# ORGANO-COBALT CLUSTERS

# DEDICATION

To my parents and brothers, Brad and Todd, for their constant support and encouragement.

#### SYNTHETIC AND MECHANISTIC STUDIES

#### OF

#### ORGANO-COBALT CLUSTERS

by

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#### A Thesis

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#### ABSTRACT

Dicobalt octacarbonyl reacts with a wide variety of molecules containing trichloromethyl functionalities to yield carbynyl tricobalt nonacarbonyl clusters of the general formula  $R-CCo_3(CO)_9$ . While these clusters have been shown to undergo many reactions, mechanistic studies on these systems are sparse. In particular, their rather facile decarbonylation processes are not well understood.

Complexes of the type Ar-CO-CCo3(CO)9 readily lose CO to produce the corresponding Ar-CCo3(CO)9 clusters but the origin of the carbon monoxide extruded was not known. Speculation had focussed on two possibilities: firstly, direct elimination of the ketonic carbonyl - perhaps via radical intermediates - and, secondly, via initial loss of a cobalt carbonyl ligand (to produce a 16-electron cobalt vertex) with subsequent migration of the original ketonic group onto the coordinatively unsaturated cobalt center. These two mechanistic possibilities are differentiable by labelling either the cobalt carbonyl sites or the ketonic position with carbon-13 and then examining the decarbonylated product to locate the isotopically enriched positions by <sup>13</sup>C NMR spectroscopy. It is shown that the carbon monoxide initially eliminated is a cobalt carbonyl and the ketonic CO migrates from its apical position onto a cobalt atom.

A second project involves the synthesis and characterization of a cobalt cluster derived from the reaction

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of dicobalt octacarbonyl with the insecticide DDT. This cluster contains the bis(4-chlorophenyl)methylcarbynyl capping group which is so bulky that it has the potential to stop the rotation of the carbynyl ligand and also prevent carbonyl exchange on the metal triangle. The DDT-tricobalt cluster was characterized by X-ray crystallography. The compound crystallizes in the space group  $P2_1/n$ : the monoclinic cell has dimensions a = 13.083 Å, b = 14.222 Å, c = 14.165 Å,  $\beta$  = 95.871° and Z = 4. The molecule adopts almost  $C_s$  symmetry except that the phenyl rings are twisted slightly so as to destroy the potential mirror plane. At low temperature, the cobalt carbonyl ligands are non-equivalent on the NMR time-scale and the possible causes for this behaviour are discussed. I am deeply indebted for the direction, encouragement and understanding provided by my research supervisor, Dr. M.J. McGlinchey. His patience in the early stages of this project, his constant encouragement, expert advice and our many stimulating discussions have influenced my development as a researcher and, as importantly, as a person.

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# CHAPTER ONE

#### 1.1 General

Transition metal cluster chemistry has developed at an ever accelerating pace over the past ten years. This has been exemplified by the number and variety of review articles pertaining to the subject; these cover the range from structures to synthesis and reactivity of transition metal clusters.<sup>1-11</sup>

F.A. Cotton has defined a cluster as a group of two or more metal atoms in which there is a system of substantial and direct bonds connecting each metal atom.<sup>12</sup> Atoms other than metals may be contained or even encapsulated within the cluster framework, these include carbon, nitrogen, oxygen, phosphorus and sulfur.

The reason for the great deal of effort which has been expended on metal clusters is their potential catalytic activity.<sup>3</sup> The metal clusters may be viewed as a bridge between the intensively studied homogeneous metallic systems and the less well understood reactions occurring on surfaces.<sup>13</sup>

# 1.2 Catalytic Applications of Organotransition Metal Clusters

German patents can be traced back to 1916 where Badische Anilin and Soda Fabrik disclosed the preparation of liquid hydrocarbons by the hydrogenation of carbon monoxide and cobalt based contact masses but under rather severe conditions (100 bar /  $300-400^{\circ}$ C). After extensive investigations, Franz Fischer and Hans Tropsch (in 1925, at the Kaiser Wilhelm Institute für Kohlenforschung, in Mühlheim an der Ruhr) found that conversion of CO / H<sub>2</sub> on certain iron and cobalt catalysts could be obtained at normal pressures at 250-300°C.<sup>13-19</sup>

The interest in this synthesis was not restricted to academics but industrialists as well since this process offered an alternative source of production of liquid hydrocarbons (fuel). In 1936, the first commercial plant was opened in Germany and by 1941, nine Fischer-Tropsch plants were operative in that country representing a substantial portion of its wartime liquid hydrocarbon fuel.<sup>19</sup>

Since carbon monoxide and hydrogen have generally been obtained from coal or oil, the use of Fischer-Tropsch catalysis for the manufacture of synthetic fuels became uneconomic by the 1950s and 1960s. This was due to the abundance and cheapness of petroleum which in turn led to the shut-down, in most countries, of these plants. The exception is in Sasolburg, South Africa, where SASOL still operates a large iron-catalyzed Fischer-Tropsch plant derived from low-cost coal.

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catalyst

- 3 - .

CO +  $H_2$  ----->  $\bigtriangleup$  / pressure

 $CH_3(CH_2)_nCH_2OH + CH_3(CH_2)_nCH=CH_2 + CH_3(CH_2)_nCH_3$ 

Scheme 1.1: Catalytic conversion of carbon monoxide and hydrogen to hydrocarbons, alkenes, oxygenated compounds.<sup>17</sup>

Research in the area of Fischer-Tropsch synthesis has always continued; in particular, an area of great interest has been the search for a homogeneous Fischer-Tropsch catalyst. Although heterogeneous catalysts are usually preferred by industry for the reasons of efficiency and ease of production, the homogeneous catalyst presents some advantages such as milder reaction conditions; temperature and pressure and may have a higher degree of selectivity. Furthermore, they may be more easily studied to yield mechanistic information.

Over the years, numerous attempts have been made to rationalize the formation of the various hydrocondensation products obtained by the catalytic conversion of carbon monoxide hydrogen. The rise and fall in the popularity of these mechanisms reflected the impact of new observations made in wider areas of physical, inorganic and organometallic chemistry.

Originally, Fischer and Tropsch proposed that carbon monoxide dissociated on the catalyst to give a carbide, then hydrogenation gave a methylene group which would polymerize to yield higher hydrocarbons.

```
H<sub>2</sub>
```

 $2CO + Co \longrightarrow CoO + "CoC" \longrightarrow Co + H_2O \longrightarrow$ 

CoCH<sub>2</sub> ----> Hydrocarbon products (Equation 1.1)

Surface carbon and surface oxygen, formed by the dissociation of CO, are currently considered as important species in the overall Fischer-Tropsch synthesis $^{20-23}$ and have been used to promote the desired organic compounds as well as some of the side reactions.



Scheme 1.2: Possible evolutions of C<sub>surface</sub> and O<sub>surface</sub> on Fischer Tropsch synthesis.<sup>22</sup>

Towards this end, transition metal carbide clusters and their derivatives have been proposed as models for key intermediates in the catalytic cycle.<sup>24</sup> This has been illustrated by the surface carbon participating with carbon monoxide to give the ketene precursors and thus give carboxylated products.



(Equation 1.2)

Strong support for this argument has been provided by Bradley and co-workers as they have shown that a soluble metal carbide cluster could be carbonylated; subsequently they isolated a methoxycarbonyl complex.<sup>25,26</sup>





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 General Properties of Alkylidynetricobalt Nonacarbonyl Complexes.

The alkylidynetricobalt nonacarbonyl complex exemplifies an interesting class of organometallic compounds. The majority of these compounds are air and thermally stable and highly coloured in the usual organic solvents and in their solid crystalline forms. This is all highly dependent upon the apical substituent which is subject to substantial steric hindrance due to the arrangement of the carbon monoxide ligands.<sup>27</sup>

An X-ray crystal structure determination illustrates that six of the nine carbon monoxide ligands are tilted slightly upward, thus playing a crucial role in the chemistry of alkylidynetricobalt nonacarbonyl complexes.<sup>28</sup>



Figure 1.1: Structure of (CO)<sub>9</sub>Co<sub>3</sub>C(CO)CH<sub>3</sub>

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Many of the alkylidynetricobalt nonacarbonyl complexes are unstable towards attack from oxidizing agents, bases or nucleophiles, but are stable towards protonic and Lewis acids --- this has been the basis for most of their chemistry.

One of the most widely used experimental methods for the investigation of organometallic compounds is the study of infrared spectra.<sup>29</sup> By means of the frequency (or more properly, the force constant, k) of the C-O absorption in the infrared, it is possible to differentiate between bridging carbonyl groups (>C=O) and terminal carbonyl groups (-C=O). Since triple bonds are stronger than double bonds, their infrared absorptions occur at higher frequency. For terminal carbonyls, the carbonoxygen stretching frequency is of the order 2000  $\pm$  100 cm<sup>-1</sup>. The bridging carbonyls, which are electronically analogous to the carbonyl groups of organic chemistry in ketones have carbon-oxygen stretching frequencies around 1800  $\pm$  75 cm<sup>-1</sup>.<sup>30</sup>

The infrared spectrum of a metal carbonyl complex can provide important information on the nature of the carbonyl groups present.<sup>31</sup> Typical terminal carbon-oxygen stretching frequencies of alkylidynetricobalt nonacarbonyl complexes show five bands in the region of 2150 to 1950 cm<sup>-1</sup>. These infrared peaks can be used to identify  $RCCo_3(CO)_9$  complexes but the shifts in these bands with different organic groups in the apical position are so

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minimal as to have no diagnostic value.

Table 1.1: IR Spectra of (OC)<sub>9</sub>Co<sub>3</sub>CR Complexes.<sup>32</sup>

R	C==O bands, cm <sup>-1</sup> (in CCl, unless specified otherwise)
СОЛН	2120 m, 2075 vs, 2055 s, 2040 sh (CHCl <sub>1</sub> )
CO2CMe2	2110 m, 2065 vs, 2044 s, 2018 w, 1980 vw
C(O)SPh	2110 m, 2065 vs, 2042 s, 2020 w, 1990 vw
CONH,	2115 m, 2066 vs, 2044 s, 2015 w
CONMer	2114 m, 2065 vs, 2044 s, 2020 w, 1990 vw
C(O)Et	2110 m, 2065 vs, 2040 s, 2020 w, 1990 vw
C(O)C,H,FeC,H;	2108 m, 2065 vs, 2045 s, 2040 sh, 1983 vw
C(O)C.H.NMer-p	2108 m, 2065 vs, 2042 s, 2020 w, 1990 vw

<sup>13</sup>C NMR spectroscopy for alkylidynetricobalt nonacarbonyl complexes is another useful tool. The signal due to the cluster carbon atoms should be a 22-line pattern resulting from spin-spin coupling to the three cobalt atoms which each possess a nuclear spin of 7/2.<sup>33</sup> Also, the line width of this carbon atom should be broadened since the cobalt atoms have a nuclear quadrupole moment.<sup>34</sup> Finally, the viscosity of the medium determines the observation of the signal in solution since the complexes have a limited molar solubility in organic solvents. These factors account for the short relaxation time of the apical carbon in solution.

For alkylidynetricobalt nonacarbonyl complexes, the  $^{13}\mathrm{C}$  NMR spectrum exhibits a broad multiplet (40-50 Hz) in width in the region of  $\delta$  255-315 ppm. These chemical shifts are typical of alkylcarbonium ions  $^{35,\,36}$  and some transition metal-carbone complexes and carbyne complexes.

(CO) <sub>5</sub> CrC(OMe)Ph	351.4	ppm <sup>37</sup>
(CO) <sub>5</sub> WC(OEt)C≡CPh	286.1	ppm <sup>38</sup>
CH <sub>3</sub> C≡W(CO) <sub>4</sub> Cl	288.8	ppm <sup>39</sup>
PhC≡W(CO) <sub>4</sub> Br	230.6	ppm <sup>38</sup>

The terminal carbonyl resonances in the <sup>13</sup>C NMR spectra were observed as a broad singlet. One would expect two terminal carbonyl carbon atom resonances in a ratio of 2:1 owing to the structure of the alkylidynetricobalt nonacarbonyl complex. However, an intramolecular exchange process takes place and even at low temperature, only a single, now sharp C=O resonance was observed.<sup>40</sup>

#### 1.4 Cluster Synthesis

The chemistry of carbyne transition metal complexes has attracted attention from many viewpoints including their use as building blocks for the synthesis of metal clusters. The preparations of alkylidyne complexes are based on the addition of substituents to atoms that are separated by two bonds (*B*-carbon atom). These syntheses can involve alkylation of carbonyl or thiocarbonyl ligands or the protonation of isocyanide ligands.<sup>41</sup>

Alkylation of a bridging carbonyl ligand exemplifies the induced shift from a double metal bridge to a triple metal bridge.

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Scheme 1.4: Alkylation of a tri-iron cluster.

Alkylation at the oxygen increases the acceptor character of CO, therefore, promoting the approach of the CO ligand to the metal centres. Protonation of isocyanide ligands at one or both nitrogen atoms leads to a ligand with carbyne-like character.



Scheme 1.5: Protonation of a coordinated nitrile.

When the isonitrile is attached to the electron rich site of a molecule, electrophilic attack is promoted.

1.5 Synthesis of Alkylidynetricobalt Nonacarbonyl

#### Complexes

The most interesting application of this concept involves the formation of these alkylidynes from metal carbynes.



The most general preparative route which has been used for a large variety of alkylidynetricobalt nonacarbonyl complexes utilizes tri- and dihalo-methyl compounds as starting materials. The proposed mechanism follows this pathway.<sup>42</sup>



(CO)3

(Equation 1.4)

In general, the product yields are only low to moderate and in some cases unsuccessful, not due to the lack of reaction but rather because of the conditions which require a rigorously anhydrous atmosphere or else the reduced products are obtained. The culprit, during the reaction or during the work-up, is believed to be  $HCo(CO)_4$ , a strong protonic acid, which is capable of destroying the cluster and / or reducing the olefin.<sup>43</sup>

There are several methods of interconverting one alkylidynetricobalt on a carbonyl complex to another. A useful method, with high (90-98%) yields, is the conversion of  $HCCo_3(CO)_9$  using arylmercuric halides or diarylmercurials as starting materials.

benzene or THF  

$$Ar_2Hg + HCCo_3(CO)_g \longrightarrow ArCCo_3(CO)_g$$
  
CO atmosphere  
2-8 hr. + ArH + Hg  
(Equation 1.5)

It has also been found that this method is useful for synthesizing specific deuterated derivatives.

 The mechanism of this reaction has not been elucidated, however there is a trend in steric hindrance. As can be seen from the Table, ortho-substituted arylmercury compounds, in general, have lower product yields than those with substituents in the meta or para positions. Also, when there are two ortho-substituents, the reaction is unsuccessful.

 Organomercurial <sup>b</sup>	R in RCCo <sub>3</sub> (CO) <sub>b</sub> produced	% Yield	
 (С.н.).на	C.H.	93	
(p-CH_OC_H_)_Hg	0-CH.OC.H.	64	
(p-CH-C-H-)-Hg	р-СН.С.Н.	92	
$(m - CH - C_{-}H_{-}) + Hg$	m - CH-C.H	96	
(0-CH-C-H.)-Hø	0-CH-C.H.	49	
(p-C)C-H_)_Hg	a-CIC.H.	83	
$(m - ClC_{-H_{-}})_{-Hg}$	m - ClC.H.	93	
(o-ClC.H.).Hg	o-ClC.H.	57	
(m-FC.H.).Hr	m-FC.H.	85	
(p-BrC.H.).Hg	p-BrC.H.	86	
(p-IC,H <sub>4</sub> ) <sub>2</sub> Hg	p-IC.H.	51	
$(C, F_{*})_{2}$ Hg	C, H,	69	
(C, H, CH <sub>2</sub> ) <sub>2</sub> Hg	C,H,CH,	75	
C <sub>s</sub> H <sub>s</sub> HgBr	C, H,	58	
p-FC <sub>5</sub> H <sub>4</sub> HgBr	p-FC.H.	57	
p-H2NC6H,HgCl	$p - H_2 NC_5 H_4$	26	
p-ClC, H, HgBr <sup>c</sup>	p-CIC,H.	54	
a-C10H7HgBr <sup>c</sup>	a-C10H7	11	
Fe Fe	Fe	14	
$\left(\begin{array}{c} \overbrace{\bigcirc}^{Cr}, \\ i \\ c \\ c$		37	
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> HgCl	сн осн сн	32	
$(n - C, \mathbf{H}_{11})$ Hg	$u = \mathbf{C}_{u} \mathbf{H}_{vv}$	32	

 Reactions were carried out under an atmosphere of carbon monoxide unless otherwise specified.

"Reaction carried out under an atmosphere of dry nitrogen.

Table 1.2: Preparation of  $RCCo_3(CO)_9$  Complexes by reaction of organo-mercurials with  $HCCo_3(CO)_9$ .<sup>32</sup> Another area in which metal clusters have found utility is as stoichiometric reagents in organic synthesis thereby introducing functionality to the cluster. The best known example is the use of a  $Co_2(CO)_6$  moiety to protect an alkyne linkage.<sup>44</sup> Typically, mestranol (an alkynyl steroid) which is widely prescribed as a contraceptive, forms a  $Co_2(CO)_6$  complex whose use as an assay for hormonal-related cancers has been advocated.<sup>45</sup>





Figure 1.2: Structure of 17ß-Propynylestra-1,3,5-(10)triene-3,17ß-diol and its Co<sub>2</sub>(CO)<sub>6</sub> complex.

Also from an organic point of view, a free-radical process has been developed utilizing  $H-CCo_3(CO)_9$  as an adduct towards an olefinic C=C bond.<sup>46</sup>



(Equation 1.8)

Having now explained the more general routes to form alkylidynetricobalt nonacarbonyl complexes, there have been serendipitous preparations as well. Typically, the very first member of this class of compounds was prepared via the protonation of (acetylene) $Co_2(CO)_6$ ;<sup>47</sup> this route can be extended to terminal acetylenes, (RC=H) $Co_2(CO)_6$ , but is highly dependent upon the nature of the substituent group with respect to conversion to the alkylidynetricobalt nonacarbonyl complex.

 $(OC)_{3}C_{0}^{---}$   $-C-H \xrightarrow{H_{2}SO_{4};}$   $H_{2}O/EtOH$   $CH_{3}CCo_{3}(CO)_{9}$ 

(Equation 1.9)

Related to this transformation is the acid induced conversion to an unsaturated cluster.  $^{\mbox{48}}$ 



(Equation 1.10)

One may note other reactions which have been reported.

 $(CO)_4 CoCF_2 CF_2 CO(CO)_4 \longrightarrow CF_3 (Co_3 (Co)_9^{49})$ 

(Equation 1.11)

hexene

 $Co_2(CO)_8 + C_6H_5SH -----> C_6H_5CCo_3(CO)_9^{50}$ 

RT

(Equation 1.12)

And finally a "supercluster" has been prepared. 46



(Equation 1.13)

1.6 Chemistry of the Tricobalt Carbon Decacarbonyl

Cation

The initial study of the chemistry of the alkylidynetricobalt nonacarbonyl complex dealt with ascertaining the electronic effects and interconversion of the substituent group attached to the apical carbon. <sup>33</sup> The accepted mechanism<sup>51</sup> for acid-catalyzed ester hydrolysis was not applicable to  $(CO)_9Co_3CCO_2R$  because of the steric hindrance inherent in the structure.



Hammett's observations had illustrated that monoprotonated result when carboxylic acids are dissolved in sulfuric acid. However, when there was a highly hindered species, a very reactive but less hindered acylium ion was formed.

$$RC \xrightarrow{O}_{OH} + H_{2}SO_{4} \rightleftharpoons \left[RC \xrightarrow{OH}_{OH}\right]^{+} + HSO_{4}^{-} \qquad (Equation 1.17)$$

$$\left[RC \xrightarrow{OH}_{OH}\right]^{+} + H_{2}SO_{4} \rightleftharpoons RC \xrightarrow{+}_{O} + HSO_{4}^{-} + H_{4}O^{+} \qquad (Equation 1.18)$$

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When this technique was applied to  $(CO)_9CO_3CCO_2R$  complexes which were then poured into ice or alcohol, generally, the acid or ester of the alcohol, respectively, was obtained in high yield. However, sulfuric acid is not a convenient solvent since it is rather reactive with most nucleophiles, 65% aqueous hexafluorophosphoric acid with propionic anhydride was chosen based on well-known techniques used in carbonium ion chemistry. The black, microcrystalline salt,  $[(CO)_9CO_3CCO]^+$   $[PF_6]^-$  salt reacted directly with the nucleophiles. The general reactions are summarized in Figure 3.



Figure 1.3: The general reactions of the salt  $[(CO)_9Co_3CCO]^+ [PF_6]^-$ 

Thus, using this route, it is possible to acylate alcohols, phenols, thicls, amines, amino acid esters and tripeptides. Reactions with mild alkylating agents were successful, but arylation reactions were successful only with highly nucleophilic aromatic substrates. Thus the reaction of this salt offers a broad spectrum of  $\alpha$ -substituted alkylidynetricobalt nonacarbonyl complexes.

Initially, Dolby and Robinson<sup>53</sup> had synthesized arylsubstituted methylidynetricobalt nonacarbonyls from a Friedel-Crafts-type reaction using both chloro- and bromo-methylidynetricobalt nonacarbonyl.

#### AlCl<sub>3</sub>

 $Cl-CCo_3(CO)_9 + ArH -----> Ar-CCo_3(CO)_9$  $CH_2Cl_2$ 

(Equation 1.19)

From known organotin chemistry, Seyferth<sup>54</sup> applied this train of thought to form alkylated methylidynetricobalt nonacarbonyl complexes,  $(R-CCo_3(CO)_9)$  in an analogous fashion to a known ketone synthesis.

AlC13

 $R_4Sn + R'COC1 \longrightarrow R'COR + R_3SnC1$ (Equation 1.20)

Instead the acetyl derivatives  $(R-C(0)-CCo_3(CO)_9)$  were the resulting products. These molecules had already been isolated and characterized from the  $[(CO)_9Co_3CCO]^+$   $[PF_6]^-$  reactions, thereby, illustrating that the same cation, was being formed from this aluminium chloride induced conversion. Table 3 summarizes these general reactions.

# with Nucleophiles

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Amt, mmol			Product, R in
CICCo,(CO),	AICI,	Nucleophile (amt)	RC(O)CCo,(CO), (% yield)
2.2	6.1	CH, OH (10 mL)	CH.O (83)
2.5	6.1	C.H.OH (20 mL)	C.H.O (78)
2.1	5.4	Me. CHOH (5 mL)	Me. CHO (78)
2.2	6.2	Mr. COH (20 ml)	Me. CO (77)
11.0	38 5	BrCH CH OH (50 mmol)	BrCH CH O (74)
2.2	27	CH -CHCH OH (73 mmol)	CH = CHCH O(66)
2.2	77		
2.2	7.7	CCI CH OH (10 mmol)	CCL CH Q (62)
1.7	1.1	C H OH (02 mmol)	
1.7	9./	C, H, OR (95 minor)	C, N, O (00)
2.2	1.1	p-CH, OC, H, OH (5 mmol)	p-CH, UC, H, U (39)
2.2	1.1	p-0, NC, H, OH (20 mmol)	p-0, NC, H, O (30)
2.2	7.7	p-MeC, H, OH (20 mmol)	p-MeC, H, O (54)
2.2	7.7	p-ClC, H, OH (20 mmol)	p-CIC, H, O (38)
2.2	7.7	Me, CSH (18.5 mmol)	Me, CS (51)
2.1	7.9	$C_{H}$ , SH (3 mL)	C, H, S (58)
4.1	9.5	NH, (large excess)	H <sub>2</sub> N (64)
2.1	5.0	(CH <sub>1</sub> ), NH (large excess)	(CH,),N (55)
2.1	7.8	Et <sub>1</sub> NH (70 mmol)	Et, N (75)
2.2	7.7	Me, CNH, (10 mmol)	Me, CNH (55)
2.6	6.9	$C_{1}H_{1}NH_{2}$ (3.5 mL)	C, H, NH (76)
2.2	7.7	0 NH (11.5 mmol)	0 N (64)
2.2	7.7	(10 mmol)	(50) N
2.3	6.3	H.O (large excess)	HO (29)
2.1	5.2	(CH.). Sn (5 mL)	CH. (61)
2.2	5.3	(C, H) Sn $(5, mL)$	C H (68)
2.2	7.7	(n-C,H) Sn (15 mmol)	n-C H (34)
2.0	6.0	(CH = CHCH) Sn (5.0 mmol)	CH = CHCH (69)
16.7	47.0	Ft SiH (S1 0 mmol)	H (68)
2.3	5.9	Ph. SiH (9.0 mmol)	H (40)
	0.0		11 (40)
2.2	6.2	Me <sub>2</sub> N-(3 mL)	Me <sub>2</sub> N-(69)
2.2	7.7	(5.0 mmol)	(47)
2.2	7.7	(5.0 mmoł)	(68)
2.0	5.0	$ \bigoplus_{F_{0}} F_{0}  (5.4 \text{ mmol}) $	$\bigvee_{Fa} \bigcirc -^{(41)}$
The proposed mechanism involves an AlX<sub>3</sub> -assisted migration of a terminal carbonyl to the electron-deficient apical carbon atom. This involves a C-Cl bond polarization of the  $(CO)_9Co_3CCl$  complex by complexing with the first molecule of AlCl<sub>3</sub> to form  $[(CO)_9Co_3CCO]^+$ .  $[AlCl_4]^-$  The second molecule of AlCl<sub>3</sub> complexes with a terminal carbon monoxide ligand and induces the migration from the cobalt to the apical carbon atom.



Figure 1.4: Bridged intermediate structure for [(CO)<sub>9</sub>Co<sub>3</sub>C]<sup>+</sup> [AlCl<sub>4</sub>]<sup>-</sup>

Possibly, the third molecule of  $AlCl_3$  complexes with a terminal carbon monoxide ligand from another molecule of  $(CO)_9Co_3CC1$  aiding a carbon monoxide transfer thereby obtaining  $[(CO)_9Co_3CC0]^+$  in high yield.



Figure 1.5: The Tricobalt Decacarbonyl cation. 54

Support for this mechanism is based on results from reactions illustrating that bridging carbonyl ligands are stronger Lewis base sites than that of terminal carbonyls in binuclear metal carbonyls,<sup>55,56</sup> and also that carbon monoxide migration from terminal to bridging positions is promoted by aluminium alkyls in binuclear ruthenium complexes.<sup>57</sup>

There are other systems which can produce the cluster acylium ion more rapidly. By simply adding a larger excess of aluminium chloride (10 molar equivalents rather than 3) or by carrying out the reaction in the presence of iodomethane or diethylamine. It is noteworthy, that  $BrCCo_3(CO)_9$  is converted to the acylium ion much faster than is  $ClCCo_3(CO)_9$ .<sup>33</sup>

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Amt, mmol			(7 viald)	
BrCCo <sub>3</sub> (CO) <sub>9</sub>	AlBr <sub>3</sub>	Nucleophile <sup>a</sup> (amt)	Product, R in RC(0)CCo <sub>3</sub> (CO) <sub>9</sub> (% yield)	
 2.0 2.0	6.0 2.0	CH <sub>3</sub> OH (5 mL) CH <sub>3</sub> OH (5 mL)	MeO (68) MeO (38) (recovery of BrCCo <sub>3</sub> (CO), was 22%)	
3.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0	9.0 6.0 5.3 6.0 6.7 6.0 6.0	$C_2H_sOH (4 mL)$ $CCl_3CH_2OH (1 mL, 10 mmol)$ $CH_2=CHCH_2OH (1 mL, 15 mmol)$ $p-CH_3C_6H_4SH (10 mmol)$ $NH_3 (large excess)$ $Et_2NH (1 mL, 20 mmol)$ $Me_3CNH_2 (10 mmol)$	$C_{2}H_{5}O$ (66) $CCI_{3}CH_{2}O$ (55) $CH_{2}=CHCH_{2}O$ (53) $p-CH_{3}C_{8}H_{4}S$ (80) $H_{2}N$ (46) $Et_{2}N$ (60) $Me_{3}CNH$ (58)	
2.0	6.04	$(1 \text{ mL})$ $H$ $H$ $Me_{2}NC_{4}H_{5}(1 \text{ mL})$	$ \begin{array}{c}                                     $	

<sup>a</sup> The reagent mixture should be chilled to 0 °C before the nucleophile is added.

Table 1.4: Reactions of the BrCCo<sub>3</sub>(CO)<sub>9</sub> / AlBr<sub>3</sub> Reagent with Nucleophiles.<sup>33</sup>

1.7 Structure of [(CO)<sub>9</sub>Co<sub>3</sub>CCO]<sup>+</sup>

Despite the great deal of chemistry that has been carried out on the tricobalt acylium ion, the actual structure of this complex is unknown.



Figure 1.6: The upright and tilted configurations of [(CO)<sub>9</sub>Co<sub>3</sub>CCO]<sup>+</sup> The two structures proposed for the  $[(CO)_9Co_3CCO]^+$ complex show that the ketenylidene ligand can be illustrated as being bonded in an upright manner with respect to the metal triangle or in a tilted configuration. From the chemistry of the cluster acylium ion one could believe that the positive charge is delocalized away from the CO substituent on the apical carbon atom, since only the most reactive aromatic nucleophilic reactions are successful.<sup>33</sup> One also finds from the infrared data, that it is arguable that there is a greater amount of positive charge residing on the cobalt since the C-O stretching frequencies are at higher frequency when compared to neutral cluster complexes.

A molecular orbital analysis on  $[(CO)_9Co_3CCH_2]^+$  had predicted the preferred conformation to be the tilted one. This was believed to be due to the interaction of a vacant orbital on the methylene carbon and a filled metal orbital, a situation only possible for the tilted configuration.<sup>58</sup> In contrast, the CCO ligand with its  $p-\pi^*$ orbitals in e pairs was thought to have no incentive to point away from a perpendicular conformation.

Finally, lending some support for the acylium ion adopting a tilted arrangement is the dynamic <sup>13</sup>C NMR study, from this laboratory,<sup>59</sup> on a <sup>13</sup>CO-enriched sample of  $[(CO)_9Co_3CCO]^+$  [AlCl<sub>4</sub>]<sup>-</sup>. Although the signal observed at room temperature for the metal carbonyls was rather broad, the <sup>13</sup>C-NMR spectrum of  $[(CO)_9Co_3CCO]^+$  has similar

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carbonyl resonance values to that of  $[(CO)_{gCo_{3}CCH_{2}]^{+}$ .<sup>60</sup> A comparison of the <sup>13</sup>C chemical shifts in several other ketenylidene clusters is found in Table 1.5. Upon cooling the sample to -110°C, the <sup>13</sup>C NMR spectrum revealed that the metal carbonyl signal had split into two resonances in a ratio of 3:6.



Figure 1.7:125 MHz Variable-Temperature <sup>13</sup>C NMR Spectra of [(CO)<sub>9</sub>Co<sub>3</sub>CCO]<sup>+</sup> [AlCl<sub>4</sub>]<sup>-.59</sup>

There are two possible explanations for this observation. The first is that the exchange between the axial and equatorial metal carbonyls has stopped on the NMR time scale; however this has never previously been observed for these cobalt clusters. Alternatively it has been proposed that at low temperature the  $[(CO)_9Co_3CCO]^+$ complex is bent in its ground state and gives two different signals for the metal carbonyls. At higher temperatures, when the carbonyls appear as a single peak, there is a rapid migration of the ketenylidene from cobalt to cobalt.

Table 1.5: Comparison of <sup>13</sup>C NMR Shifts in Ketenylidene Clusters:<sup>61-63</sup>

				metal carbonyls	
	acylium carbon	apical carbon	$J_{\rm acyl-apical},  {\rm Hz}$		
(CO) <sub>9</sub> CCO] <sup>2-</sup>	182.2	90.1	74.0	222.	.3°
$(CO)_{9}(\mu - CO)CH]^{-}$		262.4		220.	.5ª
-[000, 000]	172.5	82.8	79.4	213.	.5*
$(CO)_{6}(\mu - CO)_{3}CCO]^{2-}$	159.1	-28.3	96.0	273.3	[3] <sup>b,c</sup>
				204.0	[3]
	*			202.3	[3]
s <sub>3</sub> (CO) <sub>9</sub> CCO	160.3	8.6	86.0	175.6 [3]	165.8 [6] <sup>d</sup>
				179.6 [2]	173.0 [2]e
				169.9 [1]	168.0 [2]
		7			158.3 [2]
$(CO)_9 CCH_2]^+$	91.1	286.2		192.	78
(CO) <sub>9</sub> CCO] <sup>+</sup>	168.2	108.4		197.8 [3]	188.4 [6] <sup>h</sup>
$_{3}P)Co_{3}(CO)_{8}CCO]^{+}$	169.1			200.3 [2]	193.5 [6]
MoCo <sub>2</sub> (CO) <sub>8</sub> CCO] <sup>+</sup>	158.0			211.8 [2]	196.2 [6]

<sup>a</sup> At 67.8 MHz (corresponds to 270 MHz for <sup>1</sup>H); temperature = -40 °C. <sup>b</sup> At 67.8 MHz; temperature = -90 °C. <sup>c</sup> Numbers in square prackets denote peak intensities. <sup>d</sup> At 67.8 MHz; temperature = +25 °C. <sup>c</sup> At 67.8 MHz; temperature = -60 °C. <sup>f</sup> Methylene carbon. <sup>d</sup> At 22.6 MHz (corresponds to 90 MHz for <sup>1</sup>H). <sup>h</sup> At 125.7 MHz (corresponds to 500 MHz for <sup>1</sup>H); temperature = -110 °C. <sup>i</sup> At 62.8 MHz corresponds to 250 MHz for <sup>1</sup>H); temperature = -90 °C.

#### 1.8 Statement of the Problems

(1) In some cases, (acylmethylidyne)- and (aroylmethylidyne)tricobalt nonacarbonyl complexes have been found to undergo facile thermal decarbonylation to yield the corresponding (alkylmethylidyne) and (aroylmethylidyne)tricobalt nonacarbonyl complexes.<sup>64,65</sup>

Various mechanistic possibilities have been advanced but, in order to distinguish between these pathways, it was decided to specifically enrich the starting material in <sup>13</sup>C thereby allowing the progress of the reaction to be monitored by NMR spectroscopy.

(2) In order to probe the steric and electronic properties of the carbynyl tricobalt nonacarbonyl cluster system, we chose to attempt the incorporation of a very bulky diarylmethyl substituent at the apical position. To this end, the reaction of dicobalt octacarbonyl with the commercially available insecticide 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane, DDT, was investigated.

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## CHAPTER TWO

## DECARBONYLATION MECHANISMS

#### 2.1 Introduction

In the course of his pioneering studies on the reactivity of organic derivatives of carbynyltricobalt nonacarbonyl clusters, Seyferth<sup>64,65</sup> observed that the acyl derivatives could, in some cases, be decarbonylated to give the corresponding alkyl or aryl complexes. This was of considerable interest since such a facile thermal ketone decarbonylation is without precedent in simple, unstrained organic systems, yet is a general reaction for cobalt cluster ketones.

		% yield		
R in RC(O)CCo <sub>3</sub> (CO),	reaction time, h	RCH <sub>2</sub> - CCo <sub>3</sub> (CO),	RCH(OH)- CCo <sub>3</sub> (CO),	
Н	3	52	0	
CH,	7	8	31	
CH, CH,	7	4	23	
CH, CH, CH, CH,	6	6	26	
p-BrC, H,	3	0	79	
p-CIC, H	3	0	76	
p-FC, H	3	0	83	
C, H,	3	0	78	
p-CH,C,H,	2	0	83	

Table 2.1: Thermal Decarbonylation of RC(0)CCo<sub>3</sub>(CO)<sub>9</sub> Complexes.

# 2.2 Trends of the decarbonylation reaction

The reaction mixtures were monitored by thin layer chromatography as this technique allows the examination of the mixture for an indication of the consumption of

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the starting ketone. Thus, the reaction times given are the amount of time required for the disappearance of the starting ketone. Upon evaluation these results, one notices trends amongst the functional groups in comparison to their percentage yield and reaction time. Firstly, ArC(0)CCo<sub>3</sub>(CO)<sub>9</sub> complexes, which have an electron-releasing group on the aromatic ring, yield a product to a greater extent in a shorter reaction time. When there are electron-rich heterocyclic substituents on the ketonic carbon monoxide, the reaction times and yields are also better. Thus, electron-releasing groups on the aromatic ring and electron-rich heterocyclic substituents on the ketone, facilitate the decarbonylation reaction. In contrast, alkyl groups attached to the ketone have lower yields, even with longer reaction times and give the lowest yields. Thus, electron-withdrawing groups on the aromatic ring and alkyl substituents on the ketone inhibit the decarbonylation reaction.

## 2.3 Proposed Mechanisms

The relevance of these observations have led to the advancement of various mechanistic possibilities from an organic point of view. Most aldehydes and ketones, in inert solvents or in the gas phase, undergo one of two photoreactions, called Norrish Type I and Norrish Type II reactions. A Norrish Type I photolysis may originate from either the singlet or triplet state of the carbonyl

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compound. This is exemplified by the photodecarbonylation of 1,1,3,-triphenyl-2-propanone in benzene.

Quinkert<sup>66</sup> observed a statistical distribution of 1:2:1 in the photochemical decomposition, such that this decarbonylation and radical coupling gave rise to these products following cleavage. Seyferth<sup>65</sup>, suggested that this route could give rise to radical products after extrusion of the ketonic carbon monoxide.



Scheme 2.1: Norrish Type I photolysis of alkylidynetricobalt nonacarbonyl

A Norrish Type II photolysis arises when aldehydes or ketones are irradiated in polar hydroxylic solvents, they are often reduced to the corresponding alcohol or pinacol and/or exhibit  $\alpha$  or  $\delta$  H atom abstraction. This is exemplified by the reduction of benzophenone in the presence of isopropanol  $^{67}$ .



Scheme 2.2: Norrish Type II photolysis of benzophenone in isopropanol

Other thermal decarbonylation reactions of ketones are known. However, these reactions have low yields and are a result of a highly unstable ketene intermediate. Thus the products arise from a ketene decomposition and the result is a mixture of products. This is illustrated in a general way in Scheme 2.3 and more specifically in Scheme 2.4.



Scheme 2.3: Decarbonylation via ketene intermediates



Triphenylcrotolactone

Scheme 2.4: Decarbonylation of triphenylcrotolactone

Another related process is thermal decarbonylation of bridgehead carbonyls in bicyclic systems. Saturated bicyclic bridgehead ketones are thermally stable<sup>68</sup>, but as the degree of unsaturation increases, its thermal stability decreases. The bridge is extruded as carbon monoxide when the compound is heated and this decarbonylation is usually rapid and quantitative at 200-220°C; in favourable instances it can be detected at 75-80°C. For instance, substituted bicyclo[2.2.1]hept-2-en-7-ones will readily decarbonylate to form 1,3-cyclohexadienes in high yields once heated.



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Even the preparation of these substituted bicycloheptadienones by Diels-Alder reactions often lead to their decarbonylated products.<sup>68</sup> When styrene and tetracyclone are heated under reflux together in the absence of a solvent, carbon monoxide is rapidly given off and a



Pentaphenyldihydrobenzene (Equation 2.3)

In a study by Seyferth<sup>69</sup> the accessibility of the  $CCo_3(CO)_9$  radical was demonstrated. Thus, an attempt was made to trap this radical generated from the decarbonylation but it was unsuccessful in both allyl ether and allyl acetate.

AIBN  $CH_2=CHCH_2OR$ HCCo<sub>3</sub>(CO)<sub>9</sub> ---->  $CCo_3(CO)_9$  ----->  $ROCH_2CH_2CH_2CCo_3(CO)_9$ 80°C R=Et or Ac

(Equation 2.4)

However, the thermal decarbonylation of the carbynyltricobalt nonacarbonyls do not seem to fit any of these possibilities. The observation that the decarbonylation occurred on thermolysis, even in the dark and was not accelerated by u.v. irradiations, seemed to militate against a radical fragmentation but, nevertheless, the mechanism remained an open question.

An alternative mechanism has been proposed, from an organometallic point of view; this involves the loss of the metal carbonyl ligand with concomitant molecular rearrangement, as in Scheme 2.5 [b].



# Scheme 2.5: Decarbonylation of carbynyltricobalt nonacarbonyl

It is apparent from Scheme 2.5(b), that one way to distinguish between this pathway and that of a radical pathway (Scheme 2.5(a)) would be to isotopically label the ketonic carbonyl group and then locate the labelled carbon monoxide in the reaction products. To this end, we synthesized the starting material specifically enriched in carbon-13 with a view to monitoring the progress of the reaction by NMR spectroscopy.

### 2.4 Proposals for the Experiment

In order to differentiate between the mechanistic proposals outlined in Scheme 2.5, it is necessary to label one of the carbonyl environments and then see whether any carbonyl transfer has been effected during the decarbonylation. Thus, if the ketonic positions were enriched in <sup>13</sup>CO and if Scheme 2.5(b) were operative, then the decarbonylated product, 17(b), would possess one enriched metal carbonyl position and the normally rather weak <sup>13</sup>C NMR resonance at approximately 200 ppm would be appropriately enhanced. In contrast, if the ketonic carbon monoxide were the one eliminated, to yield 3, then no such enhancement of the 200 ppm signal would be observed.



Figure 2.1: Proposed NMR Spectra

At first sight, it might appear that one should merely synthesize a molecule of the type  $RC(0)CCl_3$  and prepare the desired cluster via the direct reaction with  $Co_2(CO)_8$ .



(Equation 2.5)

However, the cost effectiveness of such a scheme is unfavourable since the yields are low and much of the carbon-13 label would be wasted. Without ordering a specifically labelled compound, the only available starting material would be acetophenone- $\alpha$ -<sup>13</sup>C available at \$295 (US) for one gram.<sup>75</sup> This would require halogenation to form 1,1,1-trichloroacetophenone- $\alpha$ -<sup>13</sup>C. This product could then be heated under reflux with dicobalt octacarbonyl in dry tetrahydrofuran to form benzoylcarbynyl tricobalt nonacarbonyl in approximately 33% yield. Since this functional group is an aromatic ring, its reaction time is relatively fast (5 hrs) and has a respectable 66% yield. This procedure is outlined in Scheme 2.6.



Scheme 2.6 : Synthesis of enriched benzoylcarbynyl tricobalt nonacarbonyl.

The major drawback of attempting this reaction, besides hoping for ideal yields and optimum separation in each step, is that the maximum yield from one gram of acetophenone- $\alpha$ -<sup>13</sup>C would be  $\approx$  80 milligrams; as well, it would be a one shot chance to try this approach. The alternative route (see Scheme 2.7) is to use carbon-13 enriched carbon monoxide which costs \$295 (US) for one litre. Since only 50 mL of <sup>13</sup>CO is required for a reaction, this would allow us to perform the reaction at least 20 times

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Decarbonylated product (yield  $\approx$  70%) Scheme 2.7: <sup>13</sup>C enrichment / de-enrichment pathway

and still obtain a substantial yield. The extent of the reaction from one gram of the chloro-compound, 22, would be 490 milligrams of the decarbonylated product.

We have chosen  ${}^{13}C$  NMR spectroscopy as the technique for monitoring the progress of the reaction, since a 125 MHz instrument is capable of superb resolution and the technique can be used to monitor the progress of the reaction <u>in vitro</u>. This necessitates the use of  ${}^{13}CO$  since the specific labelling allows one to distinguish between the postulated mechanisms quickly and definitively. On the other hand, mass spectrometry, which is also a very powerful tool, would not be beneficial in this case. It has been our experience with these carbynyltricobalt nonacarbonyl complexes, that the terminal carbonyls are readily lost from the molecule even when using soft ionization techniques.



Thus, we would only be able to compare, with certainty the backbone of the complexes and not be able to distinguish the origin of the extruded carbon monoxide.



Figure 2.2: Clusters without terminal carbonyls 2.5 Generation of the acylium cation

It had been reported that the acylium cation  $[(CO)_9 - Co_3CCO]^+$  could be prepared by a number of techniques. The treatment of a concentrated H<sub>2</sub>SO<sub>4</sub> solution of the cluster  $(CO)_9Co_3CCO_2H$  with various alcohols led to the formation of the respective ester derivative. It was proposed that the reaction proceeded via the cation intermediate. In the same work, the isolation of the acylium cation as a salt was demonstrated. This occurred

via treatment of a propionic anhydride solution of the acid or ester derivative of the cluster with  $\mathrm{HPF_6}$ .<sup>52</sup>

HPF6

 $(CO)_{9}CO_{3}CCO_{2}R \longrightarrow [(CO)_{9}CO_{3}CCO]^{+} PF_{6}^{-}$   $(EtCO)_{2}O \qquad (Equation 2.7)$ 

The formation and stability of the acylium cation was attributed to the steric hindrance inherent to the cluster in the ester hydrolysis mechanism. The steric hindrance of the cluster is a result of six of the nine carbonyls being displaced upwards towards the apical carbon and its substituent. This prevents attack at the carbonyl position and results in protonation at the alkoxy oxygen, thereby generating the acylium cation. The presence of the acylium cation salt was confirmed by its reactions with various alcohols, amines and thiols giving the appropriate esters, amides and thioesters.<sup>33</sup> However, generation of the cation employing these methods does not enrich the acylium carbon. If the carbon monoxide in the ester group is  $^{13}\mathrm{CO}$  enriched, then the cation generated is enriched. Conversely, if the carbon monoxide in the ester group is naturally abundant  $^{12}$ CO, then the cation generated will not be enriched. Further

research from the same laboratory showed that the acylium cation could be prepared in an alternative manner.  $^{54,71}$ 

CH2C12

(Equation 2.8)

The generation of the cation using this method, rather than the one using  $HPF_6$  and a tricobalt ester derivative was chosen as it ensured that the <sup>13</sup>CO bonded to the apical carbon would be enriched.



Scheme 2.8: Generation of the acylium cation 2.6 Characteristics of the control compounds

Addition of a suitable nucleophile, such as N,Ndimethylaniline or indole leads to the Friedel-Crafts product which, in principle, could be "de-enriched" at the metal carbonyl position by treatment with <sup>12</sup>CO. Figure 2.3 shows the  ${}^{13}$ C NMR spectrum of 24a showing approximately 25%  ${}^{13}$ C enrichment for both types of carbonyl environments.



Figure 2.3: <sup>13</sup>C NMR Spectrum of <sup>13</sup>CO-enriched N,N-dimethylaminobenzoylcarbynyl tricobalt nonacarbonyl

The carbon resonances of the N,N-dimethylaminophenyl moiety were assigned by analogy to the closely related p-dimethylamino-benzaldehyde.  $^{72}$ 



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Figure 2.4: p-Dimethylamino-benzaldehyde and N,Ndimethylaminobenzoylcarbynyl tricobalt nonacarbonyl Figure 2.5 shows the  ${}^{13}$ C NMR Spectrum of 24b showing approximately 30%  ${}^{13}$ C enrichment for both types of carbonyl environment.



formylindole.<sup>73</sup>





2.33

Figure 2.6: 3-Formylindole and (3-indoloylmethylidyne) tricobalt nonacarbonyl Having assigned all the proton and carbon peaks on the respective NMR spectra and all the characteristic frequencies in the infrared spectra, we now have, in essence, control compounds which can be of use in establishing the change in the compound due to decarbonylation.

#### 2.7 De-enrichment of the enriched compounds.

A problem arose, however, in Scheme 2.7 as proposed in that the exchange of the metal carbonyl in 24 with <sup>12</sup>CO turned out to be an exceedingly slow process and even after numerous exposures to fresh <sup>12</sup>CO over a several month period, the <sup>13</sup>CO content had scarcely changed.<sup>74</sup> In retrospect, it is clear that the rate of incorporation of <sup>13</sup>CO to take a naturally abundant sample to, say, 25% <sup>13</sup>C content is much faster than that for the reverse process which takes a 75% <sup>12</sup>CO-containing molecule back up to the natural abundance level. In the latter case, 75% of the carbon monoxide molecules exchanged have no effect and the situation worsens as the reaction proceeds. The kinetics of consecutive reactions have been recently discussed by Atwood, 75 in which he had plotted the pattern for enrichment of  $^{13}$ CO molecules of the position cis to Br in  $Mn(CO)_5Br$ . The y-axis is the fraction (f) of the molecules corresponding to 0, 1, and  $3\ ^{13}\text{CO}$  molecules cis to Br. In Figure 2.7, we can see that at 25% enrichment corresponds to 12 days and that

trying to get to 17% enrichment would require 24 days according to this exponental decay curve. It is, of course, true that carbonyl ligand exchange occurs more rapidly at elevated temperatures, as illustrated for the analogous situation of substitution of  $PPh_3$  on  $V(CO)_6$ .<sup>76</sup> However, the thermal instability of these alkylidynetricobalt nonacarbonyl compounds precludes such an option.



Figure 2.7: Plots of rate versus molar concentration of PPh<sub>3</sub> for substitution on V(CO)<sub>6</sub>.

## 2.8 Adaptations to the proposed experiment

Having learnt our lesson, we followed the course outlined in Scheme 2.9 in which initial  $^{13}$ CO enrichment of the ester 30 and subsequent treatment with HPF<sub>6</sub> in propionic anhydride produced the cation 32 enriched only at the cobalt carbonyl. Reaction of 32 with N,N-di-methylaniline (or indole) gave good yields of 33a (or 33b) enriched in  $^{13}$ CO only at the cobalt carbonyls while

the ketonic carbonyl retained its normal 1% abundance. We are thus labelling the ketonic position with  $^{12}$ CO and looking for diminution of the  $^{13}$ C isotopic content at the basal carbon positions; this is merely the reverse of the original experiment which envisaged  $^{13}$ C enrichment solely at the ketonic position and then testing for enrichment at the Co(CO)<sub>3</sub> sites.

Now if the reaction were to follow a mechanism in which the ketonic carbonyl were extruded, such as the Norrish-type proposal, the ratio of the intensity of the metal carbonyl <sup>13</sup>C NMR resonance at 200 ppm to the intensities of the other peaks should be essentially unchanged on going from 33 to 34. In contrast, if a carbon monoxide ligand bonded to a cobalt were to be lost and its position taken by the former ketonic carbonyl, then, in the resulting decarbonylated molecule, 35, only eight of the terminal carbonyls will be enriched while the ninth carbon monoxide ligand would be merely naturally abundant in  $^{13}$ C. The overall result will be a diminution in the intensity of the cobalt carbonyl resonance relative to those of the remainder of the <sup>13</sup>C peaks in the spectrum by a factor of one in eight or 12.5%. It is important to note that the actual percentage of <sup>13</sup>CO enrichment is unimportant, it is merely the relative change with respect to the remaining <sup>13</sup>C nuclei in the indole which are, of course, naturally abundant.

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2.9 Assumptions when using <sup>13</sup>C NMR spectroscopy

Of course, the crucial assumption in this experiment is that the <sup>13</sup>C NMR relaxation times and relative sensitivities remain constant for the carbonylated and decarbonylated molecules. It was clearly incumbent upon us to establish whether this assumption is indeed justified and, if not, correct for it. We had two things to investigate, (a) the reproducibility of a given spectrum and (b) the constancy of the relative relaxation times. To satisfy ourselves as to the reproducibility of the given spectrum, we ran each <sup>13</sup>C spectrum three times under identical conditions. These spectra were all obtained using overnight runs on a Bruker AM500 spectrometer operating at 11.7 Tesla (500 MHz for <sup>1</sup>H, 125 MHz for <sup>13</sup>C) in order to get good signal to noise conditions. Typically, these spectra were the result of approximately 200,000 transients and, gratifyingly, the relative integrated intensities of the <sup>13</sup>C resonances separate runs differed by less than ≈1%. In each case, the integrated intensity of the cobalt carbonyl resonance was taken as the internal standard and the intensities of the resonances of the indolyl ligand were normalized to this. The internal consistency was, in fact, better than we had anticipated and is presumably a consequence of the very large number of scans and inherent sensitivity and stability of the high-field instrument.

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The second criterion, that is, the relative constancy of the relaxation times of the different <sup>13</sup>C sites in the carbonylated and decarbonylated molecules is not so trivial to establish. Clearly, this has to be accomplished on a system uncomplicated by the presence of different isotopic abundances in the ketonic and metal carbonyl positions. On the other hand, the cobalt carbonyls need to be enriched so as to give acceptable signal intensities in a reasonable time period. To achieve this, the indole complex 24b, was prepared using the sequence outlned in Scheme 2.7. By this means, the ketonic carbonyl is enriched to exactly the same extent as are the basal carbonyls since they originate from the same <sup>13</sup>C-enriched carbonyl pool, that is, from the chloro-compound 22. Now, decarbonylation of 24 made in this way gives us no information as to the origin of the carbon monoxide which is eliminated, but it does provide a standard with which to compare the relative intensities of the cobalt carbonyls and the carbon resonances of the indolyl ligand in both the carbonylated and decarbonylated molecules.

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Figure 2.8: 125MHz <sup>13</sup>C NMR spectrum of the decarbonylation product from the <sup>13</sup>CO enriched indole complex

The aromatic region of this compound was characterized by conventional heteronuclear decoupling techniques. Firstly, a <sup>1</sup>H NMR spectrum was obtained in acetone-d<sub>6</sub> and then repeated in methylene chloride-d<sub>2</sub>. This allowed assignment of the N-H peak at  $\delta$  8.3 ppm since in the presence of acetone-d<sub>6</sub>, the N-H peak undergoes exchange with the solvent. Also the singlet at 7.5 ppm corresponds to the olefinic proton on the indole ring. Since we now knew the frequencies of all the specific protons, this allowed us to irradiate these frequencies when we ran a coupled <sup>13</sup>C NMR spectrum. By doing so, the irradiation at that proton frequency would cause the C-H coupling in the <sup>13</sup>C NMR spectrum to collapse; thus a

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Figure 2.9: (3-indolylmethylidyne)tricobaltnonacarbonyl

doublet would appear as a singlet for the corresponding carbon. For instance, the assignment of carbon-4 involves irradiating proton-4 at 1089Hz, causing this doublet to collapse to a singlet. The same procedure was followed for the rest of the protons and their assignments to their respective carbons. We also chose to take advantage of one of the multipulse sequences recently developed for two-dimensional NMR spectroscopy.<sup>77,78</sup> The COSY experiment allows molecular structure elucidation through scalar coupling between protons.<sup>79,80,81</sup> Figure 2.10 shows the result of a COSY experiment presented as a contour plot in which the one-dimensional spectrum lies along the diagonal and coupling between two spins is manifested as a symmetrically positioned pair of off-diagonal peaks.

As can be seen in Figure 2.11, the superb resolution achievable at 500 MHz yields a spectrum that demonstrates

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the power of multipulse NMR techniques. Careful examination of the two-dimensional matrix clearly shows all scalar couplings and allows unequivocal assignment of the site of attachment of all protons.

Again, we were fortunate to find that the variation of the relative integrated intensities of the carbon resonances of the indolyl ligand in both clusters, normalized to those of the  $Co(CO)_3$  signals was no more than  $\pm$  1.5% in three overnight runs on the AM500. The sole exception was the C-3 carbon, that is, the nucleus which suffers the greatest change in its environment going from a position next to a ketonic carbonyl to a site contiguous to the carbonyl carbon. We could thus proceed, with some confidence, to the experiment in which the molecule enriched only at the cobalt carbonyl positions was decarbonylated.

# 2.10 The decarbonylation mechanism

In our hands, the cleanest decarbonylation process occurred for 33b to 35b, that is, where the functional group was 3-indolyl. Figure 2.16 shows the 125 MHz <sup>13</sup>C NMR spectra of the carbonylated and decarbonylated clusters and it is readily apparent that in going from 33b to 35b the ketonic carbonyl at 198.6 ppm has disappeared. Furthermore, the intensity of the 220 ppm peak in 35b has apparently been reduced with respect to the indolyl ligand resonances. In fact, the measured inte-

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Figure 2.10: Homonuclear decoupling experiment for (3indolylmethylidyne)tricobalt nonacarbonyl

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Figure 2.11: <sup>1</sup>H-<sup>1</sup>H COSY experiment of (3-indolylmethylidyne)tricobalt nonacarbonyl

grated intensities show that the cobalt carbonyl resonances in 35b has apparently been reduced with respect to the indolyl ligand resonances. In fact, the measured integrated intensities show that the cobalt carbonyl resonances in 35b have been reduced by 12-14% relative to the other <sup>13</sup>C peaks. We can thus unequivocally deduce that the carbon monoxide originally lost was a cobalt carbonyl and that its place was taken by the carbon monoxide moiety from the ketonic position. Before proposing a mechanistic rationale, we note that the rate and extent of decarbonylation are very sensitive to the identity of the acyl fragment. In particular, Seyferth has reported<sup>65</sup> (and we have confirmed) that decarbonylation is favoured when the RC=0 group contains electron-releasing substituents.

 $p-Me_2N-C_6H_4 > m-Me-C_6H_4 > C_6H_4 > C_6H_5 > p-F-C_6H_4 > pCl-C_6H_4$ 

One might envisage that loss of a cobalt carbonyl is followed by interaction of the acyl group with the vacant coordination site, as in Scheme 2.10. There must be a developing electron deficiency at the carbonyl carbon atom and this is alleviated by migration of the functional group to this terminus. The aryl functionalities listed above follow the classic pattern of migratory aptitudes for migration towards an electron-deficient centre such as a carbocation, carbene or nitrene.<sup>82</sup>



Figure 2.12: 125 MHz <sup>13</sup>C NMR spectra of the carbonylated and decarbonylated clusters


Scheme 2.10: Proposed mechanism of decarbonylation

It has been suggested that initial loss of the ketonic carbon monoxide followed by rapidly scrambling of the liberated carbon monoxide with the carbonyls of the Co(CO)<sub>3</sub> groups could account for the decreased intensity of the metal carbonyl <sup>13</sup>C NMR resonances. It was pointed out that these tricobalt clusters pick up carbon monoxide almost guantitatively as in the case of the transformation of the chloro cluster, 28, to the acylium cation 29. We note, however, that the production of 29 from 28 is essentially unaffected by the presence of free carbon monoxide.<sup>65</sup> In that reaction, which proceeds in good yields even at low temperature, the newly created vacant coordination site on cobalt must interact with a bonded carbon monoxide. Furthermore, the experimental data presented here show that, within experimental error, the entire population of ketonic <sup>12</sup>CO's is transferred to the basal position, that is, the Co(CO), peak intensity decreases by the expected 12.5% (± 1%). It is unrealistic to expect that, if initial extrusion of <sup>12</sup>CO from

the ketonic position were the predominant mechanistic process, all of this  $^{12}$ CO could successfully substitute at the coordinatively saturated Co(CO)<sub>3</sub> vertices.

Finally, it is interesting to speculate about the possibility that some of the individual steps in Scheme 2.10 are reversible. Thus, electron-donating functional groups clearly favour migration towards the carbonyl carbon with concomitant molecular rearrangement, presumably to give initially the carbonyl-bridged structure 30. One could visualize a situation where by electronwithdrawing groups might promote the reverse process in which carbonyl insertion occurs. It is particularly noteworthy that, when BrCo<sub>3</sub>(CO)<sub>9</sub>, 40, was treated with triethylamine under an atmosphere of carbon monoxide, infrared absorptions attributable to bridging carbonyls were observed. 83,84 Furthermore, it is well established that 40 reacts readily with amines to give cluster bound amides, 45, and esters, 43, respectively. 83,85 Likewise, thiols yield thioesters, but subsequent side reactions lead to complications.86

A straightforward mechanism which readily accommodates all of these observations is outlined in Scheme 2.11. If one accepts the existence of a small equilibrium concentration of the carbonyl-bridged isomer 42, then nucleophilic attack at the ketonic leads to the intermediate 44; elimination of HBr yields directly amides, 45, or esters, 43, depending on the identity of the nucleophile.

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Scheme 2.11: Reaction pathways from BrCCo3(CO)9

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Such reactions are greatly facilitated by the addition of triethylamine, whose role is presumably to accelerate the elimination of HBr. It is also easy to see why addition of a strong Lewis acid, such as aluminium trichloride, favours the generation of the ketenylidene cation 29 whose tilted geometry<sup>87</sup> is readily achievable by a very minor distortion from the carbonyl-bridged conformation 41. We suggest therefore, that decarbonylation and carbonylation reactions of the carbonyltricobalt nona-carbonyl clusters proceed via common intermediates and that the direction of the equilibrium is a consequence of the electron-withdrawing or -donating character of the apical group.

## 2.11 Conclusions and Proposals of Future Work

To conclude, we have shown that in the decarbonylation of the acyl systems  $RC(0)CCo_3(CO)_9$  to give the corresponding  $RCCo_3(CO)_9$  clusters, the carbon monoxide which is lost is derived from a tricobalt vertex. One could study the kinetics of these reactions and also synthesize acyl clusters containing a chiral functional group to see whether migration proceeds intramolecularly with retention of configuration.

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#### CHAPTER THREE

#### A COBALT COMPLEX OF DDT

### 3.1 Introduction

The observed tendency of the tricobalt nonacarbonyl group to stabilize positive charges in the  $\alpha$ -position has been attributed to its ability to delocalize the charge onto the carbonyl ligands via the cobalts. To some extent, the tetrahedral Co<sub>3</sub>C cluster can be regarded as being a three-dimensionally aromatic molecule whereby the skeletal electrons are globally-delocalized over the surface of the cluster.  $^{88}\,$  From this perspective, the  $\alpha$ position in a cluster is analogous to a benzylic site in conventional two-dimensional planar aromatic molecules. In this respect, it mirrors the behaviour of the [( $\pi$ - $C_6H_5)Cr(CO)_3$  moiety which can likewise act so as to alleviate an electronic deficiency in a neighbouring centre. The (tricarbonylchromium)phenyl system is to some extent hermaphroditic in that it can equally well tolerate a negative charge at the benzylic position. A question which therefore arises is whether the organometallic cluster or the conventional benzyl group can better stabilize an excess or deficit of electronic charge at a neighbouring centre. In effect, one needs to construct a molecule in which a phenyl ring and a nonacarbonyl tricobalt moiety are attached to the same electron-deficient center so that their relative stabil-

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izing abilities can be evaluated.

One method of probing the extent of electronic delocalization in a benzyl cation or anion is to evaluate the degree of double bond character developed between the benzylic carbon and the ipso-carbon of the phenyl ring. A simple experimental approach to doing this is to use variable temperature NMR spectroscopy to measure the rotational barrier about the "double bond" to see whether any increased resistance to rotation is detectable. Such an approach has been used previously by McGlinchey and Jaouen<sup>89</sup> to compare the abilities of the (tricarbonylchromium)phenyl and (4-trimethylsilyl)phenyl rings to delocalize the negative charge in diphenylmethyl anions.



In this case, the increased barrier to rotation of the (tricarbonylchromium)phenyl group relative to that of the (4-trimethylsilyl)phenyl ring, shows that the electron density is better delocalized onto that of the chromium-complexed ring. It therefore seemed a viable proposal to construct molecules in which one or more

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phenyl groups were bonded to a methynyl group situated in a position  $\alpha$  to the nonacarbonyltricobalt moiety. By this means, one could remove the  $\alpha$ -hydrogen either as a proton, or as a hydride to prepare a cluster-stabilized anion or cation, respectively, and then determine the barrier to phenyl rotation in each case by variabletemperature NMR measurements.



Tricobalt nonacarbonyl clusters are most easily synthesized via the direct reaction of dicobalt octacarbonyl with an appropriate trichloromethyl-containing precursor. To this end, it was decided to carry out the reaction of dicobalt octacarbonyl with l,l,l,-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) which is a cheap, readily available compound possessing a trichloromethyl substituent.

3.2 Synthesis of the Cluster (C1-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHCCo<sub>3</sub>(CO)<sub>9</sub>

The reaction of DDT with  $Co_2(CO)_8$  proceeds normally in that, upon heating, carbon monoxide is evolved; after the usual purification procedure, a mixture of black and white crystalline products is obtained. However, even after repeated attempts using column chromatography, the black product could not be cleanly separated from the accompanying white crystalline material. This separation was finally effected by manually removing the individual crystals under a microscope. The micro-analytical data (carbon, hydrogen and chlorine) on the black crystals were in accord with the expected formula, viz,  $(ClC_6H_4)_2CHCCo_3(CO)_9$ . amd the mass spectrum under mild ionization conditions exhibited a peak at m/z 648 for  $(M-CO)^+$  and a series of ions corresponding to successive losses of eight more terminal carbonyls. This mass spectrum appears as Figure 3.1.

The identity of the white crystalline material was established by its proton and carbon-13 NMR spectroscopic data. We note initially that DDT itself gives rise to a proton NMR spectrum showing multiplets at  $\delta$  7.5 (4H) and 7.3 (4H), together with a singlet at 5.5 (1H). The carbon-13 pattern for DDT is equally predictable with the expected aromatic resonances at 136 (*C*-CH), 134 (*C*-C1), 132 (*C*-H) and 128 (*C*-H); the CCl<sub>3</sub> and benzylic C-H peaks appear at 100 and 69 ppm, respectively. The white crystalline product from the reaction of DDT with dicobalt octacarbonyl with DDT, shows not only the normal resonances in the aromatic region but also two unexpected doublets at  $\delta$  6.8 and 5.5. The two-dimensional COSY spectrum shows these two anomalous protons to be coupled to each other.

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Figure 3.1 Mass Spectrum of (Cl-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHCCo<sub>3</sub>(CO)<sub>9</sub>, 3.1

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Figure 3.2 Proton and carbon-13 spectra of 1,1,1-trichloro-2,2-bis-(4-chlorophenyl)ethane (DDT).



Figure 3.3 2-Dimensional <sup>1</sup>H COSY NMR spectrum of the white product (DDD).

Correspondingly, the carbon-13 NMR spectrum of the molecule exhibits high field resonances at 71 and 64 ppm; these carbon atoms are coupled to the high field protons thus establishing the presence of a >CH-CH< unit in the molecule. These data were consistent with the assignment of the white crystals as 2,2-bis(p-chlorophenyl)-1,1- dichloroethane (DDD) and this was confirmed by comparison of the spectra with that of an authentic sample.

3.3 Carbonyl Fluxionality in the (Cl-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHCCo<sub>3</sub>(CO)<sub>9</sub> Complex.

The carbon-13 spectrum of the cobalt cluster exhibited resonances at  $\delta$  306 (apical carbon), 200 (cobalt carbonyls), 143 (C-CH), 133 (C-C1); 129 and 128 (phenyl-CH's) and 76 (benzylic CH). However, the most interesting observation was the low temperature carbon-13 NMR spectrum of the cobalt carbonyls which split into a 6:3 pattern at -120°C, as shown in Figure 3.4.



Figure 3.4 Carbon-13 NMR Spectrum of carbonyl region of the DDT-CCo<sub>3</sub>(CO)<sub>9</sub> complex at -120°C.

This rather surprising result is amenable to several interpretations; firstly, one could be stopping axialequatorial exchange of the cobalt carbonyls on the NMR timescale. Despite numerous attempts this phenomenon has not so far been unequivocally demonstrated. Secondly, one could invoke slowed rotation of the diarylmethyl-

capping group relative to the cobalt triangle. In the first instance, the molecule would maintain  ${\rm C}_{\rm 3v}$  symmetry but the cessation of the localized exchange would lead to a 6:3 pattern. This process could occur even if intermetal exchange were to continue. That is, the six aforementioned carbonyls could execute a merry-go-round process in the equatorial plane while the other three carbonyls would maintain their axial positions. The second postulated process would require that the bulky capping group rotate slowly on the NMR timescale presumably such that the predominant rotamer would be the staggered molecule as in 3.2. This situation would not demand the hitherto unknown cessation of localized rotation but merely the slowing of intermetal exchange a well established phenomenon.







Let us briefly examine the currently available evidence concerning localized and internal carbonyl exchange processes. The latter phenomenon is clearly demonstrated in, for example  $RCCo_3(CO)_7(diphos)$ , 3.3, which shows a single broad carbonyl resonance at room temperature but a 3:2:2 pattern at -90°C. This has been interpreted in terms of a  $Co(CO)_3$  (which continues to rotate) and pairs of axial-equatorial carbonyls on the phosphorus-bearing cobalts.<sup>90</sup> Furthermore, in the cluster  $Co_2Fe(CO)_9S$ , 3.4 the initial single peak at room temperature separates upon cooling into a 6:3 pattern with chemical shifts appropriate for carbonyl ligands on cobalt and iron, respectively. Further cooling splits the  $Fe(CO)_3$ resonance into a 2:1 pattern but the cobalt carbonyl signal remains sharp.<sup>91</sup>



The mixed metal ketenylidene cluster, 3.5 shows a single carbonyl resonance at high temperatures but splits into a 2:6 pattern at -100°C. Even on a 500 MHz NMR spectrometer, the carbonyl resonance remains very sharp giving no indication that axial-equatorial exchange can be stopped. The conclusions one can draw are: (a) intermetal exchange

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(which presumably involves bridging carbonyls as intermediates) has a low barrier but can be stopped on the NMR timescale; in contrast, the barrier to localized Co(CO)<sub>3</sub> exchange seems to be even smaller. It would appear, therefore, that unusual steric effects would be required to slow localized axial-equatorial exchange on the NMR timescale.



Returning to the current molecule, it is clear that we need to incorporate other probes to allow us to differentiate between these possibilities. We propose that a valuable experiment would be the reaction of the DDT-CCo<sub>3</sub>(CO)<sub>9</sub> cluster, 3.1, with the tripodal ligand;





tris(diphenylphosphine)methane,  $(Ph_2P)_3CH$ . This ligand is known to coordinate to the three cobalt atoms in a triangular face as in the known cluster  $Co_4(Co)_9(tripod)$ . In this system, one can envisage two scenarios in that, such a molecule has labelled each cobalt vertex with a NMR active nucleus, that is phosphorus-31, which will not migrate. Thus, if the 6:3 splitting in the original cluster, 3.1, is entirely attributable to axial-equatorial exchange then the phosphorus nuclei will remain equivalent at all temperatures. In contrast, if the rotation of the capping group is slowed thus generating a molecule of effective  $C_S$  symmetry, then the phosphorus environments will split 2:1.

Another approach to deciding whether unusually large steric interactions are possible is to use the CHEM-X molecular modelling programs<sup>92</sup> to produce computer-drawn structures of the possible steric interactions which might arise in the tricobalt nonacarbonyl analogue of DDT. The structure is based on the crystallographic data<sup>93</sup> for DDT but the trichloro fragment has been replaced by a nonacarbonyl tricobalt unit taken from the X-ray data for the methyl-substituted tricobalt cluster.

We note that in DDT itself this CCl<sub>3</sub> group is almost perfectly staggered with respect to the diarylmethyl fragment and the initial cluster so generated matches this conformation as in Figure 3.5.

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Figure 3.5 CHEM-X diagrams of DDT and its nonacarbonyltricobalt analogue. We then rotated the apical group and oriented one chlorophenyl ring into the worst possible position to maximize the interactions between an ortho hydrogen of an aryl ring and the carbonyl ligands. If one were to block axial-equatorial exchange, one could jam the aforementioned aryl ring either between two carbonyls on the same cobalt, as in Figure 3.6, or between two carbonyls on adjacent cobalts as in Figure 3.7.

In both cases, the ortho hydrogens of the ring come uncomfortably close to the carbonyls suggesting that such a conformation would impose a rotational barrier on the cobalt tricarbonyl group. Subsequently, we were able to grow crystals of a quality appropriate for X-ray crystallography and these were sent to Professor M.R. Churchill's laboratory at the University of Buffalo. This now provides an opportunity to compare the computer modelling results with the crystallographic data.

#### 3.4 Description of the Structure

The crystal consists of discrete units of  $Co_3(CO)_9C-$ [CH(p-C<sub>6</sub>H<sub>4</sub>Cl)<sub>2</sub>]; which have (non-crystallographic) C<sub>S</sub> symmetry. There are no abnormally short inter- or intramolecular contacts. The structure and labelling scheme is illustrated in Figure 3.8 and a stereoscopic view of the molecule appears as Figure 3.9. Interatomic distances and angles are listed in Tables III and IV of the Appendix.



Figure 3.6 CHEM-X diagram of the DDT-CCo<sub>3</sub>(CO)<sub>9</sub> complex with the phenyl ring between the two carbonyls on the same cobalt.

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Figure 3.7 CHEM-X diagram of the DDT-CCo<sub>3</sub>(CO)<sub>9</sub> complex with the phenyl ring between the two carbonyls on adjacent cobalts. The tricobalt plane has normal Co-Co bond lengths, with Co(2)-Co(3) = 2.462 (1), Co(1)-Co(3) = 2471 and Co(1)-Co(2) = 2.474(1) A. These values fall within the range reported for previous structures containing the  $Co_3(CO)_9C$  fragment, viz. (2.463(5) - 2.498(4) A). 97-103Although the variation in Co-Co bond lengths is statistically significant, it is of little chemical significance. Similar variations in chemically equivalent Co-Co bond distances have been seen previously and are probably a result of crystal packing forces. 32,94-96

The methylidyne carbon (C(l)) lies at distances of 1.914(3) to 1.92(3) A from the cobalt atoms. Again, these distances are typical. The p-chlorophenyl rings show normal distances and angles. The planar phenyl rings are "twisted" by 5° relative to their respective orientation to the tricobalt plane, removing the potential  $C_S$  symmetry of the molecule. The Co-C(1)-C(2) bond angles are:  $Co(1)-C(1)-C(2) = 127.6(2)^{\circ}$ ,  $Co(2)-C(1)-C(2) = 127.6(2)^{\circ}$ , Co(2)-C(1)-C(2),  $Co(2)-C(1)-C(2) = 127.6(2)^{\circ}$ , Co(2)-C(1)-C(2), Co(2)-C(1)-C(2), Co(2)-C(2)-C(2), Co(2)-C(2),  $C(2) = 127.8(2)^{\circ}$  and  $Co(3)-C(1)-C(2) = 139.7(2)^{\circ}$ . Since the p-chlorophenyl rings are bent towards Co(3), the increased Co(3)-C(1)-C(2) angle is probably a result of intermolecular steric forces. Axial carbonyl ligands (i.e., those trans to the apical carbon) are associated with somewhat longer cobalt-carbon distances (Co(1)-C(11))= 1.837(4) A; Co(2)-C(21) = 1.835(4) A; Co(3)-C(33) =1.839(4) A than are the equatorial carbonyl ligands (Co(1)-C(13) = 1.789(4) Å to Co(1)-C(12) 1.810(4) Å. The



Figure 3.8 ORTEP diagram of the DDT-CCo3(CO)g complex







Figure 3.10 Stereo views of the DDT-CCo3(CO)9 complex

corresponding carbon-oxygen distances show little variation: C-O(axial) = 1.129(5) A(av.) and C-O(equatorial) = 1.132(5) A(av.).

### 3.5 Concluding Remarks

The crystallographic data for the DDT-cluster molecule match rather closely the structural parameters for DDT itself. In particular, the capping group is oriented in a staggered conformer 3.2 to minimize the steric interactions. Furthermore, the two chlorophenyl rings are twisted slightly thus breaking the potential mirror symmetry of the molecule. Indeed, the X-ray data confirm the viability of molecular modelling programs such as CHEM-X to labile one to predict molecular geometries of organometallic clusters with some confidence.

## CHAPTER FOUR EXPERIMENTAL SECTION

### 4.1 General Spectroscopic Techniques

Routine proton NMR spectra were recorded on a Varian EM390 NMR spectrometer. Carbon-13 NMR spectra were recorded using Bruker AM500, WM250 and WP80 spectrometers. Proton spectra were also recorded on the Bruker AM500, WM250, and MSL100 spectrometers. Chemical shifts were all referenced to tetramethylsilane and given in  $\delta$ units (ppm). Infrared spectra were recorded on a Perkin Elmer 283 instrument using solution cells with KBr windows; mull spectra were measured using NaCl plates. Mass spectrometry was performed either on a VG Micromass 7070F (normal-geometry double-focusing mass spectrometer) equipped with a VG2035 data system or on a VG micromass ZAB-E reversed-geometry double-focusing mass spectrometer with a VG11/250 data system. Melting points of solids were measured on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected.

### 4.2 Chemicals

With the exception of tetrahydrofuran and methylene chloride, all chemicals were used as purchased. These solvents were dried by standard techniques before use.<sup>97</sup>

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#### 4.3 General Procedures

All reactions were performed under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. The progress of reactions was indicated by colour changes and was routinely monitored by thin layer chromatography (TLC) using BDH TLC plastic sheets, silica gel  $60F_{254}$  and hexane, hexane/dichloromethane (1/3), or dichloromethane as eluants.

Mixtures of reaction products were all separated by column chromatography on silica gel (60-200 mesh, Baker analyzed) using hexane, hexane/dichloromethane (1/3), or dichloromethane as eluants. Solid samples, in general, were further purified by sublimation (50-60°C, 0.02-0.07mm Hg) or by recrystallization.

## 4.4 Preparation of (CO)<sub>9</sub>Co<sub>3</sub>CCl<sup>98</sup>

Following Seyferth's general procedure,  $Co_2(CO)_8$ (18.7g, 55 mmol) and 150 mL of dry tetrahydrofuran (distilled from sodium benzophenone ketyl) was stirred until the carbonyl had dissolved. Then  $CCl_4$  (4.8g, 31 mmol) was added slowly by syringe. The reaction mixture was stirred at 50°C for 3 hrs, cooled to room temperature, then allowed to stir overnight. The solvent was removed at reduced pressure, then the sample was dissolved in hexanes and filtered under nitrogen pressure (Schlenk tube apparatus). The solvent was removed on a rotary evaporator. This residue was

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recrystallized from hexane to give 46% yield of product (mpt; 131-133°C). The infrared spectrum in benzene exhibited  $v_{CO}$  at 2140(w), 2060(vs), 2040(s) cm<sup>-1</sup>. Major mass spectral peaks occurred at m/z (%): 476 (2), 448 (38), 420 (17), 392 (20), 364 (17), 336 (38), 308 (80), 280 (46), 252 (52), 224 (100), 165 (40), 130 (60), 118 (17).

# 4.5 Preparation of $(CO)_9Co_3CCO_2C_2H_5^{-54}$

In a typical experiment,  $AlCl_3$  (0.81g, 6.1mmol) and 60mL of dry  $CH_2Cl_2$  (distilled from phosphorus pentoxide) was stirred until the solid dissolved. Then  $(CO)_9Co_3CCl$ (1.05g, 2.2mmol) was charged into the reaction vessel. The purple solution became brown after 20-30 min. The reaction was monitored via TLC, until no  $(CO)_9Co_3CCl$ remained and only a single brown spot,  $R_f = 0$ , was observed. Addition of  $C_2H_5OH$  (20mL, 342.7mmol) slowly by syringe effects an instantaneous colour change to purple and results in a homogeneous solution. This solution was stirred until only the desired products were seen on the TLC (usually 30 min.).

The reaction mixture was poured into 200mL of cold 5% hydrochloric acid, then the organic layer was separated and dried with anhydrous sodium sulfate. The solution was filtered and the solvent removed at reduced pressure. This solid was placed onto a silica column and eluted with hexane/ $CH_2Cl_2$  (1/3) to obtain the major product.

The solvent was removed under reduced pressure and the residue was recrystallized from hexane to give 78% of  $(CO)_9Co_3C-CO_2C_2H_5$ . The <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) showed a triplet at  $\delta$  1.3 (3H) and a quartet at 4.2 (2H) (J = 7.5Hz). The <sup>13</sup>C NMR spectrum (in CD<sub>2</sub>Cl<sub>2</sub>) showed peaks at  $\delta$  199.0 (terminal carbonyls), 178.4 (ester CO), 61.7 (CH<sub>2</sub>) and 13.8 (CH<sub>3</sub>). The infrared spectrum (in CCl<sub>4</sub>) exhibited  $\nu_{CO}$  at 2120(w), 2060(vs) and 2040(s) cm<sup>-1</sup>. Major mass spectral peaks occurred at m/z (%): 486 (18), 458 (30), 430 (22), 402 (10), 374 (38), 346 (100), 318 (92), 290 (48), 262 (46), 234 (50), 189 (46).

# 4.6 <sup>13</sup>CO Enrichment of $(CO)_9Co_3CR$ , where R = Cl, or R = $CO_2C_2H_5$

In this experiment a 1 mmol sample of  $(CO)_9CO_3CR$  was dissolved in 25mL of dichloromethane. The solution was degassed, then one atmosphere (760 torr) of <sup>13</sup>CO was placed over the solution. After stirring for 48 hrs. at 25°C, the exchanged carbon monoxide was removed and the solution was exposed to fresh <sup>13</sup>CO and allowed to stir for another 48 hrs at 25°C. The dichloromethane was removed at reduced pressure. (Carbon monoxide retards the decomposition of the cluster). This procedure results in approximately 30% enrichment of the cobalt carbonyls. On a Bruker WP80, an acceptable <sup>13</sup>C NMR spectrum could be obtained after 1000 scans. 4.7 Attempted De-enrichment of (<sup>13</sup>CO)<sub>9</sub>Co<sub>3</sub>C-R, where

 $R = CO_2C_2H_5$  or  $R = COC_6H_4NMe_2-p$ 

In this experiment, a 1 mmol sample of  $({}^{13}CO)_9Co_3CR$ was dissolved in 25 mL of dichloromethane. The solution was degassed, then one atmosphere (760 torr) of  ${}^{12}CO$  was placed over the solution. After stirring for 48 hrs. at 25°C, the exchanged carbon monoxide was removed and the procedure repeated. This procedure was carried out three times a week over a several month period.

4.8 Preparation of  $({}^{13}CO)_{9}Co_{3}C{}^{13}COC_{8}H_{10}N{}^{60}$ 

Following the general procedure of Seyferth, AlCl3 (10.83g, 6.2 mmol) and 60 mL of dry dichloromethane (distilled from phosphorus pentoxide) was stirred until the solid dissolved. Then  $(^{13}CO)_9Co_3CC1$  (1.05g, 2.2 mmol) was charged into the reaction vessel. The purple solution became brown after 20-30 min. Addition of dimethylaniline (3mL, 23.7mmol) was carried out slowly using a syringe then stirred until completion of the reaction. The standard work-up was followed by separating the solid by placing it on a silica column. Elution with hexane / dichloromethane (1/3) gave a single product which was recrystallized from hexane / dichloromethane to give 69% yield of red-brown solid  $(^{13}CO)_{9}Co_{3}C ^{13}$ COC<sub>8</sub>H<sub>10</sub>N. The infrared spectrum (in CCl<sub>4</sub>) exhibited  $v_{CO}$  at 2120(w), 2060(vs) and 2040(s)cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum (in acetone- $d_5$ ) shows a singlet at  $\delta$  3.02 (6H)

# 4.9 Preparation of $\left[\binom{13}{C0}_9 Co_3 CC0\right]^+ PF_6^-$

Following the general procedure of Seyferth, <sup>52</sup> a solution containing  $({}^{13}CO)_9Co_3CO_2C_2H_5$  (1.03g, 2.0mmol) in propionic anhydride (15 mL) was treated with 65% aqueous HPF<sub>6</sub> (0.23mL, 2.6mmol). Upon addition of the acid, the colour of the solution changed from purple to black and a precipitate began to form. After stirring for 30 min., 10mL of anhydrous Et<sub>2</sub>O was added three times, thereby ensuring complete precipitation of the solid. This mixture was filtered under nitrogen pressure (Schlenk tube apparatus). The product  $[({}^{13}CO)_9Co_3CCO]^+$  PF<sub>6</sub><sup>-</sup> (1.1g, 1.8mmol) was recovered in 90% yield after being washed with anhydrous Et<sub>2</sub>O and dried *in vacuo* at room temperature for 1hr.

4.10 Treatment of [(<sup>13</sup>CO)<sub>9</sub>Co<sub>3</sub>CCO]<sup>+</sup> PF<sub>6</sub><sup>-</sup> with Indole

Following the general procedure of Seyferth, a slurry of  $[(^{13}CO)_9Co_3CCO]^+ PF_6^- (1.1g, 1.8 mmol)$  in 15 mL of dichloromethane was prepared. Indole (0.6 g, 5 mmol) was dissolved in 5 mL of dichloromethane and syringed slowly into the reaction vessel. This reaction mixture was stirred for 30 min., poured into 50 mL of water and then

extracted with 50 mL of Et<sub>2</sub>O. The organic layer was washed with 20 mL portions of 10% aqueous HCl three times and then dried over anhydrous sodium sulfate. The solution was filtered and the solvent removed *in vacuo*. The product obtained was 13 ( $^{13}$ CO)<sub>9</sub>Co<sub>3</sub>CCOC<sub>8</sub>H<sub>6</sub>N in 70% yield. The infrared spectrum (in CCl<sub>4</sub>) exhibited  $v_{CO}$  bands at 2100(w), 2040(w) and 2020(s) cm<sup>-1</sup>, a ketonic carbonyl band at 1573 cm<sup>-1</sup> and  $v_{\rm NH}$  at 3479cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum (in methylene chloride-d<sub>2</sub>) showed a broad peak at  $\delta$  9.0 (NH), a multiplet at 8.35 (H-4), a doublet at 8.0 (H-2), a multiplet at 7.3 (H-7) and a multiplet at 7.1 (H-5, H-6). The <sup>13</sup>C NMR spectrum (in CDCl<sub>3</sub>) shows peaks at  $\delta$  199.3 (cobalt carbonyls), 198.6 (ketone), 136.2 (C-9), 129.9 (C-2), 126.7 (C-8), 124.1 (C-4), 123.3 (C-5), 122.8 (C-6), 115.9 (C-3) and 111.4 (C-7).

4.11 Thermal Decarbonylation of (<sup>13</sup>CO)<sub>9</sub>Co<sub>3</sub>CCOC<sub>8</sub>H<sub>6</sub>NH

Following the general procedure of Seyferth,  $^{64,65}$ ( $^{13}CO$ ) $_{9}Co_{3}CCOC_{8}H_{6}N$  was dissolved in 50 mL of benzene and heated under reflux for 4 hrs. Samples were taken every 30 min, to monitor the reaction by TLC. After 4 hrs, the starting material had been consumed, and a brown spot of lower R<sub>f</sub>, had grown. The major product was found to be ( $^{13}CO$ ) $_{8}(^{12}CO)Co_{3}CC_{8}H_{6}N$  in 70% yield. The infrared spectrum (in CCl<sub>4</sub>) exhibits  $v_{CO}$  bands at 2100(w), 2040(vs), 2020(s)cm<sup>-1</sup> and  $v_{NH}$  at 3479cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum (in methylene chloride-d<sub>2</sub>) shows a broad line at  $\delta$  8.3 (NH), a doublet at 7.7 (H-4), a singlet at 7.5 (H-2), a doublet at 7.4 (H-7) and a multiplet at 7.2 (H-5, H-6).

## 4.12 Preparation of (CO)<sub>9</sub>Co<sub>3</sub>CCH(C<sub>6</sub>H<sub>4</sub>-Cl)<sub>2</sub>

Following Seyferth's general procedure, Co<sub>2</sub>(CO)<sub>8</sub> (18.7 g, 55 mmol) and 100 mL of dry tetrahydrofuran (distilled from sodium benzophenone ketyl) was stirred until the carbonyl had dissolved. Then (Cl-C6H4)2CHCCl (10.8 g, 31 mmol) was dissolved in 50 mL of dry THF and added slowly by syringe. The reaction mixture was stirred at 50°C for 2 hrs; once the bubbling had stopped, the heat source was removed, the mixture allowed to cool to room temperature and the reaction mixture stirred overnight. After filtration under nitrogen pressure (Schlenk tube apparatus) to remove cobalt salts, the solvent was removed under reduced pressure. The residue was dissolved in hexane and filtered to remove any insoluble products. The hexane was then removed using a rotary evaporator and this solid was placed on a silica column under nitrogen. The first band eluted (using hexane) was starting material, i.e., DDT. The second band (also eluted with hexane) was repeatedly recrystallized from hexane/dichloromethane to yield (CO)<sub>9</sub>Co<sub>3</sub>C- $CH(C_6H_4Cl)_2(24\%)$ . To separate the desired cluster from DDD, the black crystals were selected under a microscope. The infrared spectrum (CCl<sub>4</sub>) exhibited  $v_{CO}$  bands at 2092 (m), 2030 (vs), 2010 (s), 1989 (w) and 1980 (w)  $cm^{-1}$ . The

<sup>1</sup>H NMR spectrum (in acetone-d<sub>6</sub>) shows a doublet at  $\delta$  7.15 (4H), a doublet at  $\delta$  6.70 (4H) and a singlet (1H) at  $\delta$  5.3. The <sup>13</sup>C NMR spectrum (in CD<sub>2</sub>Cl<sub>2</sub> / CFCl<sub>3</sub>) shows peaks at  $\delta$  305.9 (apical C), 199.1 (cobalt carbonyls), 143.7 (C-CH), 133.2 (C-Cl), 129.5 (C-2,6), 128.5 (C-3,5) [phenyl ring carbons] and 75.74 (CH-Ar). At 153 K, the cobalt carbonyl resonance is split into two peaks at  $\delta$  202.9 (3C) and 198.5 (6C). The mass spectrum exhibits m/z values of 648, 592, 564, 536, 508, 480, 452, 424, illustrating a pattern characteristic for two chlorines.

Analysis: Calculated for C<sub>22</sub>H<sub>9</sub>Cl<sub>2</sub>Co<sub>3</sub>O<sub>8</sub>: %C, 40.68; %H, 1.39; %Cl, 10.94. Found: %C, 40.77; %H, 1.33: %Cl, 10.49.

## 4.13 Collection of the X-ray Diffraction Data for Co<sub>3</sub>(CO)<sub>9</sub>C[CH(p-C<sub>6</sub>H<sub>4</sub>Cl)<sub>2</sub>]

A black crystal of approximate orthogonal dimensions 0.3 x 0.3 x 0.4 mm<sup>3</sup> was mounted along its extended axis in a thin-walled glass capillary and was aligned and centered on a Syntex P2<sub>1</sub> automated four-circle diffract-ometer. Determination of accurate unit cell dimensions and the crystal's orientation matrix were performed as described previously.<sup>99</sup> This and other details of the data collection are given in Table A-I. of the Appendix.

Examination of the data set revealed the systematic absences h0l for h + 1 = 2n + 1 and OkO for k = 2n + 1, indicating the centrosymmetric monoclinic space group  $P2_1/n$ . Data were corrected for the effects of absorption (by interpolation, in 20 and  $\phi$ , between normalized curves from -scans of six close-to-axial reflections) and for Lorentz and polarization factors. Symmetry equivalent data were averaged and the resulting unique data set was placed on an approximately absolute scale by means of a Wilson plot.

The positions of the three cobalt atoms were determined by direct methods using the program MULTAN<sup>100</sup> and a subsequent "E-map". All remaining non-hydrogen atoms were located from difference-Fourier maps. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (with hydrogen atoms included in idealized locations with d(C-H) = 0.95 A) led to convergence with  $R_F = 3.7$ %,  $R_{wF} = 3.3$ % and GOF = 1.37 for all 3434 unique data; for those 2781 data with  $|F_0| > 6\sigma (|F_C|)$ ,  $R_F = 2.5$ % and  $R_{wF} = 3.0$ %. A final difference-Fourier map showed no significant features. Final positional and thermal parameters are listed in Table A-II of the Appendix.

All calculations were performed on the SUNY-Buffalo modified Syntex XTL system. The function  $\Sigma w (|F_0| - |F_c|)^2$  was minimized during the least squares procedure; here  $w^{-1} = [\sigma(|F_0|)]^2 + [0.01 |F_0|]^2$ . The analytical form of the neutral atoms' scattering factors were corrected for both the real ( $\Delta f'$ ) and the imaginary ( $i\Delta f''$ ) components of anomalous dispersion.<sup>101</sup>

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CRYSTALLOGRAPHIC APPENDIX

Table I

Experimental Data for the X-Ray diffraction Study of

CO3(CO)<sup>6</sup>[<sup>n</sup>3-CCH(p-C<sup>6</sup>H<sup>4</sup>Cl)<sup>5</sup>]

(A) Unit Cell Data.

a	=	13.0834(27)A	crystal system: monoclinic
b	=	14.2224(16)Å	space group: P2 <sub>1</sub> /n
<u>c</u>	=	14.1649(24)Å	Z = 4
ß	=	95.871(15)°	formula C23H909Cl2C03
V	=	2621.9(8) Å <sup>3</sup>	mol. wt. = 677.01
T	=	24°C (297 K)	$D(calc'd) = 1.71 \text{ g/cm}^3$

(B) Collection of X-Ray Diffraction Data:

Diffractometer: Syntex P2,

Radiation: Mo Ka ( $\overline{\lambda}$  = 0.710730 Å)

monochromator: highly orientated (pyrolytic) graphite: equatorial mode with

 $2\theta(m) = 12.160^{\circ}$ ; assumed to be 50% perfect/50% ideally mosaic for polarization correction.

reflections meas'd: +h, +k, ±l for 20: 5 + 45°, yielding 3434 unique data. scan type: coupled  $\theta(crystal)-2\theta(counter)$ 

scan width:  $[2\theta(Ka_1) \ 1.0]^\circ \rightarrow [2\theta(Ka_2) + 1.0]^\circ$ 

scan speed: 4.0 deg/min (20)

backgrounds: stationary crystal, stationary-counter at the two extremes of

the 20 scan; each for one-quarter of the total scan time. standard reflns: three mutually orthogonal reflections collected before each set of 97 data points. No decay observed.

## Table II

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Final Atomic Parameters for  $Co_3(CO)_9[\mu_3-CCH(p-C_6H_4Cl)_2]$ .

ATOM	×	Y	Z
CD(1)	0.75321(3)	0.77559(3)	0.70445(3)
CD(2)	0.59813(3)	0.70589(3)	0.61694(3)
CD(3)	0.68006(3)	0.84436(3)	0.55199(3)
CL(1)	0.61000(9)	0.46201(9)	0.17826(7)
CL(2)	1.24577(7)	0.76571(9)	0.53301(8)
0(11)	0.66108(22)	0.91044(21)	0.83176(20)
0(12)	0.96941(22)	0.83611(21)	0.71574(19)
0(13)	0.80334(29)	0.61120(23)	0.82331(24)
0(21)	0.44731(23)	0.78707(23)	0.73630(22)
0(22)	0.47157(23)	0.66702(26)	0.43873(21)
0(23)	0.61722(24)	0.51277(20)	0.63850(24)
0(31)	0.62084(29)	0.84122(23)	0.34673(21)
0(32)	0.84784(25)	0.98068(20)	0.55602(21)
0(33)	0.51724(26)	0.96921(23)	0.61153(23)
C(1)	0.73452(22)	0.72129(19)	0.58051(19)
C(2)	0.80144(23)	0.64770(19)	0.53883(20)
C(11)	0.69695(28)	0.85838(25)	8.78422(24)
C(12)	0.88534(32)	0.81475(25)	0.70994(23)
C(13)	0.78228(32)	0.67503(29)	0.77816(25)
C(21)	0.50418(28)	0.75685(26)	0.68996(26)
C(22)	0.52092(28)	0.68233(27)	0.50731(28)
C(23)	0.60880(26)	0.58784(28)	0.66209(27)
C(31)	0.64423(31)	0.83995(26)	0.42560(28)
C(32)	0.78328(32)	0.92695(25)	0.55354(25)
C(33)	0.57991(32)	8.92276(27)	0.58873(27)

C(41)	0.75277(22)	0.60373(20)	0.44593(20)
C(42)	0.75729(28)	0.64417(24)	0.35806(23)
C(43)	0.71385(30)	0.60128(29)	0.27562(24)
C(44)	0.66504(26)	0.51678(26)	0.23153(24)
C(45)	0.65501(26)	0.47435(23)	0.35797(26)
C(46)	0.70297(26)	0.51793(22)	0.44923(22)
C(51)	0.91281(23)	0.67921(21)	0.53472(20)
C(52)	0.99082(26)	0.62745(24)	0.50351(24)
C(53)	1.09336(26)	0.65331(23)	0.53385(26)
C(54)	1.11689(24)	0.73208(25)	0.53425(24)
C(55)	1.04137(26)	0.76523(23)	0.49499(24)
C(56)	0.93999(24)	0.75867(22)	0.43552(22)
H(2)	0.8044	0.5974	0.5841
H(42)	0.7632	0.7050	0.3545
H(43)	0.7126	0.6341	0.2159
H(45)	0.6252	0.4144	0.3783
H(45)	0.7017	0.4871	0.5097
H(52)	0.9743	0.5713	0.6169
H(53)	1.1461	0.6152	0.6195
H(55)	1.0582	0.8414	0.4510
H(56)	0.8874	0.7955	8.4586

\* All hydrogen atoms were assigned an isotropic thermal parameter of B = 4.0 A

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## Table III

Interatomic Distances (in Å) for  $Co_3(CO)_9[\mu_3-CCH(p-C_6H_4Cl)_2]$ .

(A) Co-Co and Co-C(methylidyne) distances

Co(1) - Co(2)	2.474(1)	Co(1)-C(1)	1.911(3)
Co(1)-Co(3)	2.471(1)	Co(2)-C(1)	1.921(3)
Co(2)-Co(3)	2.462(1)	Co(3)-C(1)	1.914(3)

(B) Co-CO and C-O Distances

Co(1)-C(11)	1.837(4)	C(11) - O(11)	1.134(5)
Co(1)-C(12)	1.810(4)	C(12)-O(12)	1.136(5)
Co(1)-C(13)	1.789(4)	C(13)-O(13)	1.128(5)

Co(2)-C(21)	1.835(4)	C(21)-O(21)	1.126(5)

Co(2)-C(22) 1.796(4)C(22)-O(22) 1.131(5)Co(2)-C(23) 1.797(4)C(23)-O(23) 1.133(5)

Co(3)-C(31)	1.805(4)	C(31)-O(31)	1.128(5)
Co(3)-C(32)	1.791(4)	C(32)-O(32)	1.137(5)
Co(3)-C(33)	1.839(4)	C(33)-O(33)	1.126(5)

(C)	Distan	ces	Involving	the	<sup>µ</sup> 3 <sup>-C-CH-(C)</sup> 2	System	
C(1	)-C(2)	1.52	21(4)			C(2)-C(41)	1.535(4)
						C(2)-C(51)	1.531(4)

(D) Distances within  ${\rm C}_{6}{\rm H}_{4}{\rm Cl}$  systems.

C(41)-C(42)	1.378(4)	C(51)-C(52)	1.385(5)
C(42)-C(43)	1.387(5)	C(52)-C(53)	1.393(5)
C(43)-C(44)	1.368(5)	C(53)-C(54)	1.368(5)
C(44)-C(45)	1.373(5)	C(54)-C(55)	1.376(5)
C(45)-C(46)	1.381(5)	C(55)-C(56)	1.381(5)
C(46)-C(41)	1.386(4)	C(56)-C(51)	1.385(4)

 $C(44)-C\ell(1)$  1.747(4)

C(54)-Cl(2) 1.754(3)

## Table IV

Interatomic	Angles	(in	Deg.)	for	Co3(Co)9	[µ3-(	CCH(p-C <sub>6</sub> H <sub>4</sub> Cl) <sub>2</sub> ]	•
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(A) Angles within the  $Co_3(\mu_3-C)$  core.

Co(1)-Co(2)-Co(3)	60.08(2)	Co(1)-C(1)-Co(2)	80.43(11)
Co(3)-Co(1)-Co(2)	59.71(2)	Co(1)-C(1)-Co(3)	80.50(11)
Co(2)-Co(3)-Co(1)	60.21(2)	Co(2)-C(1)-Co(3)	79.86(11)

- Co(1)-Co(2)-C(1)49.59(8)Co(3)-Co(2)-C(1)49.93(8)Co(1)-Co(3)-C(1)49.70(8)Co(2)-Co(1)-C(1)49.97(8)Co(2)-Co(3)-C(1)50.20(8)Co(3)-Co(1)-C(1)49.81(8)
- (B) Co-Co-CO Angles Co(2)-Co(1)-C(11) 101.9(1) Co(3)-Co(1)-C(11) 98.1(1) Co(2)-Co(1)-C(12) 151.1(1) Co(3)-Co(1)-C(12) 101.5(1) Co(2)-Co(1)-C(13) 95.0(1) Co(3)-Co(1)-C(13) 150.0(1)

Co(1)-Co(2)-C(21)	97.0(1)	Co(3)-Co(2)-C(21)	103.7(1)
Co(1)-Co(2)-C(22)	150.3(1)	Co(3)-Co(2)-C(22)	93.2(1)
Co(1)-Co(2)-C(23)	99.6(1)	Co(3)-Co(2)-C(23)	149.1(1)

Co(1)-Co(3)-C(31)153.2(1)Co(2)-Co(3)-C(31)105.4(1)Co(1)-Co(3)-C(32)91.4(1)Co(2)-Co(3)-C(32)151.4(1)Co(1)-Co(3)-C(33)102.5(1)Co(2)-Co(3)-C(33)91.7(1)

(C) Co-C-O Angles			
Co(1)-C(11)-O(11)	178.5(3)	Co(2)-C(21)-O(21)	178.6(3)
Co(1)-C(12)-O(12)	177.1(3)	Co(2)-C(22)-O(22)	179.4(4)

Co(1)-C(13)-O(13) 177.8(4) Co(2)-C(23)-O(23) 178.0(4) Co(3)-C(31)-O(31) 177.2(4) Co(3)-C(33)-O(33) 178.4(4) Co(3)-C(32)-O(32) 178.5(4)

(D) Angles Involvi	ing the $\mu_3$ -C-CH-(C) <sub>2</sub> System	ms	
Co(1)-C(1)-C(2)	127.6(2)	C(1)-C(2)-C(41)	114.1(2)
Co(2)-C(1)-C(2)	127.8(2)	C(1)-C(2)-C(51)	113.6(2)
Co(3)-C(1)-C(2)	139.7(2)	C(1)-C(2)-H(2)	103.8
C(2)-C(41)-C(42)	123.5(3)	C(41)-C(2)-C(51)	113.6(2)
C(2)-C(41)-C(46)	119.0(3)	C(41)-C(2)-H(2)	104.8
C(2)-C(51)-C(52)	118.7(3)	C(51)-C(2)-H(2)	105.7
C(2)-C(51)-C(56)	123.4(3)		

	(E) Angles within	the C <sub>6</sub> H <sub>4</sub> Cl groups		
	C(46)-C(41)-C(42)	117.5(3)	C(56)-C(51)-C(52)	117.8(3)
	C(41)-C(42)-C(43)	121.7(3)	C(51)-C(52)-C(53)	121.2(3)
	C(42)-C(43)-C(44)	119.2(3)	C(52)-C(53)-C(54)	119.0(3)
	C(43)-C(44)-C(45)	120.7(3)	C(53)-C(54)-C(55)	121.3(3)
	C(44)-C(45)-C(46)	119.3(3)	C(54)-C(55)-C(56)	118.9(3)
	C(45)-C(46)-C(41)	121.6(3)	C(55)-C(56)-C(51)	121.7(3)
	C(43)-C(44)-Cl(1)	119.7(3)	C(53)-C(54)-Cl(2)	119.6(3)
-	C(45)-C(44)-Cl(1)	119.6(3)	C(55)-C(54)-C1(2)	119.1(3)

C(55)-C(54)-C1(2) 119.1(3)