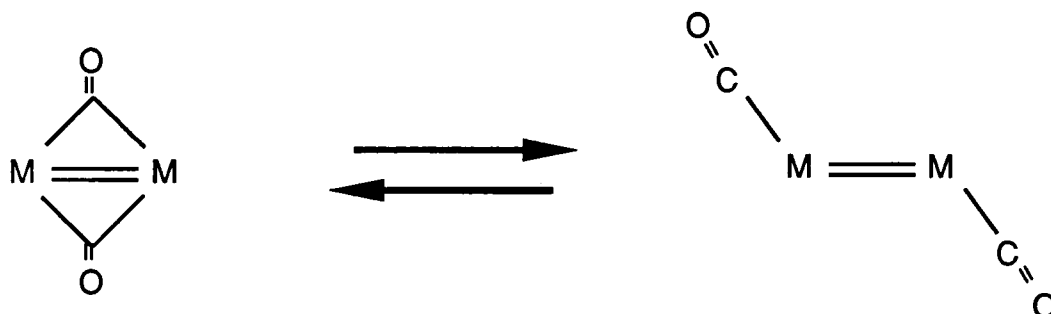


Figure 14. Terminal - bridging conformational equilibrium observed for some organometallic complexes.

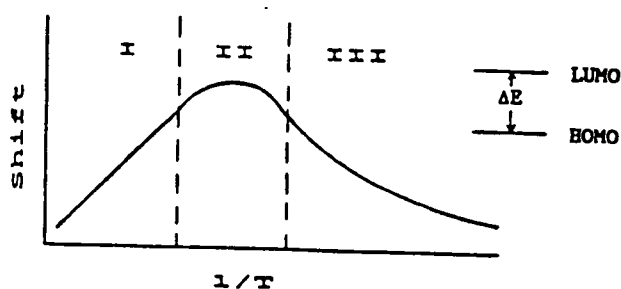
A second type of temperature dependence is that observed for Complexes 1 and 4 as shown in Figures 11 and 12, respectively. The graphs of the isotropic shift vs inverse temperature exhibit a maximum in the paramagnetically derived shift which decreases as the temperature is raised or lowered.

The third and final type of temperature dependence is that of Complex 2 shown in Figure 13. Asymptotic behavior of the isotropic shift with inverse temperature is observed over the temperature range available to the NMR. At temperatures below -50°C , the isotropic shifts are temperature

independent, and consistent with those expected for a diamagnetic complex. As the temperature is raised above -50°C , the two signals begin to move upfield (toward TMS) and show pronounced non-linear temperature dependencies. These data are consistent with the conclusion that Complex 2 exists as a ground state singlet with a low lying, thermally available triplet state which is populated at temperatures above -50°C .

A summary of the temperature dependent behaviors is shown in Figure 15. ΔE is defined as the energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Complexes which follow the behavior shown in region I are either ground state triplets due to accidental degeneracy of two molecular orbitals, i.e., ΔE is smaller than the pairing energy of electrons; or ground state singlets in which $\Delta E \ll kT$. Complexes which follow the behavior shown in region II are probably ground state singlets in which $\Delta E \approx kT$ such that there is a significant change in the populations of the HOMO and LUMO over the temperature range available to the NMR. Complexes which follow the behavior shown in region III are ground state singlets in which $\Delta E > kT$.

According to Holm and Hawkins[79], temperature dependent isotropic shifts of paramagnetic molecules are derived from Fermi contact interactions. Although no studies have been done to determine the origin of the



- I. Curie behavior (linear) expected when $\Delta E \ll kT$.
- II. Curvature with maximum shift expected when $\Delta E \sim kT$ at room temperature.
- III. Asymptotic behavior expected at low temperature when $\Delta E > kT$ at room temperature.

Figure 15. Summary of paramagnetic temperature dependent behaviors in the NMR.

magnitude and direction of the paramagnetically derived shifts for these trinuclear complexes, it is assumed that the contact interactions are dominant. Several mechanisms have been proposed to explain the contact interactions, although no one mechanism is as yet universally accepted. Levy and Orgel[80] suggest that for some organometallic complexes, if the spin density on the metal d orbital is positive, then by spin polarization through the pi system, the spin density at the Cp ring-hydrogens will be negative, leading to an upfield shift of the proton signal for a Cp ring proton, consistent with what is observed for these complexes. However, by the same spin polarization mechanism, a positive spin density on the metal d orbital will lead to a positive spin density on the Cp* methyl protons and, thus, a downfield shift of the proton signal for the

Cp* methyl protons is expected. The Cp* methyl proton signals for Complexes 1-5, however, are shifted upfield. Fritz[81] proposed that along with the Levy-Orgel spin polarization mechanism through the pi system, there is direct overlap of the methyl protons with the metal d orbitals, resulting in direct polarization such that a positive density on the metal d orbitals gives a negative spin density on the Cp* methyl protons and an upfield shift. The paramagnetically derived isotropic shift observed for the Cp* methyl protons due to polarization through the pi system is expected to be smaller than that observed for the Cp ring proton signal because the methyl protons are further removed from the metal centers. Also, the paramagnetically derived isotropic shift for the Cp* methyl protons through the pi system is expected to be in the opposite direction of the Cp ring proton shift because of a second polarization inversion. Direct polarization should lead to shift magnitudes similar to those observed for the Cp ring protons, but since both through-pi and direct polarization mechanisms are occurring and giving rise to shifts in opposite directions, a smaller net shift is observed. This explanation is consistent with the shifts observed in these complexes.

Structures

Synthetic procedures and spectroscopic data give evidence for the structures of the complexes in this series

as described below. These structures have been verified by solid state X-ray crystallography[82].

The synthesis of $^*\text{Co}_2\text{Co}$, $^*\text{Rh}_2\text{Co}$, and $^*\text{Ir}_2\text{Co}$ involves the addition of a "CpCo" fragment to the face of a parent dinuclear species, $^*\text{M}_2$. The carbonyl stretching frequencies are consistent with doubly (μ_2 -) or triply (μ_3 -) bridging carbonyl ligands; the observance of only one Cp* proton signal in the ^1H NMR indicates a plane of symmetry between the Cp* ligands in each case. In the solid state X-ray crystal structure, the metal atoms are arranged in a triangular framework with the Cp and Cp* ligands oriented perpendicular to the plane of the metals. In the cases of $^*\text{Co}_2\text{Co}$ and $^*\text{Ir}_2\text{Co}$ the two carbonyl ligands remain localized over the edge formed by the parent dinuclear and are canted only slightly toward the "CpCo" fragment as shown in the ORTEP diagrams in Figures 16 and 17. In the case of $^*\text{Rh}_2\text{Co}$, the carbonyl ligands are much more symmetrically bridged above and below the plane of the metals as shown in the ORTEP diagram in Figure 18.

The synthesis of $^*\text{CoCo}_2$, $^*\text{RhCo}_2$, and $^*\text{IrCo}_2$ involves the sequential addition of two "CpCo" fragments to a parent mononuclear dicarbonyl species. The carbonyl stretching frequencies are consistent with doubly (μ_2 -) or triply (μ_3 -) bridging carbonyl ligands. The observance of only one signal for the Cp ring protons in the ^1H NMR indicates a plane of symmetry between the Cp ligands in each case. In

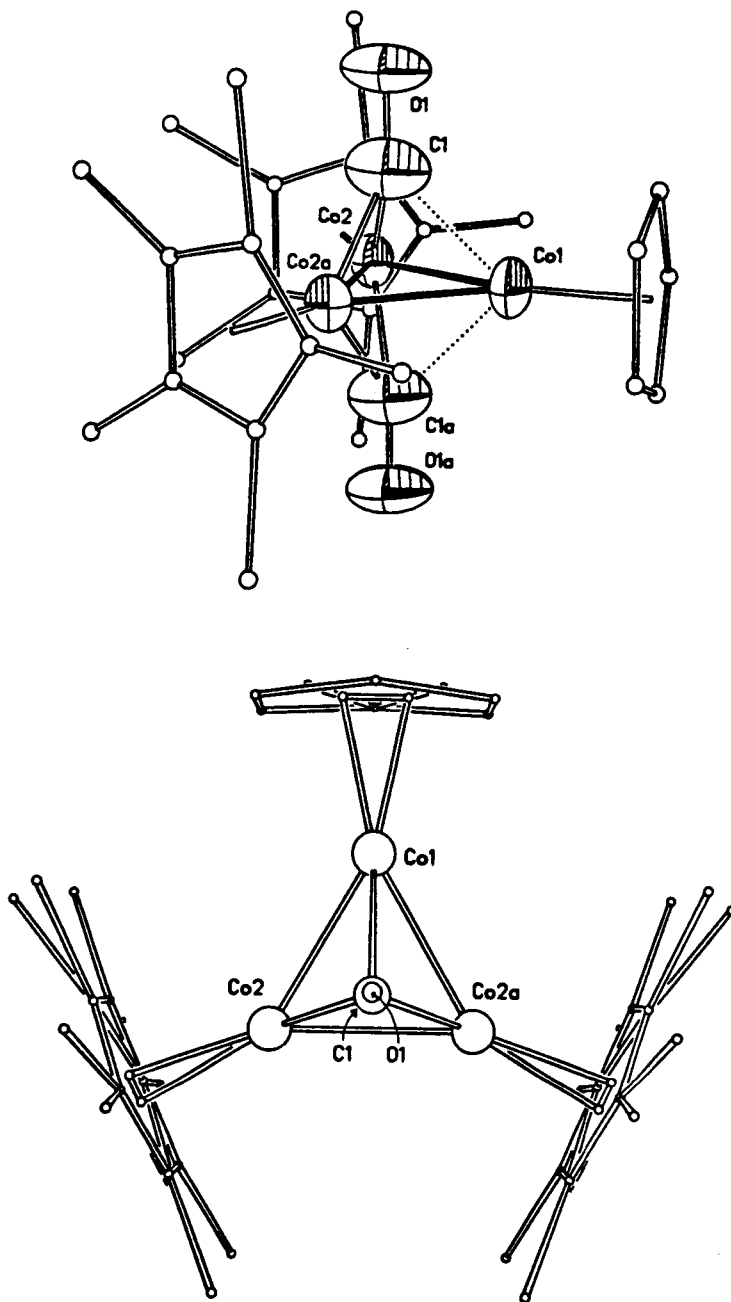
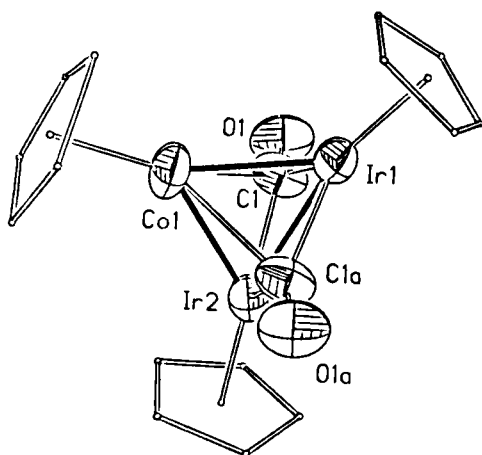


Figure 16. ORTEP diagram of Complex 3, *Co₂Co.

Structure 1



Structure 2

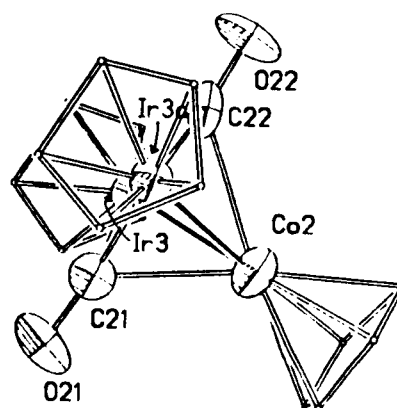
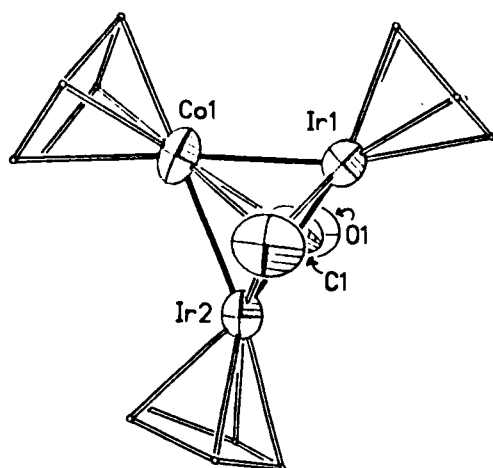
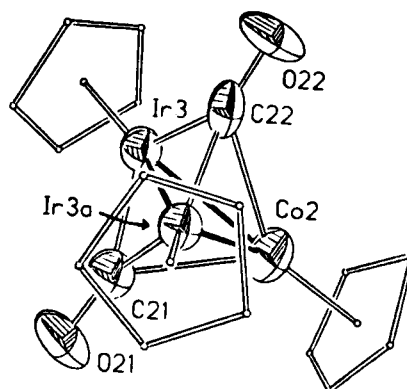


Figure 17. ORTEP diagrams of Complex 5, $^*\text{Ir}_2\text{Co}$.

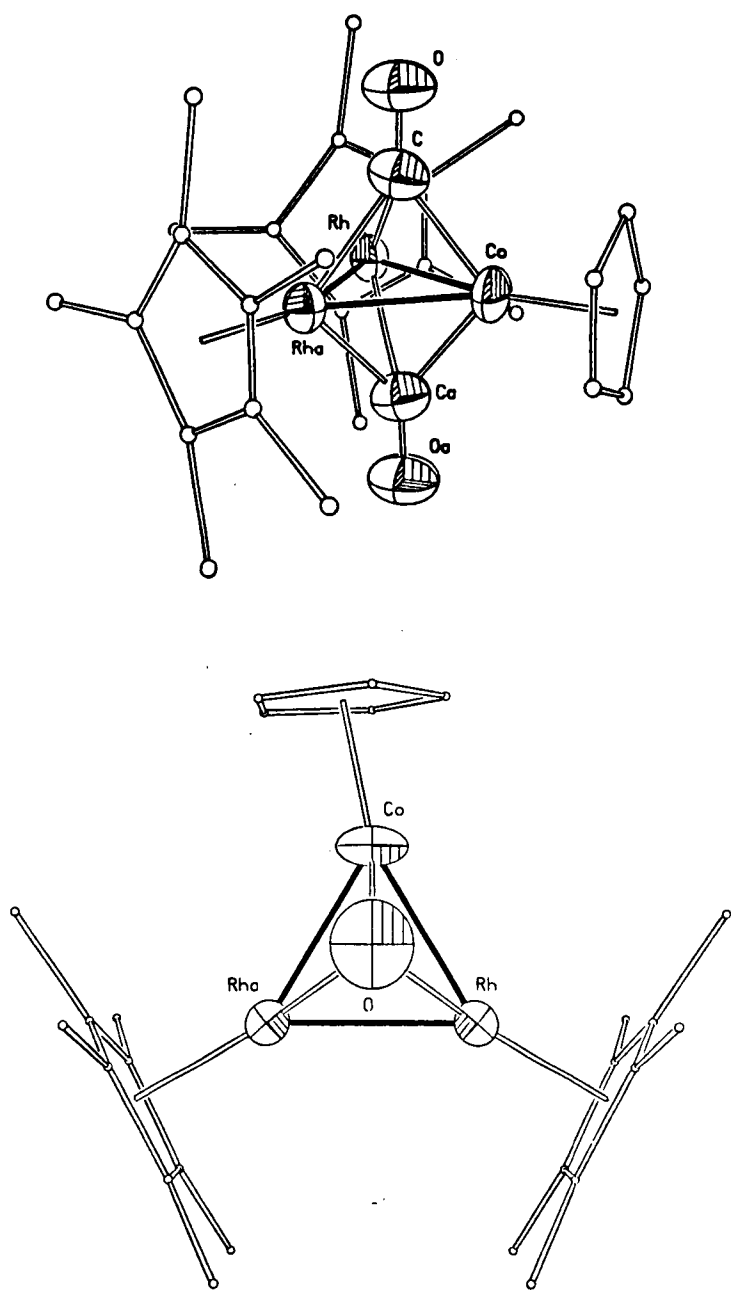


Figure 18. ORTEP diagram of Complex 4, $*\text{Rh}_2\text{Co}$.

the solid state X-ray crystal structure, the metal atoms are arranged in a triangular framework with the Cp and Cp* ligands perpendicular to the plane of the metals. For the model complex $^*\text{IrCo}_2$, the synthesis of which can also be viewed as the addition of one "CpCo" fragment to the face of a parent dinuclear $^*\text{IrCo}$, the carbonyl ligands are localized over the parent dinuclear edge and are canted toward the unique "CpCo" fragment. This structure is not consistent with the ^1H NMR spectrum observed for $^*\text{IrCo}_2$ because it does not render the Cp ring protons equivalent. This is explained by Herrmann[48] to be due to a fast CO fluctuation between the two $^*\text{IrCo}$ edges which renders the Cp ligands equivalent in solution. Another explanation is that the carbonyl ligands migrate to the Co-Co edge in solution. There are some data that support the latter suggestion. The reaction of the trinuclear cluster with CO leads to a tricarbonyl species containing one terminal carbonyl ligand localized on the iridium and two bridging carbonyl ligands localized over the Co-Co edge. For $^*\text{CoCo}_2$ and $^*\text{RhCo}_2$ the carbonyl ligands, which were originally associated with the unique metal in the mononuclear precursor, are localized over the edge joining the two "CpCo" fragments and are canted toward the unique Cp*M fragment. This configuration is the result of a carbonyl migration from the Cp*M fragment to the Co-Co edge. The ORTEP diagrams for $^*\text{CoCo}_2$ and $^*\text{RhCo}_2$ are shown in Figures 19 and 20, respectively.

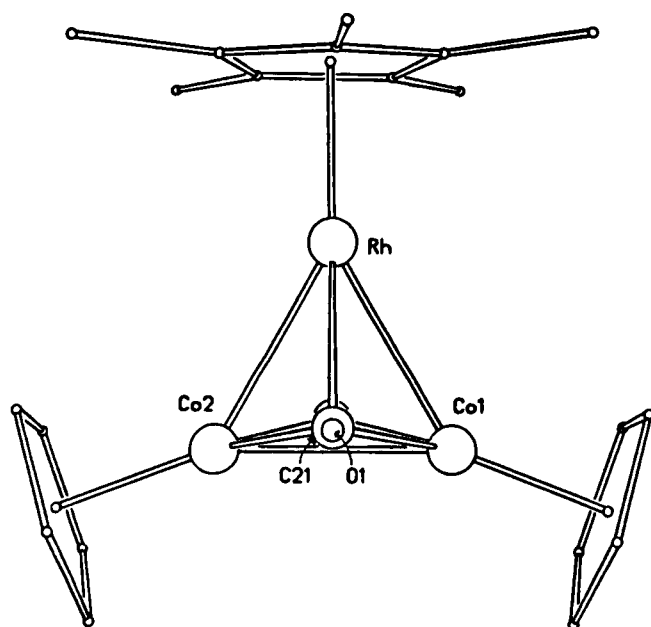
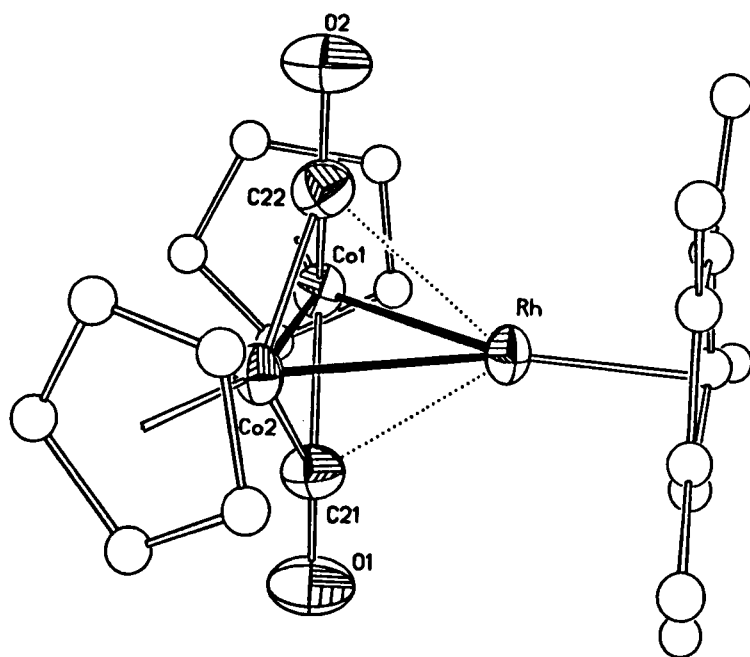


Figure 20. ORTEP diagram of Complex 2, $^*\text{RhCo}_2$.

Bond lengths and angles for Complexes 1-5 are listed in **Appendix B**.

CHAPTER IV

REACTION WITH TWO ELECTRON DONOR LIGANDS

Introduction

Complexes 1-5 are 46 electron complexes and are therefore two electrons short of the desired 48 valence electrons for a stable trinuclear metal cluster containing three metal-metal bonds. The reaction of these complexes with a simple two electron donor ligand such as carbon monoxide is expected to result in tricarbonyl adduct of the parent trinuclear complexes. Sinolar trinuclear tricarbonyl complexes are already known[13,16-18,47]. The reaction of organometallic complexes with diazoalkanes is expected to result in carbene species[41-54]. In the case of a di- or trinuclear complex, a bridging carbene species is expected[41-54]. The study of such alkylidene complexes could lead to a better understanding of the role of metals in catalysis.

Reaction with Carbon Monoxide

The reaction of each of the trinuclear complexes with carbon monoxide in THF yields a trinuclear tricarbonyl species. The reactions were carried out at low temperature and warmed slowly to room temperature under CO. There was only one major product formed in each reaction isolated in virtually quantitative yield. The products 6-10 were

purified by anaerobic column chromatography and were recrystallized from hexane. The model complex $^*\text{IrCo}_2$ reacts with CO to give a diamagnetic 48 electron trinuclear tricarbonyl complex containing one terminal carbonyl and two bridging carbonyl ligands[48]. Complexes 1-4 also react with CO to yield diamagnetic 48 electron trinuclear tricarbonyl species. However, there is no evidence in the infrared spectra for a terminal carbonyl ligand. Instead, there is strong evidence for doubly bridging and triply bridging carbonyls. Complexes 6-9 exhibit very similar carbonyl stretching frequencies as shown in Table 9. The ^1H NMR spectrum for each product contains only one Cp and one Cp^* signal, indicating a plane of symmetry in each product. Although the X-ray structures have not been obtained for Complexes 6-9, two types of structures may be proposed which are consistent with the spectroscopic data. These are shown in Figure 21. Type 3 is the product formed by the reaction of Type 1 clusters with CO, and Type 4 is the product formed by the reaction of Type 2 clusters with CO. All spectroscopic data are consistent with the proposed structures.

The reaction of Complex 5, $^*\text{Ir}_2\text{Co}$, with CO is different. Anaerobic chromatography of the crude reaction mixture yields only one band. Only one Cp ring proton signal and one Cp^* methyl proton signal are observed in the ^1H NMR spectrum which suggests that only one species is present. The infrared spectrum, however, contains several

Table 9. Infrared and ^1H NMR spectroscopic data for Complexes 6-10

Complex 6, $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\mu\text{-CO})_2(\mu_3\text{-CO})\text{Co}_2(\eta^5\text{-C}_5\text{H}_5)_2$

^1H NMR (C_6D_6)	δ	IR	$\nu(\text{CO})$
Cp	1.390	KBr	1830, 1780, 1675
Cp*	4.619	CH_2Cl_2	1825, 1778, 1675

Complex 7, $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CO})_2(\mu_3\text{-CO})\text{Co}_2(\eta^5\text{-C}_5\text{H}_5)_2$

^1H NMR (C_6D_6)	δ	IR	$\nu(\text{CO})$
Cp	1.559	KBr	1800, 1760, 1650
Cp*	4.619	CH_2Cl_2	1828, 1780, 1670

Complex 8, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Co}_2(\mu\text{-CO})_2(\mu_3\text{-CO})\text{Co}(\eta^5\text{-C}_5\text{H}_5)$

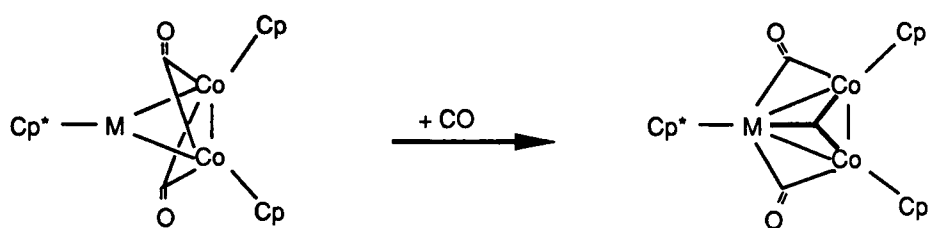
^1H NMR (C_6D_6)	δ	IR	$\nu(\text{CO})$
Cp	1.466	KBr	1815, 1772, 1660
Cp*	4.703	CH_2Cl_2	1815, 1765, 1665

Complex 9, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CO})_2(\mu_3\text{-CO})\text{Co}(\eta^5\text{-C}_5\text{H}_5)$

^1H NMR (C_6D_6)	δ	IR	$\nu(\text{CO})$
Cp	1.627	KBr	1823, 1782, 1668
Cp*	4.689	CH_2Cl_2	1815, 1770, 1655

Complex 10, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2(\mu\text{-CO})_2(\mu_3\text{-CO})\text{Co}(\eta^5\text{-C}_5\text{H}_5)$

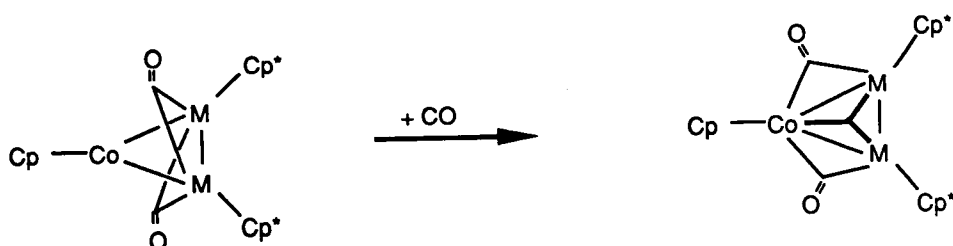
^1H NMR (C_6D_6)	δ	IR	$\nu(\text{CO})$
Cp	1.779	CH_2Cl_2	1930, 1778,
Cp*	4.771		1725, 1612



M = Co, Rh

Type 1

Type 3



M = Co, Rh

Type 2

Type 4

Figure 21. Reactions of Type 1 and Type 2 clusters with CO.

terminal and bridging carbonyl stretches which suggests that more than one species may be present. Due to a lack of material complete identification of the product(s) has not been possible.

Reaction with a Diazoalkane

The model complex $^*\text{IrCo}_2$ was shown to react with diazomethane to give a bridging methylene complex[48]. The diazoalkane selected for this study is 4,4'-dimethyldiazo-benzophenone (4,4'DMB) because it is more stable and is easily synthesized and purified. The reactions were run at room temperature in an inert atmosphere box. The products of these reactions were separated and collected by anaerobic column chromatography. In only one case has it been possible to identify all of the products in the reaction of these trinuclear cluster complexes with 4,4'DMB. Complex 5 has not, as yet, been reacted with the diazoalkane.

The reactions of Type 2 clusters and the model complex, $^*\text{IrCo}_2$, with 4,4'DMB resulted in the fragmentation of the trinuclear framework. The major product in each case was the parent dinuclear. Other products were collected in such small yield (< 5%) that identification was not possible.

The reaction of $\text{Cp}^*\text{Co}(\mu\text{-CO})_2(\text{CoCp})_2$ with the diazoalkane has been the most thoroughly studied, and all major products have been identified. Anaerobic column chromatography yielded three major products.

Fraction 1 was eluted with a 75/25 mixture of hexane and methylene chloride and was purple in color. The infrared spectrum indicated the presence of a doubly bridging carbonyl ligand, $\nu(\text{CO})$ 1780 (s). The ^1H NMR spectrum exhibited one Cp and one Cp^* signal. The relative integrations of the two signals was one to three which indicated that the trinuclear framework had been fragmented and that the product was a dinuclear complex containing one Cp ligand and one Cp^* ligand. Also present in the ^1H NMR was the expected pattern for a symmetric *p*-tolylcarbene; there were two sets of doublets in the aromatic region and a singlet around 2ppm, where methyl proton signals are commonly observed. The IR and ^1H NMR are depicted in Figure 22. The structure shown in Figure 23 is consistent with the spectroscopic and elemental analysis data.

Fraction 2 was eluted with pure methylene chloride and was dark yellow-brown. Initial spectroscopic data indicated that there were two species present. Upon fractional recrystallization two products were separated. The minor product was identified as dimethylbenzophenone azine $((\text{CH}_3\text{Ph})_2\text{CN-NC}(\text{PhCH}_3)_2)$. The major product was identified by IR and ^1H NMR as the CO adduct of Complex 1.

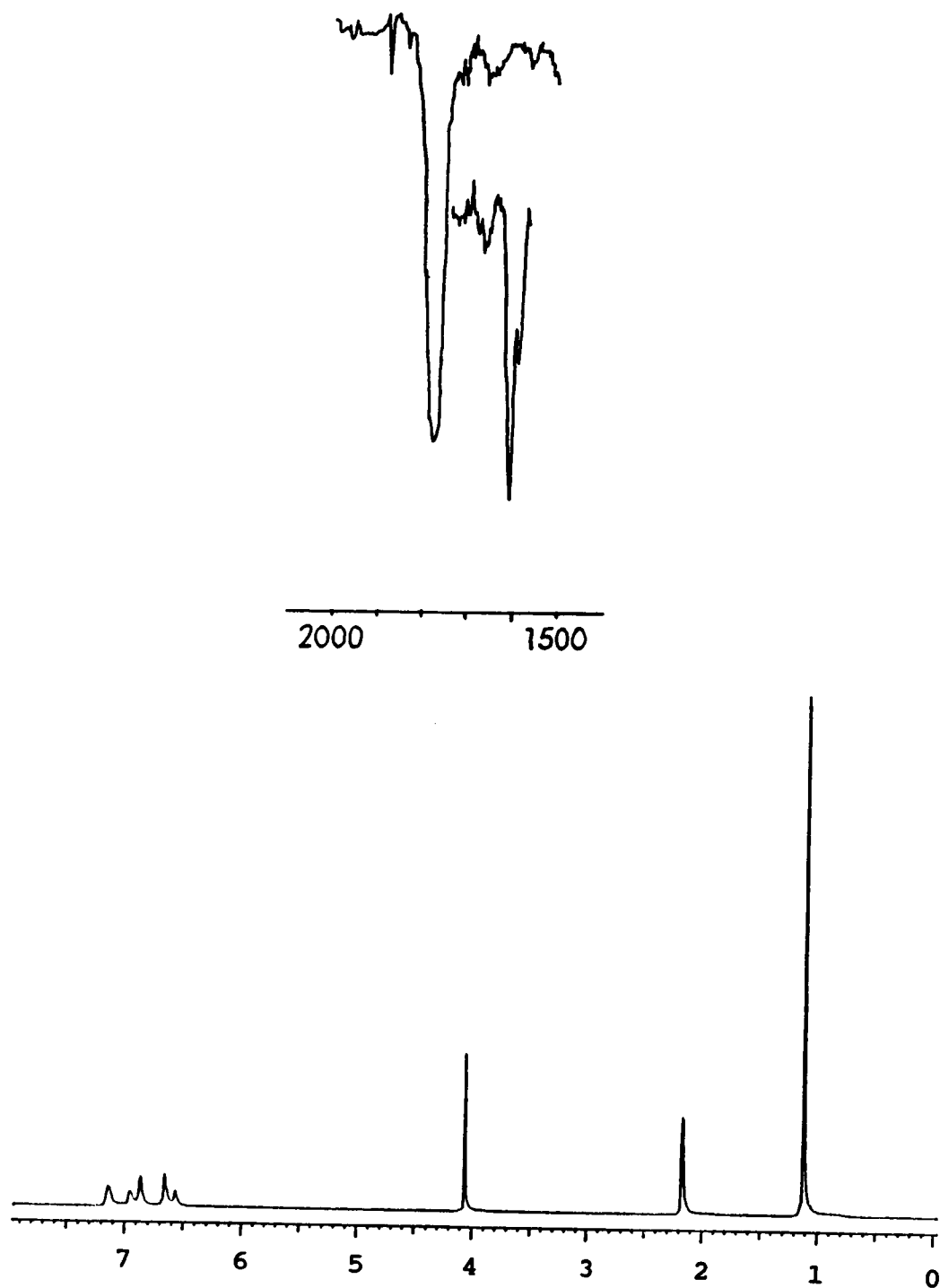


Figure 22. IR and ¹H NMR spectra for Fraction 1 from the reaction of Complex 1, ⁶⁰CoCo₂, with 4,4'DMB.

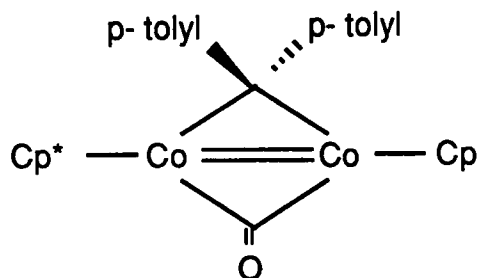


Figure 23. Proposed structure for Fraction 1 from the reaction of Complex 1, $^*\text{CoCo}_2$, with 4,4'DMB.

Fraction 3 was eluted with hexane with a trace of THF (1%) and was dark yellow-brown. The IR spectrum indicated the presence of a triply bridging carbonyl ligand, $\nu(\text{CO})$ 1675 (s). The ^1H NMR indicated the trinuclear framework was still intact with equivalent Cp ligands. There was also an asymmetrical carbene unit present; the aromatic region contained two doublets and a multiplet which was interpreted as a pair of overlapping doublets. Since only one signal was observed for the methyl protons, it was concluded that the two signals were overlapping. The IR and ^1H NMR spectra are shown in Figure 24. Based on these data alone, it appeared that the bridging carbene adduct had been synthesized. However, elemental analysis data indicated the presence of nitrogen in the complex. The mass spectrum gave a parent ion of mass 692. If nitrogen were present in the complex, then based on the mass spectrum, only one carbonyl ligand could be present. Herrmann[46] has reported the isolation of a monocarbonyl trinuclear complex containing a

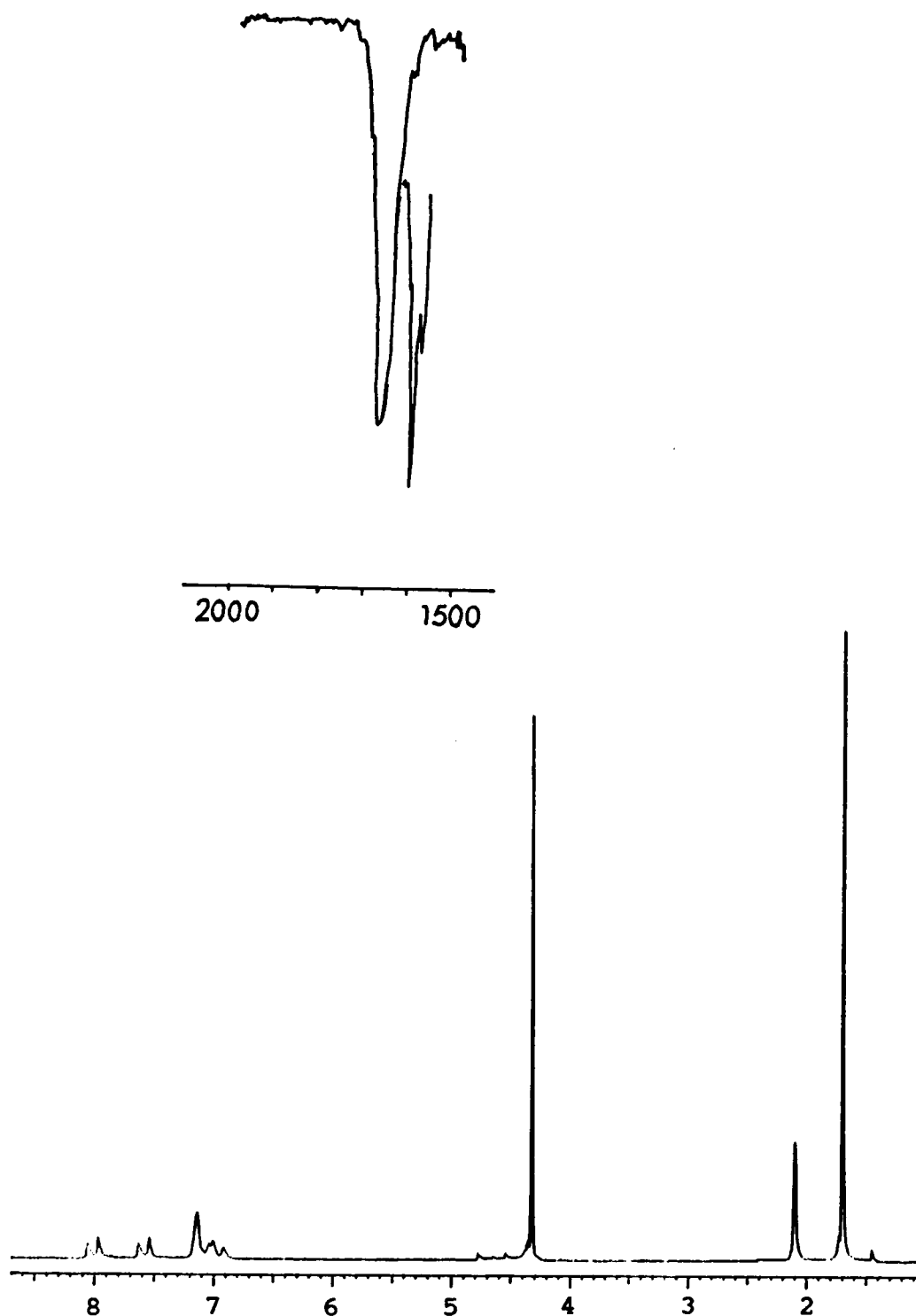


Figure 24. IR and ^1H NMR spectra for Fraction 3 from the reaction of Complex 1, $^*\text{CoCo}_2$, with 4,4'DMB.

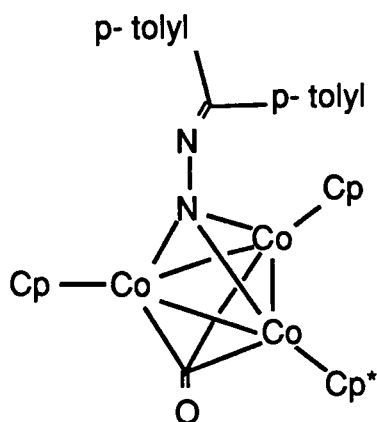


Figure 25. Proposed structure for Fraction 3 from the reaction of Complex 1, $^*\text{CoCo}_2$, with 4,4'DMB.

triply bridging diazoalkane from the low temperature photolysis of $\text{CpCo}(\text{CO})_2$ and diphenyldiazomethane in THF. Based on the spectral and elemental analysis data, a similar structure is proposed for this product as shown in Figure 25. The X-ray crystal structure of this species is currently under investigation.

The reaction of $^*\text{RhCo}_2$ with the diazoalkane is similar to that of Complex 1, but the products have not yet been identified. Separation of the reaction products by anaerobic column chromatography yielded three major fractions and one minor fraction.

Fraction 1, the minor fraction, was eluted from the column with a 50/50 mixture of hexane and methylene chloride and was violet red. The ^1H NMR spectrum indicated the trinuclear framework had been degraded and that a symmetric carbene unit was present. There was, however, no evidence

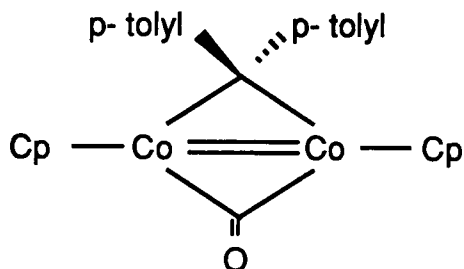


Figure 26. Proposed structure for Fraction 1 from the reaction of Complex 2, Cp^*RhCo_2 , with 4,4'DMB.

for a Cp^* ligand. Due to a lack of material, no further characterization was possible. Because of the similarities in the chromatographic and NMR characteristics, the structure shown in Figure 26 is proposed.

Fraction 2 was eluted with a mixture of hexane and methylene chloride with an increasing amount of methylene chloride and was intense blue in color. A ^1H NMR of the residue indicated the presence of three products. Two of the products could be identified from the proton signals as $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$ and $\text{CpCo}(\mu\text{-CO})_2\text{CoCp}$. The third product is proposed to be the unknown dinuclear species $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{CoCp}$ because of the Cp to Cp^* ratio, 1:3[83]. Further attempts to separate and isolate the three products lead to decomposition, and the only product isolated was the homodinuclear complex $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$.

Fraction 3 was eluted with pure methylene chloride and was olive green in color. The major product was

identified by ^1H NMR as unreacted trinuclear complex, $^*\text{RhCo}_2$, which appears to be the only trinuclear complex in this series that is stable towards chromatography.

Fraction 4 was greenish brown and eluted with hexane and THF (1%). A ^1H NMR spectrum of the collected product indicated that the trinuclear framework was intact and that an asymmetric carbene unit was present. Crystallization attempts yielded two different types of crystals, neither of which had the same ^1H NMR spectrum as the initial spectrum. Due to a lack of material, complete identification has not been possible. Spectroscopic data do indicate, however, that the crude product is a complex analogous to the triply bridging diazoalkane adduct isolated in the case of $^*\text{CoCo}_2$, as described above.

Conclusions

The trinuclear complexes in this series do react with carbon monoxide to yield tricarbonyl trinuclear species. The reaction of $(\text{Cp}^*\text{Ir})_2(\mu\text{-CO})_2\text{CoCp}$ with carbon monoxide is unique in that it results in the formation of at least two different tricarbonyl isomers. If the proposed equilibrium between the bridging and terminal carbonyl configurations of Complex 5 does occur in solution, then the two products which are formed could be carbonyl adducts of the two species involved in the equilibrium (Figure 27). A preparative scale reaction of the trinuclear complex with CO

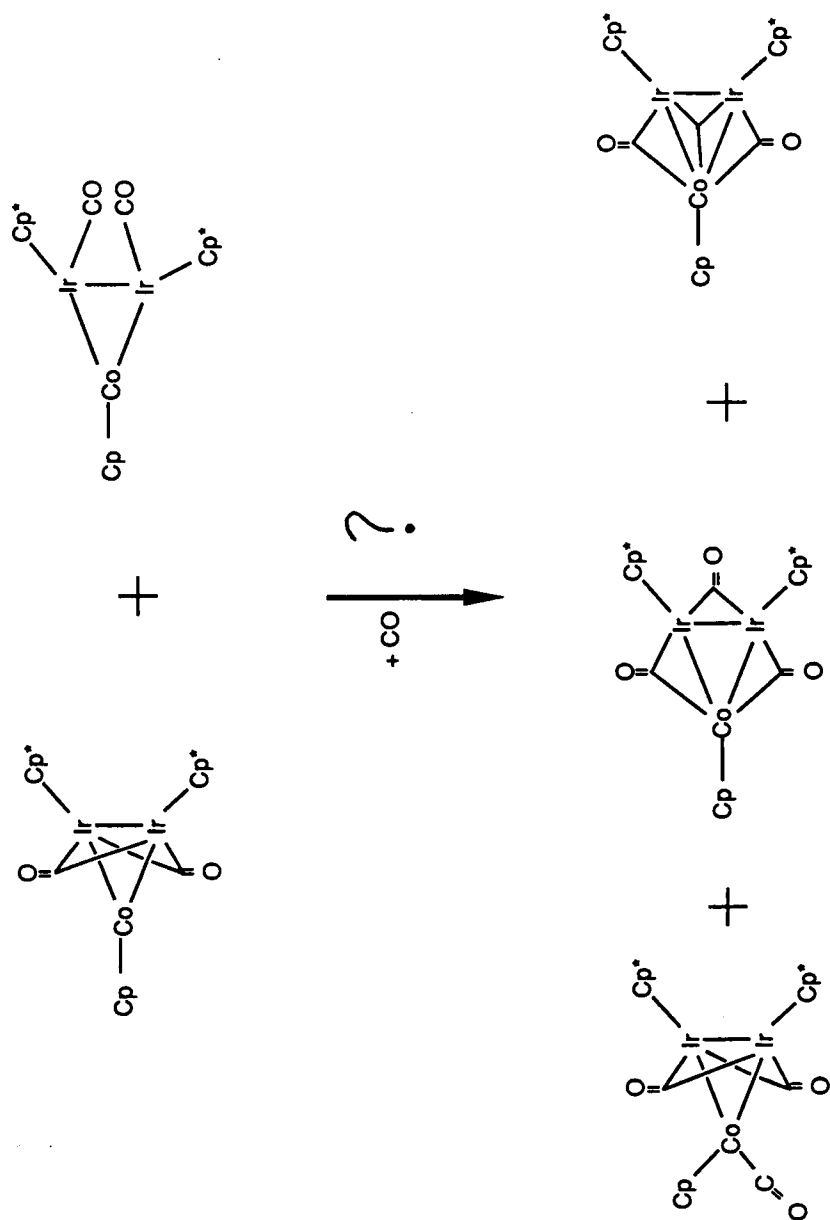


Figure 27. Addition of CO to terminal and bridging conformations of Complex 5, Ir_2Co .

should allow for the isolation and identification of the product(s) which could lead to a better understanding of what types of processes involving the carbonyl ligands occur in solution.

It was surprising that none of the reactions between the trinuclear complexes and the diazoalkane resulted in the expected bridging alkyldine species. It is widely believed that diazoalkane adducts are formed initially in the reaction of diazoalkanes with organometallic complexes; however, these adducts are usually not stable and generally decompose, releasing nitrogen gas and give rise to a bridging carbene complex[41-54]. The isolation of a triply bridging diazoalkane adduct is uncommon. One explanation for this unexpected product is that the steric hindrance (between the Cp* ligands and the aryl groups within the carbene unit) prevents the carbene unit from coming close enough to the trinuclear framework to initiate the release of nitrogen gas and the formation of a μ -alkyldine product. These observations may be contrasted to the reaction of *IrCo₂ with diazomethane[48] to give a bridging methylene trinuclear complex; the expected product does result when diazoalkanes with small substituents are reacted with the trinuclear cluster complex. The following question then arises: If the diazoalkane adduct is unstable and if steric hindrance prevents the formation of a bridging alkyldine complex, then why is any reaction observed? One possible

answer is that the 48 electron diazoalkane adduct, however unstable, is more stable than the original 46 electron trinuclear cluster complex.

CHAPTER V

OLEFIN-LIKE EXCHANGE

Introduction

Transition metal olefin complexes of the form CpML_2 ($\text{M} = \text{d}^8$ transition metal, $\text{L} = \text{olefin}$) are known to exchange coordinated olefin ligands for uncoordinated olefins. Although no mechanism for this exchange is known which accounts for all cases studied thus far, there are at least two possible mechanisms as shown in Figure 28[84]. The first is a dissociative mechanism in which the CpML_2 complex loses an olefin ligand in the rate determining step to form a 16 electron intermediate, CpML . A new olefin ligand (L') is then added in a subsequent fast step. The second is an associative mechanism in which a new olefin ligand is coordinated with simultaneous slippage of the Cp ring from the η^5 - to η^3 -coordination mode to form the intermediate $\text{CpML}_2\text{L}'$, and then one of the original olefin ligands is lost with the simultaneous slippage of the Cp ring back to the η^5 - coordination mode. While none of the clusters in this series contain olefin ligands, most do contain an olefin-like fragment. The dinuclear fragment in these clusters that was described earlier has frontier orbitals and electron occupancy which are similar to those of ethylene. Thus, the dinuclear fragment is isolobal with ethylene. The interaction of a CpCo fragment with the dinuclear complex

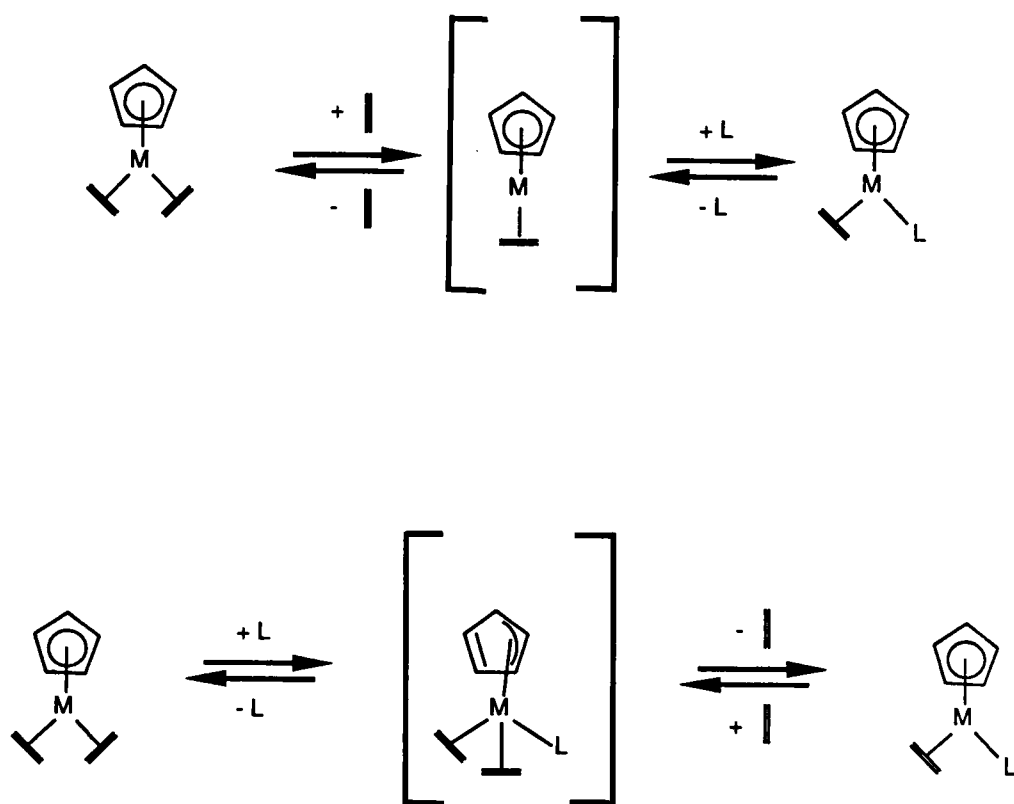
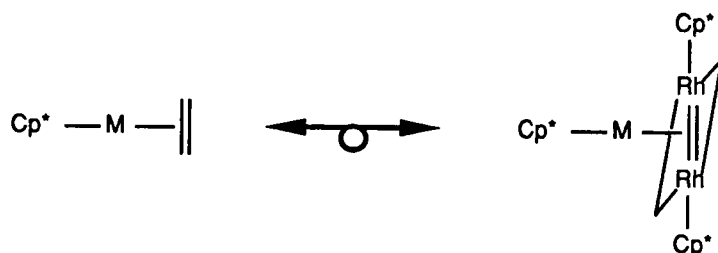


Figure 28. Two possible mechanisms for olefin exchange in organometallic complexes.

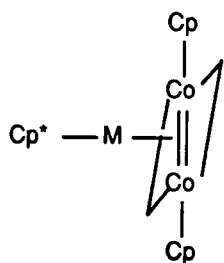
$(\text{Cp}^*\text{Rh})_2(\mu\text{-CO})_2$, or an analogous dinuclear complex of cobalt or iridium, should be isolobal to a CpCo fragment interacting with an ethylene ligand. These isolobal analogies are shown in Figure 29.

In the solid state, the carbonyl ligands in Complexes 1 and 2 bridge the Co-Co edge, whereas in the complex $^*\text{IrCo}_2$, the carbonyl ligands bridge one of the Ir-Co edges in the solid state. The exact structures of these complexes in solution are not known. In order to allow for the possible fluctuation of the carbonyl ligands in solution, two views of Type 1 clusters are considered: Type 1a and Type 1b. Type 1a clusters have a Cp^*M fragment interacting with the olefin-like dinuclear complex $(\text{CpCo})_2(\mu\text{-CO})_2$. Type 1b clusters have a CpCo fragment interacting with the olefin-like dinuclear complex $\text{Cp}^*\text{M}(\mu\text{-CO})_2\text{CoCp}$. Type 2 clusters have a CpCo fragment interacting with the olefin-like dinuclear complex $(\text{Cp}^*\text{M})_2(\mu\text{-CO})_2$.

The Cp^*M fragment of Type 1a clusters is a good π -donor relative to the CpCo fragments of Type 1b and Type 2 clusters. The olefin-like dinuclear fragment of Type 1a clusters is electron deficient relative to the olefin-like dinuclear fragments of Type 1b and Type 2 clusters, and therefore it is a better π -acceptor. Thus, it is expected that the $\text{Cp}^*\text{M}-||$ bond in Type 1a clusters is stronger than the corresponding $\text{CpCo}-||$ bonds in Type 1b and Type 2 clusters.

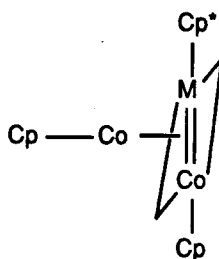


Type 1a

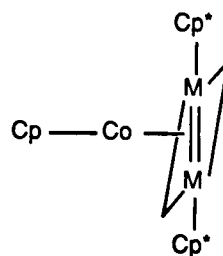


1. Electron rich dinuclear fragment - poor π -acceptor
2. Cp-Co fragment - poor π -donor
3. Cp-Co-olefin bond - weak

Type 1b



Type 2



1. Electron deficient dinuclear fragment - good π -acceptor
2. Cp*-M fragment - good π -donor
3. Cp*-M-olefin bond - strong

Figure 29. Isolobal analogies of Type 1a, Type 1b, and Type 2 clusters with organometallic complexes containing ethylene.

Type 1a and Type 2 clusters present the two extremes with respect to this type of LM-olefin interaction, whereas Type 1b clusters should be intermediate between the two. With these analogies in mind, it would be interesting to see if the unique metal fragment will undergo olefin-like exchange, analogous to the olefin exchange mechanisms, when the trinuclear species is exposed to different dinuclear species.

Reactivity Results

Based on the isolobal analogies above it is expected that olefin-like exchange should occur more readily for Type 2 clusters than for Type 1a or Type 1b clusters and more readily for Type 1b clusters than for Type 1a clusters. Sealed NMR tube reactions were investigated using various combinations of the six trinuclear complexes and the four known dinuclear precursors in the deuterated solvents benzene, toluene and THF (see Chapter II). All of the reactions appeared to be under equilibrium control in that mixtures of the products and reactants were observed when these reactions were complete. Higher rates of reaction were observed in THF as opposed to benzene or toluene, possibly due to the stabilization of reaction intermediates by solvent coordination. Reactions were clean (no decomposition was observed) when temperatures were kept at ambient temperature (22°C) or below.

The most thoroughly studied system to date is the reaction of Complex 3, $^*\text{Co}_2\text{Co}$, with the dinuclear species $(\text{Cp}^*\text{Rh})_2(\mu\text{-CO})_2$ to give the cobalt dinuclear species $(\text{Cp}^*\text{Co})_2(\mu\text{-CO})_2$ and Complex 4, $^*\text{Rh}_2\text{Co}$. This reaction is illustrated in Figure 30 and the NMR data is shown in Figure 31. The reaction occurs most readily in THF with little change in the relative amounts of products and reactants after three hours. The same reaction in benzene does not reach equilibrium in twelve hours. In toluene, the reaction of the trinuclear complex with the dinuclear species (10:1), is very slow, requiring 65 hours to reach equilibrium. At equilibrium, reaction is essentially complete (90%); there is only a very small amount of the original dinuclear complex remaining. In toluene, with a 3:2 ratio of the trinuclear complex to the dinuclear complex, equilibrium is reached after 60 hours and only about 10% reaction is observed.

Complex 3 shows insignificant reaction with the iridium dinuclear complex, $(\text{Cp}^*\text{Ir})_2(\mu\text{-CO})_2$, in THF. However, if a small amount of $\text{CpCo}(\text{C}_2\text{H}_4)_2$ is added to the reaction mixture, significant reaction yielding the cobalt dinuclear species $(\text{Cp}^*\text{Co})_2(\mu\text{-CO})_2$ and Complex 5, $^*\text{Ir}_2\text{Co}$, is observed in just three hours. This reaction is illustrated in Figure 32 and the NMR data is shown in Figure 33. The reverse reaction is observed to occur in the absence of $\text{CpCo}(\text{C}_2\text{H}_4)_2$. The NMR data is shown in Figure 34.

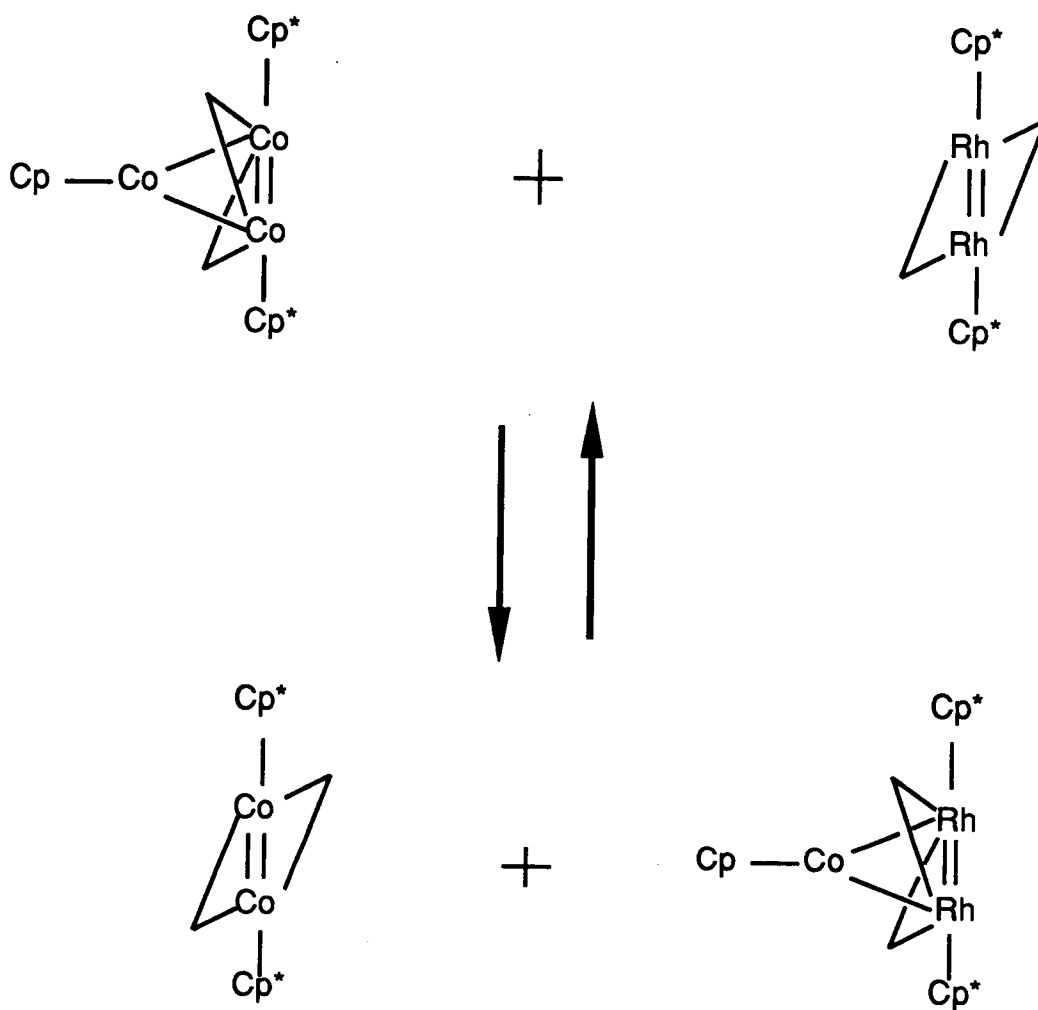


Figure 30. Scheme illustrating the reaction of Complex 3, $^*\text{Co}_2\text{Co}$, with $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$.

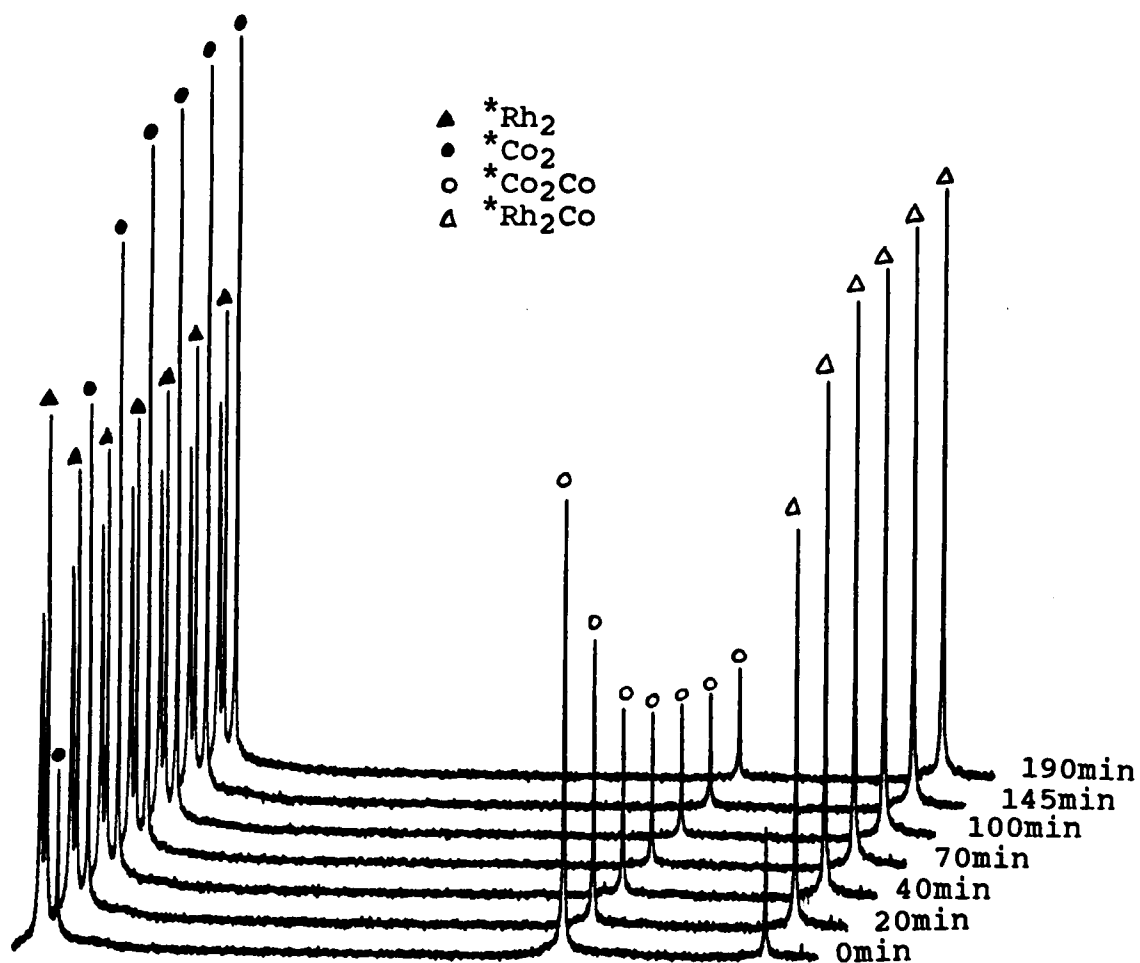


Figure 31. Stacked plot of the reaction of Complex 3, $^*\text{Co}_2\text{Co}$, with $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$ in THF-d_8 as followed by ^1H NMR.

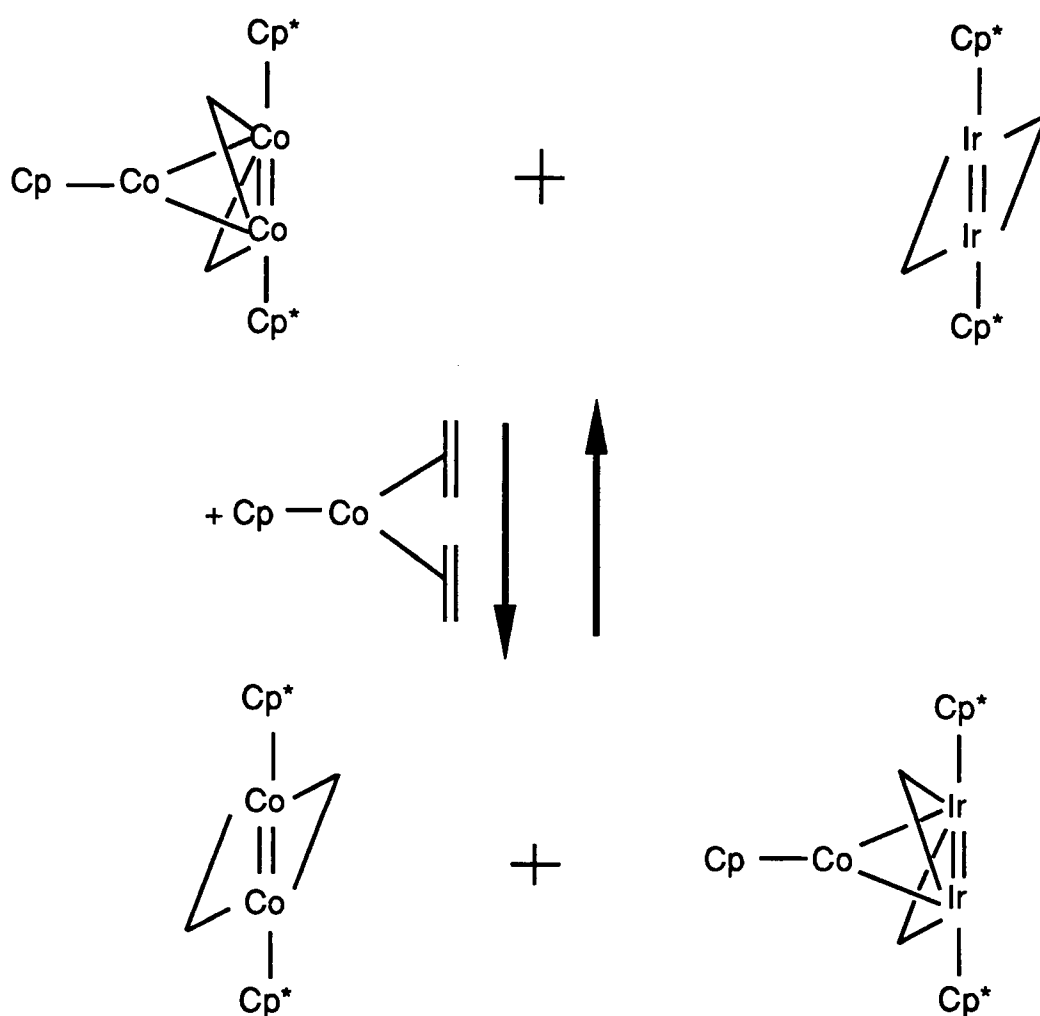


Figure 32. Scheme illustrating the reaction of Complex 3, $^*\text{Co}_2\text{Co}$, with $\text{Cp}^*\text{Ir}(\mu\text{-CO})_2\text{IrCp}^*$ catalyzed by $\text{CpCo}(\text{C}_2\text{H}_4)_2$.

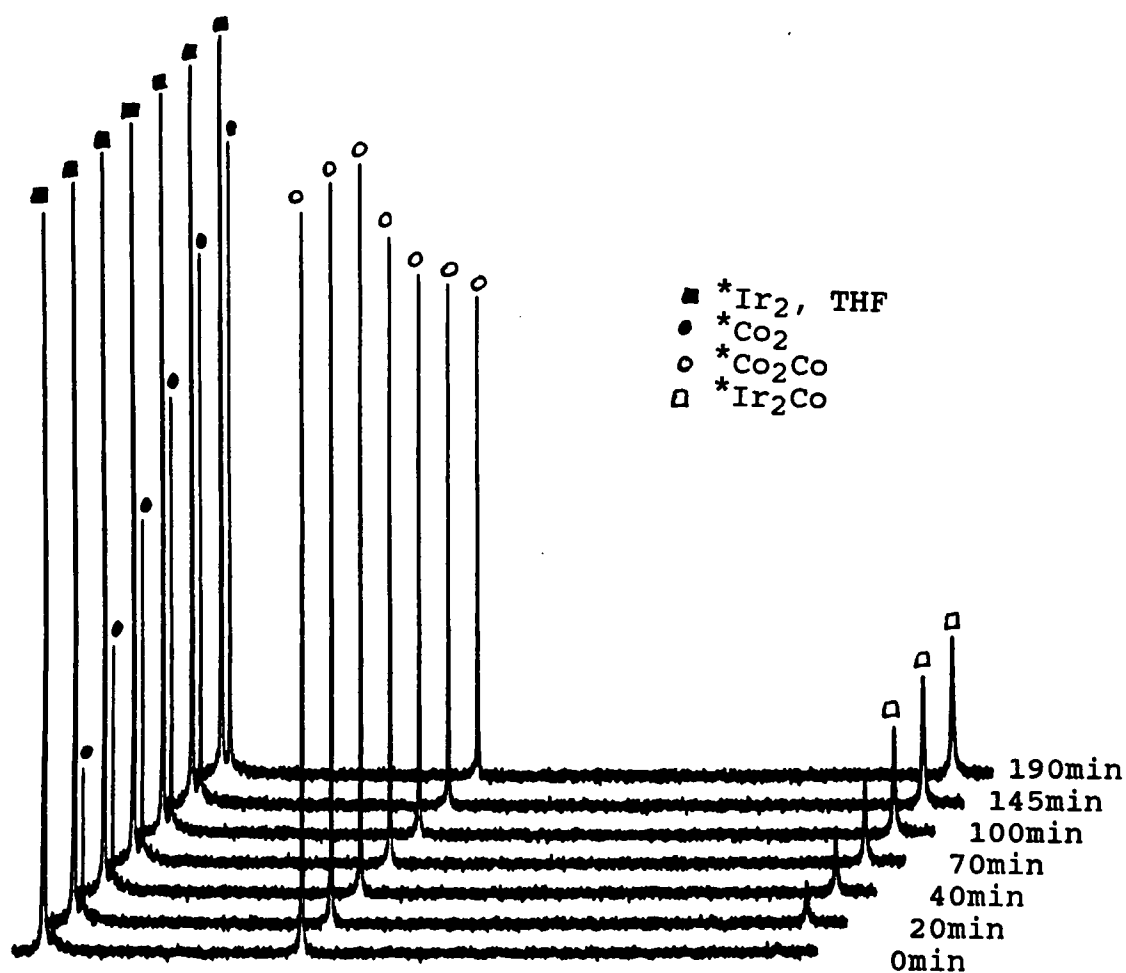


Figure 33. Stacked plot of the reaction of Complex 3, $^*\text{Co}_2\text{Co}$, with $\text{Cp}^*\text{Ir}(\mu\text{-CO})_2\text{IrCp}^*$ catalyzed by $\text{CpCo}(\text{C}_2\text{H}_4)_2$ in THF-d_8 as followed by ^1H NMR.

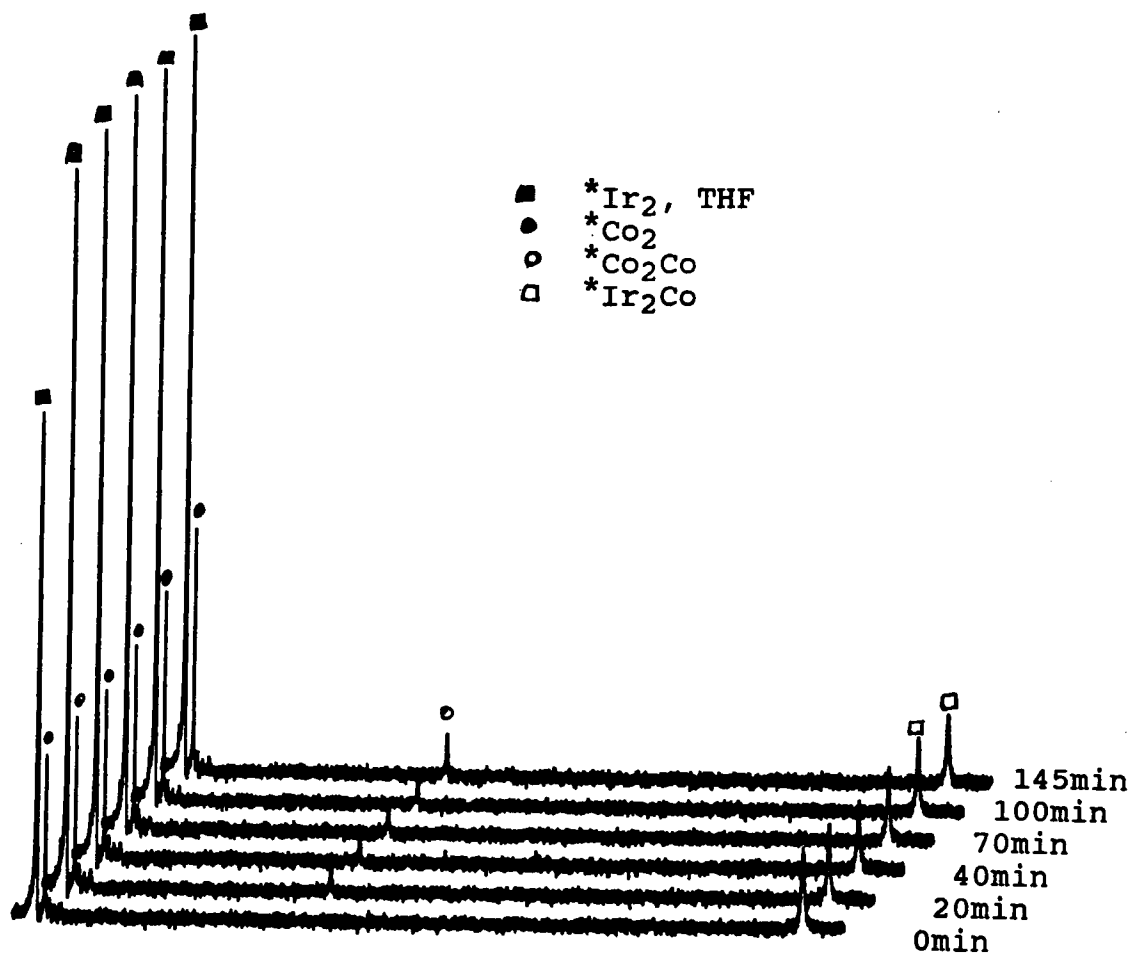


Figure 34. Stacked plot of the reaction of Complex 5, $^*\text{Ir}_2\text{Co}$, with $\text{Cp}^*\text{Co}(\mu\text{-CO})_2\text{CoCp}^*$ in THF-d_8 as followed by ^1H NMR.

A possible mechanism for the ethylene catalyzed exchange of a dinuclear fragment as observed in the reaction of Complex 3 with $\text{Cp}^*\text{Ir}(\mu\text{-CO})_2\text{IrCp}^*$ is shown in Figure 35.

A second set of equilibrium reactions involves the reaction of Complex 4, $^*\text{Rh}_2\text{Co}$, with the iridium dinuclear complex and the reverse reaction of Complex 5, $^*\text{Ir}_2\text{Co}$, with the rhodium dinuclear complex as shown in Figures 36-39. The reaction of the rhodium trinuclear with the iridium dinuclear complex is slow, and there are signs of decomposition upon heating to 50°C , whereas the reverse reaction occurs smoothly in only three hours. One explanation as to why the forward reaction is slow is based on the solid state structure of the two trinuclear complexes involved. Complex 4, $^*\text{Rh}_2\text{Co}$, contains fully triply bridging carbonyl ligands whereas Complex 5, $^*\text{Ir}_2\text{Co}$, contains doubly bridging carbonyl ligands which interact with the CpCo fragment only slightly. Thus, Complex 5, $^*\text{Ir}_2\text{Co}$, undergoes olefin-like exchange more readily. It is not known at this time whether the barrier to exchange of Complex 4, $^*\text{Rh}_2\text{Co}$, is thermodynamic or kinetic. Nevertheless, beginning with a trinuclear complex, $(\text{Cp}^*\text{M})_2(\mu\text{-CO})_2(\text{CoCp})$ and a dinuclear complex, $(\text{Cp}^*\text{M}')_2(\mu\text{-CO})_2$, olefin-like exchange does occur to give a trinuclear complex $(\text{Cp}^*\text{M}')_2(\mu\text{-CO})_2(\text{CoCp})$ and a dinuclear complex $(\text{Cp}^*\text{M})_2(\mu\text{-CO})_2$. Each of these reactions involves a Type 2 cluster undergoing olefin-like exchange to give a new Type 2 cluster.

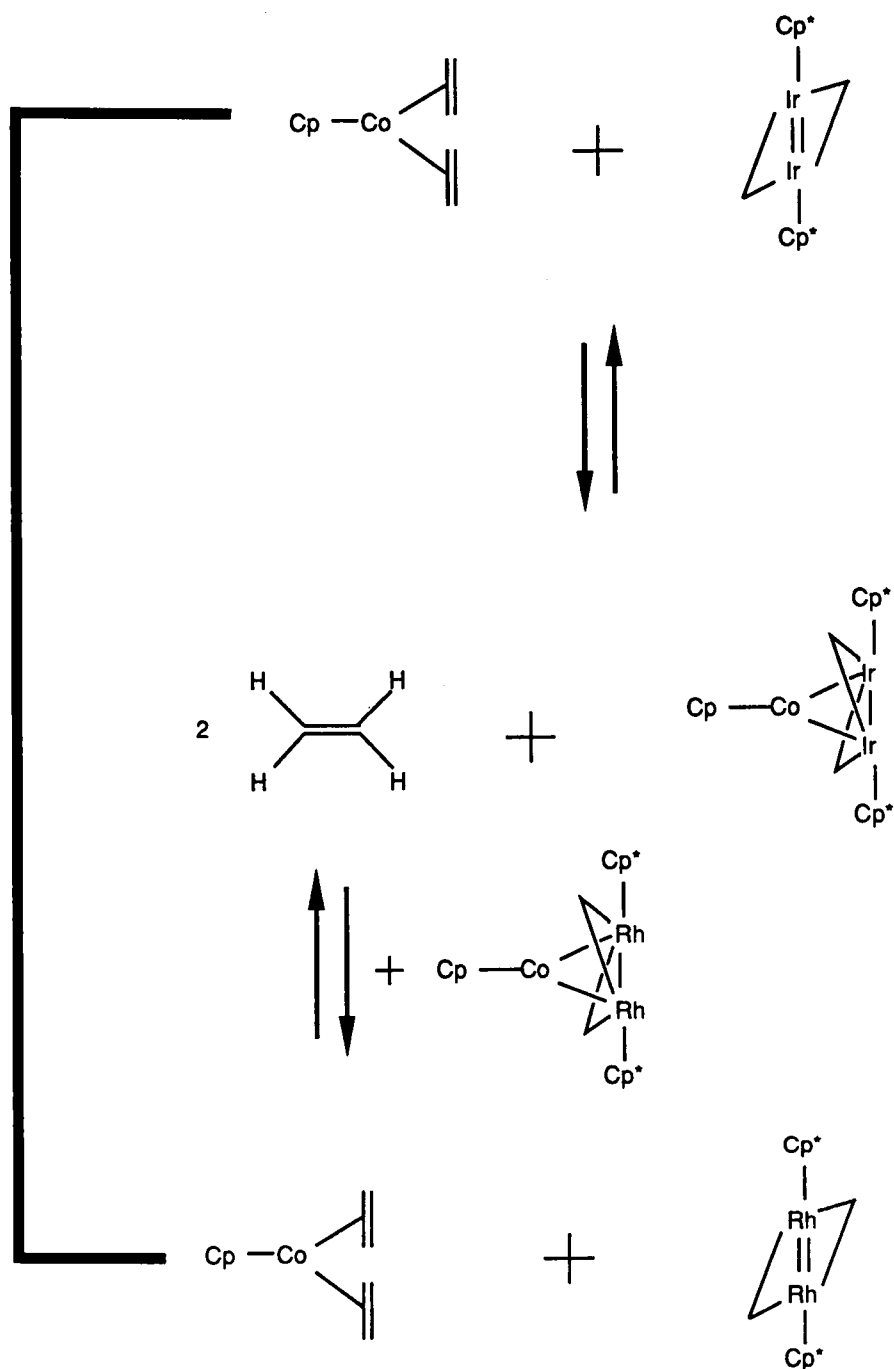


Figure 35. A possible mechanism for the ethylene catalyzed exchange of a dinuclear fragment for these trinuclear complexes.

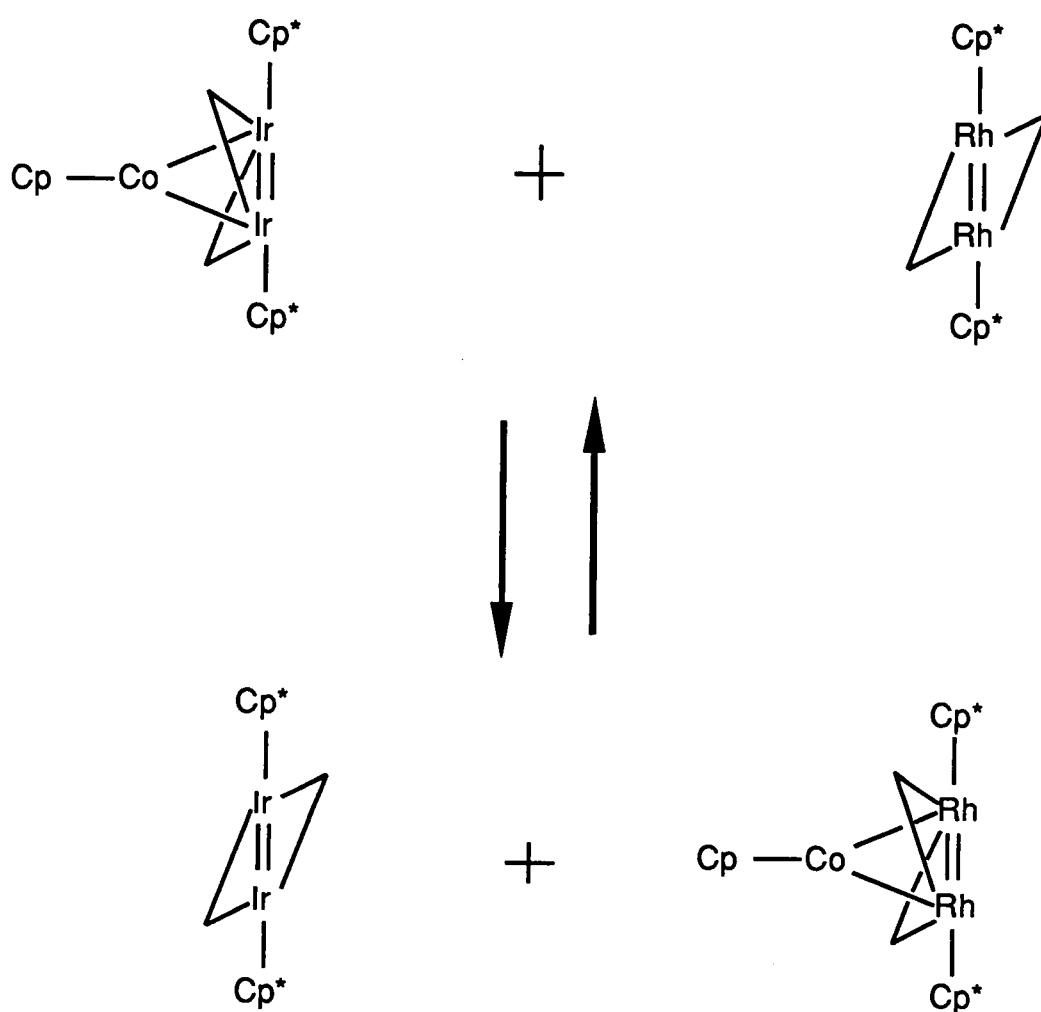


Figure 36. Scheme illustrating the reaction of Complex 5, $^*\text{Ir}_2\text{Co}$, with $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$.

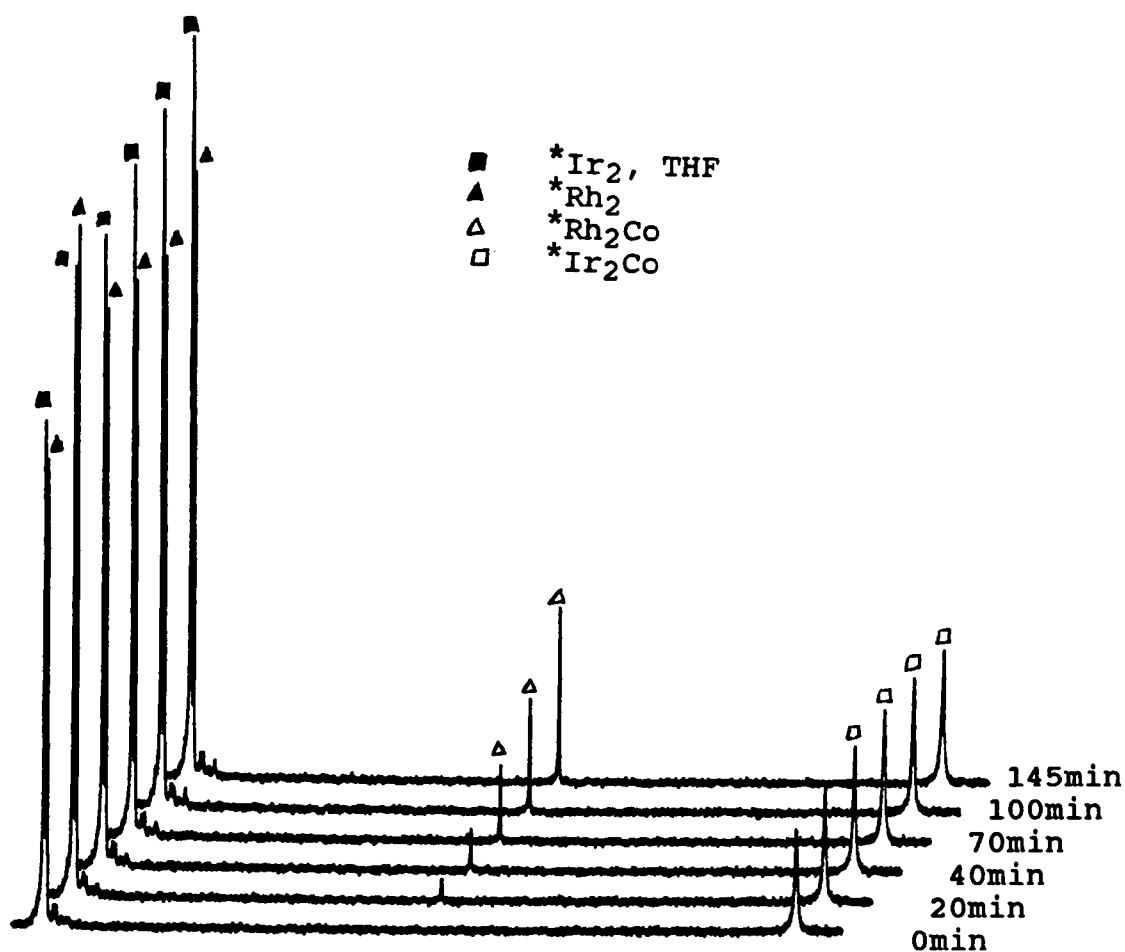


Figure 37. Stacked plot of the reaction of Complex 5, $^*\text{Ir}_2\text{Co}$, with $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$ in THF-d_8 as followed by ^1H NMR.

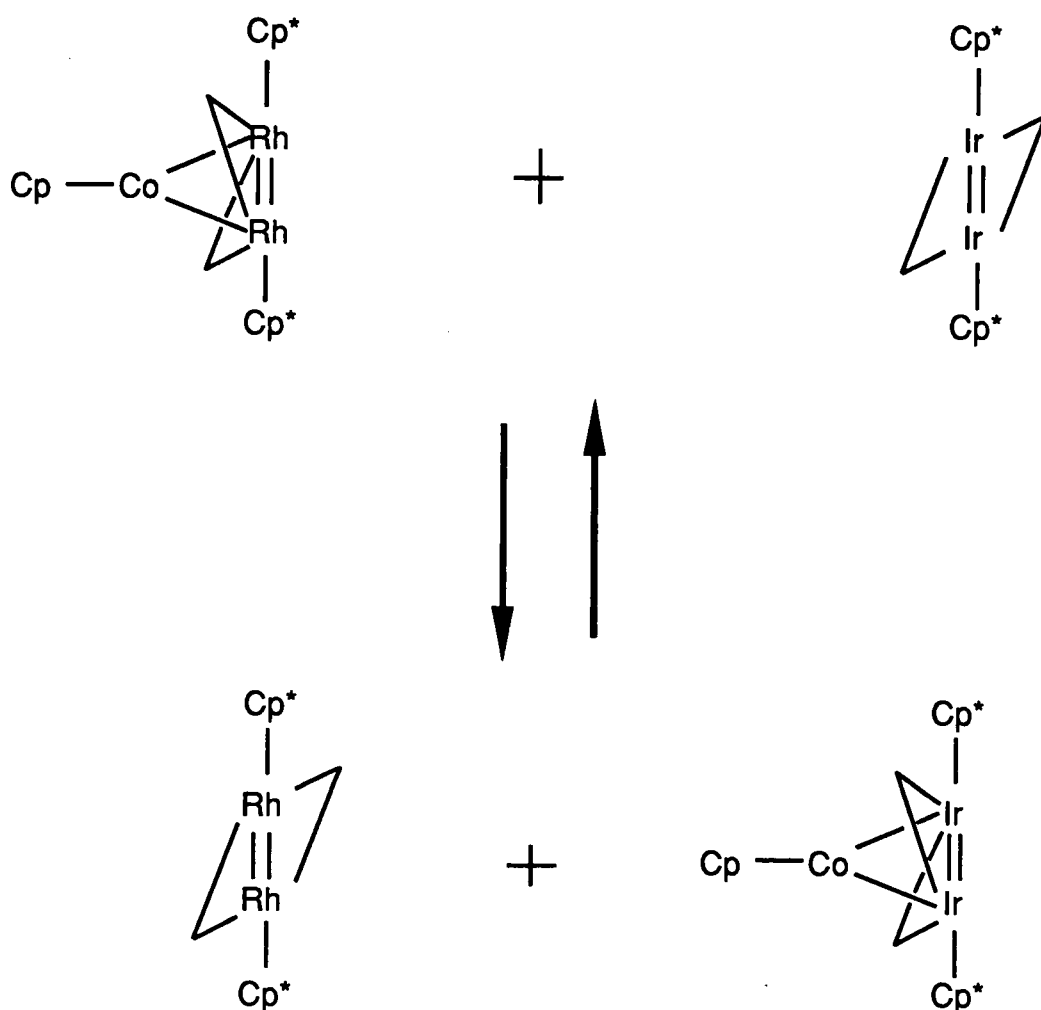


Figure 38. Scheme illustrating the reaction of Complex 4, $^*\text{Rh}_2\text{Co}$, with $\text{Cp}^*\text{Ir}(\mu\text{-CO})_2\text{IrCp}^*$.

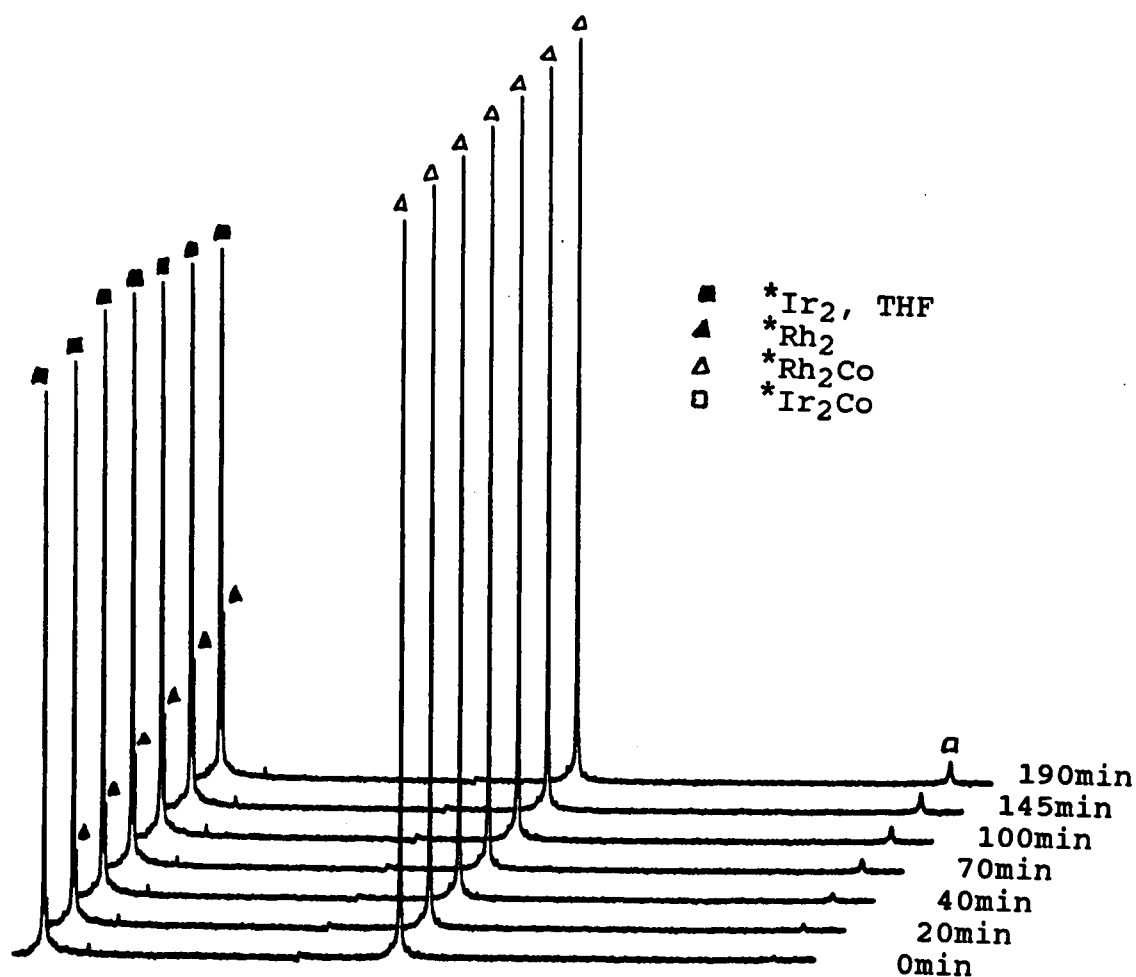


Figure 39. Stacked plot of the reaction of Complex 4, $^*\text{Rh}_2\text{Co}$, with $\text{Cp}^*\text{Ir}(\mu\text{-CO})_2\text{IrCp}^*$ in THF-d_8 as followed by ^1H NMR.

The reaction in THF of the cobalt trinuclear Complex 3 with the dinuclear complex $\text{Cp}^*\text{Ir}(\mu\text{-CO})_2\text{CoCp}$, illustrated in Figure 40, occurs cleanly for the first four hours, but unidentifiable side products are present before equilibrium is reached.

The reaction of a Type 1b cluster, $^*\text{MCo}_2$, with an olefin-like dinuclear complex should result in a new trinuclear complex and the dinuclear species $^*\text{MCo}$. In the cases of the cobalt and rhodium Type 1 clusters, the dinuclear products $\text{Cp}^*\text{M}(\mu\text{-CO})_2\text{CoCp}$ have not been independently synthesized. The success of an olefin-like exchange reaction would provide ^1H NMR evidence for the unknown dinuclear species $^*\text{MCo}$ where $\text{M} = \text{Co}$ or Rh .

The reaction in benzene of Complex 2, $^*\text{RhCo}_2$, with the rhodium dinuclear species $(\text{Cp}^*\text{Rh})_2(\mu\text{-CO})_2$, illustrated in Figure 41, does appear to give Complex 4, $^*\text{Rh}_2\text{Co}$, and some other species which, based on NMR evidence (positions and relative integrations of the proton signals), may be the unknown dinuclear complex $(\text{Cp}^*\text{Rh})(\mu\text{-CO})_2(\text{CoCp})$. [Further evidence for the unknown dinuclear complex is provided by the reaction of Complex 2 with 4,4'-dimethyldiazobenzophenone which, as described in Chapter IV, gives a product with the same proton NMR shifts and has the chromatographic properties of a dinuclear species, being eluted with two other dinuclear complexes, $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$ and $\text{CpCo}(\mu\text{-CO})_2\text{CoCp}$.]

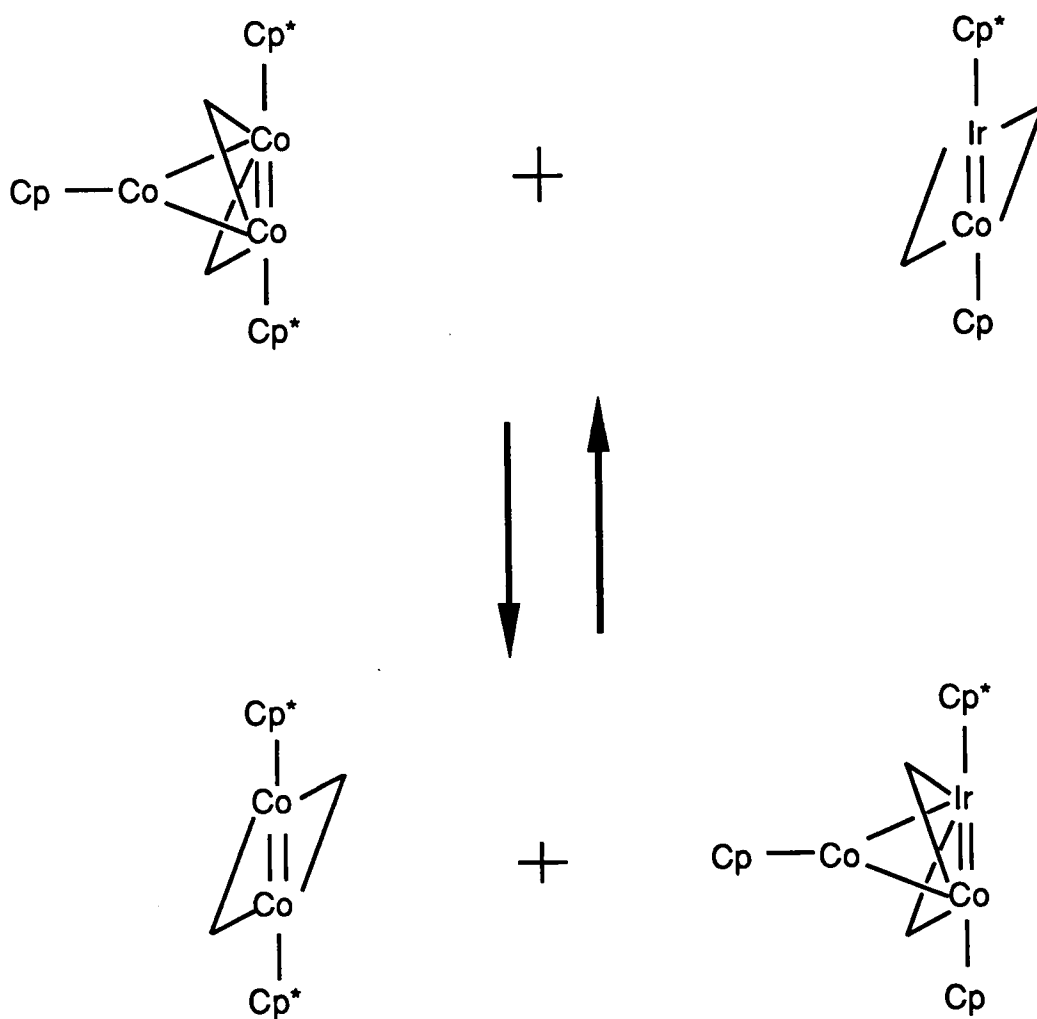


Figure 40. Scheme illustrating the reaction of Complex 3, $^*\text{Co}_2\text{Co}$, with $\text{Cp}^*\text{Ir}(\mu\text{-CO})_2\text{CoCp}$.

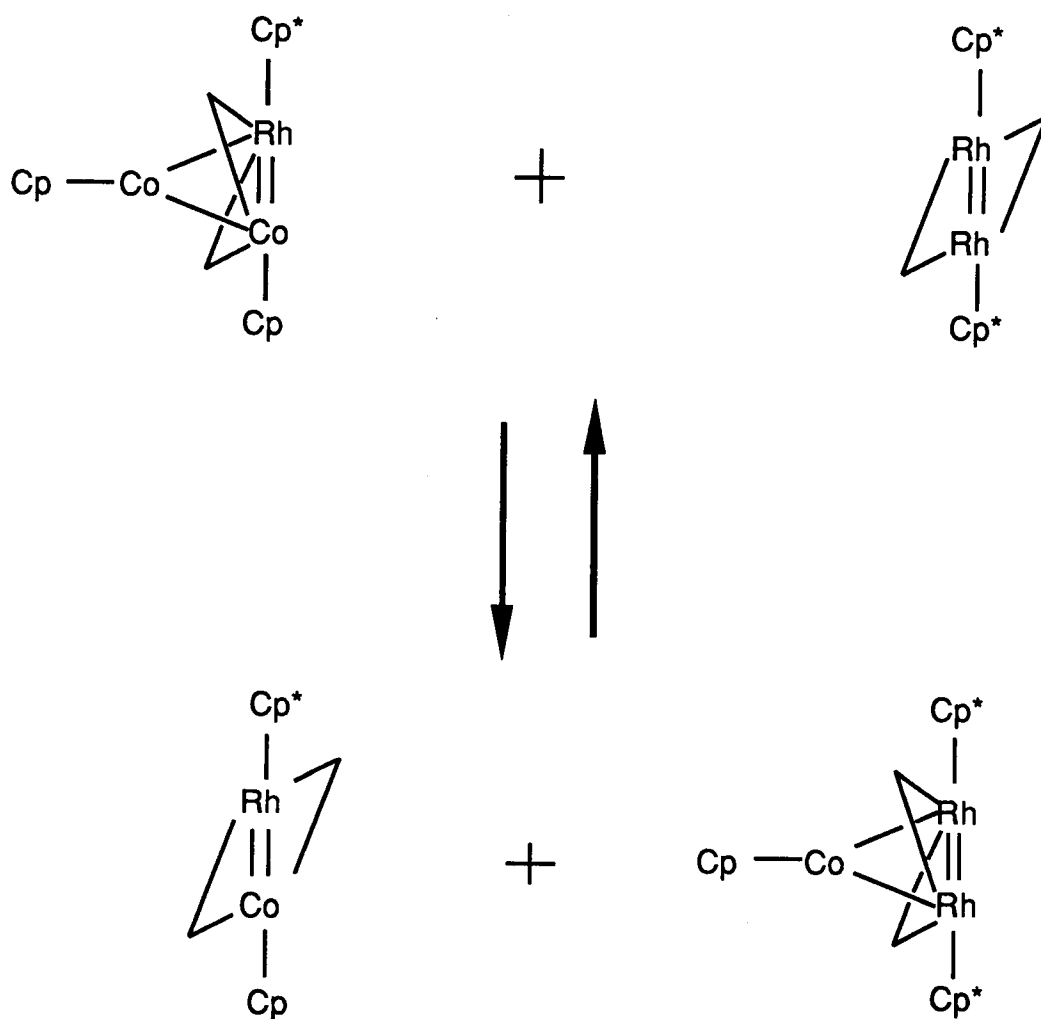


Figure 41. Scheme illustrating the reaction of Complex 2, Cp^*RhCo_2 , with $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$.

The reaction in benzene of Complex 1, $^*\text{CoCo}_2$, with the rhodium dinuclear complex, illustrated in Figure 42, gives Complex 4, $^*\text{Rh}_2\text{Co}$, as expected. There is also NMR evidence for the unknown dinuclear species $\text{Cp}^*\text{Co}(\mu\text{-CO})_2\text{CoCp}$.

The reactions shown in Figures 41 and 42, however, do not appear to occur in toluene and have not been attempted in THF. An example of a Type 1b trinuclear complex undergoing olefin-like exchange in THF is the reaction of the model complex $^*\text{IrCo}_2$ with the rhodium dinuclear species $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$. This reaction is illustrated in Figure 43 and the NMR data is shown in Figure 44. This reaction appears to occur slowly but cleanly and goes essentially to completion in about two weeks (Figure 45).

At this time there is no evidence for the olefin-like exchange of the $\text{CpCo}(\mu\text{-CO})_2\text{CoCp}$ dinuclear fragment of Type 1a for a $\text{Cp}^*\text{M}(\mu\text{-CO})_2\text{MCp}^*$ dinuclear complex as shown in Figure 46. There are no proton signals in the NMR which could be due to the trinuclear complex $(\text{Cp}^*\text{M})_2(\mu\text{-CO})_2(\text{M}'\text{Cp}^*)$ [38] or the dinuclear complex $\text{CpCo}(\mu\text{-CO})_2\text{CoCp}$ [51].

Conclusions

The trinuclear cluster complexes described here appear to undergo clean exchange of various dinuclear fragments within the triangular framework when exposed to appropriate dinuclear complexes. The mechanism for these

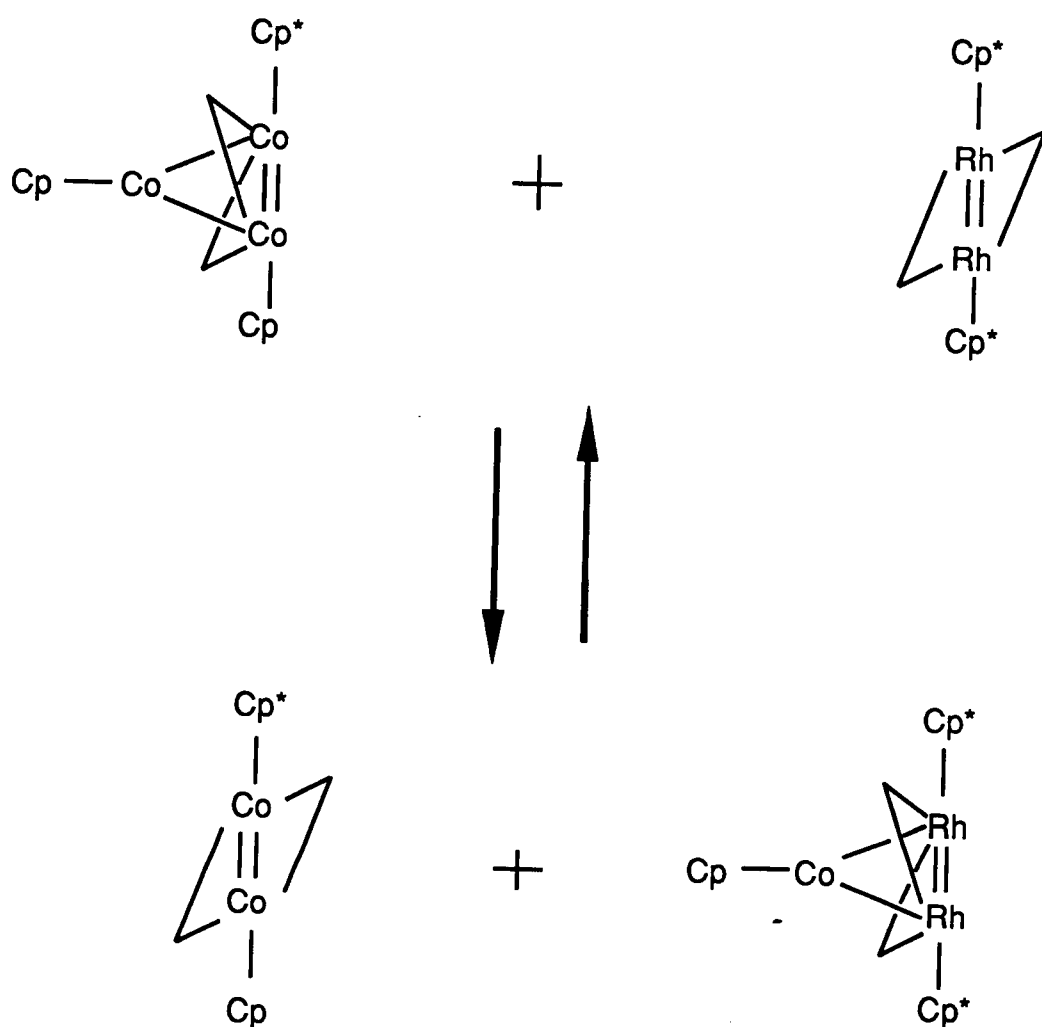


Figure 42. Scheme illustrating the reaction of Complex 1, $^*\text{CoCo}_2$, with $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$.

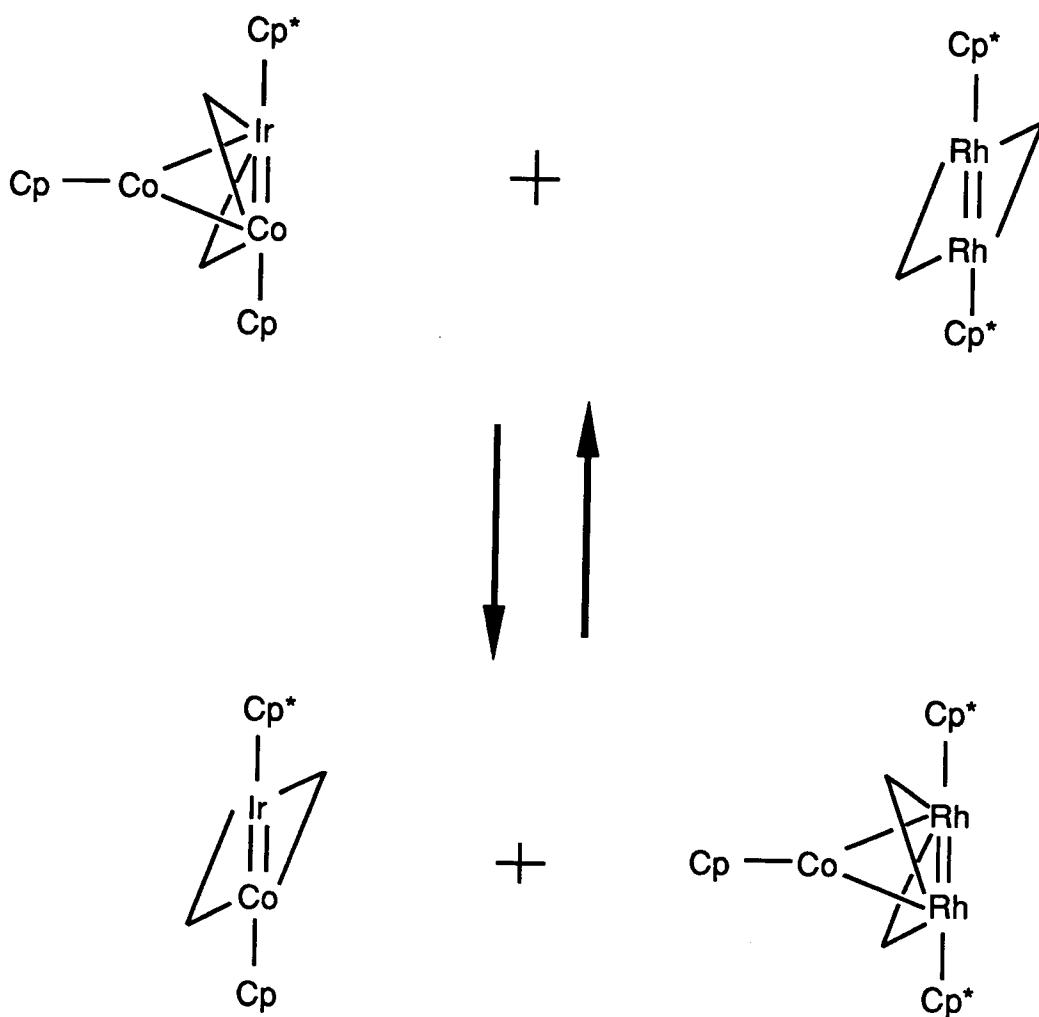


Figure 43. Scheme illustrating the reaction of the model complex, $^*\text{IrCo}_2$, with $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$.

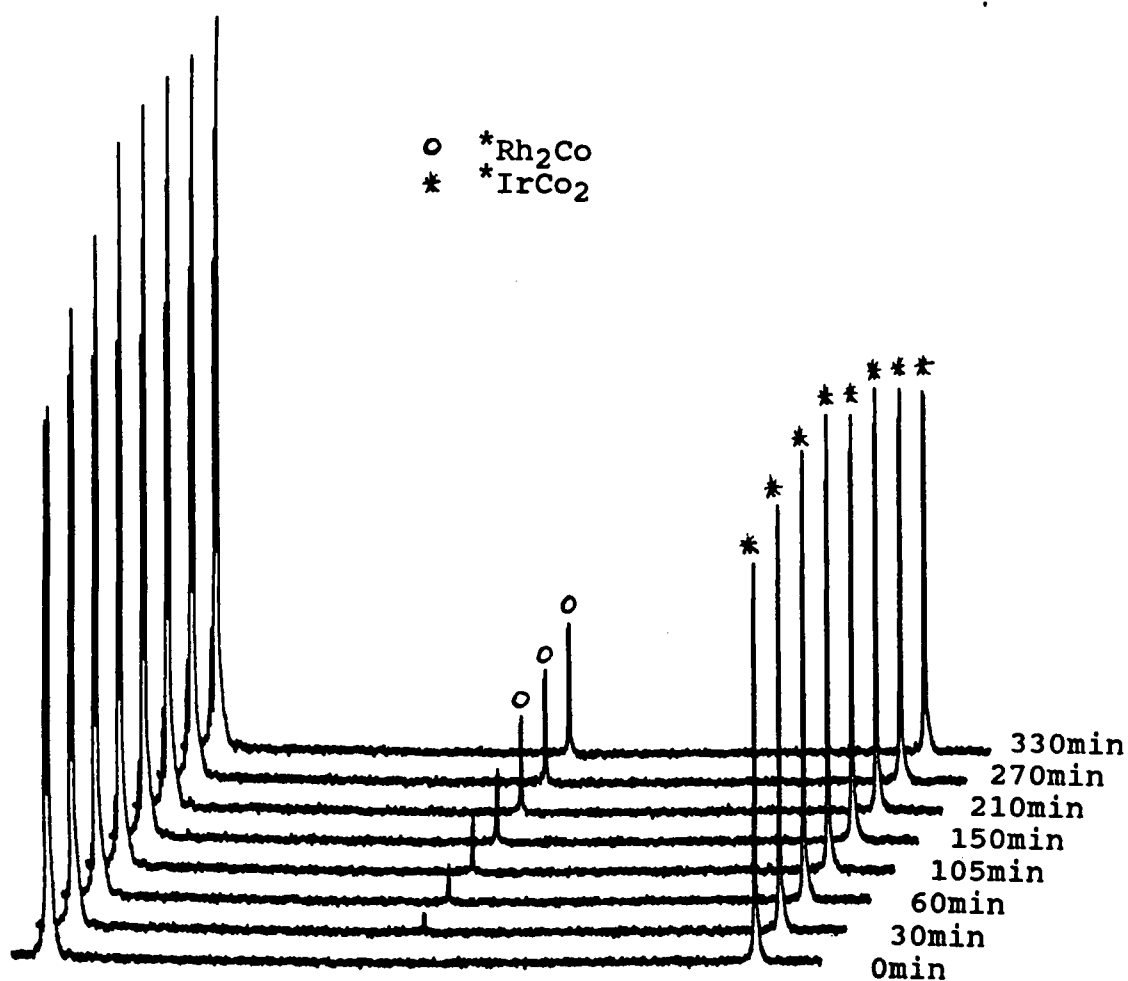


Figure 44. Stacked plot of the reaction of the model complex, $^*\text{IrCo}_2$, with $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$ in THF-d_8 as followed by ^1H NMR.

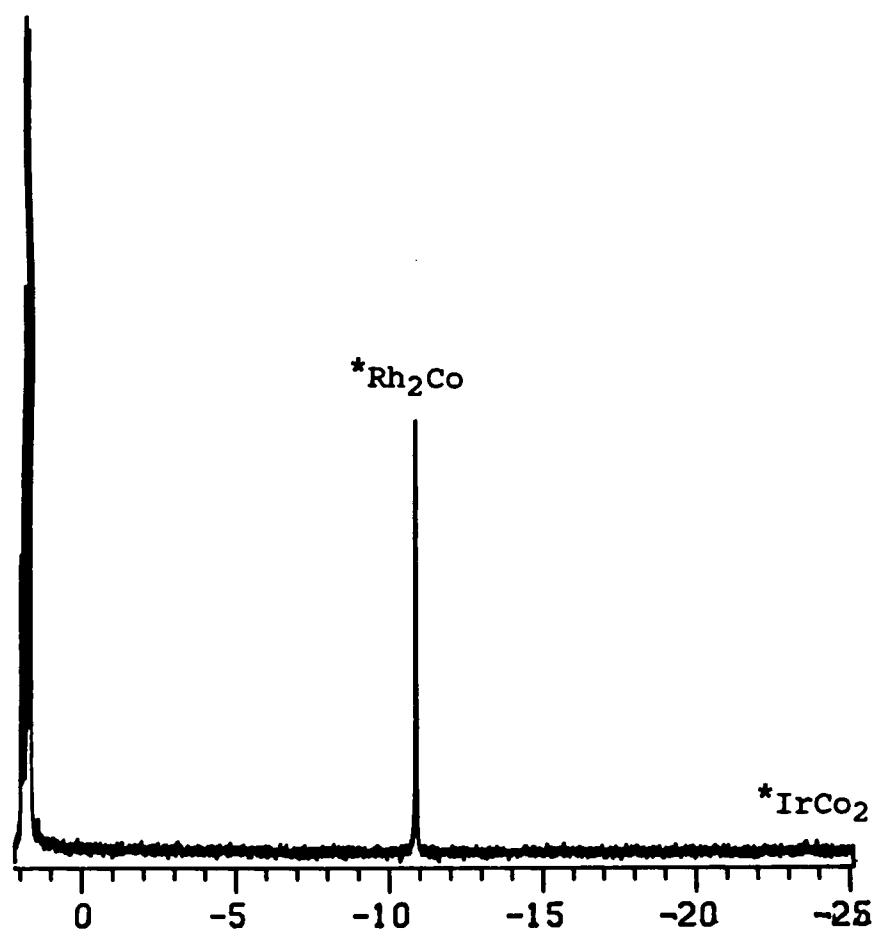


Figure 45. ^1H NMR spectrum of the reaction of the model complex, $^*\text{IrCo}_2$, with $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2\text{RhCp}^*$ after two weeks.

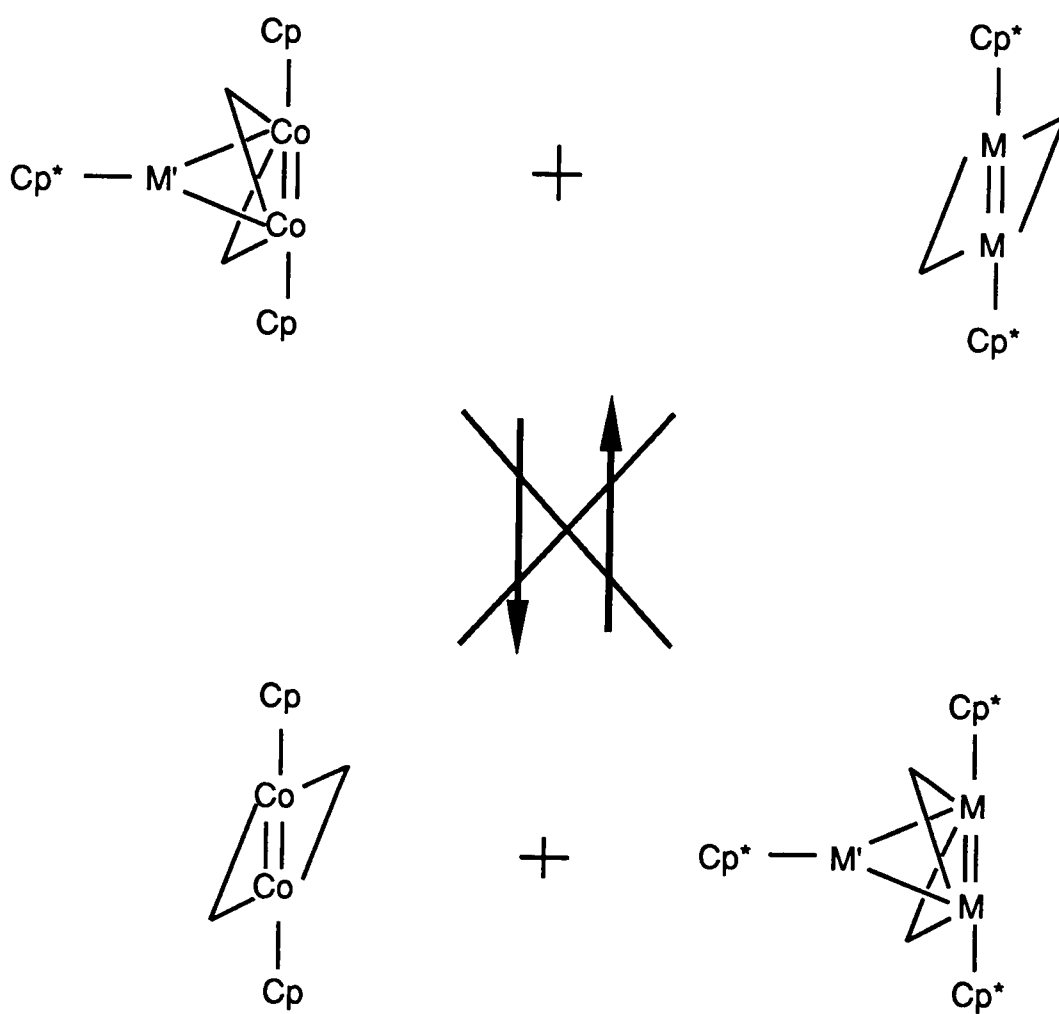
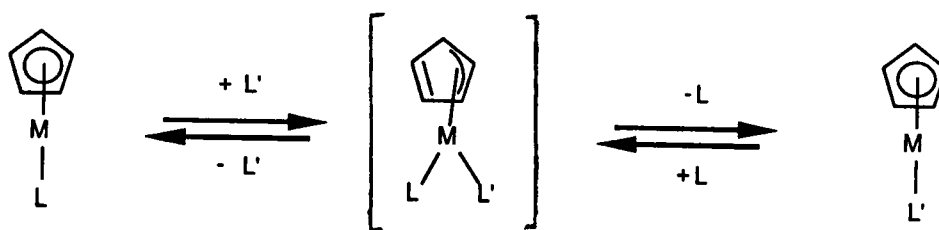


Figure 46. Scheme illustrating the reaction of a Type 1a cluster, $\text{Cp}^*\text{M}'\text{Co}_2$, with $\text{Cp}^*\text{M}(\mu\text{-CO})_2\text{MCp}^*$.



L, L' = olefin-like dinuclear fragment

Figure 47. Proposed mechanism for the olefin-like exchange process exhibited by Complexes 1-5.

observed exchange reactions is not known with certainty. The mechanism shown in Figure 47 is proposed on the basis of the analogy (structural and isolobal) that appears to exist between these trinuclear complexes and the CpML species. This observation of olefin-like exchange provides the basis for more detailed studies of the reactions including determinations of the equilibrium constant and reaction kinetics. It will be interesting to see if Complex 4, $\text{*Rh}_2\text{Co}$, is indeed a thermodynamic "sink" in these reactions by virtue of its triply bridging carbonyl ligands.

Stone[2-10] and others[11-27] have used the Isolobal Theory of Hoffmann[1] to aid in the synthesis of new organometallic cluster complexes. Here the theory is used to predict the reactivity of organometallic cluster complexes with respect to olefin or olefin-like exchange.

A further understanding of this process may lead to a broader understanding of the fundamental processes involved in cluster formation and degradation.

CHAPTER VI

SUMMARY

The synthesis of five new trinuclear organometallic complexes of iridium, rhodium, and cobalt has been described. These complexes, taken together with $^*\text{IrCo}_2$, form a series of six cluster complexes containing both cyclopentadienide and pentamethylcyclopentadienide ligands. Each complex reacts with carbon monoxide to form tricarbonyl trinuclear complexes. The reactions of Type 2 clusters with 4,4'-dimethyldiazobenzophenone cause fragmentation of the trinuclear framework and give rise primarily to the dinuclear precursors. Both Complex 1 and Complex 2 react with 4,4'-dimethyldiazobenzophenone to yield dinuclear μ -alkylidene products and triply bridging diazoalkane trinuclear products. Future studies of the reactions of these complexes with two electron donor ligands include diazoalkanes with smaller organic substituents and nitric oxide.

These complexes have been shown to undergo olefin-like exchange when exposed to different dinuclear species which are isolobal to ethylene. This process is believed to be similar to the type of reactivity involved in the fundamental processes of cluster formation and degradation which are ever present in organometallic chemistry. Detailed thermodynamic and dynamic studies are included in

future research which should lead to a further understanding of these processes.

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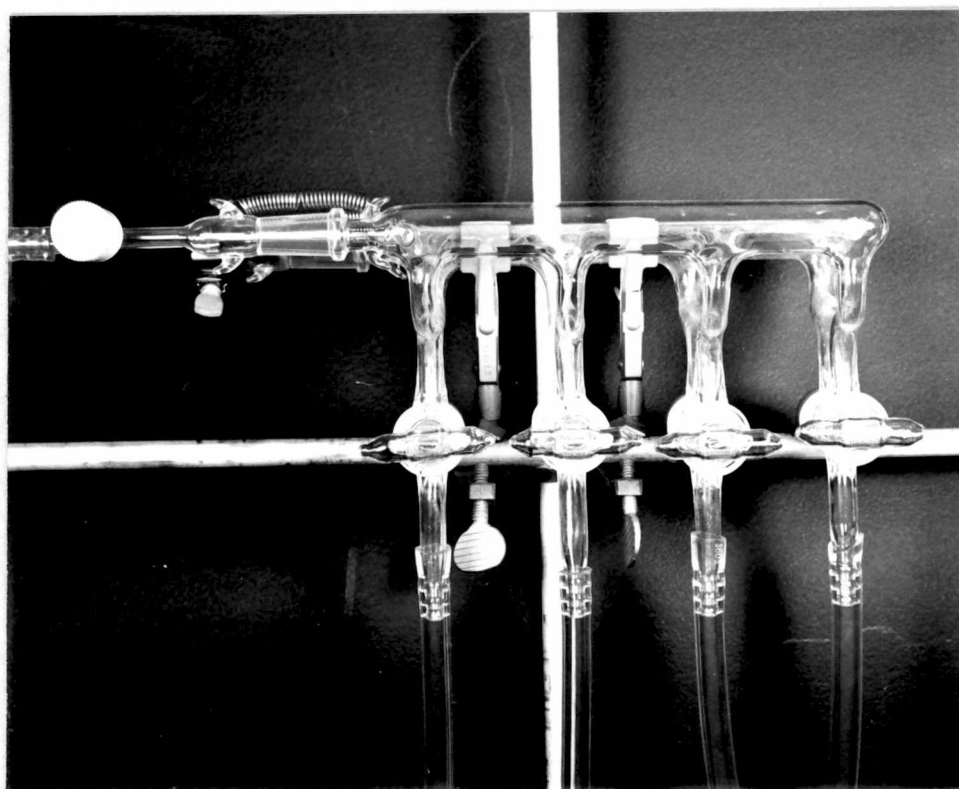
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APPENDIXES

APPENDIX A

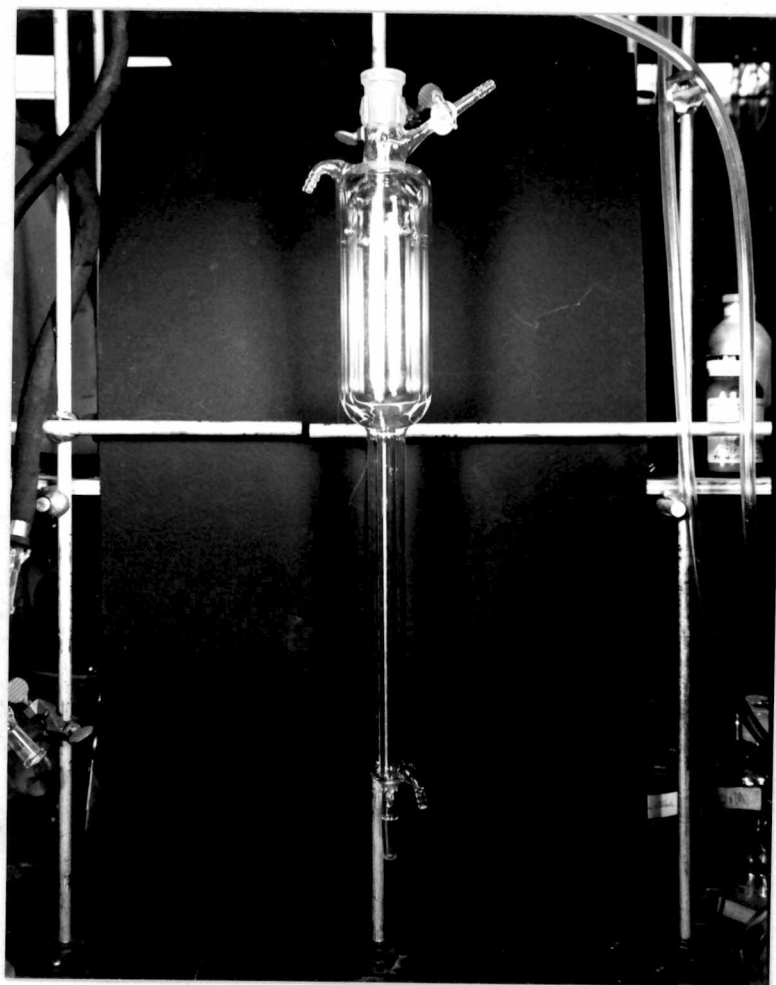
Special Glassware



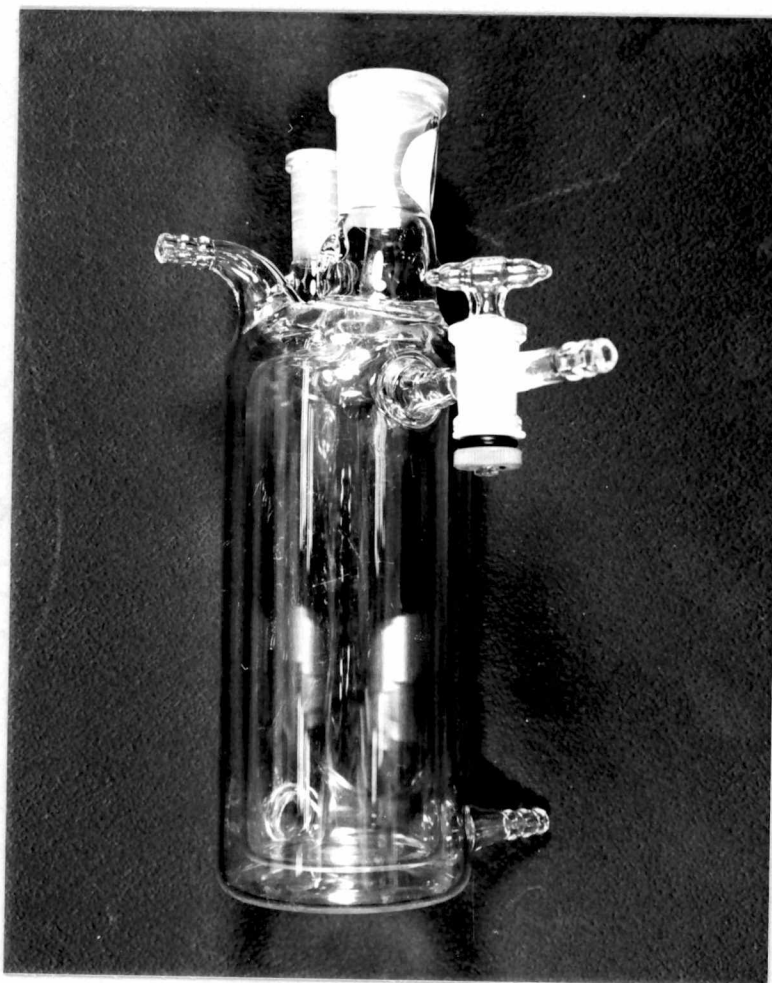
Vacuum/Nitrogen Manifold



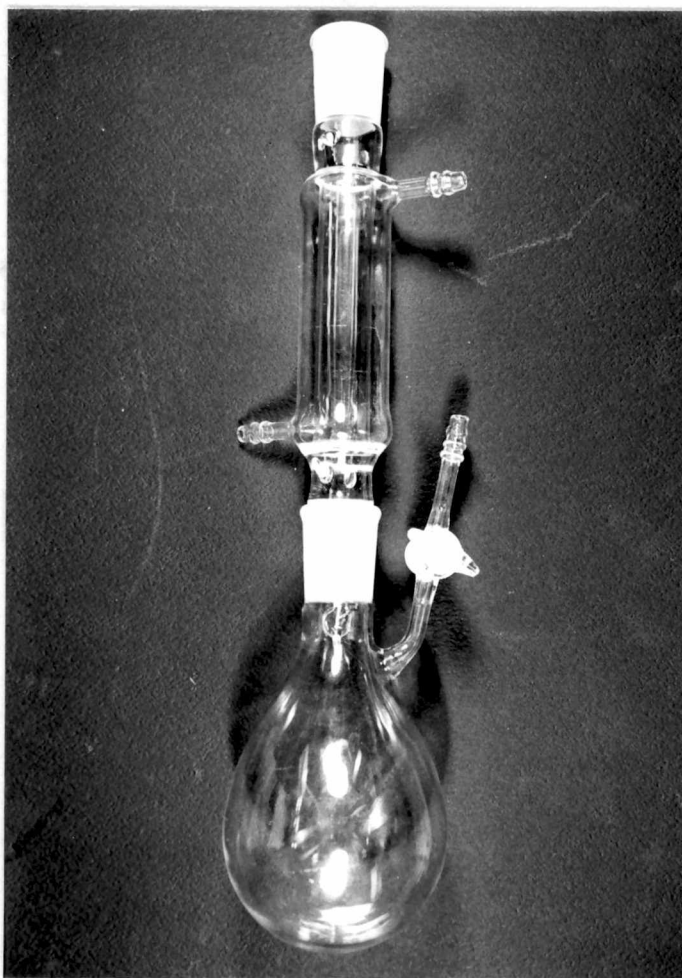
100mL Schlenk Vessel



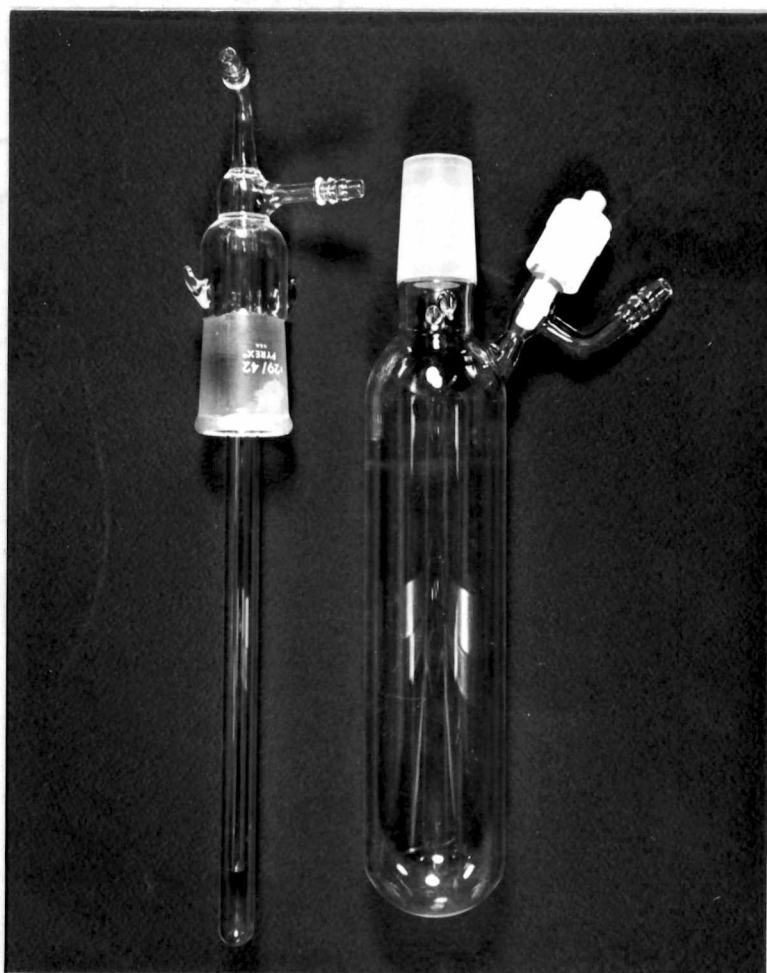
Jacketed Flash Chromatography Column



500mL Jacketed Schlenk Vessel



Sublimation Bottom and Condensor



Sublimation Cold Finger and 500mL Schlenk Vessel

APPENDIX B
Bond Lengths and Angles
for Complexes 1-5

Bond Lengths and Angles for Complex 1, Cp*Co(μ -CO)₂(CoCp)₂

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
			Co2	Co2a	Cb	Cba
Co1	Co2	2.305				
Co1	Co2a	2.305	62.9			
Co1	Cb	2.160	49.8	50.1		
Co1	Cba	2.160	50.1	49.8	82.0	
Co1	Cnt1	1.679	143.0	153.1	132.8	144.6
			Co1	Co2a	Cb	Cba
Co2	Co1	2.305				
Co2	Co2a	2.405	58.5			
Co2	Cb	1.884	61.1	50.7		
Co2	Cba	1.894	61.0	50.3	97.2	
Co2	Cnt2	1.725	144.9	156.4	132.8	129.0
			Co1	Co2	Cb	Cba
Co2a	Co1	2.305				
Co2a	Co2	2.405	58.5			
Co2a	Cb	1.894	61.0	50.3		
Co2a	Cba	1.884	61.1	50.7	97.2	
Co2a	Cnt3	1.725	144.9	156.4	129.0	132.8

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
			Ob	Co1	Co2
Cb	Ob	1.174			
Cb	Co1	2.160	129.2		
Cb	Co2	1.884	139.3	69.1	
Cb	Co2a	1.894	138.9	68.9	79.1

			Oba	Co1	Co2
Cba	Oba	1.174			
Cba	Co1	2.160	129.2		
Cba	Co2	1.894	138.9	68.9	
Cba	Co2a	1.884	139.3	69.1	79.1

Bond Lengths and Angles for Complex 2, $\text{Cp}^*\text{Rh}(\mu\text{-CO})_2(\text{CoCp})_2$

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
			Co1	Co2	C21	C22
Rh	Co1	2.433				
Rh	Co2	2.431	59.8			
Rh	C21	2.322	46.9	46.3		
Rh	C22	2.319	46.6	46.7	75.2	
Rh	Cnt3	1.815	150.9	149.2	142.5	142.3

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
			Co2	Rh	C21	C22
Co1	Co2	2.426				
Co1	Rh	2.433	60.0			
Co1	C21	1.896	49.5	63.5		
Co1	C22	1.884	49.9	63.5	97.0	
Co1	Cnt1	1.725	159.3	140.7	130.6	131.3

			Co1	Rh	C21	C22
Co2	Co1	2.426				
Co2	Rh	2.431	60.1			
Co2	C21	1.872	50.4	63.8		
Co2	C22	1.884	49.9	63.5	97.9	
Co2	Cnt2	1.720	159.5	140.3	131.6	129.6

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>	
			O1	Co1	Co2	
C21	O1	1.188				
C21	Co1	1.896	139.2			
C21	Co2	1.872	138.7	80.2		
C21	Rh	2.322	126.7	69.6	69.9	

			O2	Co1	Co2	
C22	O2	1.182				
C22	Co1	1.884	139.2			
C22	Co2	1.884	138.1	80.2		
C22	Rh	2.319	127.8	69.9	69.8	

Bond Lengths and Angles for Complex 3, (Cp*Co)₂(μ-CO)₂CoCp

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
			Co2	Co2a	C1	C1a
Co1	Co2	2.335				
Co1	Co2a	2.335	61.0			
Co1	C1	2.081	50.6	50.6		
Co1	C1a	2.081	50.6	50.6	85.2	
Co1	Cnt1	1.804	159.8	139.2	136.4	136.4
			Co1	Co2a	C1	C1a
Co2	Co1	2.335				
Co2	Co2a	2.370	59.5			
Co2	C1	1.902	57.7	51.5		
Co2	C1a	1.902	57.7	51.5	95.5	
Co2	Cnt2	1.698	147.3	153.2	132.1	132.1
			Co1	Co2	C1	C1a
Co2a	Co1	2.335				
Co2a	Co2	2.370	59.5			
Co2a	C1	1.902	57.7	51.5		
Co2a	C1a	1.902	57.7	51.5	95.5	
Co2a	Cnt3	1.698	147.3	153.2	132.1	132.1

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
			O1	Co2	Co2a
C1	O1	1.207			
C1	Co2	1.902	137.5		
C1	Co2a	1.902	137.5	77.1	
C1	Co1	2.081	133.2	71.6	71.6
			O1a	Co2	Co2a
C1a	O1a	1.207			
C1a	Co2	1.902	137.5		
C1a	Co2a	1.902	137.5	77.1	
C1a	Co1	2.081	133.2	71.6	71.6

Bond Lengths and Angles for Complex **4**, (Cp^{*}Rh)₂(μ-CO)₂CoCp

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
			Rha	Co	C	Ca
Rh	Rha	2.559				
Rh	Co	2.469	58.8			
Rh	C	2.124	52.9	48.8		
Rh	Ca	2.124	52.9	48.8	87.0	
			Rh	Rha	C	Ca
Co	Rh	2.469				
Co	Rha	2.469	58.8			
Co	C	1.925	48.8	48.8		
Co	Ca	1.925	48.8	48.8		

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
			O	Rh	Rha
C	O	1.129			
C	Rh	2.124	134.4		
C	Rha	2.124	134.4	74.1	
C	Co	1.925	137.7	75.0	75.0

Bond Lengths and Angles for Complex 5, (Cp*Ir)₂(μ-CO)₂CoCp

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
Structural Type 1					
			Ir2	Co1	C1
Ir1	Ir2	2.657			
Ir1	Co1	2.462	57.8		
Ir1	C1	2.011	48.4	65.2	
Ir1	C1a	2.011	48.4	65.2	96.2
			Ir1	Ir2	C1
Co1	Ir1	2.462			
Co1	Ir2	2.478	65.1		
Co1	C1	2.440	48.8	48.1	
Co1	C1a	2.440	48.4	48.1	75.7

		<u>angst.</u>	<u>deg</u>	<u>deg</u>	<u>deg</u>
			O1	Ir1	Ir2
C1	O1	1.182			
C1	Ir1	2.011	137.6		
C1	Ir2	2.004	137.4	82.9	
C1	Co1	2.440	132.3	66.3	66.9

Structural Type 2

			Ir3a	Co2	C21
Ir3	Ir3a	2.634			
Ir3	Co2	2.476	57.9		
Ir3	C21	1.989	48.6	64.8	
Ir3	C22	1.968	48.0	66.0	95.9
			O21	Ir3	Ir3a
C21	O21	1.232			
C21	Ir3	1.989	138.0		
C21	Ir3a	1.968	138.0	82.9	
C21	Co2	2.426	128.1	67.4	67.0

VITA

Michelle Royster Dial was born in Columbia, South Carolina in 1962. Shortly thereafter, her family moved to Misenheimer, North Carolina. She graduated from North Stanly High School in 1980. She attended Pfeiffer College where she pursued with a Bachelor of Science degree in mathematics and chemistry. In the summer of 1983 she received an undergraduate research assistantship at the University of Tennessee. In the fall of 1983 she returned to Pfeiffer College with the desire to pursue a graduate degree in chemistry. In May of 1984, her B.S. was conferred, and she enrolled in the graduate program in chemistry at the University of Tennessee.

In the course of graduate studies, one learns many things. But, the most valuable lesson is to shoot your best shot, because no one can take that away from you.