

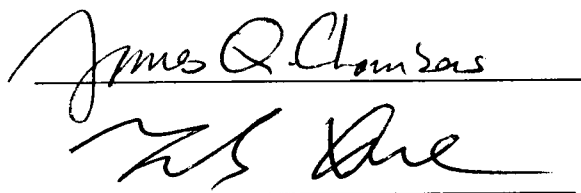
To the Graduate Council:

I am submitting herewith a thesis written by Michael Joseph Player entitled "Reaction of 1,3,4,5-Tetramethylimidazole-2-Ylidene with Cyclopentadienyl Cobalt Carbonyl Complexes: Characterization of a Novel Dinuclear Carbene Adduct. 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, Major Professor

We have read this thesis
and recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor
and Dean of The Graduate School

**REACTION OF 1,3,4,5-TETRAMETHYLIMIDAZOLE
2-YLIDENE WITH
CYCLOPENTADIENYL COBALT CARBONYL
COMPLEXES: CHARACTERIZATION
OF A NOVEL
DINUCLEAR CARBENE ADDUCT**

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

Michael Joseph Player
December 1997

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ACKNOWLEDGMENTS

I would like to thank my major professor, Dr. Craig E. Barnes, for his assistance and patience. Appreciation is extended to Dr. Anthony Arduengo for the generous supply of imidazole carbene. I would also like to thank my committee members, Dr. Jim Chambers and Dr. Ben Xue, for their helpful input. I am also grateful for the financial support from Department of Chemistry with regard to the instrument position of student operator for the 200 MHZ NMR and for GTA funding. To Bill Gurley, I appreciate all the help on the Nicolet and sundry computer related problems. To Bobby Daryl, and Roy Hodges in chemistry stores and to John, Eddie, and Tim in the machine shop thanks for all friendly service.

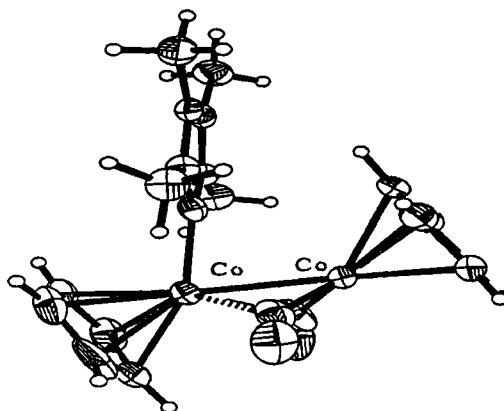
To those who left the lab before me, Bill King, Holger Foersterling, Stephe Vierkotter and Martina Ralle, I hope for the best in all your future endeavors. For the ones who will remain, I wish the graces of goddess fortuna. A special thanks to Kris Scaboo for his friendship and concern. To the golfing community, it has been a pleasure to get out and hit the links with you once and a while.

To Bruce Lysek alias the WAR chemist, my carousing comrade back home, I certainly have appreciated your sage advise, humorous e-mails, and tremendous friendship.

Last and by no means least, I am enormously grateful to my parents, Jovita and James. To my siblings, Jim, Michelle, Melissa, Cindy, John, David, and Jane, I have borrowed your best qualities and am still trying to make them my own. For this am also thankful.

ABSTRACT

The synthesis and characterization of an unusual dinuclear organometallic complex derived from $\text{Cp}_3\text{Co}_3(\text{CO})_2$ **1** is presented. Reaction of **1** with 1,3,4,5-tetramethylimidazole-2-ylidene **2** was anticipated to form a trinuclear carbene adduct. The actual product arises from fragmentation of the trinuclear cluster **1** to form the dinuclear monocarbene adduct $\text{Cp}_2\text{Co}_2(\text{CO})_2(\text{C}_7\text{H}_{12}\text{N}_2)$ **3**. The x-ray crystal structure of **3** has been determined and an ORTEP illustration of the structure in the solid state is shown below.



The x-ray crystal structure of the adduct was solved (space group P-1; $a = 8.8600$ Å, $b = 9.0374$ Å, $c = 12.1181$ Å; $\alpha = 92.300$; $\beta = 103.979$; $\gamma = 109.514$; 2403 reflections; $R = 0.0220$). As the illustration shows, one atom of the imidazole ring, the carbene carbon is coordinated to just one of the cobalt atoms at a distance of $1.899(5)$ Å. The tilt of the ligand towards the other cobalt atom is approximately 10° such that this center is $2.788(5)$ Å away. The Co-Co bond ($2.432(1)$ Å) is asymmetrically bridged by the two carbonyl ligands. The average $\text{C}_{\text{CO}}\text{-Co}$ distances are of 1.955 Å ($\text{C}_{\text{CO}}\text{-Co}_1$) and 1.602 Å ($\text{C}_{\text{CO}}\text{-Co}_2$). The dinuclear adduct **3** can also be made by adding the carbene to $\text{Cp}_2\text{Co}_2(\text{CO})_2$. The complex is also formed by fragmentation of electronically saturated

$\text{Cp}_3\text{Co}_3(\text{CO})_3$ and $\text{Cp}_4\text{Co}_4(\text{CO})_2$ in the presence of 2. The imidazole carbene adduct decomposes at room and low temperatures in solution. One of the decomposition products, $\text{CpCo}(\text{CO})(\text{C}_7\text{H}_{12}\text{N}_2)$ 4, will be discussed briefly.

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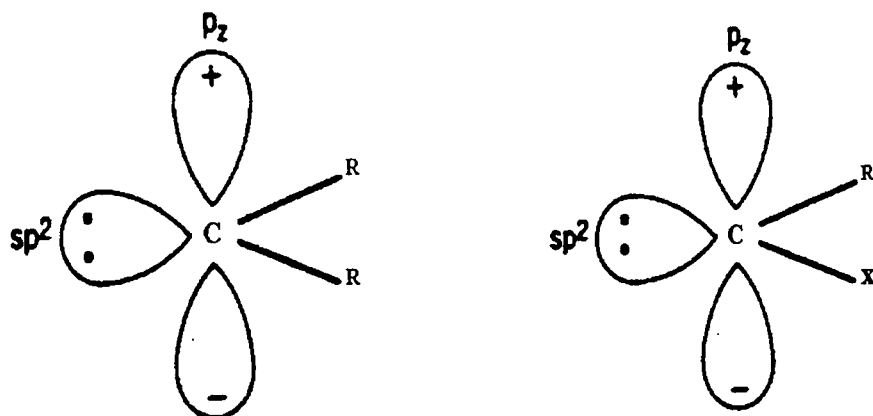
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Chapter One

Introduction

A. CARBENE LIGANDS

Carbenes are organic molecules which contain a carbon that violates the eight valence electron rule and are thus unusually reactive. Recently, however, Arduengo and coworkers have investigated the properties of a new family of stabilized Fischer carbenes derived from the imidazole ring¹. These molecules derive their reactivity and stability from steric and electronic factors. Steric protection of the carbene center is imparted by the substituents attached to α -nitrogen atoms on the carbene carbon, generally bulky alkyl or aryl groups and electronic stabilization is afforded by orbital contributions from the electron rich π -system ($\text{N}=\text{C}=\text{N}$). Carbene ligands are generally divided into two main categories: alkylidenes and Fischer carbenes. Alkylidenes in organometallic complexes refer to carbenes where the substituents bound to the carbon are alkyl, aryl or hydrogen. Fischer carbenes refer to carbenes where one or both of the substituents contain a main group element, usually from groups V, VI, or VII.⁹ A generic structural representation of these two types of ligands is illustrated in Figure 1.



R=Alkyl or Aryl

Alkylidene

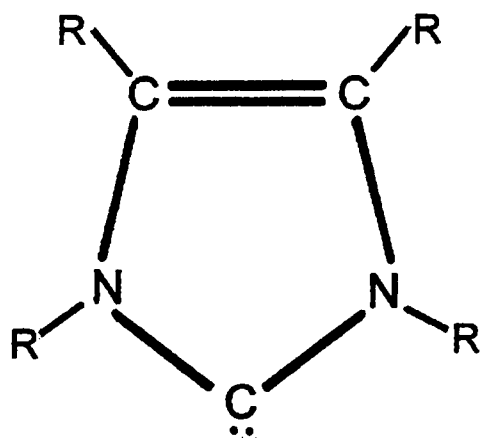
X=N, O, S, or P

Fischer Carbene

Figure 1. Orbital representation for carbene types.

Formally a carbene contains a carbon atom with only six valence electrons. Two of these electrons are localized in a sp^2 hybridized nonbonding orbital, thereby creating a singlet spin state and leaving one p-orbital unoccupied. The p-orbital may interact with an extended (d-p) π -systems on a metal atom. The accessibility of an empty orbital and a pair of electrons make carbenes exemplary ligands which exhibit strong σ donation to a metal atom while also engaging in strong $M \rightarrow C$ π -back bonding.

A new series of stable nucleophilic carbenes has been isolated and structurally characterized.² These new carbenes are based upon the framework of imidazole-2-ylidenes (Figure 1.2). Prior to the discovery of these compounds, investigations of free



R= Alkyl or Aryl

Figure 2. A representation of a generic imidazole-2-ylidene carbene.

carbenes had been limited to matrix isolation studies.³ Early theoretical investigations centered upon methylene (:CH_2). From those calculations some understanding was gained about how the singlet state is stabilized relative to the triplet state.⁴ The analysis of these new ylidenes revealed that small bond angles near 100° at the carbene carbon are indicative of singlet states, whereas angles in molecules with triplet ground states are in the range of 120° to 130° .¹

Carbenes have been employed as ligands in a prodigious number of organometallic complexes. When carbenes are added to the framework of a transition metal complex they can do so via two main coordination modes, terminal and bridging. The latter is subdivided into additional modes. Figure 3 illustrates these basic coordination modes.

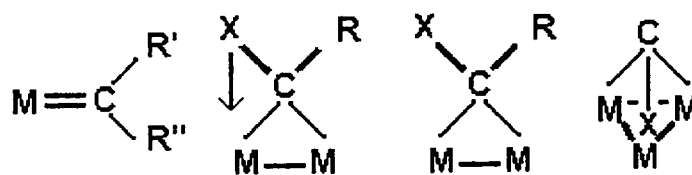


Figure 3. Coordination modes of carbene ligands.

B. ELECTRON COUNTING FORMALISMS

With regard to electronic configuration, the metal center in a complex seeks to achieve the effective atomic number (EAN) of 18. EAN is defined as the sum of the valence electrons on the metal plus the electrons donated from surrounding ligands. In organometallic chemistry this has been translated into the concept referred to as the *18 electron Rule*.⁵ This electron counting rule states that an electronic configuration of $ns^2 (n-1)d^{10}np^6$ (18 valence electrons) creates a stable, closed configuration. In the case of complexes where there is more than one metal atom, one must consider the contribution of a possible M-M bond to the formal valence electron count. One should view the representation of M-M bonds within the context of electron counting schemes with caution. The multiple bonds between metal atoms are quite distinct from that of say ethyne or ethylene since there is a wide variability in the lengths which constitutes multiple M-M bonds.⁶ This formalism is best employed as an indicator of reactivity as opposed to an indication of the nature of bonding. In these instances the electron count for a saturated complex can be calculated using the following formula:

$$\text{Electron count} = 18n - 2m$$

where **n** represents the number of metal atoms and **m** the number of M-M bonds. Thus for a dinuclear complex with a double M-M bond, **n** and **m** are equal to two. Thus, 32 valence electron are expected. One can determine the total number by counting the individual electron contributions for each metal and ligand and summing them. There are two formalisms as to whether the metal and ligands are counted as covalent or ionic species, as displayed in figure 4. Unless specified otherwise, the ionic formalism will be followed for the complexes presented in this work.

C. CARBENE COMPLEXES

Mononuclear carbene complexes are by far the most common and have dominated much of the research done in this area for the past few decades. However, incorporation of carbenes into cluster complexes has lead to unusual properties such as fluxionality and new varieties of catalysts.⁷ Carbene complexes have also been conjectured to be intermediates or transition states in many catalytic processes.

2Cp	2 x 5 = 10	2Cp ⁻	2 x 6 = 12
2CO	2 x 2 = 4	2CO	2 x 2 = 4
2M	2 x 9 = 18	2M ⁺	2 x 8 = 16
Total	32	Total	32
Covalent		Ionic	

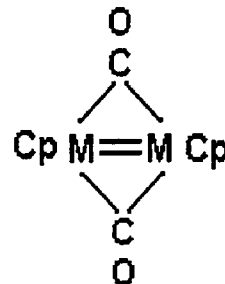


Figure 4. Example of electron counting formalisms.

There is a close relationship between metal clusters and the surfaces of bulk metals which lead Muetterties to formulate the "cluster-surface analogy".⁸ This novel concept views metal clusters as tiny metal pieces with chemisorbed species residing on the periphery. Thus, investigation of carbene complexes has permitted a better approximation of how organic molecules interact and become transformed via heterogeneous catalysts.

The first official carbene complexes were reported by Fischer and Maasböl in 1964.⁹ Initially these compounds were unstable acylpentacarbonyl tungstates. With further investigation stable complexes were isolated via the reactions of the carbene precursor with diazomethane. Other metal hexacarbonyls (Cr and Mo) and bimetallic decacarbonyls (Mn, Tc, Re)^{10,11} were soon discovered. These novel compounds were soon found to be more stable with regard to carbanion addition and alkylation. Furthermore, these types of complexes were found to be diamagnetic, soluble in common organic solvents and sublimable which greatly facilitated their ease of handling and characterization.

Today there are numerous examples of homonuclear bimetallic carbene complexes of the genre $\text{Cp}_2\text{M}_2\text{CR}_2(\text{CO})_n$, a few of these have been studied previously by members of Barnes group.^{12,13} As stated previously, carbenes can adopt a bridging or terminal geometry as ligands on polynuclear complexes. In the latter case structurally characterized examples are quite rare. The closest homo dinuclear species that resemble the terminally coordinated complex featured within this work are a dinuclear molybdenum complex¹⁴ having a cyclopentadienyl carbene and a dinuclear cobalt complex with phosphine as a ligand.¹⁵ These analogous complexes are featured in figure 5. The

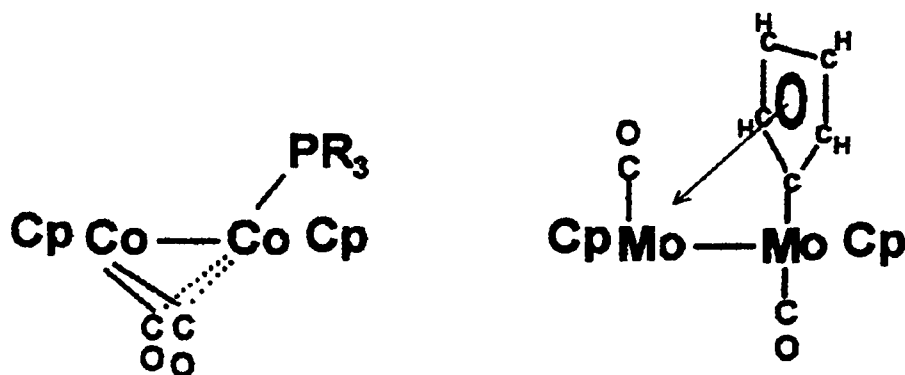


Figure 5. Examples of similar dinuclear complexes.

terminal carbene of the cyclopentadienyl ligand is bent close enough to the second Mo atom so that the 5 carbons of the cyclopentadienyl ring function as a η^5 -system.¹⁴ Furthermore, carbonyl ligands can coordinate in a terminal or a symmetrically bridged fashion in addition to a semi bridged mode which has been observed for the phosphine complex.

This thesis will give an account of the synthesis and characterization a novel dinuclear cobalt carbene complex which, in the solid state, has a rare example of a terminally coordinated carbene ligand. In solution, however, it appears that their ligand either assumes a symmetrical bridging coordination geometry or is rapidly equilibrated between terminal coordination to either of the two metal centers.

Chapter Two

Experimental

A. INTRODUCTION

Infrared (IR) spectra were acquired as KBr pellets using a Bio-Rad FT 60A Fourier transform IR spectrometer. Nominal and high resolution mass spectra were taken with a VG ZAB-EQ hybrid high performance mass spectrometer using electron impact ionization. Single crystal x-ray diffraction data were collected using a Nicolet R3 diffractometer. Structure solutions and refinements were performed on a PC using the SHELXTL-93 suite of programs.

Routine proton NMR spectra were recorded using a Bruker AC-250 spectrometer. Carbon-13 as well as all variable temperature NMR experiments were performed on a Bruker AMX-400WB spectrometer operating at 400.13 MHz for proton (100.62 MHz for carbon-13) using a 5 mm quadronuclear probehead (QNP).

The nitrogen gas used in Schlenk vessel manipulations was filtered through a column containing vermiculite coated with activated manganese oxide to remove oxygen followed by a column with molecular sieves to remove water. Chromatography was performed using silica that had been degassed under dynamic vacuum overnight and was

stored under nitrogen. Separation and elution of the reaction mixture components was accomplished by increasing solvent polarity in the order hexane, 10%, 20% and 30% hexane/ether. Methylene chloride was distilled over calcium hydride. All other solvents were distilled from Na/K alloy under nitrogen..

Cyclic voltammetric information was acquired using a BAS 100 electro chemical analyzer. The electrochemical cell used was a special design which afforded an air free environment.¹⁶ Concentrations of analyte were kept within a range of 3-5 mmol in the presence of 100 mmol concentration of supporting electrolyte, tetramethylammonium hexafluorophosphate. The solvent (THF) used in these measurements was treated with sodium /potassium alloy prior to being vacuum transferred into the cell.

NMR samples of air sensitive compounds were prepared by vacuum transfer of the deuterated solvent on a diffusion pump vacuum line followed by flame sealing of the tube.

B. SYNTHETIC PROCEDURES.

Cobalt(II)-hexamine chloride $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$

In a wide bottom Schlenk 40 g of hexaquo-cobalt(II)-chloride, $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ was added to 200-250 mL of aqueous concentrated (15M) ammonium hydroxide solution and stirred for several hours. The resulting pink colored precipitate was allowed to settle and the slightly colored solution above the material was removed by cannulation. The pink solid was washed with 3 X 100 mL portions of dry methanol followed again by cannulation. The material was then filtered excluding air and then dried under vacuum

overnight. The hexamine yield was 36 g of a finely divided salmon pink material (94 % yield).

Cobaltocene

In a glove box, 9.81 g of cobalt(II)-hexamine chloride (41.3 mmol) was combined with 8.90 g cyclopentadienyl-sodium, CpNa (123.7 mmol) in a Schlenk vessel. The Schlenk vessel was removed from the box and connected to a nitrogen gas line. While purging with nitrogen, 200 mL of dry tetrahydrofuran was added with concomitant gas evolution. The mixture was refluxed for 1.75 hours followed by removal of solvent under vacuum. The residue was taken back into the glove box and transferred into a 250 ml round bottom flask that was fitted with a condensor and stopcock joint. The arrangement was then connected to a high-vacuum line and the residue was sublimed at 65 °C and less than 0.5 mtorrr onto a condensor at -10 °C, yielding 6.50 g (34.3 mmol, 83.% of theoretical) .

Cyclopentadienyl Cobalt(I) bis-dicarbonyl CpCo(CO)₂

In the glove box, 10 g of dicobalt octacarbonyl was placed into a Schlenk vessel. The vessel was then connected to a nitrogen line. Under N₂ purge, 200 mL of dry methylene chloride was added. The dark solution was refluxed overnight. The solvent was removed. One hundred fifty mL of dry hexane was then added to the viscous residue and filtered into a clean Schlenk vessel followed by evacuation of solvent. The remaining reddish/ orange liquid was then transferred to a vacuum distillation apparatus. The red

dicarbonyl was collected into a receiver at 77 K. The yield was 2.0 ml or 3.81 g, 40 % of theoretical.

Cyclopentadienyl-cobalt(I) bis-ethylene, $\text{CpCo}(\text{C}_2\text{H}_2)_2$ ¹⁷

In a jacketed Schlenk vessel which was connected to a ethylene cylinder and a vacuum line, 6.50 g of cobaltocene was dissolved in 200 mL of dry ether. Then a brief vacuum was pulled on the solution and the vessel refilled with ethylene. The solution was then stirred and cooled to -10 °C, maintaining 1 atm overpressure of ethylene. Over a period of three days, 3-4 g of potassium was added in 0.5 g portions. The color changed from a dark purple/red to a bright orange. Stirring was stopped and the precipitate (KCp) allowed to settle to the bottom of the vessel. The solution was then cannulated into another Schlenk which was precooled to -78 °C. Two thirds of the solvent were removed under vacuum without heating. Hexane was added and the remaining ether was pulled off until crystallization began. The solution was then filtered through a cotton plugged, pouring spout into a clean Schlenk vessel. The hexane was removed leaving a flaky, dark orange solid. The material was stored in the refrigerator under ethylene gas. The yield was 4.5 g crystalline product (63% theoretical yield).

Tris(cyclopentadienylcobalt(I)-dicarbonyl, $\text{Cp}_3\text{Co}_3(\text{CO})_2$ ¹⁸

In a glove box, 500 mg of cyclopentadienylcobalt(I)-dicarbonyl, $\text{CpCo}(\text{CO})_2$, (2.76 mmol) was taken up in 15 mL of hexane. Cyclopentadienyl-cobalt(I) bis-ethylene, $\text{CpCo}(\text{C}_2\text{H}_2)_2$, 1000 mg in 75 ml of hexane was then added to the Schlenk vessel via

filtration through a pipet containing a cotton plug. The volume of the mixture was then decreased 50 % followed by filtration on a medium frit. The jet black microcrystalline material was washed with a small amount of hexane to remove trace impurities. One gram of product was obtained (92 % yield).

1, 3, 4, 5-tetramethylimidazol-2-ylidene (C₇H₁₂N₂) 2

This material was obtained as a research sample from Dr. Anthony J. Arduengo at Dupont Research division in Wilmington, DE. ¹HNMR was used to check purity of the material. Shifts in benzene-d₆ are 3.36 and 1.57 which correspond to the methyl groups attached to the nitrogen and olefin carbons respectively.

Survey Reactions of 2 with other Cobalt Complexes

Reactions of 2 with CpCo(CO)₂, Cp₂Co₂(CO)₂ and Cp₃Co₃(CO)₂, Cp₃Co₃(CO)₃, and Cp₄Co₄(CO)₂ were carried out in sealed nmr tubes which were kept at 77 K until insertion into the spectrometer. The first spectrum was obtained within five minutes and subsequent spectra were taken at ten minute intervals for about two hours. After that period of time no major changes were observed.

Cp₂Co₂(CO)₂ (C₇H₁₂N₂) 3 from reaction of Cp₃Co₃(CO)₂ 1 with 2

The investigation of the reactivity of the imidazole carbene's reactivity began by treating it with Cp₃Co₃(CO)₂. The imidazol carbene (29 mg; 0.233mmol) was dissolved in 10 mL of dry toluene. One mole-equivalent Cp₃Co₃(CO)₂ was dissolved in 20-30 mL of

toluene. The carbene solution was then added to the $\text{Cp}_3\text{Co}_3(\text{CO})_2$ solution. The combined solution was stirred for five minutes and then chromatographed on an air free column. The red product was eluted with a mixture of hexane:ether (3:1). The red fraction must be cooled immediately since the adduct is unstable at ambient temperatures. Spectral data (NMR, IR, MS) for **3** are summarized in table 3.2 (pp 9) in chapter three.

Reaction of $\text{Cp}_2\text{Co}_2(\text{CO})_2$ with **2**

The dinuclear carbene adduct **3** can also be synthesized by combining the imidazole carbene with $\text{Cp}_2\text{Co}_2(\text{CO})_2$. When dissolved in solution, this dinuclear reactant gives an intense green solution that changes to a red color almost immediately upon addition of the carbene. The reaction is also fast at lower temperatures, -10 to -20 °C. This method produces the carbene adduct cleanly with yields better than 95%.

$\text{CpCo}(\text{CO})(\text{C}_7\text{H}_{12}\text{N}_2)$ **4** from **3**

This complex can be obtained from the mother liquor of a recrystallization or decomposition of **3** at room temp.

Electrochemical surveys of **3** and **4**

The analyte and supporting electrolyte, 3 mg and 40 mg respectively, were added to cell in the dry box. The working electrode was polished on a polishing pad with 0.3 micron alumina for five minutes and was taken into the box and attached to the cell. Solvent was then quickly transferred into the cell on diffusion pump vacuum line after

pumping the box gases out of the cell. The cell was chilled at -5 °C with a salt/ice mixture during the solvent transfer and measurement of 3. Measurements of the decomposition product 4 were obtained after letting the cell warm to room temperature and sit out on the bench for 8 to 10 hours.

Recrystallization of 3 at low temperature (-20 °C) from ether/hexane solutions provided single crystals suitable for x-ray diffraction studies. The structure was solved by direct methods followed by anisotropic refinement on all non hydrogen atoms. Appendices A-E summarize data collection and final refinement parameters.

Chapter Three
Reactions of 1,3,4,5-Tetramethyl-
imidazole-2-Ylidene
with CpCo carbonyl Complexes

A. DINUCLEAR ADDUCT CHARACTERIZATION

In this chapter various aspects of the synthesis and characterization of the dinuclear carbene adduct $\text{Cp}_2\text{Co}_2(\text{CO})_2 (\text{C}_7\text{H}_{12}\text{N}_2)$ **3** will be summarized first. Second, a brief description of the decomposition of **3** to form a mononuclear carbene $\text{CpCo}(\text{CO}) (\text{C}_7\text{H}_{12}\text{N}_2)$ **4** is presented. Finally, a short discussion is given concerning several survey reactions of the imidazole carbene with other cluster complexes.

The formation of the adduct is rapid at ambient temperatures, but must be quickly separated from side products when it is generated via $\text{Cp}_3\text{Co}_3(\text{CO})_2$. When the carbene adduct is dissolved in solution, it must be kept at -10 to -20 C because it decomposes to mononuclear and tetranuclear species as well as insoluble materials at room temperature or above.

There are several methods of producing the carbene adduct. A general outline of preliminary investigations of the imidazole carbene with $\text{CpCo}(\text{CO})_2$, $\text{Cp}_2\text{Co}_2(\text{CO})_2$,

$\text{Cp}_3\text{Co}_3(\text{CO})_2$, $\text{Cp}_3\text{Co}_3(\text{CO})_3$, and $\text{Cp}_4\text{Co}_4(\text{CO})_2$ is given in the following pages. The most efficient of these methods for obtaining the adduct employs the reaction of the carbene with freshly prepared dinuclear complex, $\text{Cp}_2\text{Co}_2(\text{CO})_2$. The reaction with other starting materials containing cobalt generate additional products which must be removed from 3.

The imidazole carbene adduct 3 derived from $\text{Cp}_3\text{Co}_3(\text{CO})_2$ 1 and the imidazole carbene 2 exhibits interesting spectroscopic and structural properties. There are three peaks in the ^1H NMR spectra of 3 and 4. For compound 3 the chemical shifts of the methyl groups, $\text{N}-\text{CH}_3$ and $\text{C}=\text{C}-\text{CH}_3$, are 3.67 and 1.33 ppm respectively. The Cp shift for 3 is 4.57 ppm and the one for 4 is 4.85 ppm.

The ^{13}C NMR assignments for the methyl groups bound to nitrogen and olefin positions in 3 are 34.5 and 14.5 ppm, while the corresponding groups for 4 have shifts of 35.7 and 8.8 ppm. The carbene carbon for 3 appears at 167.8 ppm. The carbene carbon signal for 4 was not observed. The carbonyl shifts for the dinuclear adduct complex have a chemical shift of 240.5 ppm while the one for the mononuclear complex was too weak to be observed. Olefin carbons in each complex have signals at 129.4 and 124.8 ppm while the Cp ligands appear at 88.9 and 81.0 ppm for 3 and 4, respectively. Figure 6 shows the ^{13}C NMR of 3 at -20°C .

B. STRUCTURE

The solid state structure of 3 is interesting on several other accounts. The cyclopentadienyl ligands are canted in opposite directions from an imaginary line extending through the cobalt atoms. The two carbonyl ligands are coordinated in a semi-bridging fashion where the $\text{Co}(2)$ to $\text{C}(8)$ and $\text{C}(9)$ distances are 0.2 - 0.3 Å shorter than

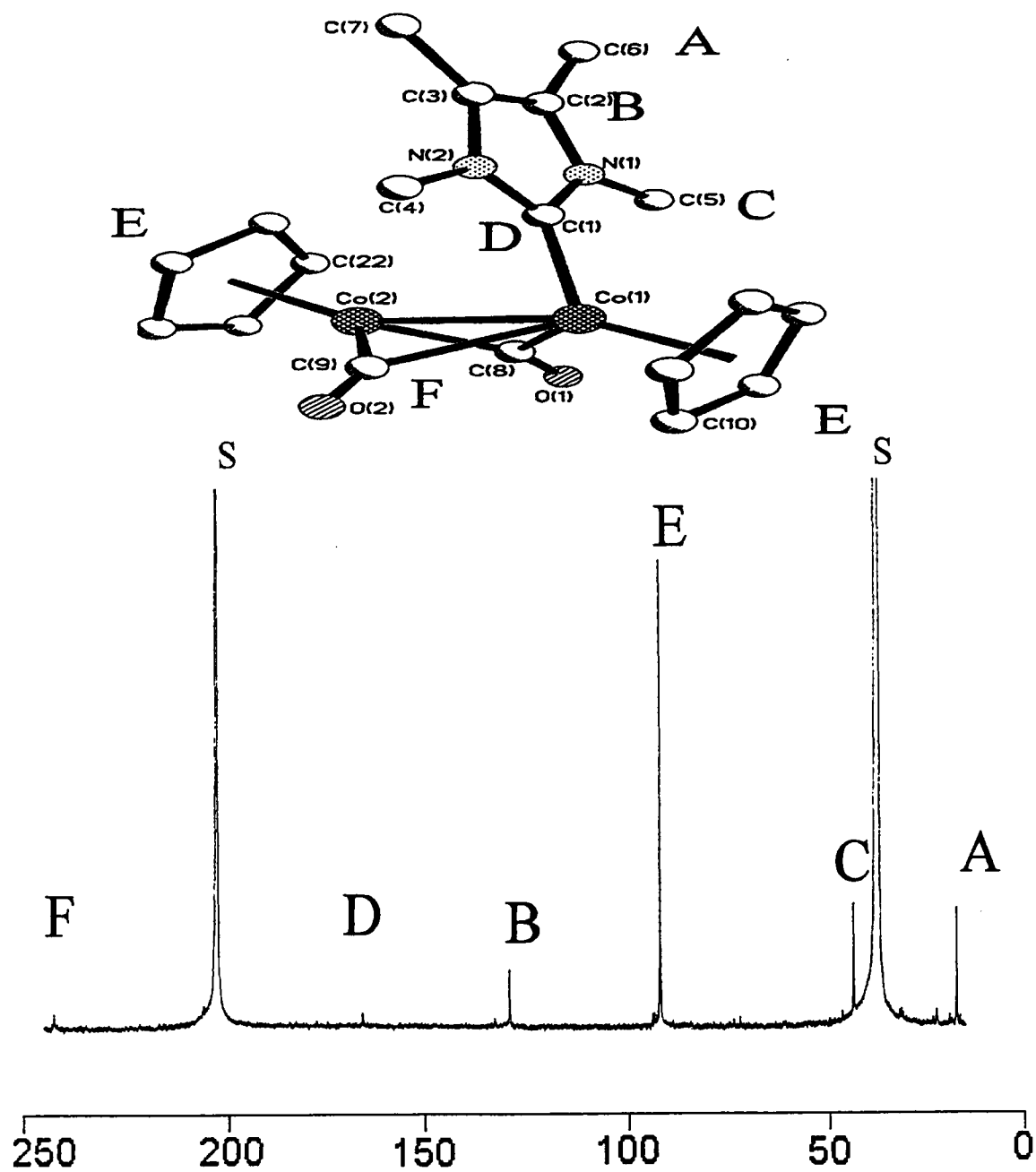


Figure 6. ^{13}C spectrum of the dinuclear carbene adduct **3** with peaks marked as S arising from acetone- d_6 .

the corresponding bonds to Co(1). The carbene is ligand tilted at 10 degrees towards the second cobalt atom. This tilting angle is not large enough such that interaction of the imidazole nitrogens or the olefin portion can contribute to the formal valence count of the second metal atom. Furthermore, the carbene carbon is sufficiently separated from the other cobalt atom by a distance of 2.788 Å such that no bond is formed. An ORTEP illustration of **3** is featured in figure 7. Table 1 lists pertinent bond angles and distances.

The ^1H NMR of **3** shows the presence of a single peak for the Cp hydrogens which was quite interesting with regard to the structure of the complex in solution. One would expect to observe two Cp signals in the region of 4-5 ppm, based upon the solid state structure. These peaks should be of equal intensity and area. To explain the observation of only one peak, we proposed that the carbene ligand is fluxional in solution. If the carbene ligand was fluxional at room temperature, then only an averaged signal should be observed if molecular motion is faster than the NMR time scale. To test this hypothesis, NMR spectra were recorded at lower temperatures. However, no coalescence behavior was observed within the temperature range of -20 to -90°C. Therefore we concluded that either the carbene moves instantaneously to adopt a symmetrical μ^2 -bridging coordination mode when dissolved or that the fluxional process of the ligand remains fast at all temperatures investigated.

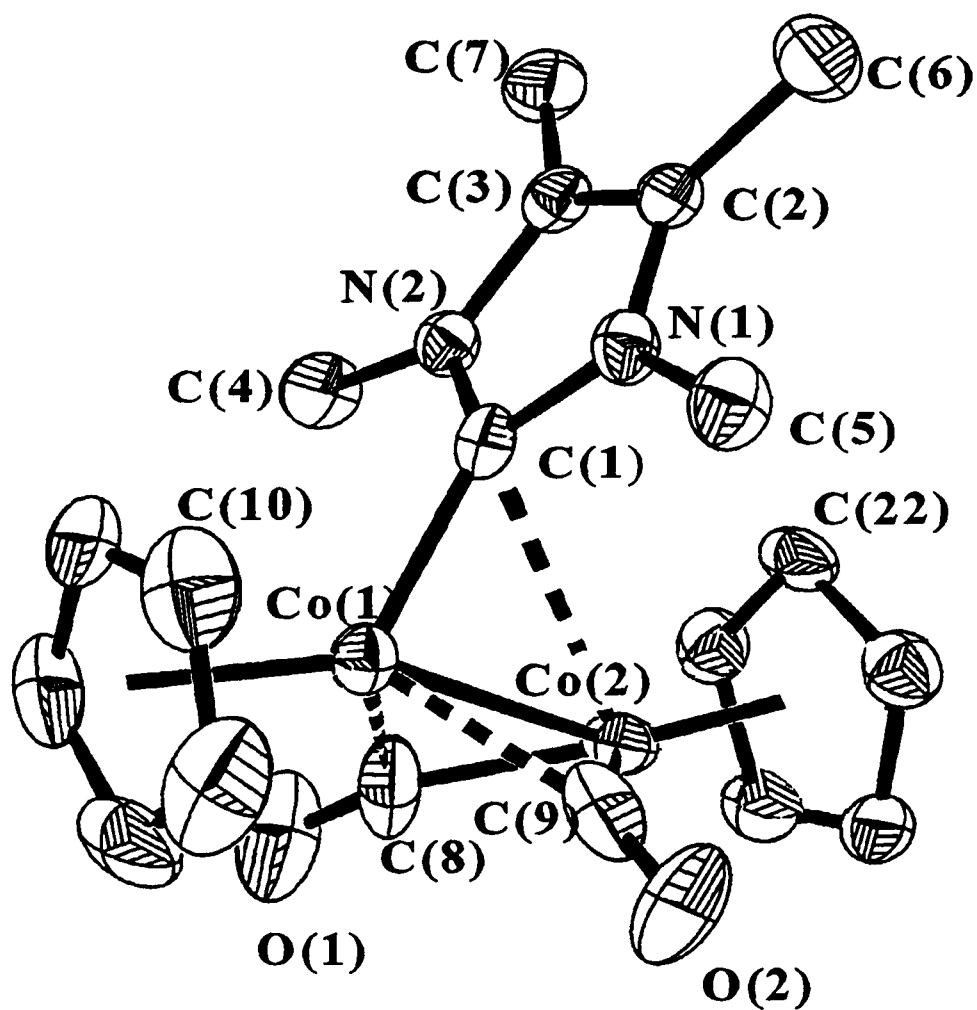


Figure 7. Crystal Structure of the Tetramethylimidazole-2-Ylidene adduct **3**.

Table 1. Selected bond distances and angles

Bond Distances in Å			
Co(1)-C(1)	1.899(5)	Co(1)-Co(2)	2.432(1)
Co(1)-C(8)	1.989(6)	Co(1)-C(9)	2.192(7)
Co(1)-C(10)	2.081(6)		
Co(2)-C(1)	2.788(4)		
Co(2)-C(9)	1.759(6)	Co(2)-C(8)	1.815(6)
N(1)-C(1)	1.356(6)	N(2)-C(1)	1.352(6)
N(1)-C(2)	1.383(6)	N(2)-C(3)	1.401(6)
C(8)-O(1)	1.174(6)	C(9)-O(2)	1.152(7)
Bond Angles °			
Co(1)-C(1)-Co(2)	79.08(14)	C(1)-Co(1)-C(10)	157.78(22)
C(1)-Co(1)-C(8)	99.90(20)	C(1)-Co(1)-C(9)	103.08(20)
Co(1)-C(8)-O(1)	135.48(42)	Co(1)-C(9)-O(2)	129.54(42)
Co(2)-C(8)-O(1)	145.14(46)	Co(2)-C(9)-O(2)	155.35(52)
N(1)-C(1)-N(2)	103.43(37)		

Figure 8 shows a set of spectra which define the upper and lower limits of the temperature study.

For the proposed solution structure, the ring plane of the carbene ligand is perpendicular to the M-M bond. This arrangement minimizes the steric interaction of the methyl groups and the Cp ligands and creates the symmetry necessary to yield only one Cp signal in the NMR spectra. Figure 9 illustrates a comparison of structures. Table 2 summarizes relevant spectral data.

Another interesting observation is that the imidazole carbene **2** causes fragmentation of complex **1**. It is well known that diazomethane reacts with this material and produces an unfragmented 48-electron cluster where the carbene bridges one of the Co-Co edges¹². However, if a trinuclear adduct forms it is very short lived due to the steric interaction of the N-CH₃ groups with other groups attached to the complex. Another possible explanation for product formation might be due to the nature of the ligand. The carbene ligand is such a strong donor ligand that it could generate the adduct and a solvated CpCo fragment in a concerted fashion. The CpCo fragment eventually reacts to form a tetranuclear species. Trinuclear complex **1** is quite prone to such fragmentation/recombination reactions. When **1** is dissolved in benzene or THF, solvent assisted fragmentation is observed to occur.^{19, 20} There are also a few interesting points about the mononuclear species which results from the decomposition of **3**. This complex has only one carbonyl stretch near 2000 cm⁻¹. If two carbonyl ligands were present in this complex, then an asymmetric, two peak pattern would have been expected. The ¹HNMR of the mononuclear adduct **4** is similar to **3** in that it has three signals with one

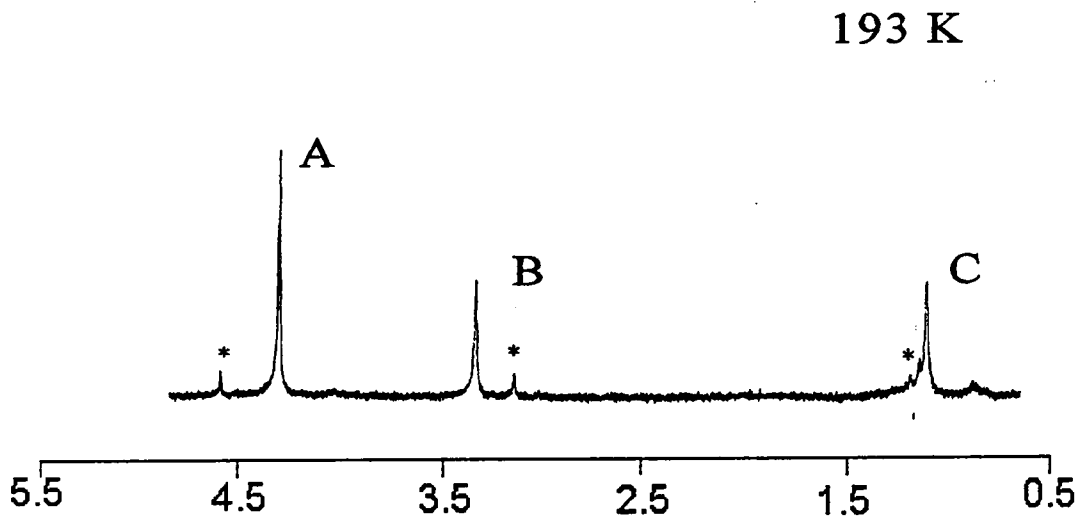
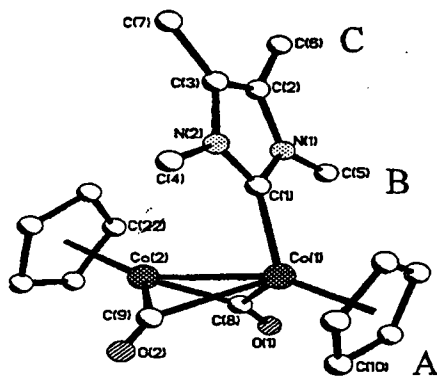
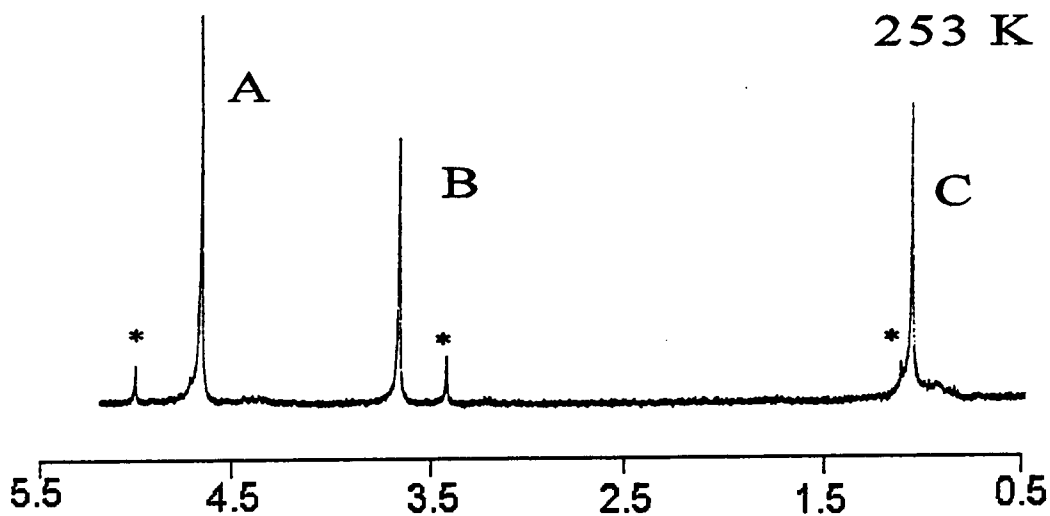
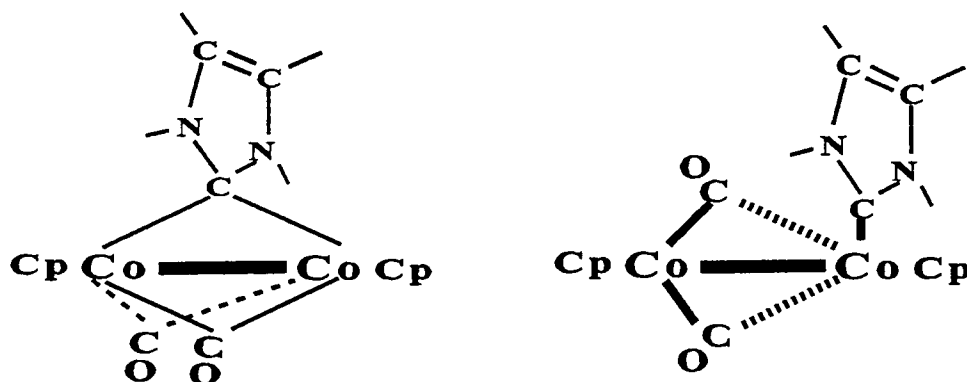


Figure 8. ^1H NMR of the carbene adduct **3** at 253 and 193 K in acetone- d_6 ; * denotes impurity.



Proposed solution structure

Solid state structure

Figure 9. Comparison of structures

the mononuclear adduct 4 is similar to 3 in that it has three signals with one assigned to the Cp ligand protons and one for each set of methyl groups with integrated intensities consistent with a Cp/imidazole ligand ratio of 1:1. Although we have not yet isolated crystals for a x-ray study, this complex is anticipated to closely resemble same basic structure of a mesityl imidazole CpCo complex that has recently been characterized by x-ray diffraction.²¹

C. SURVEY ELECTROCHEMISTRY

Cyclic voltammetric surveys scans of complexes 3 and 4 were recorded in THF solution using TBAP as a supporting electrolyte. The complexes, based upon the scan rate dependence for the first oxidative wave, exhibit electrochemical behavior that is

Table 2. Spectral Data for Carbene Adducts

Adduct	Proton ^a	¹ H NMR	Carbon ^b	¹³ C NMR	ν_{CO} ^c	MS ^{d,e,f}
<u>3</u>	Cp	4.57	Cp	88.9	1675	NPIO
	NCH ₃	3.67	NCH ₃	34.5		124
	CH ₃	1.33	CH ₃	14.3		189
			C=C	129.4		494
			C:	167.8		552
			C=O	240.5		
<u>4</u>	Cp	4.85	Cp	81.0	1891	
	NCH ₃	3.44	NCH ₃	35.7		
	CH ₃	1.36	CH ₃	8.8		
			C=C	124.8		
			C=O			
			C:			

^a Proton NMR were acquired in toluene-d₈.^b Carbon-13 NMR were acquired in acetone-d₆.^c KBr^d Mass spectrum were obtained via electron ionization technique.^e No Parent Ion Observed for mass of 428^f the ions listed represent the main peaks detected

consistent with quasireversible oxidation. For 3 the first oxidative wave appears at potential of 250 mV with a peak separation of 125 mV when scanned at 100 mV/s. At 1000 mV/s the first wave appears at 200 mV with a peak separation of 200 mV. The position of a second oxidative wave for 3 is complicated. At slow or fast scan rates the potential would appear to be close 1125 mV. In the former case no return wave is seen. However, for the faster scan rate (1000 mV), the second feature appears to be a set of overlapping waves. For complex 4 at scan rate of 100 mV/s, the first oxidative wave appears at potential of 600 mV with a peak separation of 130 mV. At 1000 mV/s, the oxidative wave is observed at 585 mV with a separation of 180 mV. A second oxidative wave for 4 again exhibits complicated redox behavior. For the 1000 mV/s scan, the potential seems to be close quite to 1500 mV. Figures 10 through 13 feature cyclic voltammetric survey scans of complexes 3 and 4.

D. SURVEY REACTIONS

A series of reactions of 2 with several CpCo-based cluster complexes has been investigated in sealed NMR tubes. When mixed with $\text{Cp}_3\text{Co}_3(\text{CO})_3$ or $\text{Cp}_4\text{Co}_4(\text{CO})_2$ rapid disappearance of both starting complexes is observed. As described earlier, reaction with 2 causes fragmentation and formation of a dinuclear adduct as well as other products. However, after about 30 to 40 minutes $\text{Cp}_3\text{Co}_3(\text{CO})_3$ and $\text{Cp}_4\text{Co}_4(\text{CO})_2$ reappear in each reaction, respectively. $\text{Cp}_3\text{Co}_3(\text{CO})_3$ has even been observed to form in the reaction of 1 with 2 at longer reaction times (>2 hours). Figure 14 provides a view of the respective reactions at five minutes while figure15 shows changes which have occurred after two hours. $\text{Cp}_4\text{Co}_4(\text{CO})_2$ does not appear in the spectra where $\text{Cp}_3\text{Co}_3(\text{CO})_3$ reacts with the 2.

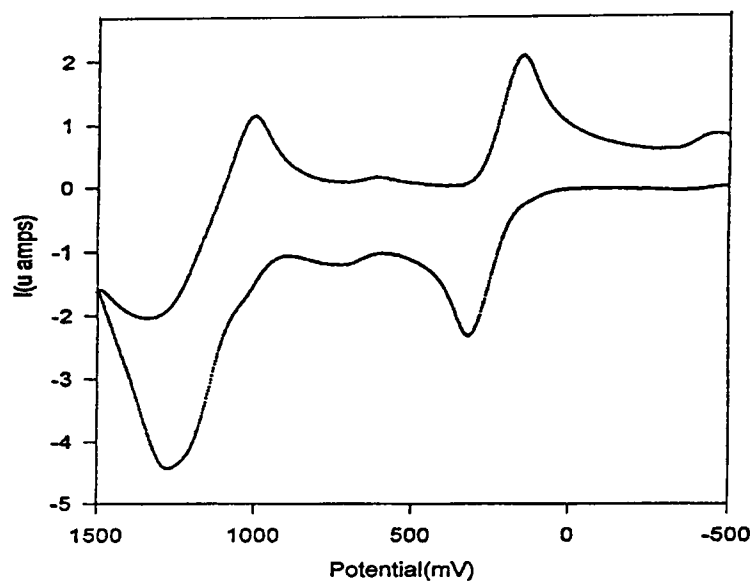


Figure 10. Cyclic Voltammetry of **3** in THF at -5 °C and 1000 mV/s.

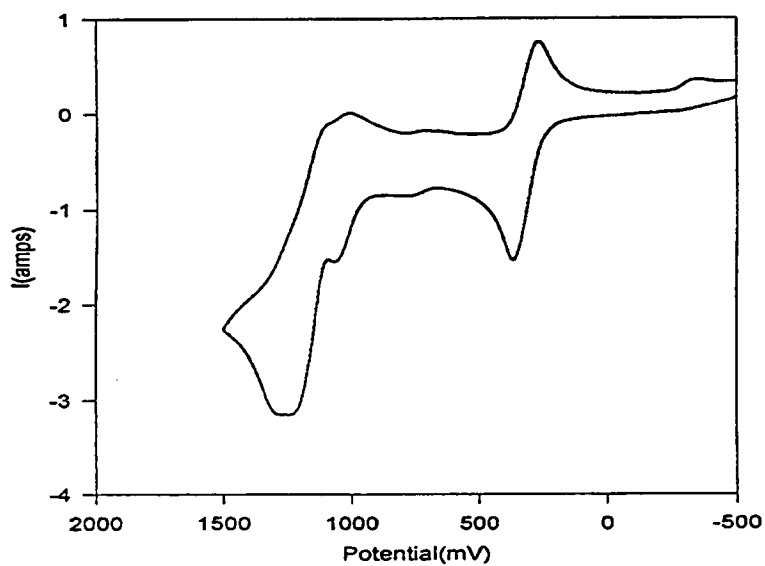


Figure 11. Cyclic Voltammetry of **3** in THF at -5 °C and 100 mV/s.

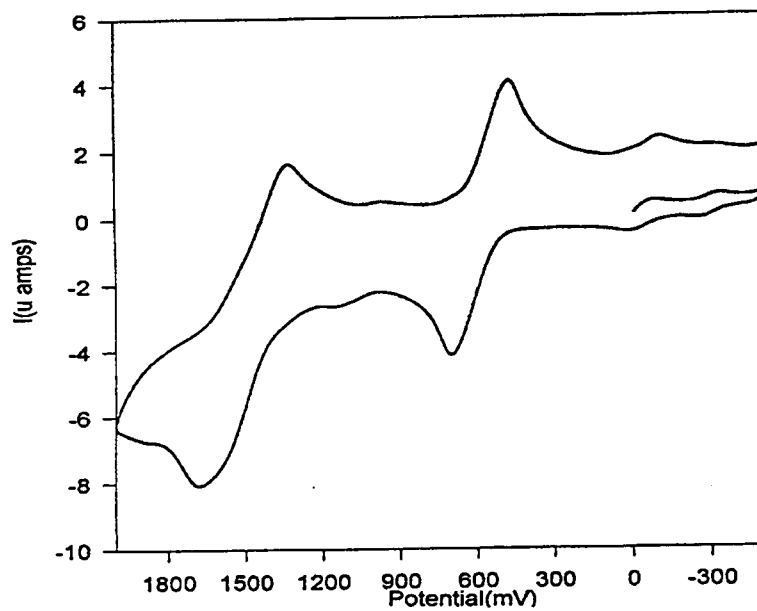


Figure 12. Cyclic Voltammetry of 4 in THF at -5 °C and 1000 mV/s.

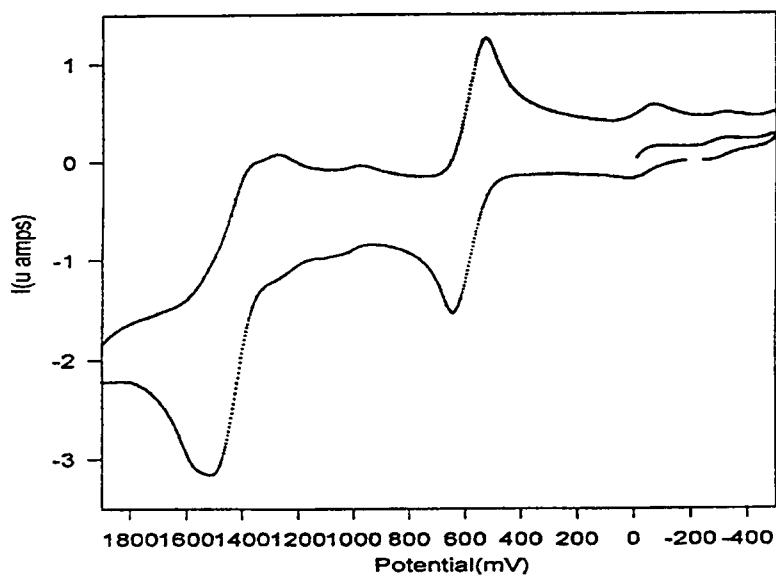


Figure 13. Cyclic Voltammetry of 4 in THF at -5 °C and 100 mV/s.

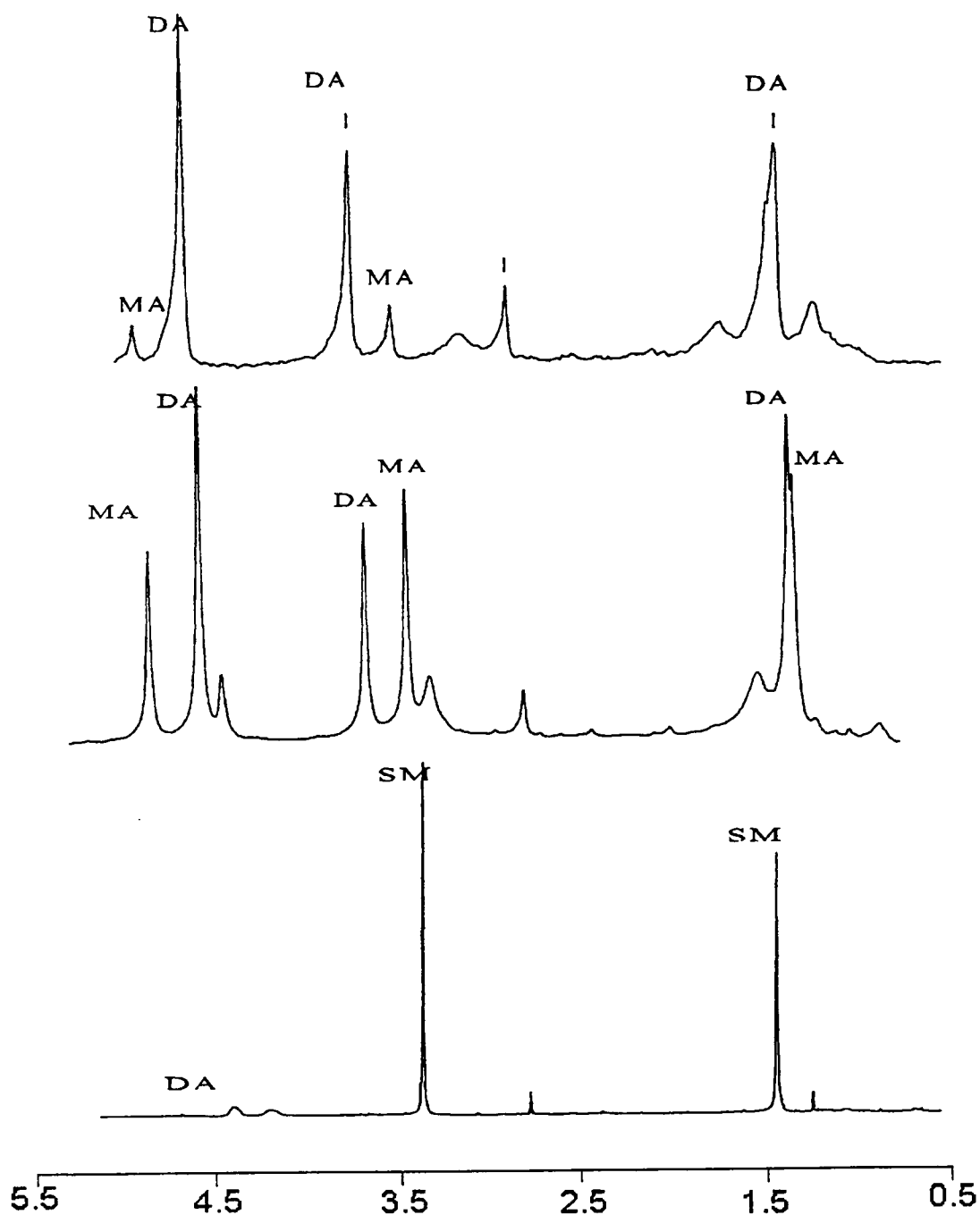


Figure 14. ^1H NMR at five minutes for Cp₃Co₃(CO)₂ (TOP), Cp₃Co₃(CO)₃ (MIDDLE), and Cp₄Co₄(CO)₂ (BOTTOM) in d^6 -benzene, room temperature. DA, MA, and SM denote Dinuclear Adduct, Mononuclear Adduct, and Starting Material respectively.

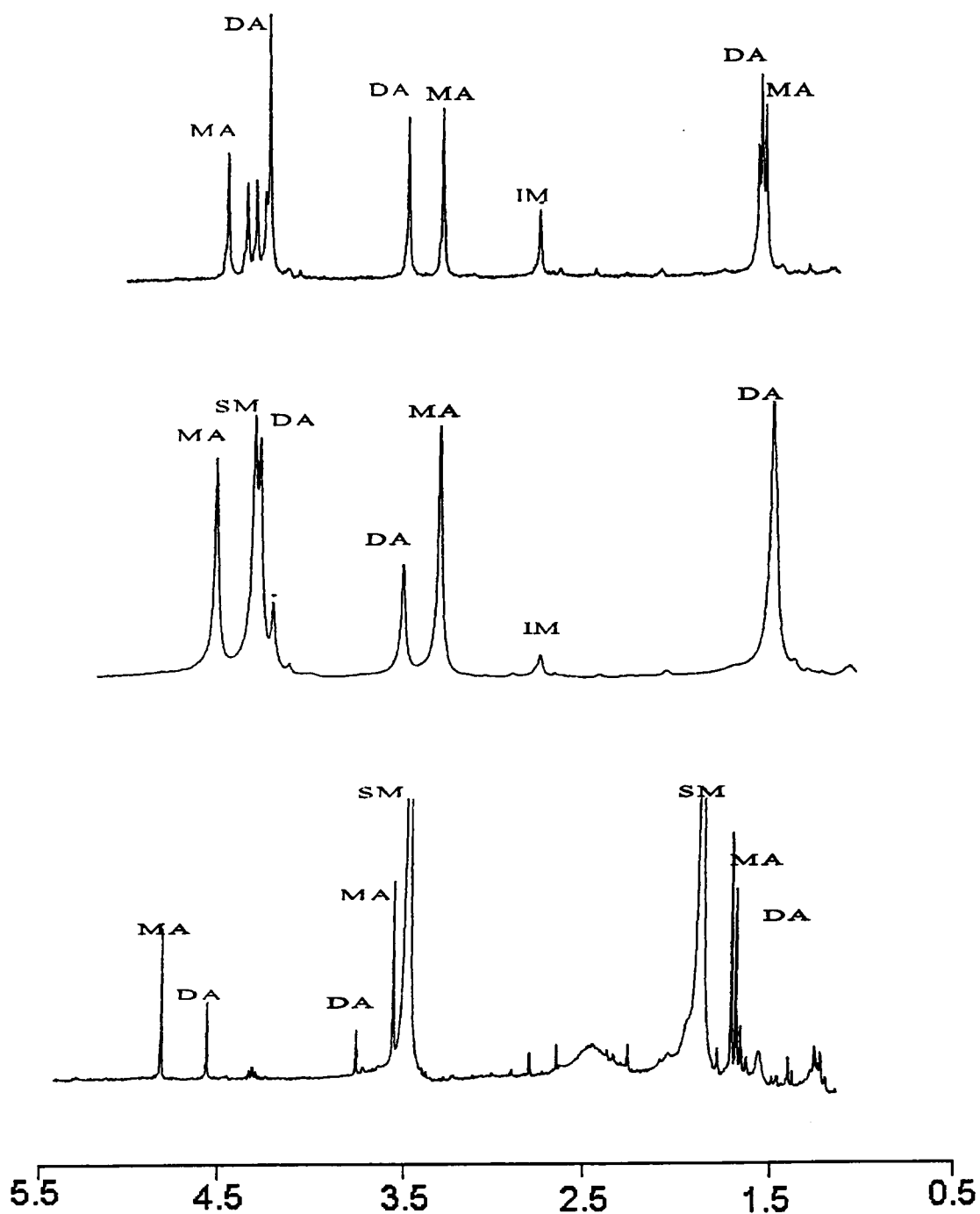


Figure 15. ^1H NMR at two hours for $\text{Cp}_3\text{Co}_3(\text{CO})_2$ (TOP), $\text{Cp}_3\text{Co}_3(\text{CO})_3$ (MIDDLE), and $\text{Cp}_4\text{Co}_4(\text{CO})_2$ (BOTTOM) in d^6 -benzene, room temperature. DA, MA, SM, and IM denote Dinuclear Adduct, Mononuclear Adduct, Starting Material, and IMPurity respectively.

Figures 16 through 18 illustrate the main products observed when 2 reacts with cobalt carbonyl complexes.

Suggestions for Future Studies.

It would be interesting to investigate the reaction of the imidazole carbene with an arene complex such as $\text{CpCo}(\text{C}_6(\text{Ph})_6)$. Since the arene does not have any carbonyl ligands, the reaction may not generate as many side products. These reactions might yield a complex in which a bridging carbene ligand can be observed. The reaction 2 with the ethylene complex $\text{CpCo}(\text{C}_2\text{H}_4)_2$ would also be of interest in this respect.

Other investigations could focus on the reactivity of the 2 other homo and hetero metallic cluster systems. Furthermore, mechanistic studies could also yield significant information with regard to intermediates in future catalytic systems based upon these types of compounds.

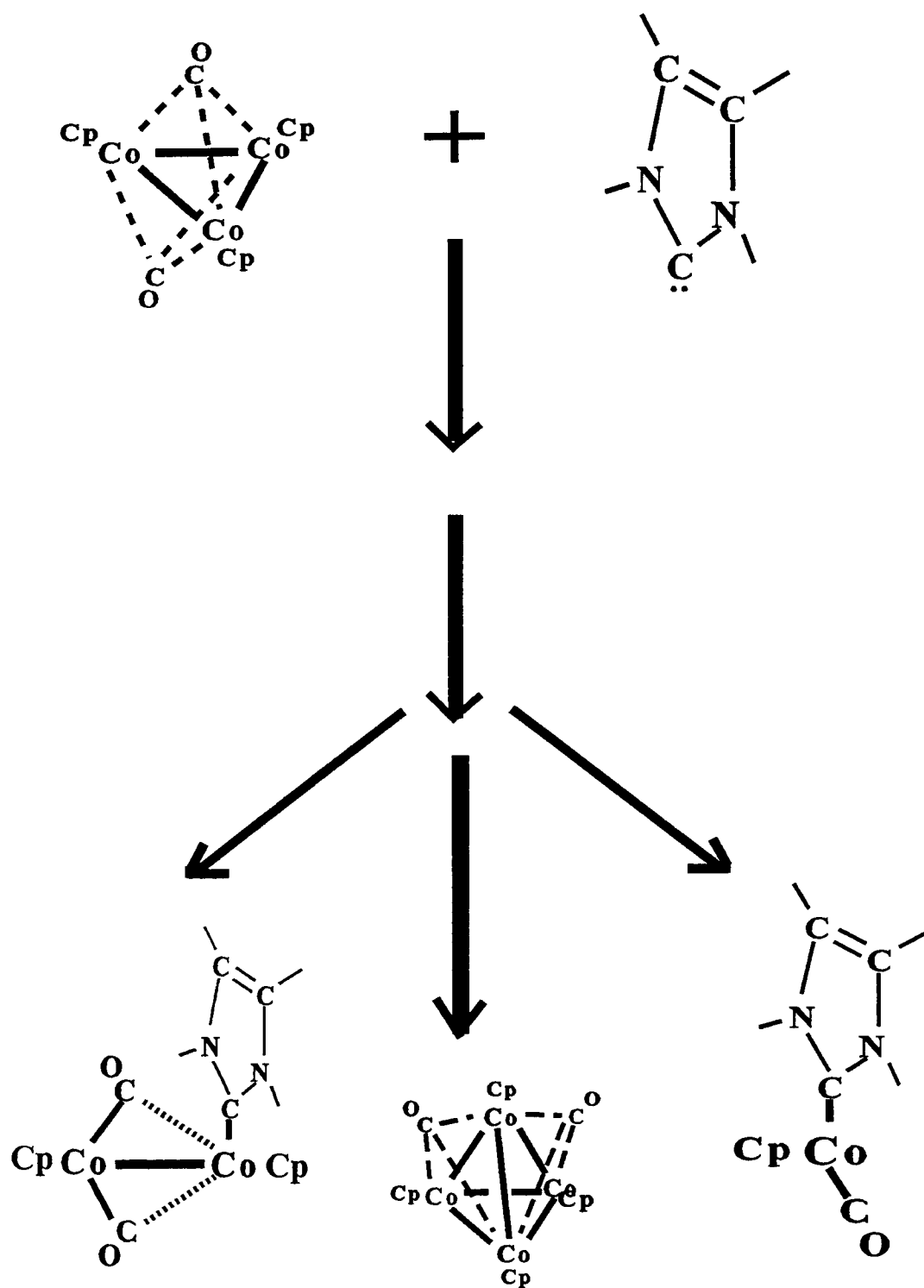


Figure 16. Reaction of 2 with a trinuclear dicarbonyl complex.

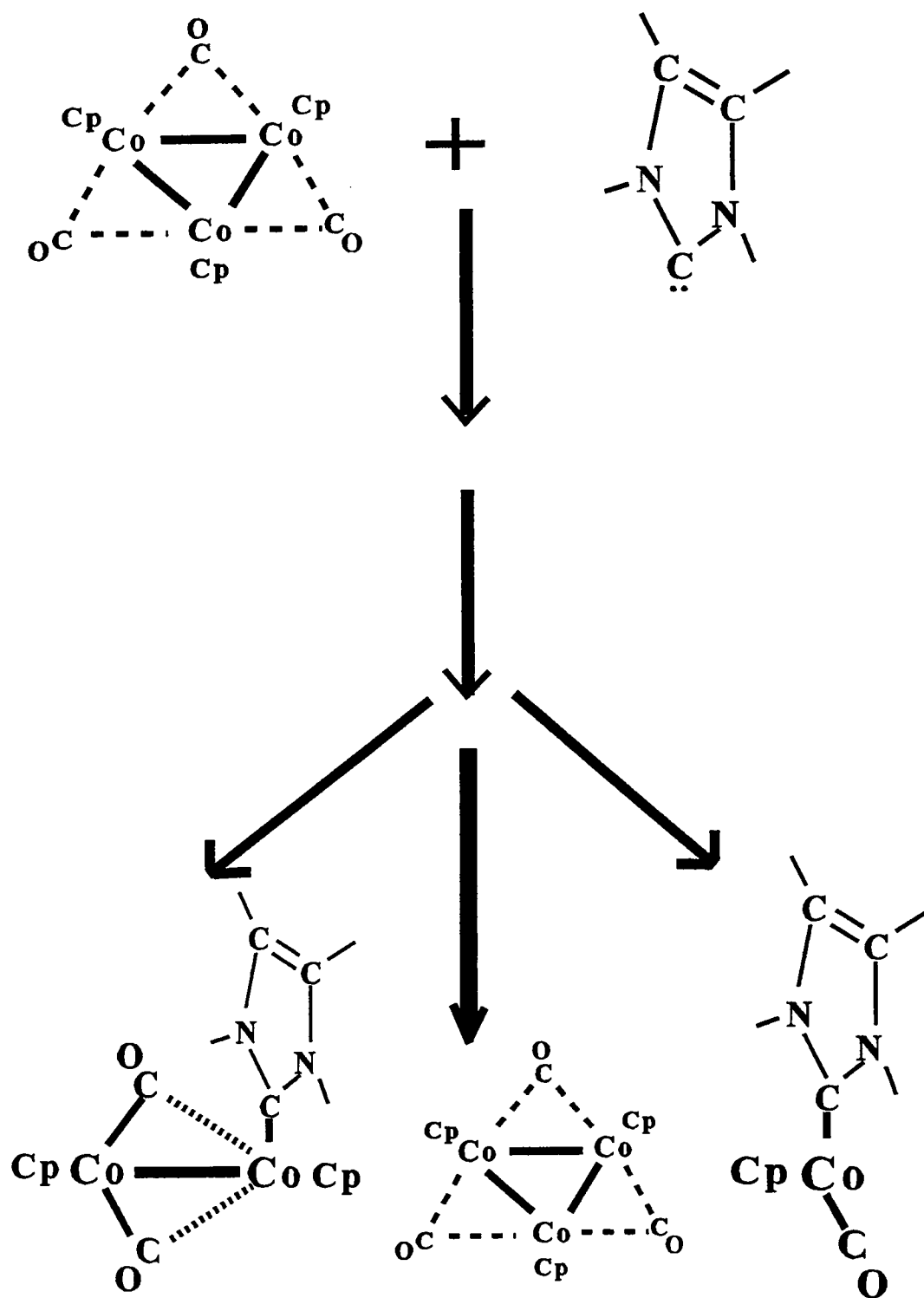


Figure 17. Reaction of 2 with trinuclear tricarbonyl complex.

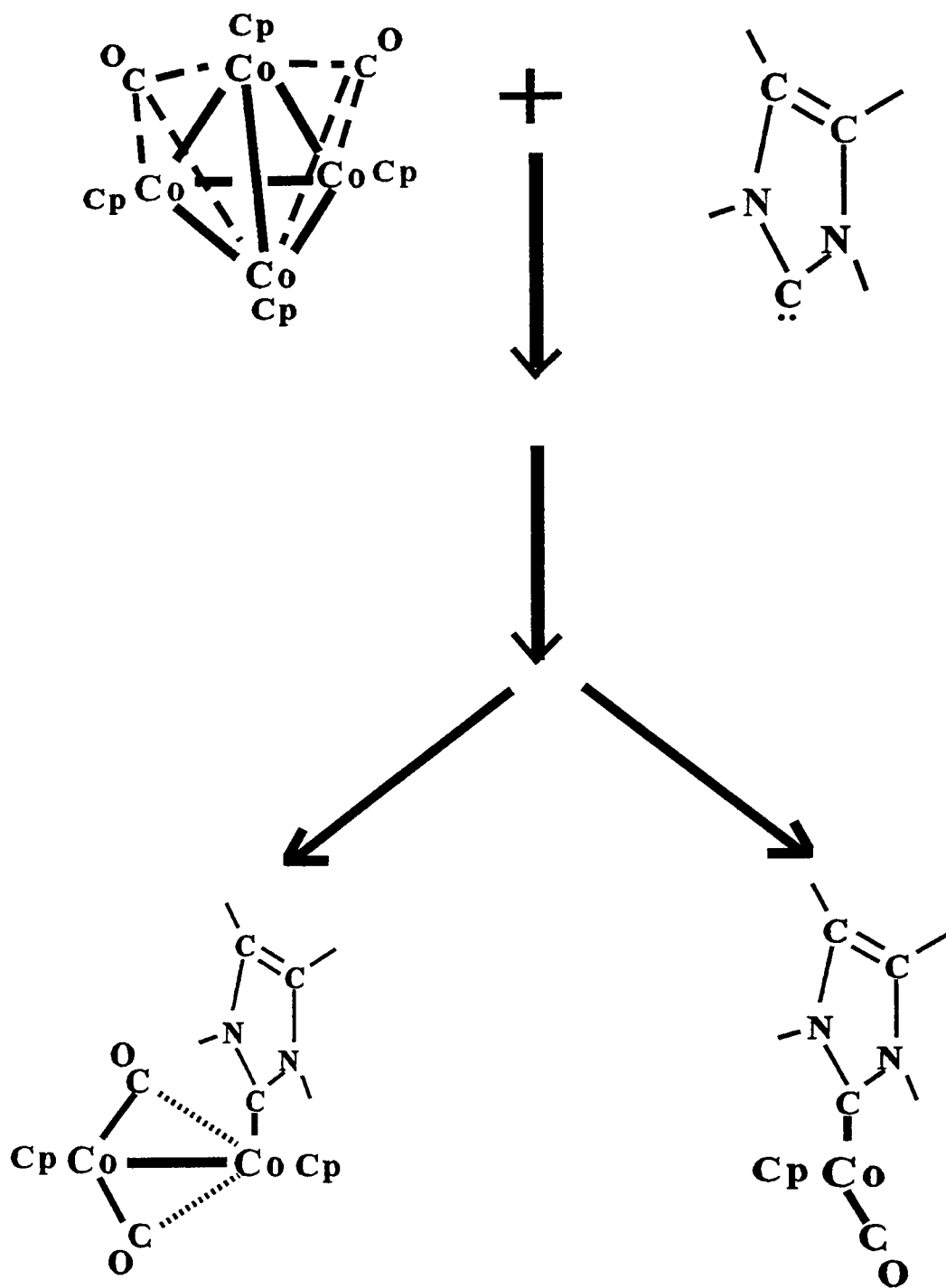


Figure 18. Reaction of 2 with tetranuclear dicarbonyl complex.

Chapter Four

Summary and Conclusions

The reaction of 1, 3, 4, 5-tetramethylimidazole-2-ylidene ($C_7H_{12}N_2$) **2** with $Cp_3Co_3(CO)_2$ **1** was expected to generate 48 electron trinuclear adduct. Instead, a 34 electron dinuclear species **3** was isolated and characterized. $Cp_3Co_3(CO)_2(C_7H_{12}N_2)$ compound **3** has an unusual crystal structure from which insight to its reactive nature was obtained. In contrast to the solid state structure, the solution structure indicates that the carbene ligand may be involved in a fluxional process which variable low temperature NMR studies were unable to resolve. An alternative explanation for the discrepancy between the solution and solid state structure could be that the carbene adopts a bridging coordination upon being solvated. This dinuclear complex is temperature sensitive and will decompose in solution even at low temperatures.

Instability of the dinuclear adduct may result from steric and electronic factors. The methyl groups of the imidazole carbene extend far enough such that they can interact with the cyclopentadienyl ligands. Metal to carbene ligand backbonding may not be efficient due to the pseudo aromatic stability within the ring. Thus, the p-orbital on the carbene carbon is not "free" enough to engage in d-p π backbonding effectively.

Mono-, di-, tri-, and tetra- nuclear cobalt carbonyl complexes also react with 2. The initial product that forms is 3, but in time and at ambient temperatures and below, converts to a mononuclear carbene complex 4. The $\text{CpCo}(\text{CO})_2$ and $\text{Cp}_2\text{Co}_2(\text{CO})_2$ cobalt complexes react rapidly with the imidazole carbene whereas the trinuclear and tetranuclear complexes react more slowly to generate the dinuclear and mononuclear carbene adducts.

Cyclic voltammetric surveys of complexes 3 and 4 were conducted at 1000 and 100 mV/s. The first oxidative wave for each complex is well defined and corresponds to a quasireversible process. The second oxidative wave is complicated and is best described as an irreversible process.

Reaction 1,3,4,5-tetramethylimidazole-2-ylidene carbene with cyclopentadienyl cobalt carbonyl complexes is challenging, but also quite intriguing. Additional studies are needed to probe more thoroughly the various aspects of the carbene's reactivity with organometallic compounds.

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APPENDICES

Appendix A. Crystal data and structure refinement for 3

Empirical Formula	$C_{19}H_{22}Co_2 N_2O_2$
Formula Weight	428.10
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	$a = 8.860(2)$ $\alpha = 92.30(30)^\circ$ $b = 9.037(2)$ $\beta = 103.98(3)^\circ$ $c = 12.118(2)$ $\gamma = 109.51(3)^\circ$
Volume, Z	879.7(3) Å ³ , 2
Density (calculated)	1.617 Mg/m ³
Absorption coefficient	1.900 mm ⁻¹
F(000)	440
Crystal size	0.25 x 0.25 x 0.10 mm
Θ range for data collection	1.75 to 22.55°
Limiting indices	$-1 \leq h \leq 9, -9 \leq k \leq 9, -13 \leq l \leq 12$
Reflections collected	2403
Independent reflections	2313 ($R_{int} = 0.0136$)
Absorption correction	Semi-empirical from psi-scans
Max. and mm. transmission	0.9793 and 0.6299
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2311 / 0 / 230
Goodness-of-fit on F^2	1.112
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0414, wR2 = 0.0997$
R indices (all data)	$R1 = 0.0523, wR2 = 0.1107$
Largest diff. peak and hole	0.496 and -0.709 eÅ ⁻³

Appendix B. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A \times 10^3$] for **3**. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Co(1)	4211(1)	2488(1)	1809(1)	25(1)
Co(2)	5843(1)	1933(1)	3556(1)	33(1)
N(1)	6621(5)	5724(4)	2631(3)	26(1)
N(2)	7580(4)	4355(4)	1720(3)	26(1)
C(1)	6229(5)	4249(5)	2089(4)	25(1)
C(2)	8196(6)	6709(5)	2631(4)	27(1)
C(3)	8822(5)	5857(5)	2062(4)	27(1)
C(4)	7742(6)	3034(6)	1085(4)	36(1)
C(S)	5527(6)	6215(6)	3175(4)	35(1)
C(6)	8900(7)	8409(6)	3136(5)	43(1)
C(7)	10459(6)	6282(7)	1800(4)	42(1)
C(8)	3962(7)	2388(6)	3395(5)	41(1)
O(1)	2993(5)	2535(5)	3861(3)	55(1)
C(9)	5059(6)	536(8)	2315(5)	49(2)
O(2)	4835(6)	-640(5)	1783(3)	67(1)
C(10)	1950(8)	811(8)	872(6)	63(2)
C(11)	1684(7)	2186(10)	1203(5)	68(2)
C(12)	2602(7)	3411(7)	719(5)	51(2)
C(13)	3385(7)	2767(7)	61(4)	42(1)
C(14)	2975(7)	1193(7)	141(5)	48(2)
C(20)	7333(6)	1055(6)	4758(4)	35(1)
C(21)	6685(6)	1971(6)	5324(4)	33(1)
C(22)	7278(6)	3533(6)	5065(4)	38(1)
C(23)	8329(6)	3585(6)	4349(4)	36(1)
C(24)	8352(6)	2057(6)	4142(4)	39(1)

Appendix C: Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **3.****Bond Lengths:**

Co(1)-C(1)	1.899(5)	Co(1)-C(8)	1.989(6)
Co(1)-C(10)	2.082(6)	Co(1)-C(11)	2.099(5)
Co(1)-C(12)	2.108(5)	Co(1)-C(13)	2.122(5)
Co(1)-C(14)	2.130(5)	Co(1)-C(9)	2.192(7)
Co(1)-Co(2)	2.4322(11)	Co(2)-C(9)	1.759(6)
Co(2)-C(8)	1.815(6)	Co(2)-C(21)	2.087(5)
Co(2)-C(20)	2.088(5)	Co(2)-C(22)	2.119(5)
Co(2)-C(24)	2.127(5)	Co(2)-C(23)	2.161(5)
N(1)-C(1)	1.357(6)	N(1)-C(2)	1.383(6)
N(1)-C(5)	1.463(6)	N(2)-C(1)	1.352(6)
N(2)-C(3)	1.401(6)	N(2)-C(4)	1.460(6)
C(2)-C(3)	1.343(6)	C(2)-C(6)	1.491(7)
C(3)-C(7)	1.486(7)	C(8)-O(1)	1.174(6)
C(9)-O(2)	1.152(7)	C(10)-C(14)	1.390(9)
C(10)-C(11)	1.400(10)	C(11)-C(12)	1.383(9)
C(12)-C(13)	1.399(8)	C(13)-C(14)	1.359(8)
C(20)-C(21)	1.395(7)	C(20)-C(24)	1.424(7)
C(21)-C(22)	1.410(7)	C(22)-C(23)	1.409(7)
C(23)-C(24)	1.401(7)		

Bond Angles:

C(1)-Co(1)-C(8)	99.9(2)	C(1)-Co(1)-C(10)	157.8(2)
C(8)-Co(1)-C(10)	101.0(3)	C(1)-Co(1)-C(11)	134.3(3)
C(8)-Co(1)-C(11)	89.5(2)	C(10)-Co(1)-C(11)	39.1(3)
C(1)-Co(1)-C(12)	99.3(2)	C(8)-Co(1)-C(12)	114.8(2)
C(10)-Co(1)-C(12)	65.0(2)	C(11)-Co(1)-C(12)	38.4(3)
C(1)-Co(1)-C(13)	94.0(2)	C(8)-Co(1)-C(13)	152.3(2)
C(10)-Co(1)-C(13)	63.9(2)	C(11)-Co(1)-C(13)	64.0(2)
C(12)-Co(1)-C(13)	38.6(2)	C(1)-Co(1)-C(14)	121.5(2)
C(8)-Co(1)-C(14)	138.5(2)	C(10)-Co(1)-C(14)	38.5(3)
C(11)-Co(1)-C(14)	64.4(2)	C(12)-Co(1)-C(14)	64.1(2)
C(13)-Co(1)-C(14)	37.3(2)	C(1)-Co(1)-C(9)	103.1(2)
C(8)-Co(1)-C(9)	78.2(2)	C(10)-Co(1)-C(9)	88.4(2)
C(11)-Co(1)-C(9)	122.6(3)	C(12)-Co(1)-C(9)	151.6(2)
C(13)-Co(1)-C(9)	121.8(2)	C(14)-Co(1)-C(9)	89.2(2)
C(1)-Co(1)-Co(2)	79.08(14)	C(8)-Co(1)-Co(2)	47.2(2)
C(10)-Co(1)-Co(2)	121.1(2)	C(11)-Co(1)-Co(2)	133.1(2)
C(12)-Co(1)-Co(2)	160.2(2)	C(13)-Co(1)-Co(2)	160.4(2)
C(14)-Co(1)-Co(2)	133.5(2)	C(9)-Co(1)-Co(2)	44.33(14)
C(9)-Co(2)-C(8)	95.4(2)	C(9)-Co(2)-C(21)	137.8(3)
C(8)-Co(2)-C(21)	103.2(2)	C(9)-Co(2)-C(20)	105.5(3)
C(8)-Co(2)-C(20)	137.9(2)	C(21)-Co(2)-C(20)	39.0(2)
C(9)-Co(2)-C(22)	167.5(2)	C(8)-Co(2)-C(22)	97.1(2)
C(21)-Co(2)-C(22)	39.2(2)	C(20)-Co(2)-C(22)	65.4(2)
C(9)-Co(2)-C(24)	102.7(2)	C(8)-Co(2)-C(24)	161.5(2)

Appendix C continued

C(21) -Co(2) -C(24)	65.5(2)	C(20)-Co(2) -C(24)	39.5(2)
C(22) -Co(2) -C(24)	64.8(2)	C(9)-Co(2)-C(23)	130.8(2)
C(8) -Co(2)-C(23)	124.7(2)	C(21) -Co(2) -C(23)	64.9(2)
C(20)-Co(2)-C(23)	64.9(2)	C(22)-Co(2) -C(23)	38.4(2)
C(20) -Co(2) -Co(1)	165.2(2)	C(22)-Co(2)-Co(1)	127.31(14)
C(24) -Co(2)-Co(1)	134.13(14)	C(23)-Co(2)-Co(1)	119.03(14)
C(1) -N(1) -C(2)	111.9(4)	C(1)-N(1)-C(5)	124.3(4)
C(2)-N(1)-C(5)	123.7(4)	C(1)-N(2)-C(3)	111.9(4)
C(1)-N(2) -C(4)	123.6(4)	C(3)-N(2)-C(4)	124.4(4)
:			
N(2) -C(1) -N(1)	103.4(4)	N(2) C(1) -Co(1)	127.7(3)
N(1) -C(1) -O(1)	128.7(3)	C(3)-C(2)-N(1)	106.9(4)
C(3) -C(2) -O(6)	130.5(4)	N(1) -C(2) -C(6)	122.5(4)
C(2)-C(3) -N(2)	105.8(4)	C(2)-C(3)-C(7)	131.1(4)
N(2)-C(3)-C(7)	123.1(4)	O(1)-C(8)-Co(2)	145.2(5)
O(1) -C(8)-Co(1)	135.5(4)	Co(2)-C(8)-Co(1)	79.3(2)
O(2) -C(9) -Co(2)	155.4(5)	O(2)-C(9)-Co(1)	129.5(4)
O(2)-C(9) -Co(1)	75.1(2)	C(14)-C(10) -C(11)	107.7(6)
C(14)-C(10)-Co(1)	72.6(3)	C(11)-C(10)-Co(1)	71.1(3)
C(12) -C(11) -C(10)	107.9(6)	C(12)-C(11)-Co(1)	71.1(3)
C(10) -C(11)-Co(1)	69.7(3)	C(11) -C(12)-C(13)	107.0(5)
C(11) -C(12) -Co(1)	70.5(3)	C(13)-C(12)-Co(1)	71.2(3)
C(14) -C(13)-O(12)	109.3(5)	C(14)-C(13) -Co(1)	71.7(3)
C(12)-C(13)-Co(1)	70.2(3)	C(13) -C(14)-C(10)	108.0(5)
C(13) -C(14) -Co(1)	71.0(3)	C(10)-C(14) -Co(1)	68.8(3)
C(21)-C(20)-C(24)	107.9(5)	C(21)-C(20) -Co(2)	70.4(3)
C(24) -C(20) -Co(2)	71.7(3)	C(20) -C(21)-C(22)	108.3(5)
C(20) -C(21) -Co(2)	70.5(3)	C(22)-C(21)-Co(2)	71.6(3)
C(21) -C(22) -C(23)	107.9(5)	C(21)-C(22)-Co(2)	69.2(3)
C(23) -C(22) -Co(2)	72.4(3)	C(24) -C(23)-C(22)	108.1(5)
C(24) -C(23) -Co(2)	69.6(3)	C(22)-C(23)-Co(2)	69.2(3)
C(23) -C(24) -C(20)	107.7(5)	C(23)-C(24)-Co(2)	72.2(3)
C(20) -C(24) -Co(2)	68.8(3)		

Symmetry transformations used to generate equivalent atoms:

Appendix D. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for **3**

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [(ha^*)^2 U_{11} + \dots + 2hka^*b^*U_{12}]$$

	U11	U22	U33	U23	U13	U12
Co(1)	23(1)	30(1)	21(1)	1(1)	4(1)	10(1)
Co(2)	27(1)	31(1)	29(1)	10(1)	-1(1)	3(1)
N(1)	31(2)	26(2)	22(2)	-1(2)	7(2)	13(2)
N(2)	27(2)	28(2)	23(2)	0(2)	10(2)	10(2)
C(1)	27(2)	34(3)	17(2)	1(2)	5(2)	16(2)
C(2)	30(3)	26(3)	21(2)	6(2)	2(2)	8(2)
C(3)	26(2)	33(3)	22(2)	6(2)	6(2)	11(2)
C(4)	40(3)	38(3)	38(3)	-1(2)	20(2)	18(2)
C(S)	43(3)	37(3)	33(3)	-2(2)	15(2)	21(2)
C(6)	50(3)	32(3)	38(3)	2(2)	0(3)	12(3)
C(7)	31(3)	50(3)	38(3)	7(3)	13(2)	5(3)
C(8)	42(3)	30(3)	41(3)	-7(2)	-7(3)	14(3)
O(1)	70(3)	82(3)	35(2)	9(2)	26(2)	47(2)
C(9)	35(3)	80(5)	25(3)	-12(3)	0(2)	21(3)
O(2)	107(4)	72(3)	40(2)	-2(2)	3(2)	66(3)
C(10)	40(3)	53(4)	58(4)	21(3)	-23(3)	-8(3)
C(11)	27(3)	139(7)	42(4)	15(4)	0(3)	43(4)
C(12)	56(4)	55(4)	44(3)	1(3)	-7(3)	37(3)
C(13)	45(3)	52(4)	22(3)	7(2)	0(2)	15(3)
C(14)	60(4)	45(4)	32(3)	-12(3)	-9(3)	27(3)
C(20)	31(3)	34(3)	34(3)	8(2)	-1(2)	8(2)
C(21)	31(3)	37(3)	25(3)	8(2)	3(2)	8(2)
C(22)	36(3)	35(3)	36(3)	3(2)	1(2)	11(2)
C(23)	26(3)	33(3)	34(3)	6(2)	-5(2)	-1(2)
C(24)	30(3)	49(3)	31(3)	3(2)	3(2)	10(2)

Appendix E. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3.

	x	y	z	U(eq)
H(4A)	6643(8)	2344(22)	615(22)	54
H(4B)	8224(38)	2429(24)	1626(4)	54
H(4C)	8469(34)	3443(6)	588(22)	54
H(SA)	4445(15)	5355(16)	3014(24)	52
H(SB)	5376(33)	7158(23)	2868(21)	52
H(SC)	6028(20)	6459(37)	4005(S)	52
H(6A)	10038(17)	8882(12)	3070(28)	65
H(6B)	8909(41)	8489(6)	3946(9)	65
H(6C)	8214(26)	8973(11)	2722(20)	65
H(7A)	11174(17)	7349(17)	2182(25)	62
H(7B)	10294(7)	6255(41)	969(5)	62
H(7C)	10987(20)	5522(25)	2077(27)	62
H(10A)	1509(8)	-200(8)	1105(6)	76
H(11A)	994(7)	2263(10)	1677(5)	81
H(12A)	2686(7)	4487(7)	816(5)	61
H(13A)	4092(7)	3339(7)	-374(4)	51
H(14A)	3328(7)	479(7)	-236(5)	58
H(20A)	7129(6)	-43(6)	4781(4)	42
H(21A)	5967(6)	1605(6)	5802(4)	39
H(22A)	7016(6)	4398(6)	5326(4)	45
H(23A)	8920(6)	4497(6)	4058(4)	44
H(24A)	8942(6)	1745(6)	3674(4)	47

VITA

Michael Joseph Player entered this realm of existence in the sleepy little town of Milton, Florida on February 13, 1970. He attended elementary school in the Santa Rosa County School District. He obtained his high school diploma in June 1989. He immediately began his college education at Pensacola Junior College. Two years later he received an Associate of Arts degree and then transferred to the University of West Florida and in August of 1994 he graduated with a Bachelor of Science degree in Chemistry. He then began graduate studies in chemistry at the University of Tennessee, Knoxville and received a Master of Science degree in December 1997.