To the Graduate Council:

I am submitting herewith a thesis written by Jane Doll entitled "Synthesis and Characterization of alkyne adducts of $Cp^*Co(CpCo)_2(CO)_2$." 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.

Craig E Barnes

Dr. Craig E. Barnes, Major Professor

We have read this thesis and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor
and Dean of The Graduate School

SYNTHESIS AND CHARACTERIZATION OF ALKYNE ADDUCTS OF $Cp^*Co(CpCo)_2(CO)_2$.

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Jane Doll

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DEDICATION

I would like to dedicate this thesis to my family, who no matter how far away are always close to my heart.

I would also like to dedicate this thesis to my husband, Fred. Getting married in the same semester that I was graduating probably wasn't the best idea we've ever had. Then again, we were never the ones to take the path most trodden and it can only get better from here!

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Last but by no means least I wish to express my appreciation to my husband, Fred, who was there to see me through both the good and the bad.

ABSTRACT

This thesis describes the continuation of research performed in the laboratories of Dr. Barnes. Previous work has concentrated on the synthesis and characterization of cluster complexes with the general formula $Cp^*M_m(CpCo)_{3-m}(CO)_2$ where M = Co, Rh, Ir, m = 0 - 2, Cp = cyclopentadiene and Cp^* = pentamethylcyclopentadiene. Of this series of complexes, the reactions of one in particular, $(Cp)_3Co_3(CO)_2$, (Co_3), have been studied in great detail. This complex contains no pentamethylcyclopentadiene ligands and all three metals are the same. Therefore, this complex may be considered to be the "simplest form" of the general formula given above. Studies of Co_3 have concentrated on two types of reactions: two and four electron donor ligand addition and cluster fragmentation.

This thesis involves the study of the reaction of alkynes (R-C≡C-R′) with the complex $Cp^*Co(CpCo)_2(CO)_2$, ($^*CoCo_2$). This complex was chosen as it was thought that the presence of the bulky pentamethylcyclopentadiene ligand on the trinuclear complex may sterically hinder the addition of alkynes to the complex in the formation of alkyne adducts. Three alkynes were chosen that were of similar electronic nature but with relatively well defined differences in the size of their respective R groups. Described herein is a description of the formation of the alkyne adducts, their characterization and

the results of their respective reactions with $^{*}CoCo_2$.

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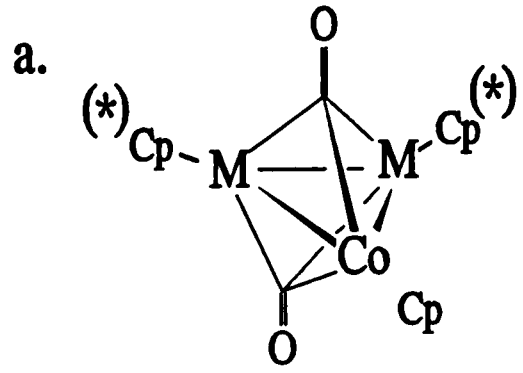
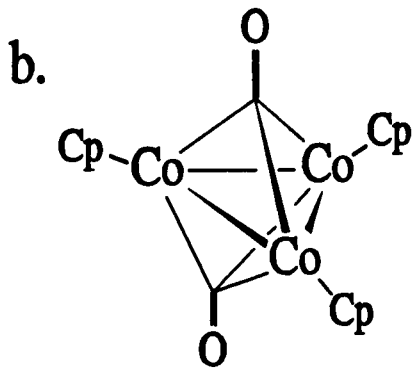
CHAPTER 1

INTRODUCTION

One of the major themes in the research efforts of Dr Barnes' group has been studying and understanding the properties of various reactive organometallic cluster complexes. A cluster complex is essentially one made up of three or more transition metal atoms and organic ligands. Previous work has concentrated on the synthesis and characterization of cluster complexes with the general formula $Cp^*M_m(CpCo)_{3-m}(CO)_2$ where M = Co, Rh, Ir, m = 0 - 2, Cp = cyclopentadiene and Cp^* = pentamethylcyclopentadiene (see Fig 1.1)[1]. All of the complexes in this series contain at least one CpCo and are 46 electron complexes. In accordance to the 18 electron rule, they are considered to be electron deficient and therefore very reactive.

Of this series of complexes, the reactions of one in particular, $(Cp)_3Co_3(CO)_2$, abbreviated herein as Co_3, have been studied in great detail. As can be seen in Fig 1.1 this complex contains no pentamethylcyclopentadiene ligands and all three metals are the same. Therefore this complex may be considered to be the "simplest form" of the general formula given above. As with other complexes in this series, Co_3 is





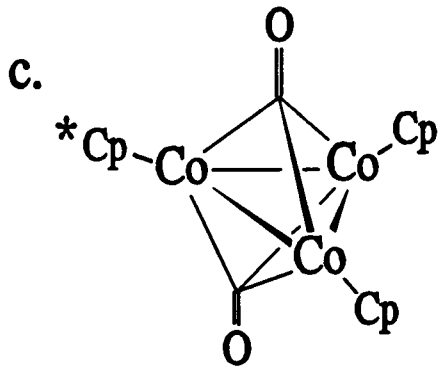


Figure 1.1 Structures of the 46 electron trinuclear complexes discussed in this thesis, a, general formula, b, $Cp_3Co_3(CO)_2$, Co_3, c, $Cp^*Co(CpCo)_2(CO)_2$, $^*CoCo_2$.[4]

deficient by two electrons and is, as one would expect, very reactive with electron donating ligands. Studies of Co_3 have concentrated on two types of reactions: two and four electron donor ligand addition and cluster fragmentation. These will be discussed in turn in the following paragraphs.

It has been found that the reaction of Co_3 with carbon monoxide, a two electron donor ligand, yields a tricarbonyl trinuclear complex, $(Cp)_3Co_3(CO)_3$. Reaction with diazomethane, also a two electron donor ligand, yields carbene and hydrazone complexes. The trinuclear complex Co_3 has also been reacted with a wide variety of alkynes ($R-C\equiv C-R'$)[5]. Alkynes are four electron donors and add to the cluster core with the elimination of one carbonyl ligand to form "alkyne adducts". The alkyne adducts when heated in refluxing decalin to approximately 200°C undergo elimination of a second CO to form "scission" (bis-alkylidyne) complexes.[3] These reactions are summarized in a general reaction scheme in Fig 1.2.

Co_3 has also been found to undergo a unique, solvent induced two-step fragmentation to yield $(C_5H_5)_2Co_2(CO)_2$, a dinuclear complex and $(C_5H_5)_4Co_4(CO)_2$ a tetranuclear complex.[3] As can be seen in Figure 1.3, the fragmentation mechanism proceeds via the initial reversible attack of the solvent on the Co_3, resulting in the formation of the dinuclear complex and a solvated mononuclear intermediate. This intermediate subsequently reacts with a second Co_3 to form the tetranuclear complex with recovery of the solvent molecule. It should be

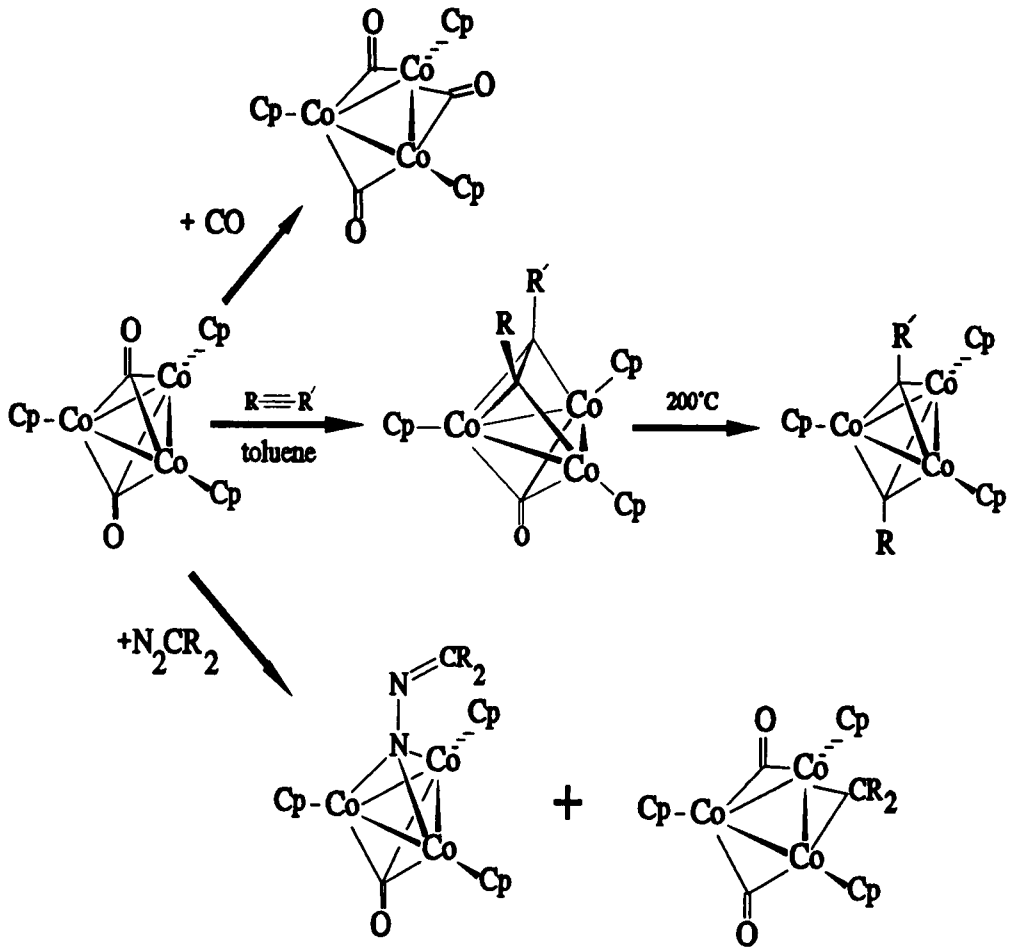


Figure 1.2 General reaction scheme for Co_3.[2,3,6]

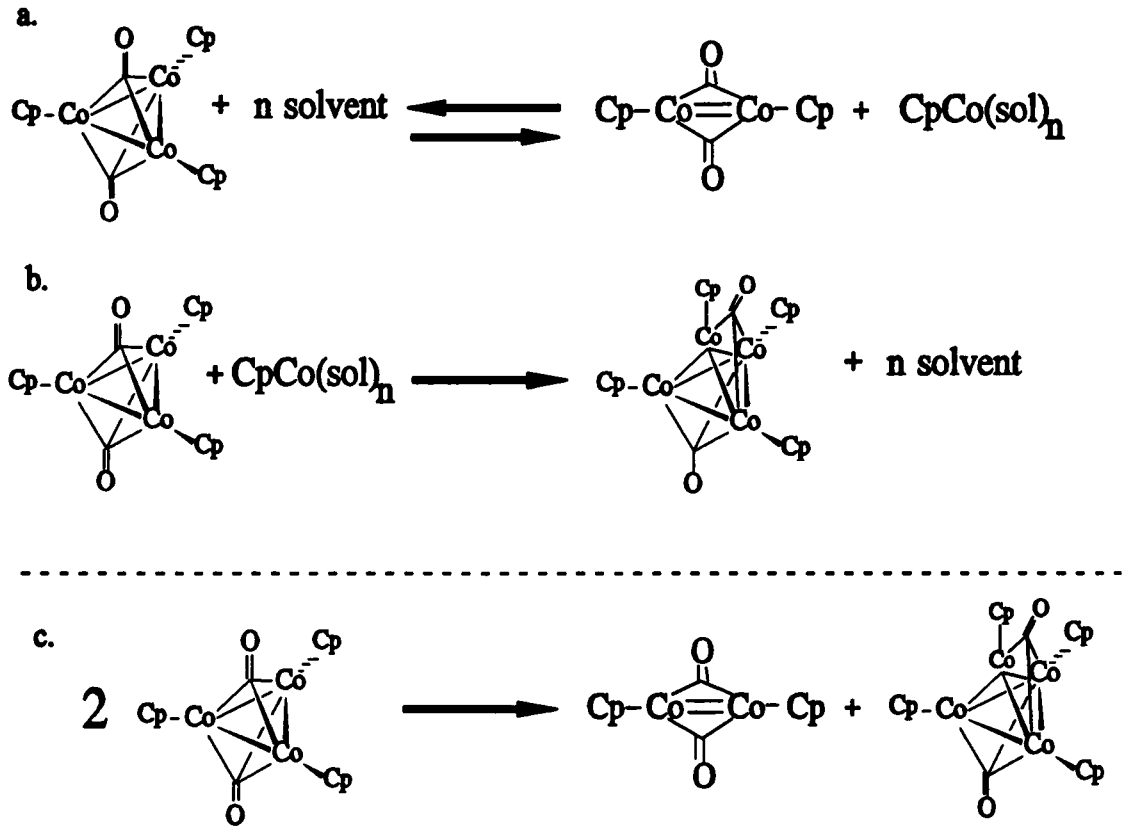


Figure 1.3 Mechanism for the solvent induced fragmentation of Co_3 a, initial reversible attack of solvent, b, attack of solvated mon-nuclear intermediate on Co_3, c, the overall net reaction.[5]

noted that the rate of fragmentation when compared to aromatic solvents, such as benzene, shows considerable acceleration in tetrahydrofuran (THF).

The research described in this thesis involves the study of the reaction of alkynes with a complex analogous to Co_3 this being $Cp^*Co(CpCo)_2(CO)_2$, abbreviated herein as $^*CoCo_2$, (refer back to Figure 1.1). As can be seen this trinuclear complex differs from Co_3 by the replacement of one cyclopentadiene ligand with a pentamethylcyclopentadiene ligand. Whilst the basic premises behind the reactivity of the complex remain unchanged, ie. it is also a 46 electron complex, it is thought that this "substitution" will have two marked effects on the stability and reactivity of $^*CoCo_2$. The first involves the electronic nature of the complex. Given that the pentamethylcyclopentadiene is a better electron donor than the cyclopentadiene ligand, it follows that the $^*CoCo_2$ should be inherently more stable than Co_3. This may be illustrated by the fact that $^*CoCo_2$ is stable even in refluxing THF whereas Co_3 rapidly decomposes when exposed to THF at room temperature. Second, it can be seen that the cyclopentadiene and the pentamethylcyclopentadiene ligands differ greatly in size. The pentamethylcyclopentadiene ligand is much larger than the cyclopentadiene ligand due to the replacement of the five hydrogens with five methyl (CH_3) groups. It is thought that this size difference may bring into play certain steric factors when considering the reactions of the $^*CoCo_2$. This

thesis therefore essentially concentrates on understanding the effects this "substitution" has on the reaction of $^{*}CoCo_2$ with alkynes to form alkyne adducts.

If one considers the reaction of $^{*}CoCo_2$ with various alkynes as illustrated in Figure 1.4, it can be seen that the bulky Cp^{*} group may sterically hinder the addition of the alkyne to the complex if the R groups of the alkyne are also large. In fact it may also be predicted that the amount of steric hinderance should increase with increasing size of the R groups on the alkyne and it follows therefore that the yield of the adduct may be inversely affected ie. the yield should decrease with increasing size of the R groups. This then is the basis of the research described herein. In order to carry out this investigation the alkynes used needed to be of a similar electronic nature with only relatively well defined differences in the size of their respective R groups. To this end three alkynes were chosen:

H-C≡C-H acetylene

H-C≡C-Ph phenylacetylene

Ph-C≡C-Ph diphenylacetylene

It can clearly be seen that the R groups increase in size from R=H to R=Ph. Based on this increase in size the yield is therefore expected to decrease as we progress from the acetylene/$^{*}CoCo_2$ adduct to the phenylacetylene/$^{*}CoCo_2$ adduct

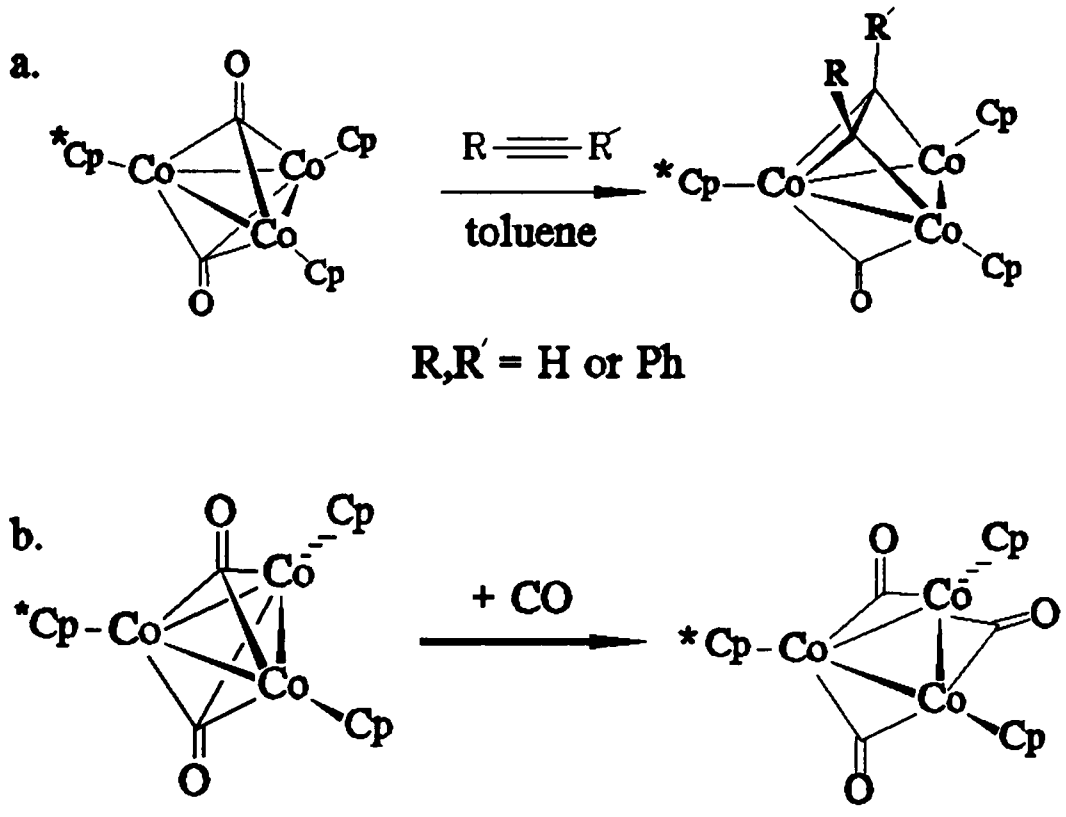


Figure 1.4 a, general reaction for the formation of the $^{*}CoCo_2$ alkyne adducts, b, competing side reaction which takes place during the formation of the adducts forming a tricarbonyl trinuclear complex.[2,3]

with the lowest yield being given for the diphenylacetylene/$^{*}CoCo_2$ adduct.

The basic reaction of $^{*}CoCo_2$ with alkynes proceeds in a similar fashion to Co_3 and it should be noted that in both cases carbon monoxide is liberated during the reaction. This free CO molecule may react with the parent trinuclear in a competing side reaction to form a tricarbonyl trinuclear complex, $(Cp)_3Co_3(CO)_3$ in the case of Co_3 and $Cp^{*}Co(CpCo)_2(CO)_3$ in the case of $^{*}CoCo_2$. The competing side reaction that occurs in the case of $^{*}CoCo_2$ is illustrated in Figure 1.4. This competing side reaction reduces the maximum expected yield of the Co_3 alkyne adducts to approximately 50 - 60% in most cases.

CHAPTER 2

EXPERIMENTAL PROCEDURES

Introduction

The majority of compounds discussed in this thesis are, to some extent air and/or water sensitive, that is, exposure to either of these entities causes decomposition of the compound. To this end therefore, it is necessary to employ specialized techniques in the production, handling and storage of these compounds.

The most air sensitive compounds are handled in an inert atmosphere glove box filled with helium. For compounds that are less sensitive it is possible to handle them outside the glove box by using Schlenk techniques. A Schlenk vessel is essentially a glass flask fitted with a ground glass joint and a teflon stopcock. The Schlenk vessels are used in connection with a vacuum/nitrogen manifold. Sealing the Schlenk vessel with a rubber stopper makes it possible to evacuate the air by pulling a brief vacuum on the Schlenk vessel, which may then be replaced with nitrogen. This creates an inert atmosphere in which reactions involving the less air sensitive compounds may be carried out, compounds stored etc. These techniques prove to be adequate for the less air sensitive compounds where transfer from the storage Schlenk vessel to the reaction

Schlenk vessel may be facilitated using a pouring spout and a continuous nitrogen purge in order to minimize the risk of contact with air or moisture.

The nitrogen used for the manifold is of a prepurified grade but it is further purified in the lab by passing it over a manganese oxide catalyst to remove any trace amounts of oxygen and over molecular sieves to remove trace amounts of water. The vacuum on the manifold is not only used for the evacuation of Schlenk vessels but may also be used by employing a dual trap to remove solvents.

All of the solvents employed are reagent grade which have been distilled from a sodium/potassium alloy or calcium hydride (in the case of methylene chloride) to eliminate oxygen and water. Solvents are stored either in two litre Schlenk vessels under a nitrogen atmosphere or in the glove box. Nuclear magnetic resonance (NMR) solvents are prepared and dried in a similar fashion.

During several reactions and in particular with adduct formation reactions, where side reactions and some decomposition of the starting material is seen to occur, purification of the final product is necessary. Purification is achieved by chromatographic separation under anaerobic conditions using silica gel as the separation medium. The silica gel is prepared by placing it in a two litre Schlenk vessel and alternately pulling vacuum and refilling with nitrogen over a period of approximately twenty-four hours. The

anaerobic columns are prepared in hexane and the compounds eluted by slowly increasing the polarity of the solvent from hexane through methylene chloride to ether and finally to THF.

Synthetic procedures

Di-μ-carbonyl-bis(cyclopentadienide)-dicobalt-pentamethylcyclopentadienide-cobalt, $(\eta^5\text{-}C_5(CH_3)_5)Co(\mu\text{-}CO)_2Co_2(\eta^5\text{-}C_5H_5)_2$, ($^*CoCo_2$). In an inert atmosphere box, 0.313g of cyclopentadiene cobalt bis-ethylene, $CpCo(C_2H_4)_2$, was dissolved in approximately 30ml hexane (See note). This solution was stirred and a solution of 0.215g of pentamethylcyclopentadiene cobalt dicarbonyl, $Cp^*Co(CO)_2$, was added portionwise. A slight vacuum was pulled following each addition in order to remove ethylene which is liberated in the reaction. After the final addition was made the mixture was stirred for a further 15 mins. The solvent was then drawn off under vacuum and the reaction mixture concentrated to approximately 5 - 10ml. At this point stirring was stopped and a microcrystalline precipitate settled out of solution. The solution was pipetted away from the precipitate and the precipitate dried under vacuum. The yield was 0.396g (81%). Analysis by ^1H NMR identified the product as $^*CpCo(CpCo)_2$, ($^*CoCo_2$).[1,4] The product was stored in a vial in the glove box. ^1H NMR (C_6D_6, 25°C) δ -2.24 (s, 15H), δ -11.25 (s, 10H).

NOTE. When using cyclopentadiene cobalt bis-ethylene, $CpCo(C_2H_4)_2$, in subsequent reactions, it should not be

dissolved in ether. Impurities present in samples of $CpCo(C_2H_4)_2$ that arise due to decomposition are readily soluble in ether but insoluble in hexane. Therefore, dissolution in hexane followed by filtration allows for adequate removal of these impurities.

$^*CoCo_2$/alkyne adducts. All of the alkyne adducts described in this thesis are synthesized using the same basic procedure. They do, however, differ in the number and nature of the fractions seen when chromatographed. Slight differences are also observed in the solvents which were used to elute the different fractions from the anaerobic column and this will be discussed in turn later.

The initial reaction is carried out in the glove box. In general a 1-2 fold excess of the alkyne is dissolved in approximately 10 - 15ml of toluene. As this is stirred 0.3 - 0.4g of $^*CoCo_2$ is added portionwise, a slight vacuum is pulled between additions in order to remove any liberated CO and therefore attempt to minimize any competing side reaction that may occur. The reaction is allowed to stir for about five minutes and then the Schlenk vessel is removed from the box and the toluene is removed under vacuum. The reaction mixture is then placed at the head of an anaerobic column in a solvent mixture of hexane with just enough methylene chloride added to completely dissolve the product. The product was then eluted from the column by slowly increasing the polarity of the solvent. Each fraction eluted from the column is collected

into a Schlenk vessel under nitrogen, the solvent removed under vacuum and the fraction characterized via NMR, IR, MS and elemental analysis.

Acetylene/$^*CoCo_2$ adduct. Three fractions were eluted from the column. The first small fraction, which was bright green in colour, was eluted in a mixture of 90% hexane and 10% methylene chloride. As this fraction was so small it was not collected, however the intense green colour indicates that it is the dinuclear complex $(Cp^*Co)_2(CO)_2$. The second fraction was eluted in a 50:50 hexane, methylene chloride mixture. The solvent was removed and analysis via ^1H NMR revealed this fraction to be the tricarbonyl trinuclear complex, $Cp^*Co(CpCo)_2(CO)_3$, ^1H NMR (C_6D_6, 25°C) δ 4.614 (s, 10H), δ 1.388 (s, 15H). The third reddish brown fraction was eluted from the column in methylene chloride. The solvent was removed to give 0.144g (38%) of the desired product. ^1H NMR (C_6D_6, 25°C) δ 9.785 (s, 2H), δ 4.496 (s, 10H) δ 1.518 (s, 15H); ^{13}C NMR C≡C δ 145.171, C-H of Cp δ 94.380, quaternary C of $^*Cp$ δ 84.3667, CH_3 on $^*Cp$ δ 10.302; (KBr) ν(CO) 1656.1 cm^{-1}. High resolution mass spectrum: parent ion calculated for $Co_3C_{23}H_{27}O$ = 496.0058 (Dalton). Found 496.0048. A brief overview of the mass spectral data is given in Table 2.1.

Table 2.1 Mass spectral data for the acetylene/$^*CoCo_2$ adduct.

Ion	Mass
Parent ion M^+	496
$[M-CO]^+$	468
$[Cp^*CpCo]^+$	259
$[Cp_2Co]^+$	189

Phenylacetylene/$^*CoCo_2$ adduct. Four fractions were eluted from the column. The first fraction was eluted in hexane and analysis revealed this to be excess phenylacetylene. The second small fraction, which was bright green in colour, was eluted in a mixture of 90% hexane and 10% methylene chloride. As this fraction was so small it was not collected, however the intense green colour indicates that it is the dinuclear complex $(Cp^*Co)_2(CO)_2$. The third fraction was eluted in a 50:50 hexane, methylene chloride mixture. The solvent was removed and analysis via ^1H NMR revealed this fraction to be the tricarbonyl trinuclear complex, $Cp^*Co(CpCo)_2(CO)_3$, ^1H NMR (C_6D_6, 25°C) δ 4.614 (s, 10H), δ 1.388 (s, 15H). The fourth reddish brown fraction was eluted from the column in methylene chloride. The solvent was removed to give 0.114g (28%) of the desired product. ^1H NMR (C_6D_6, 25°C) δ 9.795 (s, 1H), aromatic

range δ 7.235 - 7.706, δ 4.431 (s, 10) δ 1.462 (s, 15H); ^{13}C NMR C≡C δ141.35, C-H of Cp δ85.440, quaternary C of $^{*}Cp$ δ 94.466, CH_3 on $^{*}Cp$ δ9.566, aromatic carbon range δ 125 - 130; (KBr) ν(CO) 1661.2 cm^{-1}. High resolution mass spectrum: parent ion calculated for $Co_3C_{29}H_{31}O$ = 572.0371 (Dalton). Found 572.0366. A brief overview of the mass spectral data is given in Table 2.2.

Table 2.2 Mass spectral data for the phenylacetylene/$^{*}CoCo_2$ adduct.

Ion	Mass
Parent ion M^+	572
$[M-CO]^+$	544
$[Cp^{*}CpCo]^+$	259
$[Cp_2Co]^+$	189

Diphenylacetylene/$^{*}CoCo_2$ adduct. Three fractions were eluted from the column. The first fraction was eluted in hexane and analysis revealed this to be excess diphenylacetylene. The second large fraction which was bright green in colour, was eluted in a mixture of 90% hexane and 10% methylene chloride. The solvent was removed and analysis via ^1H NMR revealed this fraction to be the dinuclear complex $(Cp^{*}Co)_2$, ^1H NMR (C_6D_6, 25°C) δ 1.416. The third reddish brown

fraction was eluted in a 50:50 hexane, methylene chloride mixture. The solvent was removed to give a very small amount (<10%) of the desired product. ^{1}H NMR (C_6D_6, 25°C) aromatic region, range δ 7.060 - 7.463, δ 4.528 (s, 10H) δ 1.360 (s, 15H); ^{13}C NMR C≡C δ150.452, C-H of Cp δ86.941, quaternary C of $^{*}Cp$ δ 95.026, CH_3 on $^{*}Cp$ δ9.496, aromatic carbon range δ 124 - 131; IR (KBr) ν(CO) 1639.8 & 1659.6 cm^{-1}. High resolution mass spectrum: parent ion calculated for $Co_3C_{35}H_{35}O$ = 648.0684 (Dalton). Found 648.0654. A brief overview of the mass spectral data is given in Table 2.3.

Table 2.3 Mass spectral data for the diphenylacetylene/$^{*}CoCo_2$ adduct.

Ion	Mass
Parent ion M^{+}	648
$[M-CO]^{+}$	620
$[Cp^{*}CpCo]^{+}$	259
$[Cp_2Co]^{+}$	189

CHAPTER 3

DISCUSSION OF RESULTS

In the previous discussion it was said that the large bulky pentamethylcyclopentadiene group may sterically hinder the addition of alkynes in their reaction with $^{*}CoCo_2$. It may also be predicted that the amount of steric hinderance between these ligands should increase with increasing size of the R groups on the alkyne and it follows therefore that the yield of the adduct will be inversely affected, i.e. the yield should decrease with increasing size of the R groups. Within the series of alkyne adducts, acetylene, phenylacetylene and diphenylacetylene we expected that the yield would decrease as we progressed from the acetylene adduct to the phenylacetylene adduct with the lowest yield being obtained for the diphenylacetylene adduct. One should also be reminded at this point of the competing side reaction which occurs in nearly all adduct formation reactions. When carbon monoxide is liberated during the adduct formation it subsequently reacts with the parent trinuclear complex to form a tricarbonyl trinuclear complex. In fact, formation of the tricarbonyl trinuclear complex may be seen as an indicator that the reaction is proceeding in a "normal" fashion.

Table 3.1 Adducts of $^{*}CoCo_2$ and their percent yields

$^{*}CoCo_2$ adduct	Percentage yield
acetylene adduct	38%
phenylacetylene adduct	28%
diphenylacetylene adduct	< 10%

As can be seen in Table 3.1 the expected yields of the three adducts do decrease as expected. The yields of these adducts are also consistently lower than the yields obtained for the corresponding Co_3 adducts. For the Co_3 acetylene adduct it is found that due to the small size of the acetylene molecule, it is able to compete with the liberated carbon monoxide, thereby minimizing the effects of the competing side reaction and increasing the yield to approximately 80%.[3]

The adduct formation for both the acetylene and phenylacetylene adducts proceeded in a "normal" manner, i.e. approximately equal amounts of the adduct and the tricarbonyl complex were obtained. In the case of the diphenylacetylene adduct, however, the reaction did not proceed in the same fashion. Large amounts of the intense green dinuclear complex, $(Cp^{*}Co)_2(CO)_2$, were obtained and the yield of the alkyne adduct, as expected, was very low. The yield for the diphenylacetylene adduct is so low that barely enough compound was obtained to allow for purification by recrystallization.

The product is therefore relatively impure when compared to the acetylene and phenylacetylene adducts.

It is thought that the results of the reaction of the diphenylacetylene with $^{*}CoCo_2$ may be explained in a similar fashion to the solvent induced fragmentation of Co_3. The reaction proceeds via initial attack of the diphenylacetylene on the $^{*}CoCo_2$ complex. Due to the steric factors involved, (i.e. the interaction of the large phenyl groups and the pentamethylcyclopentadiene ligand), instead of forming the adduct the complex fragments to give a dinuclear complex, $(Cp^{*}Co)_2(CO)_2$ and a mononuclear species which in this case does not appear to undergo further reaction with a second $^{*}CoCo_2$ to form a tetranuclear complex as is the case in Co_3. Evidence for this may be seen in the colour of the reaction mixture in the initial stages. At first, the reaction mixture is the expected reddish brown colour of the adduct, this colour rapidly disappears and is replaced by the intense green colour of the dinuclear complex. The nature of the transient mononuclear is as yet undetermined. It appears that it is not stable enough to be chromatographed and NMR of the crude reaction mixture does not allow for the definition of this species indicating the possibility that it undergoes further fragmentation to species that are insoluble.

The $^{*}CoCo_2$ adducts were all analyzed using both ^{1}H and ^{13}C NMR spectroscopy. The chemical shifts for the alkyne protons in the acetylene and phenylacetylene adducts are found to be

shifted down field from, δ 2.5 - 3.0, in the uncomplexed alkyne to, δ 9.5 - 10.5, in the adduct as has been observed for similar adducts of Co_3.[1,3] This then gives a good indication that the adduct has been formed.

For all the adducts described in this thesis only one peak is found for both cyclopentadiene ligands. There are two possible explanations for this observation. The first is that the alkyne is held stationary above the trinuclear complex in such a way that the two cyclopentadiene ligands become equivalent. The second is that the alkyne undergoes motion that is fast on the NMR time scale, again leading to a 'time averaged' signal and the two cyclopentadiene ligands appearing to be equivalent.

When attempting to look at the adducts in three dimensions it is possible to simplify matters by viewing the trinuclear complex as a triangle with the alkyne above it as can be seen in Figure 3.1 and 3.2.

With this in mind, let us now consider the above explanations for the two cyclopentadiene ligands becoming equivalent. Figure 3.1 gives a number of stylized representations of the alkyne held in a stationary position above the trinuclear complex. In Figure 3.1 a, with the alkyne held in the position shown (the alkyne R groups point up and out of the page), both cyclopentadiene ligands would be equivalent. Unfavourable steric interactions of the bulkier R and R' groups with the pentamethylcyclopentadiene ligand can

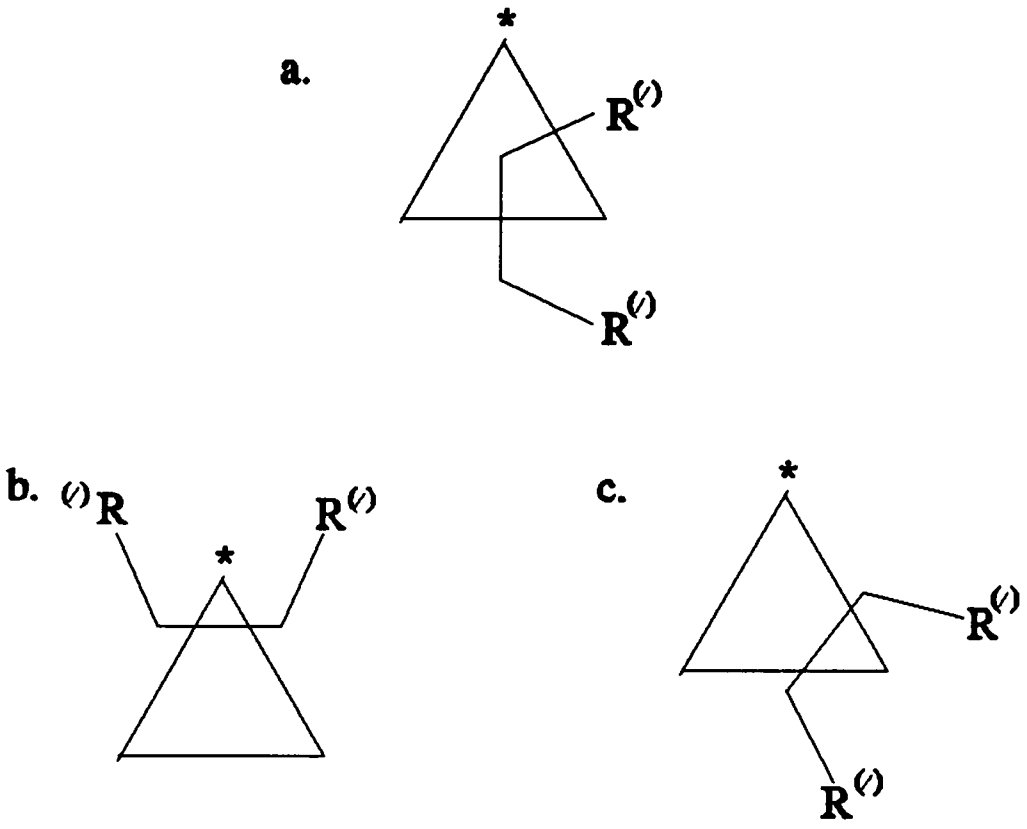


Figure 3.1 Representations of $^{*}CoCo_2$ adducts, with the alkyne stationary above the trinuclear complex.

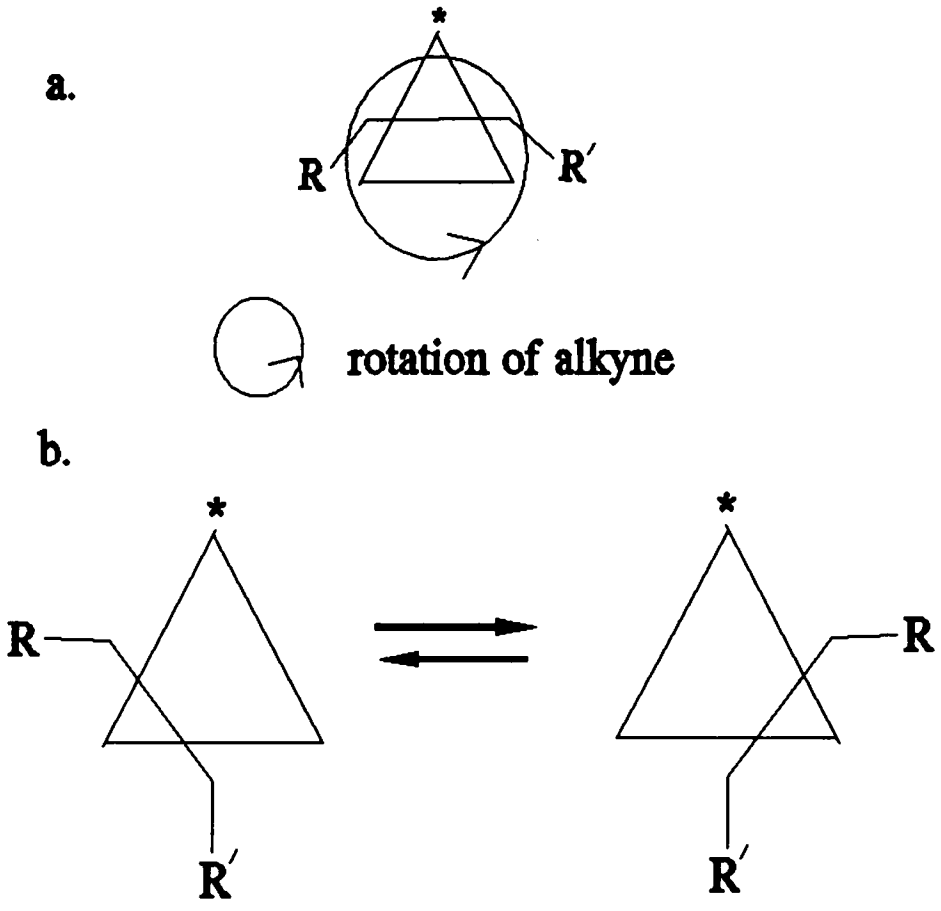


Figure 3.2 Two possible modes of fluxionality thought possible for the alkyne in the $^{*}CoCo_2$/alkyne adducts.

be minimized by placing the bulkier group facing away from the pentamethylcyclopentadiene ligand, whose position is indicated by a * in the stylized representations. In both Figure 3.1 b and c the position of the alkyne does not render the two cyclopentadiene ligands equivalent when R and R′ are different. This is not consistent with the observation of only one NMR signal for the Cp ligands and therefore they are not considered to be possible structures.

Figure 3.2 shows two forms of motion (or fluxionality) of the alkyne that would give rise to a 'time averaged' signal and the two cyclopentadiene ligands appearing to be equivalent. In Figure 3.2 a, the alkyne may be seen to rotate through 360°, in a fashion that can be likened to the rotation of helicopter blades. Earlier studies have been performed that show this to be the case for Co_3 where all three cyclopentadiene ligands are equivalent.[3] In the case of $^*CoCo_2$ this form of fluxionality may be prevented due to the interaction of the R and R′ groups with the pentamethylcyclopentadiene ligand, especially in the case of the phenylacetylene and diphenylacetylene adducts. Figure 3.2 b, shows a second possible form of motion of the alkyne, in this case the alkyne may be viewed as flipping backwards and forwards across the complex in a motion somewhat similar to that of the windshield wipers on a car. This would be the more favoured type of fluxionality for $^*CoCo_2$ adducts, as interaction the R and R′ groups with the

pentamethylcyclopentadiene ligand could be minimized by placing the bulkier R or R′ group facing away from the pentamethylcyclopentadiene ligand, as was seen earlier. As prior investigation for other trinuclear complexes has shown in nearly all cases that the cyclopentadiene ligands are rendered equivalent via some form of motion of the alkyne one would tend to favour that explanation in this also. Investigations into the fluxionality of the alkyne may be done using low temperature NMR techniques, where at low enough temperatures the motion would be "frozen" out and the two cyclopentadiene ligands would no longer be equivalent.

Similar trends are also observed in the ^{13}C NMR spectra. Again only one signal is observed for both cyclopentadiene ligands. In a similar fashion to that observed for the acetylene and phenylacetylene protons the chemical shifts for the alkyne triple bond carbons in all three adducts are found to be shifted down field from, δ 60 - 90, in the uncomplexed alkyne to, δ 140 - 155, in the alkyne adduct as has been observed for similar alkyne adducts of Co_3.[1,3] These data indicate that the alkyne adduct has been formed. ^{13}C atoms undergo relaxation via dipole-dipole interaction with directly attached hydrogens, therefore, nonprotonated carbon atoms typically have longer relaxation times the consequence of which is smaller peaks than is generally observed for protonated carbons.[8] It is therefore possible to recognize nonprotonated carbons by their lower intensities and for this

reason then the Cp carbons are found to be of greater intensity than the *Cp ring carbons and this difference allows them to be easily distinguished from one another despite their similar chemical shifts. It should also be noted that the carbonyl carbon is also expected to be shifted downfield from δ 200 - 220 to an observed δ 270 - 280. As is often the case, a very weak signal is obtained for the single, non-protonated, carbonyl carbon and, as commonly occurs, it may in fact be lost in the baseline. This was found to be the case for all three alkyne adducts despite attempting to use high numbers of pulses and long relaxation delays.

Examination of the stretching frequencies of the CO ligand may reveal certain insights into the structure of the complex and also the electronic interactions therein. The interactions between carbonyl ligands and metals may be formally separated into two parts, 1), sigma donation of two electrons to the metal and, 2), the back donation from occupied d-orbitals on the metal into empty antibonding orbitals of the carbonyl ligand. This back donation results in a weakening of the carbon-oxygen double bond, formally decreasing the bond order and lowering the observed stretching frequency in the IR. Therefore, increased amount of back-donation from metal to ligand will further lower the stretching frequency. It is for this reason then that the

stretching frequency is found to follow the form:

terminal	> doubly bridging	> triply bridging
~2000 cm^{-1}	~1800cm^{-1}	~1700cm^{-1}

For all the alkyne adducts discussed in this thesis carbonyl stretching frequencies are found to be in the range of 1700-1650cm^{-1}. This information indicates that the carbonyl is triply bridging and consistent with the proposed structure which has a triply bridging CO ligand on opposing side of the triangular metal plane to the conjugated alkyne. It is also thought that the presence of electron donating substituents on the alkyne will lead to greater donation of electrons from the alkyne to the metals and consequently from the metal to the carbonyl, thereby decreasing the bond order of the carbon, oxygen bond and lowering the stretching frequency. This, however, is not found to be the case for the alkyne adducts described in this thesis as can be seen in table 3.2.

In fact the trend in the CO stretching frequencies for these alkyne adducts is found to be the opposite of that which is expected. This may be due to steric factors, i.e. repulsive interaction between the R and R′ groups with the pentamethylcyclopentadiene ligand may increase the distance between the alkyne and the metals of the trinuclear complex thereby decreasing the extent of electron donation from the alkyne to the metals. With the data in hand it is difficult to

alkyne to the metals. With the data in hand it is difficult to

Table 3.2 Observed carbonyl stretching frequencies for the $^{*}CoCo_2$ adducts discussed in this thesis.

$^{*}CoCo_2$ adduct	$\nu CO/cm^{-1}$
acetylene	1656.1
phenylacetylene	1661.2
diphenylacetylene	1659.6

separate the electronic and steric factors at play within this particular series of alkyne adducts. The data does, however indicate that both are important factors in gaining understanding of the interaction between the trinuclear complex and the conjugated alkyne.

Examination of the mass spectra of the adducts reveals certain interesting facts regarding the alkyne adducts apart from the mass peak of the parent ion ($[M]^{+}$). In all cases a second mass peak is observed for $[M-CO]^{+}$, i.e. the elimination of the second CO ligand from the alkyne adduct. As was previously mentioned, alkyne adducts when heated in refluxing decalin undergo elimination of the second CO ligand to form "scission" (bis-alkylidyne) complexes. It has been found that presence of the $[M-CO]^{+}$ peak in the mass spectrum indicates that the adduct complex is capable of undergoing such a

Suggestions for further work

Further work in this area may proceed in one of two directions. First, further study into the properties of the $^*CoCo_2$ alkyne adducts described in this thesis is possible and second similar studies as those described here using a second trinuclear complex $(Cp^*Co)_2CpCo(CO)_2$.

As has already been mentioned one area that requires further study is the fluxionality of the alkyne. Further work would require the use of low temperature NMR techniques, where at low enough temperatures the motion of the alkyne would be "frozen" out, the two cyclopentadiene ligands would no longer be equivalent and two peaks would be observed in the NMR.

A second area of study involving the would be to investigate if the formation of the alkyne scission (bis-alkylidyne) complexes is indeed possible as is indicated by the mass spectral data obtained for the alkyne adducts.

Further work in this area could be done using the trinuclear complex, $(Cp^*Co)_2CpCo(CO)_2$. Again, this is also a 46 electron complex that in this case differs from $Cp_3Co_3(CO)_2$ by the presence of two pentamethylcyclopentadiene ligands. similar reactions and studies could be carried out using this complex and the same three alkynes described in this thesis, the results should show a similar but more pronounced trend in the decreasing yield of the adduct obtained. In this case it may not possible to obtain a diphenylacetylene adduct at all.

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VITA

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