1986

An Investigation Of Dinuclear Alkylidene-bridged Carbonyl Complexes

William John Laws

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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS REÇUE
AN INVESTIGATION OF DINUclear
ALKYlidene-BRIDGEd CARBONYl COMPLEXES

by

William John Laws
Department of Chemistry

Submitted in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Ontario

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rearrangement of the fluxional methylene bridges in \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})]\) was observed for the \textit{bis}(\mu-methylene)dicobalt dmpm congener. The first example of a cluster incorporating a bridging dmpm ligand was isolated and identified as \([\text{Co}_2(\text{CO})_7(\mu_3-\text{COO}_2\text{Et})(\mu-\text{dmpm})]\).

Reaction of the dianionic complexes \([\text{Co}_2(\text{CO})_6(\mu-L)]^2^-\) (\(L=\text{dppm, dmpm}\)) with diiodomethane or \(\sigma,\sigma\)-diidoalkanes did not produce the expected dicobaltacycles. Excess \(\text{I}(\text{CH}_2)_n\text{I}\) \((n=1,3)\) reacts with \([\text{Co}_2(\text{CO})_6(\mu-\text{dmpm})]^2^-\) to yield \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dmpm})]\) and the novel complex \([\text{Co}_2\text{I}_4(\mu-\text{dmpm})_2]\). Similarly, reaction of excess \(\text{I}(\text{CH}_2)_n\text{I}\) \((n=1,3-5)\) or \(\text{R}\text{I} (\text{R}=\text{Me, Et})\) with the dianionic dppm derivative generates \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]\), \textit{trans}-\([\text{Co}_2\text{I}_2(\text{CO})_2(\mu-\text{CO})_2(\mu-\text{dppm})_2]\) and an unidentified species. Halogen abstraction is suspected to arise from an electron transfer process.
This work is dedicated to my
dear mother, my father and Lori.
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triplet $^1$H N.M.R. resonance exhibiting a large J(PH) value, considered diagnostic for that $\mu$-alkylidene proton extending over the diphosphine ring.

The chemical reactivity of these ($\mu$-alkylidene)dicobalt complexes was investigated with particular emphasis on possible mechanistic analogies to the Fischer-Tropsch synthesis on metal surfaces. Carbon-carbon coupling reactions occur at room temperature in reactions of $[\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)]_2(\mu-\text{dppm})$ with alkynes to give ethylene and $[\text{Co}_2(\text{CO})_4(\mu-\text{RCCR})(\mu-\text{dppm})](\text{R}=\text{CF}_3, \text{Ph})$, with ethylene to give propylene, and, at higher temperature, with hydrogen to yield the first example of formation of ethane from a bis($\mu$-methylene) transition metal complex. Deuterium-labelling studies reveal that the remarkably easy methylene coupling reactions to give ethylene from $[\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)]_2(\mu-\text{dppm})$ involve a complex, intermolecular coupling process associated with a large isotope effect. In all cases, small molecule addition, specifically carbon monoxide, sulfur dioxide or hexafluoro-2-butyne to the ($\mu$-alkylidene)dicobalt complexes induces coupling of the alkylidene unit with a carbonyl ligand and subsequent ketene elimination to form $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]$, $[\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)_2(\mu-\text{dppm})]$ and $[\text{Co}_2(\text{CO})_4(\mu-\text{CF}_3\text{CO}_2\text{CF}_3)(\mu-\text{dppm})]$ respectively. Each ketene derivative was trapped via methanolysis and the respective alkyl acetate formed was identified by $^1$H NMR spectroscopy.

The differences in structure and stability noted from the identical diazoalkane additions to the analogous complex $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dmpm})]$ were attributed to the higher basicity and smaller steric effects introduced by dmpm as compared to dppm. A similar
rearrangement of the fluxional methylene bridges in \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})]\) was observed for the bis(\(\mu\)-methylene)dicobalt dppm congener. The first example of a cluster incorporating a bridging dppm ligand was isolated and identified as \([\text{Co}_3(\text{CO})_7(\mu_3-\text{COO}_2\text{Et})(\mu-\text{dppm})]\).

Reaction of the dianionic complexes \([\text{Co}_2(\text{CO})_6(\mu-L)]^{2-}\) (L=dppm, dmpm) with diiodomethane or \(\alpha,\omega\)-diiodoalkanes did not produce the expected dicobaltacycles. Excess \(\text{I}(\text{CH}_2)_n\text{I}\) \((n=1,3)\) reacts with \([\text{Co}_2(\text{CO})_6(\mu-\text{dppm})]^{2-}\) to yield \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]\) and the novel complex \([\text{Co}_2\text{I}_4(\mu-\text{dppm})]\). Similarly, reaction of excess \(\text{I}(\text{CH}_2)_n\text{I}\) \((n=1,3-5)\) or \(\text{RI} (\text{R}=\text{Me, Et})\) with the dianionic dppm derivative generates \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]\), \(\text{trans}\cdot[\text{Co}_2\text{I}_2(\text{CO})_2(\mu-\text{CO})_2(\mu-\text{dppm})_2]\) and an unidentified species. Halogen abstraction is suspected to arise from an electron transfer process.
I wish to express my sincere appreciation, gratitude and, perhaps above all, admiration to my supervisor Dr. R.J. Puddephatt. His patience, timely encouragement and immeasurable guidance have contributed greatly to this work.

Many thanks are also extended to the faculty, staff and graduate students of the Chemistry Department at The University of Western Ontario for their advice, assistance and friendship; most notably Drs. P.K. Monaghan, S.S.M. Ling and J.T. Burton. The contribution of Mrs. Janis Zaborniak in the typing of the manuscript is especially appreciated.

Finally, I would like to acknowledge my wife, Lori, and my parents for their unbounded optimism and unfaltering patience throughout the duration of this thesis.
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**CHAPTER 2 - FORMATION AND REACTIVITY OF THE NOVEL METALLACYCLE**

(HCO)₄(μ-C(O))R(μ-dempp)₂

(R=H, Me₃C₂Et)

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Key Abbreviations

dmpm = bis(dimethylphosphino)methane
dppm = bis(diphenylphosphino)methane
R = alkyl or aryl group
Me = methyl
Et = ethyl
Pr = propyl
Bu = butyl
Ph = phenyl
Cp = cyclopentadienyl
η^5-C₅Me₅ = pentamethylcyclopentadienyl
THF = tetrahydrofuran
TLC = thin layer chromatography
psi = pounds per square inch
MS = mass spectrum

M⁺ = parent ion

IR = infrared
s = strong
vs = very strong
m = medium
w = weak
vw = very weak
br = broad
sh = shoulder

cm⁻¹ = reciprocal centimeters

NMR = nuclear magnetic resonance
s = singlet
d = doublet
t = triplet
q = quartet
qu = quintet
m = multiplet
Hz = hertz
ppm = parts per million

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CHAPTER 1

ALKYLIDENE-BRIDGED COMPLEXES

The rapid depletion of oil and natural gas reserves has rekindled interest in coal. In the assessment of coal as a world energy source, attention has been focused on coal's conversion to synthesis gas, which is then used as a feedstock for the petrochemical industry.

Reductive polymerization of carbon monoxide to yield hydrocarbons is called the Fischer-Tropsch synthesis.\(^1\) Classical Fischer-Tropsch catalysts (Fe, Co and Ru) are heterogeneous, non-selective systems, which produce a mixture of hydrocarbons and oxygen-containing organic compounds, the exact nature of the product mixture depending on the reaction conditions employed. Since high selectivity is a feature of successful homogeneous catalysts, the search for soluble liquid phase counterparts to classical Fischer-Tropsch catalysts is very active.

Although the mechanism of the Fischer-Tropsch synthesis is not established, it has been suggested\(^2\) that carbon monoxide is first converted to \(\text{CH}_2\) units at the metal surface and carbon-carbon bond formation occurs later. A \(\text{CRR'}\) unit bound to one metal is usually termed a carbene complex and the first such complex was discovered in 1964.\(^3\) However, on a metal surface, a \(\text{CRR'}\) unit is considered to bridge between two metal atoms.\(^2\) Such complexes are called \(\mu\)-alkylidene complexes or, when \(R=R'=\text{H}\), \(\mu\)-methylene complexes. They may also be called dimetallacyclop propane.\(^4\)
The aim of the work described in this thesis was to synthesize novel binuclear transition metal complexes containing one or two \( \mu \)-alkylidene groups, and to study the chemical reactions of these complexes. The formation of carbon-carbon bonds by coupling of two \( \mu \)-alkylidene ligands, or of carbon monoxide with a \( \mu \)-alkylidene ligand, was of especial interest since such reactions would model proposed steps in the Fischer-Tropsch synthesis.

This introductory chapter presents an overview of the syntheses and structures of dimetallacyclopropane-type compounds. Emphasis is focused on the most versatile synthetic method for \( \mu \)-alkylidene construction; carbene transfer from highly reactive diazoalkane precursors to appropriate organometallic substrates. The bonding, as derived from Hückel MO calculations for \([\text{Cp}_{2}\text{Rh}(\text{CO})_2(\mu-\text{CH}_2)]^4\) and geometry of known \( \mu \)-alkylidenes, is also discussed. Finally, an outline of the spectroscopic data provides evidence for the significantly increased electron density for the nearly \( \text{sp}^3 \)-hybridized bridging carbon of \( \mu \)-alkylidene complexes. By contrast, the Fischer-type metal carbenes contain an \( \text{sp}^2 \)-hybridized, electron deficient carbene unit attached to a mononuclear metal fragment.
1.1 Syntheses of $\mu$-Alkyldiene Transition Metal Complexes

From the various routes accessible for the preparation of $\mu$-alkyldiene complexes, two distinct classifications have emerged; notably the direct and the indirect methods. The direct methods are subdivided into three different synthetic types and each of these three direct synthetic pathways is reviewed, although only the Diazooalkane (1.1.1.1) and the Dihaloalkane (1.1.1.2) routes were studied with at least one organodimetal system in this work. The number of indirect methods as an access to alkyldiene-bridged complexes is considerably larger. Only the two more common methods are reviewed in Chapter 1 since they have received the most attention.

As the source of a carbene precursor in organic chemistry, diazoalkanes are the starting materials of choice since the preparation of the first unsubstituted $\mu$-methylen complex in 1974 demonstrated that carbene (\(-\text{CH}_2\)) could be transferred from its diazo precursor to organometallic compounds. The versatility of the functional group attached to the diazo carbon center produces a variety of ligand systems capable of selective coordination with organometallic substrates. A second direct synthetic route employs the numerous geminal dihaloalkanes \(\text{CX}_2\text{RR}'\), although side reactions originating from halogen transfer must be controlled.\(^6\)\(^7\) By adding more methylene units to the bridging \(\text{CH}_2\) function, isomeric $\alpha,\omega$-dihaloalkanes provide a convenient route to binuclear alkane-bridged organometals ($\mu(\alpha,\omega)$-alkanediyl complexes) of general formula \(\text{L}_n\text{M}(\text{CH}_2)_m\text{ML}_n\) (Section 6.1.1). The transfer of a Wittig reagent's ylide functionality to a metal carbonyl constitutes the final direct $\mu$-alkyldiene preparative method.\(^8\)\(^9\)
Only the indirect "carbene path" method appears to have a limitless range of applicability owing to the large number of characterized mononuclear metal carbenes. The "carbene path" method involves addition of electrophilic Fischer-type carbenes to coordinatively unsaturated transition metal complexes and consequently provides a valuable route to dimetallacyclopropane complexes containing heteronuclear metal-metal bonds. The second type of indirect method capable of synthesizing \( \mu \)-alkylidene complexes to be discussed is the "acetylene path", characterized by initial insertion of alkynes into metal-ligand bonds and subsequent metallacycle rearrangement. Other indirect synthetic approaches to \( \mu \)-alkylidene complexes with limited synthetic range have been reviewed by Herrmann and include organolithium reagents, ketenes, organomercurials, dimethylmagnesium, strained hydrocarbons and rearrangement reactions. Furthermore, Tebbe's reagent \([\text{Cp}_2\text{Ti}(\mu-\text{CH}_2)_2(\mu-\text{Cl})\text{AlMe}_2]\) (1.1), a molecule exhibiting ylide behaviour, represents a mixed main group element transition metal \( \mu \)-methylene complex.

1.1.1 Direct Methods

1.1.1.1 The Diazo Route

Diazo compounds appear to be a rich source of bridged alkylidene complexes and a range of complexes has been obtained. The numerous synthetic uses of diazoalkanes in organometallic syntheses has recently been reviewed. Perhaps the most intriguing feature of diazoalkanes is their ability to undergo metal-induced nitrogen elimination with concomitant carbene transfer to the metal substrate. Herrmann has proposed that a definite prerequisite for
diazooalkane bridge formation is the generation of an unsaturated transition metal substrate. This generation of a metal carbene or methylene species from diazo precursors is dependent on: 21, 23

a) exchange of a readily replaceable two-electron ligand of the organometallic reactant for the carbene unit of the diazo precursor, or

b) simple addition of the carbene unit preformed in the diazoalkane to the unsaturated metal metal frames.

This hypothesis is supported by the following literature precedents.

1.1.1.1 Activation by Photolysis or Thermolysis

The preparation of μ-alkylidene complexes from diazoalkane precursors generally requires mild conditions. When an unsaturated metal substrate contains a metal-metal multiple bond, no activation of the substrate is necessary and diazoalkanes react at low temperatures. Therefore, a comparable rate between the generation of an unsaturated metal substrate by either a metal-metal multiple bond or a ligand, typically carbonyl, loss followed by dinitrogen elimination from the diazo substrate may lead to high yields of μ-alkylidene complexes. However, this only holds if the newly formed mononuclear species has sufficient lifetime to allow metal-metal bond formation. 21 Consequently the reaction conditions are as mild as possible to avoid uncontrolled diazoalkane decomposition. Activation via photolysis to induce an unsaturated organometal substrate may promote a light-induced decomposition of the diazoalkane (e.g., CH₂N₂).

Treatment of both the cis- and trans-μ-vinylidene complexes [CP₂Fe₂(CO)₂(μ-CH)₂(μ-CH₂)] with excess diazomethane in ether produced
no reaction. However, cuprous chloride was found to be an effective catalyst for the smooth conversion of the bridging vinylidene to bridging cyclopropylidene with diazomethane\(^{25}\) (equation 1.1.1)

![Chemical structure](image)

Similarly, an anionic trinuclear \(\mu\)-alkylidene complex was synthesized with formulation \([\text{Fe}_3(\text{CO})_{10}(\mu-H)(\mu-\text{CHO}_{2}\text{Et})]^-\) (1.2) via carbene addition from ethyl diazoacetate to the corresponding metalcarbonyl framework of the anionic \([\text{HFe}(\text{CO})_{11}]^-\) precursor with carbonyl loss. The structure of (1.2) was inferred from spectroscopic data.\(^{26}\)

Both Shapley et al.\(^{27}\) and Johnson, Lewis et al.\(^{28}\) independently synthesized the cluster \([\text{Os}_3(\text{CO})_{11}(\mu-\text{CH}_2)]\) (1.3) by the addition of diazomethane to \([\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})]\), although this same \(\mu\)-methylene osmium trimer (1.3) had earlier been prepared via ketene addition to the cluster \([\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]\)\(^{29}\) or excess phosphoric acid addition to solutions of \([\text{Os}_3(\text{CO})_{11}(\text{CHO})]\)^{30}\.

\[
[\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})] + \text{CH}_2\text{N}_2 \xrightarrow{\text{N}_2} [\text{Os}_3(\text{CO})_{11}(\mu-\text{CH}_2)] + \text{CH}_3\text{CN}
\]

(1.3)  1.1.2
Addition of diazomethane to an unsaturated tetranuclear heterometallic cluster \([\text{Os}_3\text{Pt}(\text{CO})_{10}(\mu-\text{H})_2\{\text{P(C}_6\text{H}_{11}\}}_3]\) (1.4) led to the first tetranuclear heterometallic \(\mu\)-methylen cluster \([\text{Os}_3\text{Pt}(\text{CO})_{10}-(\mu-\text{H})_2(\mu-\text{CH}_2)\{\text{P(C}_6\text{H}_{11}\}}_3]\) (1.5), an orange product which isomerizes in solution to a second red isomer (1.6). X-ray crystallography combined with \(^1\text{H}\) and \(^2\text{H}\) NMR spectroscopy to reveal evidence for a transient \(\mu\)-methyl species, postulated in Scheme 1.1 to account for \(^2\text{H}/^1\text{H}\) scrambling between \(\mu\)-\text{CH}_2 and \(\mu\)-\text{H} sites.\(^{31}\)

A \(\mu\)-methylene ligand, bridging an Ir-Co bond in the heteronuclear timer \([\text{CpIr}(\mu-\text{CO})_2(\mu-\text{CH}_2)\text{Co}_2\text{CP}_2]\), was obtained in quantitative yield from diazomethane addition to the trinuclear cluster \([\text{CpIr}(\mu-\text{CO})_2\text{Co}_2\text{CP}_2]\) without degradation of the former.\(^{32}\)

The addition of diazomethane to \([\text{Au}_2\text{Br}_2(\mu-\text{CH}_2\text{PPh}_2\text{CH}_2)]\) (1.7) occurs readily in THF at \(-78^\circ\text{C}\) to produce the \(\mu\)-methylen gold(III) complex (1.8)\(^{33}\), as illustrated in equation 1.1.5.
Scheme 1.1: (i) CH₂N₂, (ii) rotation of Pt(CO){P(C₆H₁₁)₃} fragment about an axis perpendicular to the Os₃ plane. L=P(C₆H₁₁)₃ and CO ligands are omitted for clarity.
For the preparation of the (μ-alkylidene)dicobalt complexes from diazoalkane precursors contained in this thesis, the generation of the unsaturated metal substrate by a carbonyl ligand loss in situ required only mild reaction conditions. When more drastic conditions are required to generate an unsaturated metal species in situ, diazoalkanes of higher thermal stability (e.g., diazomalonates, diazoacetates) are utilized to afford alkylidene-bridged dimers. 

The dimetallacycle \([\text{Cp}_2\text{Ru}_2(\text{CO})(\mu-\text{CO})(\mu-\text{C}O)\text{C}_2\text{Ph}_2)]\) is readily obtained from, and is much more reactive than, \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})_2]\). However, the thermal conditions required to generate the unsaturated \([\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{Ru}_2(\text{CO})_3]\) unit via diphenylacetylene displacement from \((1.9)\) prevent the synthesis of \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CH}_2)]\) (1.11a) from diazomethane addition by this route (see sections 1.1.1.2, 1.1.1.3^3). Consequently, only the more thermally stable diazoalkanes produce μ-alkylidene complexes from \((1.9)\). Thus ethyl diazoacetate produces \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHCO}_2\text{Et})]\) in a 2:1 ratio of cis and trans isomers^9, illustrated in equation 1.1.6.
Similarly, solution $^1$H and $^{13}$C($^1$H) NMR spectra from the products from reaction of (1.9) with diphenylidazomethane identified only the cis-$[\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu\cdot\text{CO})(\mu\cdot\text{CPh}_2)]$ (1.12) isomer formation, presumably in order to minimize steric interactions between the phenyl and Cp groups, and complex (1.13) (equation 1.1.7). The decarbonylation of (1.12) to yield (1.13) was interpreted to reveal that crowding is lessened by carbonyl ejection and that decarbonylation takes precedence over the resonance energy retention of the phenyl ring.

If thermolysis reactions prove inefficient, then the application of photolysis techniques may be necessary. Low temperature ultra violet photolysis was employed in the low yield synthesis of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\cdot\text{CO})(\mu\cdot\text{CHCO}_2R)]^{n}$ (1.15).
\[
\text{[Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2] + N_2\text{CHCO}_2R \xrightarrow{\text{N}_2} \text{[Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHCO}_2R)]}
\]

(1.14)

(1.15): R=Et, t·Bu

Hence, if the organometallic reagent is more photosensitive than the diazo precursor, photolysis may induce a \(\mu\)-alkylidene species from diazoalkane attack.

The rhodium complex [CpRh(CO)\(_2\)](1.16a) further illustrates this phenomenon since it can be photochemically transformed via carbonyl substitution by the alkyl esters of diazoacetates into the bis(methoxycarbonyl)methylene complex (1.17a) with concomitant dinitrogen loss\(^ {37,38}\), as shown in Scheme 1.2. Alternatively the homologous cobalt compound [CpCo(CO)\(_2\)](1.16b) yields the alkylidene-bridged complex (1.17b) under thermal conditions only, with similar diazo precursors, also depicted in Scheme 1.2. The complex trans-[Cp\(_2\)Co\(_2\)(CO)\(_2\)(\mu-\text{CR'-CO}_2R)](1.17b) was formed in high yield and its structure was elucidated from IR, \(^1\text{H}\) and \(^{13}\text{C}(\text{\textsuperscript{1}H})\) NMR data,\(^ {39}\) and from an X-ray diffraction study.\(^ {40}\)

The photolysis of ethyl or t-butyldiazoacetate with (1.16b) below -80°C (Scheme 1.2) affords a unique ester-bridged compound, \(\mu-(1,3\text{-dioxoindane\)-\(\mu\)-ylidene\) complex (1.18)\(^ {41}\), as an intermediate which undergoes an irreversible, intramolecular rearrangement in solution at ambient temperatures to form the alkylidene-bridged species (1.17b). This five-membered metallacycle in (1.18) arises from an unprecedented [2+3]-cycloaddition of the carbonyl-flanked carbenes onto a Co-C(CO) bond.\(^ {42}\) However, both thermolysis and photolysis of (1.16b) with diphenyldiazo methane produces the decarboxylated \(\mu\)-alkylidene...
Scheme 1.2: (i) $\text{hv}/15^\circ\text{C}/\text{THF}$, (ii) $80^\circ\text{C}/\text{C}_6\text{H}_6$,
(iii) $\text{hv}/<80^\circ\text{C}/\text{THF}: R=H; R'=\text{Et, t-Bu}$, (iv) $\text{hv}/\text{THF}: R=\text{CO}_2\text{R}$; $R'=\text{CO}_2\text{R}'$, (v) $\text{hv}/\text{THF}: R=R'=\text{Ph}$, (vi) $R=\text{Me}$; $R'=\text{Me, Bu/R=Et; R'=Et, Bu/R=Bu; R'=Me, Bu/R=\text{CO}_2\text{Et; R'=OEt.}$
derivative of (1.17b)\textsuperscript{a,b}, \([\text{Cp}_2 \text{Co}_2 (\mu - \text{CO})(\mu - \text{CPh}_2)]\) in Scheme 1.2, suspected to lack the structural prerequisites necessary for the \(\mu\)-heterocarbene-type derivatives like (1.18).\textsuperscript{21}

Scheme 1.2 also illustrates the mononuclear metallaacycle

\([\text{CpCo(CO)} (\text{C(O)C(CO}_2 \text{R})_2)\]) (1.19) derived from photolysis (\(\lambda > 300\) nm) of (1.16b) in the presence of diazoacetates or -malonates possessing oxygen-containing substituents capable of coordination.\textsuperscript{42,44} A metal-mediated carbylation of the respective carbenes accounts for the metallaacycle formation in (1.19). This metallaacycle in (1.19) is thermally cleaved along the cobalt-oxygen bond in refluxing benzene to give (1.17b).\textsuperscript{42}

Herrmann and co-workers\textsuperscript{37,45} have synthesized alkylidene-bridged rhodium dimers (1.20) using N-alkyl-N-nitrosourea derivatives, generally the diazoalkane precursors, as the organic reagent (equation 1.1.9). The yield of (1.20) increases significantly if \([\text{Cp}_2 \text{Rh}_2 (\text{CO})_2 (\mu - \text{CO})]\), formed under thermal or photochemical conditions from \([\text{CpRh(CO)}_2]\) (1.16a), is the metal source.\textsuperscript{46}

\[
(\text{1.16a}) \quad [\text{CpRh(CO)}_2] + \text{RCH}_2 \text{NH(NO)} \text{CONH}_2 \rightarrow \text{trans-}[\text{Cp}_2 \text{Rh}_2 (\text{CO})_2 (\mu - \text{CHR})]
\]

(1.19) \quad (1.20): R=H, Me

It has been deduced on the basis of deuterium labelling experiments that the alkylidene-bridge source is the alkyl group of the nitroso reagent; it does not originate from the reduction of a carbonyl group.\textsuperscript{37} The mechanism proposed by these authors centers on the alkyl group transfer from the urea to the coordinatively unsaturated intermediate \(\text{CpRh(CO)}\), followed by \(\alpha\)-hydrogen abstraction. Similar
reaction conditions had previously demonstrated that alkyl nitrosourea
possess very mild nitrosylating power toward the analogous cobalt
system (1.1.6b) in equation 1.1.10, even in the presence of excess
nitroso reagent.\textsuperscript{47}

\[
[CpCo(CO)_{2}] + RCH_2N(NO)CONH_2 \rightarrow [Cp_2Co_2(\mu-CO)\mu(NO)]
\] 1.1.10

(1.1.6b)

1.1.1.1.2 Carbene Addition to Metal-Metal Double Bonds

The synthetic method of using carbenes as electron acceptors to
add across electron rich metal-metal bonds parallels the documented
cyclopropanation of alkenes\textsuperscript{48} in organic chemistry, as illustrated in
equation 1.1.11.

\[
\begin{array}{c}
R \begin{array}{c}
\text{C} \\
\text{C}^{'}
\end{array} \\
\text{C} \begin{array}{c}
\text{C} \\
\text{C}^{'}
\end{array}
\end{array}
\]

\[
L_nM = \text{ML}_n + N_2CRR' \xrightarrow{-N_2} L_nM \xrightarrow{N_2} ML_n
\]

This direct addition of diazoalkanes to unsaturated metal-metal bonds
provides alkylidene-bridged A-frame complexes directly and many
examples of this reaction type are cited in the literature.

Complexes of composition [Cp_2Fe_2(NO)_{2}(\mu-CRR')] possessing nitrosyl
ligands in terminal and bridging positions are accessible by carbene
transfer from the appropriate diazoalkanes to the metal-metal double
bond of [Cp_2Fe_2(\mu-NO)_2]. No isomerization or thermolysis was noted for
either system shown by equations 1.1.12 and 1.1.13. Herrmann et al.\textsuperscript{49}
have also proven that nitrosyl bridge opening is more resistant than
the structurally analogous carbonyl bridge utilizing these products (1.21) and (1.22) from reaction equations 1.1.12 and 1.1.13 respectively.

\[
\begin{align*}
[Cp_2Fe_2(\mu-NO)_2] + CH_2N_2 & \overset{\text{-N}_2}{\longrightarrow} \text{trans-[Cp}_2\text{Fe}_2(\text{NO})_2(\mu-\text{CH}_2)] \quad 1.1.12 \\
[Cp_2Fe_2(\mu-NO)_2] + C_5H_4N_2 & \overset{\text{-N}_2}{\longrightarrow} \quad \text{1.1.13}
\end{align*}
\]

Applying the diazo method to the trinuclear osmium dihydride \([H_2Os_3(CO)_{10}] (1.23)\) reveals the hetero substituents in the diazoalkane influence the product structure. Ethyl diazoacetate gives the C,O-bridged compound \([Os_3(CO)_{10}(\mu-H)(\mu,\eta^2-CH_2CO_2Et)]^{50}\) which is structurally related to complex (1.18). However, a net carbene addition via diazo methane to the Os=Os double bond in (1.23) produces a solvent-dependent equilibrium mixture between a bridging methylene and its interconversion with a methyl ligand by methylene insertion into an Os-H single bond.\(^{51}\) In an elegant study involving \(^{13}\)C(\(^1\)H) NMR\(^{51,52}\) and X-ray and neutron diffraction,\(^{53}\) the cluster (1.25) was shown to adopt, through hydrogen atom transfer, the \(\mu\)-methyl (1.24), the \(\mu\)-methylene(1.25), and under appropriate thermal conditions, the irreversibly decarbonylated \(\mu\)-methylidyne cluster (1.26) molecules
This type of $\text{M(\text{CH}_3)} \rightleftharpoons \text{H}_2\text{M(\text{CH}_2)}$ tautomerism may serve as a model for mechanistic interpretation of hydrocarbon interaction with transition metal surfaces\(^3\) and suggests a possible role for alkylidene-bridged species in catalysis.

An array of triply bridged carbene addition products has been isolated from direct reaction of the unsaturated complex \([\text{Cp}_2\text{Rh}_2(\mu-\text{CO})_2]\)\(^{(1.27)}\) with a variety of diazo reagents $\text{N}_2\text{CRR'}$ via dinitrogen elimination.\(^{54}\) Scheme 1.3 illustrates this reaction sequence. Even the bulkier methylene ligands tetrabromo-cyclopentadienyliyldene(1) or 9-anthrone-10-ylidene(2) generate spectroscopic data indicative of the triply bridged geometry in \((1.28),^{54}\) verified by an X-ray structure.\(^{55}\) A 1,3-dipolar addition of $\text{N}_2\text{CRR'}$ across the Rh=Rh double bond in \((1.27)\) to form a five-membered dimetallacycle \((1.A)\), common in organic chemistry,\(^{48}\) is the suspected intermediate prior to the rapid, low temperature elimination of dinitrogen from even the most stable diazoalkane to yield \((1.28).^{54,55}\) However, not one organometallic substrate possessing such a dimetallacycle has yet been isolated.
Scheme 1.3: Diazaalkane addition to the unsaturated complexes $[\eta^5$-C$_5$Me$_5]$M$_2$(μ-CO)$_2$(N=Rh:Co) where $R=H, Me, CO_2Et; R'=H, CO_2Et$.

$R_1 (1.29) M=Rh$

$R_2 (1.30) M=Rh$

$R_3 (1.31) M=Co$

$R_4 (1.32) M=Co$

$R_5 (1.33) M=Co$

$R_6 (1.34) M=Co$

$R_7 (1.35) M=Co$
After formation of (1.28), decarbonylation results from bulky methylene ligands (1) and (2) in Scheme 1.3 to give complex (1.30). Alternatively at ambient reaction temperatures, an intramolecular isomerization of the triply bridged products (1.28) in Scheme 1.3 occurs to give the singly bridged counterparts (1.29) if sterically allowed.\textsuperscript{54} A $^{13}$C($^1$H) NMR study has revealed too bulky methylene substituents prevent isomerization between the structurally identical complexes $[\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mu-\text{CH}_2)]$ and $[(\eta^5-\text{C}_5\text{Me}_5)_2\text{Rh}_2(\text{CO})_2(\mu-\text{CH}_2)]$, or their CRR', derivatives.\textsuperscript{21,23,54} The carbonyl bridge opening to initiate isomerization is accompanied by a movement of the bulky $\text{C}_5\text{Me}_5$ ligand from positions exactly perpendicular to the metal-metal vector in (1.28) into positions above or below the $\text{Rh}_2\text{C}$ plane in (1.30). Hence the $\text{C}_5\text{Me}_5$/CRR' approach necessary for carbonyl bridge opening is governed by the steric demands of the methylene substituents R and R'.

Herrmann et al.\textsuperscript{57} utilized the decarbonylation of the diphenyl-methylene-bridged derivative of (1.29) to regenerate the metal-metal double bond in (1.30), which subsequently allowed addition of a second alkylidene unit to generate the mixed CR$_2$/CPh$_2$ derivative (1.31), shown in Scheme 1.4. The overall reaction in Scheme 1.4 replaces two carbonyl ligands with isolobal alkylidene ligands and was the first example of consecutive carbene addition.

Similarly a series of $\mu$-alkylidene cobalt complexes has been
Scheme 1.4: Formation of the mixed bis-(u-alkylidene) complex (1.31).
synthesized when the dinuclear cobalt complex \([\eta^5-C_5Me_5]_2Co_2(\mu-CO)_2\) (1.32) adds, when treated with various diazoalkanes under mild reaction conditions, carbenes of diversified structures to the metal-metal double bond\(^{38}\) (Scheme 1.3). Following elimination of dinitrogen, the stable triply bridged derivatives (1.33) are isolated. Consecutive structural isomerization and/or decarbonylation yield the secondary products of type (1.34) and (1.35) in Scheme 1.3. Decarbonylation on thermolysis of dinuclear \(\mu\)-alkylidene complexes (1.34) \((R,R'\neq H)\) also leads to stable, unsaturated \(\mu\)-alkylidene complexes (1.35).\(^{39}\) Furthermore, the \(\mu\)-alkylidene complexes (1.34) \((R=H,R'=H,CF_3)\), in a manner previously observed for (1.29) in Scheme 1.4, yield the bis(\(\mu\)-alkylidene) derivatives (1.36) when the precursors (1.34) \((R=H,R'=H,CF_3)\) are treated with diazomethane or (1.34) \((R=R'=H)\) is treated with excess diazoethane.\(^{38}\)

![Diagram](image)

(1.36) \(R=CF_3, Me\)

Open-chained \(\alpha\)-ketodiazaoalkanes, \(R-C(=N)\)-Cl(=O)R', are recognized starting materials for suitable syntheses of the respective ketenes, RR'\(\text{C}=\text{C}=\text{O}\).\(^{40}\) The facile Wolff rearrangement of ketocarbenes, derived from their noncyclic \(\alpha\)-ketodiazaoalkanes by dinitrogen loss, produces ketenes, a process favoured over 1,3-dipolar additions.\(^{23}\) Scheme 1.5 depicts the novel metallacycles (1.38) arising from attack on a rhodium
Scheme 1.5: $R = R' = \text{Me}, \text{Ph}, p$-MeOC$_6$H$_4$; $R, R' = \text{Ph}$.
carbonyl function (1.37) by the nucleophilic ketocarbene oxygen atom, subsequent to the ketocarbene complexation to the Rh=Rh-double bond in (1.27). An X-ray structure determination of (1.38) (R=R' =Ph) revealed the presence of a folded five-membered ring system Rh-CR=CR-O-C=O, a stable (2+3)-cycloaddition product that acts as a π-olefin-type ligand to the other Rh metal center. It should be noted that the bridgehead carbon atom, as a result of the steric constraints imposed by the cycloaddition, has lost its μ-methylene character in accordance with the orthogonality criterion described in section 1.3.

The cobalt analogue [η⁵-C₅Me₅]₂Co₂(μ-CO)₂ (1.32) of (1.27) shows no metallacycle formation on reaction with noncyclic α-ketodiazokanes. Alternatively the exclusive products (>96% yield) are the respective μ-ketomethylene complexes (1.37) of cobalt. The differences between these two metal systems under similar reaction conditions with α-ketodiazokanes are attributed to the less electrophilic carbonyl ligands in (μ-alkylidene)dicobalt complexes as compared to their rhodium analogues:

1.1.1.1 Carbene Addition to Metal-Metal Triple Bonds

It is generally believed that diazoalkane complexes are formed first but rarely are such complexes isolated. Usually dinitrogen is lost to yield a μ-alkylidene complex, as was described in the preceding sections. Since transition metal complexes have been extensively used to catalyze carbene moiety transfer from diazoalkanes to alkenes, it is often assumed that the metal center attacks the carbon of the diazoalkane, displacing dinitrogen. The results reviewed in this section and in section 2.1.1 suggest this view may be naive; the
Figure 1.1: Initial Coordination of the Intact Diazo Unit to $\left[ (\eta^5-C_5X_5)M_0(\eta^5-C_5X_5) \right]$. 

(1.C): $X = H, Me$

(1.B): $X = H, Me$
catalytically active species may be nitrogen bonded or polynuclear.

According to the simple formalism that carbenes can add across electron rich metal-metal bonds,49,51,54-59,61 reaction of diazoalkanes with metal-metal triple bonds, an unsaturated metal substrate, should produce dimetallacycloprenenes. Considering the results obtained with the sterically demanding methyl derivative [(η⁵-C₅H₅)₂Mo₂(CO)₄] as a substrate,62-68,70,71 the diazoalkane reactions are envisioned to occur through an initial coordination of the intact diazo unit via one or both nitrogen atoms as a bridging ligand to form (1.B) or (1.C) respectively, shown in Figure 1.1.

The type of secondary reaction experienced by the intermediate adducts (1.B) and (1.C) is strongly influenced by the nature of the bridging methylene substituents R,R' and the peripheral ligands. Relevant examples for each of the four types of secondary reaction routes are discussed in the following subsections (1.1.1.1.3.1-1.1.1.1.3.4).

1.1.1.1.3.1 N₂-Elimination with Bridging Alkylidene Derivative Formation

The first intermediate diazoalkane complex characterized was isolated from reaction of bis(p-toly1)- or diphenyldiazomethane, which is generally less reactive in cyclopropanation than the parent diazomethane,48 with the metal substrate [CP₂Mo₂(CO)₄] (1.40) without nitrogen loss.62 The crystallographically characterized intermediate [CP₂Mo₂(CO)₄(μ-N₂CPh₂)] (1.41) exhibited a similar symmetric bonding arrangement (1.B) of the diphenyldiazomethane bridging entity as that also reported for [CP₃Co₃(μ-CO)(μ-N₂CPh₂)] (1.39).63

The intermediate adducts (1.41) are thermally62 or photo-
Scheme 1.6: M=CpMo(CO)_2 R=Ph, p-MeC_6H_4; R'=H, Me
lytically decomposed in benzene with intramolecular loss of dinitrogen to afford the stable, red $\mu$-alkylidene species $[\text{Cp}_2\text{Mo}_2\text{(CO)}_4(\mu-\text{CR}_2)]$, (R=Ph, p-Me-Ph) (1.42) in high yield. The absence of nitrogen in the elemental analyses of (1.42) supported their formulation as $\mu$-alkylidene complexes and this was confirmed by $^1$H and $^{13}$C NMR spectroscopy, as well as single crystal X-ray diffraction.

The proposed mechanism (Scheme 1.6) involves initial diazoalkane coordination through the terminal nitrogen (1.41), followed by a cyclic 1,3-dipolar addition transition state as in (1.A), elimination of dinitrogen and formation of the alkylidene bridge (1.42).

The X-ray crystal structures of both (1.41) and (1.42) did not reveal the formal, anticipated Mo=Mo double bond of dimetallacyclopropanes. Consequently the bridging diazoalkane ligand in (1.41) acts as a four- as opposed to a two-electron ligand via its terminal nitrogen atom. Furthermore the methylene ligand in (1.42) incorporates the phenyl ring's bonding reserves to establish a $\sigma$-alkyl/$\pi$-alkyl type four-electron system. Hence the complexation of the $\mu$-alkylidene (1.42) is stabilized by the participation of the substituent phenyl groups, observed earlier with the ruthenium dimer (1.13). Addition of 1 equiv of (p-MeC$_6$H$_4$)$_2$CN$_2$ to a benzene or ether solution of the $\mu$-di-p-tolylmethylen complex $[\text{Cp}_2\text{Mo}_2\text{(CO)}_4(\text{CR}_2)]$ (R=p-MePh) (1.42) yields carbon monoxide and complex (1.43) of molecular composition $[\text{Cp}_2\text{Mo}_2\text{(CO)}_3(\text{CR}_2)(\text{N}_2\text{CR}_2)]$ in 75% yield (equation 1.1.15).

$$[\text{Cp}_2\text{Mo}_2\text{(CO)}_4(\text{CR}_2)] + \text{R}_2\text{CN}_2 \rightarrow [\text{Cp}_2\text{Mo}_2\text{(CO)}_3(\text{CR}_2)(\text{N}_2\text{CR}_2)]$$

(1.42)  \hspace{1cm} (1.43) R=p-Me-Ph
Scheme 1.7: Probable Mechanism for formation of (1.43) from (1.42)

\[ \text{[Cp}_2\text{Mo}_2\text{O}_2\text{[CO]}_4\text{[CR}_2\text{]_2]} + \text{N}_2\text{CR}_2 \]

(1.42) \( R = \text{Ph}, \text{p-Me-Ph} \)

(1.43)
Insufficient information for determining the diazoalkane coordination mode necessitated a single-crystal X-ray diffraction study. The key results of the molecular structure determination were the presence of terminal alkylidene and N-terminal diazoalkane ligands on the same molybdenum atom (1.43). The authors proposed a mechanism for this bridge (1.42) to terminal (1.43) alkylidene conversion as shown in Scheme 1.7.

1.1.1.3.2 Simultaneous CO/N₂-Elimination with Diazoalkanes whose Carbene Moieties Aromatize

Diazocyclopentadiene also evades simple carbene addition on reaction with (1.40). The X-ray structure reveals the product 
\[ \text{[Cp}_2\text{Mo}(\text{CO})_3(\mu-\text{C}_5\text{H}_4)] \] (1.44) has lost one carbonyl group to form a unique six-electron cyclic ligand bridging the Mo-Mo single bond (equation 1.1.16). The cyclopentadienyldiene ligand acts as an aromatic η⁵-system bound to the CpMo(CO) unit and a terminal-type \( \sigma^*\)-alkyl to the \( \text{CpMo}_2(\text{CO})_2 \) fragment in (1.44).

![Image](1.1.16)

1.1.1.3.3 Irreversible N-N Bond Cleavage of Coordinated Heterocumulene

Addition of 2-diazopropane to (1.40*) produced the novel coordination mode (1.40). The dinuclear 1:1 addition product (1.45)
isolated was structurally characterized by a bent, four-electron type
$\eta^1,\eta^2$-diazoalkane ligand (1.C), with the terminal nitrogen atom
symmetrically bridging the metal-metal single bond (d(Mo-Mo)305.0(2) pm)
and the second nitrogen atom being bonded to one molybdenum atom only.
Thermolysis in toluene promotes an irreversible nitrogen-nitrogen bond
fragmentation of the metal coordinated heterocumulene in (1.45) with
subsequent rearrangement of the intermediate species to yield a
terminal isocyanato ligand and a Mo=Mo double bond (d(Mo-Mo)274.5(2)
pm), symmetrically bridged by a 2-propylidene amido fragment (1.46).\textsuperscript{67}
A chemical test for the Mo=Mo double bond in (1.46) was verified by
reversible addition of carbon monoxide to give [Mo$\alpha$(CO)(N=CMe$_2$)(NCO)]
(1.47).\textsuperscript{67} A bridging methylene between two Mo atoms in which there is
no metal-metal bond (1.48) was obtained from addition of diazomethane
to (1.45) with concomitant loss of nitrogen. Scheme 1.8 illustrates
the reaction scheme of complexes (1.45) through (1.48).

Addition of excess diazomethane to the unsaturated metal-metal
triple bond of (1.40\textsuperscript{6}) was shown by IR, $^1$H and $^{13}$C($^1$H) NMR spectroscopy
to reveal a product (1.49) containing two ($\eta^5$-C$_3$Me$_6$)Mo(CO)$_2$ moieties
held together by a methylene, CH$_2$, and its diazoprecursor, CH$_2$N$_2$,
briding ligands (equation 1.1.17).\textsuperscript{68} Although an X-ray structure
analysis was not undertaken to distinguish between the two possible
coordination modes of the intact diazoalkane ligand ((1.B),(1.C)) for
(1.49), the spectroscopic data suggest a structure similar to that
exhibited for (1.48), presumably also passing through an intermediate
similar to the structure for (1.45) shown in Scheme 1.8.
Scheme 1.8: $M = (n^5-C_5Me_5)Mo(CO)_2$
\[
(1.40) + 2\text{CH}_2\text{N}_2 \rightarrow [(\eta^3 - \text{C}_5\text{Me}_5)_2\text{Mo}_2(\text{CO})_4(\text{CH}_2)(\text{CH}_2\text{N}_2)]
\]

(1.49)

Insertion of a nitride metal moiety into a methylene bridge was first observed from a rearrangement process from complex (1.49) resulting in the dinuclear bis(methylene) amido derivative (1.50), which was characterized by means of X-ray diffraction techniques\(^6\)\(^7\) (equation 1.1.18).

\[
(1.49) \xrightarrow{\Delta} (1.50)
\]

The rearrangement process proposed to convert (1.49) to (1.50) involves a mechanism which initiates from an isomer of (1.49) possessing an \(\eta^1: \eta^2\)-diazomethane ligand (1.4) only.

An extremely facile nitrogen-nitrogen bond rupture to generate complex (1.52) occurs with the metal-metal triple bond of \([(\eta^3 - \text{C}_5\text{Me}_5)_2\text{W}(\text{CO})_2]_2\) (1.51) in the presence of 2-diazopropane or diazocyclopentadiene (equation 1.1.19). This process with subsequent intramolecular rearrangement is particularly facile, even at temperatures well below 0°C and hence the intermediate species, suspected to be structurally analogous to (1.45), could not be isolated.\(^6\)
1.1.1.1.3.4 Rupture of the Metal-Metal Bond

The synthesis of novel O,N-chelate complexes (1.53) containing six-electron donor diazoalkane bridges has been obtained via irreversible cleavage of the metal-metal triple bond of (1.40°) by an unusual insertion reaction of α-keto diazoalkanes into the metal-metal triple bond of (1.40°) (equation 1.1.20). Since it appears that this particular metal-metal bond does not obey a uniform reactivity pattern, in the sense that the diazoalkane's nature bears a decisive influence upon the final products, these insertion reactions of α-ketodiazooalkanes appear to be of general applicability. Although proposed as an intermediate species in equation 1.1.20, neither three membered Mo₃N-ring was observed with either structure (1.B) or (1.C) in the final products of equation 1.1.20. However, these same authors suggest a subsequent rearrangement of the non-isolobal intermediate possessing either structure (1.B) or (1.C) with concomitant metal-oxygen bond making and metal-metal bond cleavage to produce the observed complex (1.53).
1.1.1.4 Carbene Addition to Complexes Constrained by the dppm Ligand

The preference of bis(diphenylphosphino)methane, dppm, for coordinating to metal centers either as a monodentate ligand or as a bridging ligand, as opposed to forming the sterically strained four-membered chelate ring, has invoked extensive organometallic reaction chemistry on the constrained bimetallic core $M_2(\mu$-dppm)$_2$ ($M=$Pt,Pd,Rh,Ir,Mn or Re)$^{72-78}$ involving the two locked metal atoms in close proximity. This bridging ligand offers some degree of molecular flexibility in spanning a range of different metal-metal distances, and has enabled the development of a rich coordination chemistry.$^{77}$ There are some dppm systems which add small molecules, often reversibly, and exhibit catalytic activity in solution for carbon dioxide reduction and the water gas shift. Current emphasis centers on the syntheses, characterization and reaction of heterobimetallic dppm systems.$^{79}$

Carbene or alkylidene, $\text{CRR'}$, or an equivalent two-electron donor ligand addition to a metal-metal single bond is expected to produce an unstable dinuclear species since all known stable dimetallacyclopropane complexes contain either a metal-metal bond or diphosphine bridges to rigidly pin the two metal atoms in close proximity. Indeed it has been postulated that these are necessary structural features to stabilize
\( \mu \)-alkylidene complexes.\(^{21} \) However, the report of the isolation and characterization of the \( \mu \)-methylene complex \([\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu-\text{CH}_2)]\) (1.66) without these features is a known exception.\(^{50} \)

1.1.1.1.4.1 Compounds without Metal-Metal Bonds or Other Bridging Groups

Complexes with two trans \( \mu \)-dppm ligands are most common since complexes with two cis bridging dppm ligands are restricted to the dimethylplatinum(II) derivative \([\text{Pt}_2\text{Me}_4(\mu-\text{dppm})_2]\)\(^{61} \) and the \( \pi \)-allylrhodium(I) complex \([\text{Rh}_2(\eta^3-\text{CH}_2\text{CHMeCH}_2)_2(\mu-\text{dppm})_2]\).\(^{62} \)

The addition of diazomethane to the precursor \([\text{Pt}_2\text{Cl}_2(\mu-\text{dppm})_2]\) (1.54) produces the complex \([\text{Pt}_2\text{Cl}_2(\mu-\text{CH}_2)(\mu-\text{dppm})_2]\) (1.55) without the metal-metal single bond (equation 1.1.21). An X-ray structure determination of (1.55) supported the absence of the Pt-Pt single bond since a Pt-Pt distance of 3.16\( \AA \) and the \( \angle \) (PtCt) of 102\(^\circ \) predominated.\(^{63} \) The mechanism of molecular A-frame formation by methylene insertion into the Pt-Pt single bond of \([\text{Pt}_2\text{X}_2(\mu-\text{dppm})_2]\) (X=Cl,Br,I) has also been studied.\(^{64} \)

![Diagram](image)

Up to three methylene groups from diazomethane have been incorporated into hydridodiplatinum(I) complexes by insertion into metal-metal and metal-ligand bonds,\(^{65} \) as shown in equation 1.1.22.
Although this synthesis is more relevant to the halomethane route discussed in Section 1.1.1.2, the oxidative addition of CHRX₂ (X=Cl, Br, I; R=H, Me) to one of only two known complexes containing three \( \mu \)-dppm ligands, \([M_2(\mu \text{-dppm})_3]\), \(M=\text{Pd}^{88} \) or \( \text{Pt}^{89} \), (1.57), results in complete dissociation of one dppm ligand from the Pd(0) specie (equation 1.1.23) with oxidation at each palladium metal atom by two units in (1.58). 88

1.1.1.4.2 Compounds without Metal-Metal Bonds but with Other Bridging Groups

A novel binuclear rhodium complex containing bridging methylene and acetylene ligands, \([\text{Rh}_2\text{Cl}_2(\mu \text{-CH}_2)(\mu \text{-HFB})(\mu \text{-dppm})_2]\), HFB=CF₃C≡C≡C≡F, (1.59), 88 was one of the first bridging methylene complexes without an accompanying metal-metal bond to be characterized by X-ray crystal-
lography (equation 1.1.24). This unambiguous confirmation that a μ-methylene species could be synthesized without accompanying metal-metal bonds re-emphasizes the ability of the bridging dppm ligand to stabilize unusual ligand geometries and bonding modes by fixing the metal atoms at the required separation.

\[ \text{CH}_2\text{N}_2 \xrightarrow{-78^\circ\text{C}} \]

(1.59); R=CF₃

1.1.24

1.1.1.1.4.3 Compounds with Metal-Metal Bonds and Other Bridging Groups

The reversible addition of small diazoalkane molecules to the vacant 'pocket' site between two rhodium metal atoms to yield A-frame complexes is illustrated in equation 1.1.25. The presence of the metal-metal bond in (1.60) is predictable in terms of the normal electron counting procedures.⁹⁰
1.1.1.2 The Dihaloalkane Method

Dihalomethane and its derivatives are another possible carbene source (equation 1.1.26)

\[
[M-M]^2^- + X_2CRR' \xrightarrow{-2X^-} M \quad \text{(1.1.26)}
\]

This reaction type of using geminal dihaloalkanes for the introduction of \( \mu \)-alkylidene moieties into organometallic substrates has not been as extensively studied as that of the diazo method. This is presumably due to reports that only a successful suppression of halogen transfer to the metal centers will encourage high yields of methyleneated products.\(^6\) Furthermore, small yields of desired \( \mu \)-dihalomethylene complexes are observed from reaction of a neutral as opposed to an anionic organometal with the respective dihaloalkanes. This fact is supported by the negligible yields of speculated difluoromethylene-bridged species [Co\(_2\)(CO)\(_6\)(\( \mu \)-CF\(_2\))\(_2\)] and [Fe\(_2\)(CO)\(_6\)(\( \mu \)-CO)-\( \mu \)-CF\(_2\))\(_2\)] from reported photolysis of [Co(CO)\(_3\)NO]\(^9\) and of [Fe(CO)\(_3\)]\(^9\) respectively in the presence of CF\(_2\)Br\(_2\), both metal substrates with pronounced dehalogenation tendencies.

A 0.6% yield of the target complex cis-[Cp\(_2\)Fe\(_2\)(CO)\(_4\)(\( \mu \)-CO)-\( \mu \)-C(CN)\(_2\))] from the reaction of the highly nucleophilic [CpFe(CO)\(_4\)] anion and Br\(_2\)C(CN)\(_2\), along with the principal reaction products, coupling adduct [Cp\(_2\)Fe\(_2\)(CO)\(_4\)] and [CpFe(CO)\(_3\)Br], was attributed to the halogenating tendencies of the organic precursor due to the relatively positive bromine substituents.\(^9\)
Dihalomethane has been used in reactions with $[\text{Fe}_2(\text{CO})_6]^{2-}$, 
$[\text{Os}_2(\text{CO})_6]^{2-}$ and the radical anion $[\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2]^-$ (1.63) to form the 
methylene-bridged species (1.61), (1.62) and (1.64) respectively 
(equations 1.1.27, 1.1.29); each product exhibiting a metal-metal bond.

No mechanistic details are available for any of these reactions.

However, replacement of the cation $\text{Na}^+$ with $\text{NET}_4^+$ in the dinuclear iron 
complex $[\text{Fe}_2(\text{CO})_6]^{2-}$ drastically increases the yield of $[\text{Fe}_2(\text{CO})_6$
$(\mu-\text{CH}_2)],$ (1.61). Since the disodium salt did not allow the isolation 
of (1.61), an undetermined side reaction between (1.61) and NaI is 
suspected; NaI is more soluble in acetone or THF than Et$_4$NI.

\[
(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{CO})_6] + \text{CH}_2\text{I}_2 \rightarrow [\text{Fe}_2(\text{CO})_6(\mu-\text{CH}_2)]^+ \quad \text{1.1.27}
\]

\[
\text{Na}_2[\text{Os}_2(\text{CO})_6] + \text{CH}_2\text{I}_2 \rightarrow [\text{Os}_2(\text{CO})_6(\mu-\text{CH}_2)] + 2\text{NaI} \quad \text{1.1.28}
\]

\[
\text{Na}[\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2]^+ + \text{CH}_2\text{I}_2 \rightarrow \text{trans-}[\text{Cp}_2\text{Co}_2(\text{CO})_2(\mu-\text{CH}_2)] + \quad \text{1.1.29}
\]

\[
[\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2] + 2\text{NaI} \quad \text{1.1.29}
\]

By contrast, the $\mu$-methylene complex $[\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu-\text{CH}_2)]$ (1.66),
containing neither a metal-metal bond or an additional bridging ligand,
was prepared by reacting Na\([\text{CpRu(CO)}_2]\) with 0.5 equivalent of dichloromethane at \(-35^\circ C\) in THF (equation 1.1.30). Complex (1.66) decomposes over a 24 h period, yet can be kept indefinitely at \(-35^\circ C\). Equation 1.1.31 illustrates that photolysis of (1.66) yields the cis and trans isomers of the metal-metal bonded \(\mu\)-methylene dimer (1.67)\(^a\), earlier prepared from the appropriate Wittig reagent and complex (1.9)\(^b\), as shown by equation 1.1.37.

\[
\text{Na[}\text{CpRu(CO)}_2]\text{ + }\frac{1}{2}\text{CH}_2\text{Cl}_2 \rightarrow \frac{1}{2}\text{[Cp}_2\text{Ru}_2(\text{CO})_4(\mu-\text{CH}_2)]} \quad 1.1.30
\]

(1.66)

\[
\begin{align*}
\begin{array}{c}
\text{OC} \quad \text{CO} \\
\text{Ru} \quad \text{Ru} \\
\text{Cp} \quad \text{Cp} \\
\text{CH}_2 \\
\text{C} \\
\text{O} \\
\end{array}
\end{align*}
\quad \text{hv} \quad \begin{align*}
\begin{array}{c}
\text{OC} \\
\text{Ru} \quad \text{Ru} \\
\text{Cp} \quad \text{Cp} \\
\text{CH}_2 \\
\text{C} \\
\text{O} \\
\end{array}
\end{align*}
\quad \begin{align*}
\begin{array}{c}
\text{OC} \quad \text{CO} \\
\text{Ru} \quad \text{Ru} \\
\text{Cp} \quad \text{Cp} \\
\text{CH}_2 \\
\text{C} \\
\text{O} \\
\end{array}
\end{align*}
\quad \begin{align*}
\text{CpRu} \quad \text{RuCp} + \text{CO} \\
\text{C} \\
\text{O} \\
\end{align*}
\quad 1.1.31
\]

(1.66) (1.67)

Treatment of the radical anion [\(\text{Cp}_2\text{CO}_2(\mu-\text{CO})_2\)] (1.63) with gem-diodoalkanes (\(\text{RR'}\text{Cl}_2; \text{R}=\text{H}, \text{alkyl}\)) leads to a class of dicobalt \(\mu\)-alkylidene complexes (Scheme 1.9). For \(\mu\)-alkylidene complexes (1.68) containing one hydrogen atom of diiodomethane replaced by an alkyl group, spectroscopic studies revealed isolated materials from the reaction of \(\text{RCI}_2; \text{R}=\text{H}, \text{Et}, \text{n-Bu}, \text{t-Bu}\) with (1.63) are all mixtures of cis (ca. 5%) and trans isomers in all but the neopentyl-substituted complex (\(\text{R}=\text{H}, \text{R'}=\text{t-Bu}\)), which is apparently bulky enough to shift this equilibrium to a 20% cis content. Decreases in the yields of (1.68) parallel a more sterically demanding methylene alkyl substituent.
Scheme 1.9: Diolefin addition to the radical anion [Co₂(CO)₆⁻].

(168): R = H, Et, n-Bu, i-Bu

(169): R = R' = Me, Et, CD₃Me

(170): R = R' = Me, Et

(163):

Na
Substitution of both hydrogen atoms of diiodomethane with alkyl groups produces a mixture on reaction with Na\(\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2\)\(\text{I}_2\). The major product is the trans isomer (1.69) whose carbonyl stretching frequencies indicate both terminal and bridging carbonyl structures exist in solution, presumably interchanging rapidly on the NMR time scale. The minor product (1.70), also generated by decarbonylation via photolysis or thermolysis of (1.69), is a stable, unsaturated \(\mu\)-alkylidene complex.\(^5\)

Scrambling of [\(\text{Cp}_2\text{Co}_2(\mu-\text{CH}_2)\)] (1.64) and [(\(\eta^5-\text{C}_5\text{Me}_5\))\(\text{Co}_2(\mu-\text{CH}_2)\)] (1.34) occurs with the formation of [\(\text{CpCo(\mu-\text{CH}_2})\text{Co}(\eta^5-\text{C}_5\text{Me}_5)(\text{CO})\)] (1.71). Also treatment of (1.64) with [\(\text{CpRh(\mu-\text{CH}_2})\text{Rh(\mu-\text{CH}_2})\text{Cp})\)] (1.16a) leads to metal-metal exchange reactions (equation 1.1.33) resulting in the formation of (1.16b), a heteronuclear \(\mu\)-methylene complex (1.72) containing a Co-Rh bond, and the structurally analogous homonuclear complex [\(\text{Cp}_2\text{Rh}_2(\mu-\text{CH}_2)\)] (1.20).\(^5\)

\[
\begin{align*}
\text{[Cp}_2\text{Co}_2(\mu-\text{CH}_2)] & + [(\eta^5-\text{C}_5\text{Me}_5)_2\text{Co}_2(\mu-\text{CH}_2)] & \rightarrow & \\
(1.64) & & (1.34) & \\
2[\text{CpCo}(\mu-\text{CH}_2)\text{Co}(\text{CO})](\eta^5-\text{C}_5\text{Me}_5)] & & (1.71) & \\
& & (1.1.32) & \\
(1.64) + [\text{CpRh(\mu-\text{CH}_2})\text{Rh(\mu-\text{CH}_2})\text{Cp})] & \rightarrow & \text{[Cp}_2\text{Rh}_2(\mu-\text{CH}_2)] & + \\
(1.16a) & & (1.20) & \\
[\text{CpCo}(\mu-\text{CH}_2)\text{Rh(\mu-\text{CH}_2})\text{Cp})] & + & [\text{CpCo(\mu-\text{CH}_2})\text{Rh(\mu-\text{CH}_2})\text{Cp})] & \\
(1.72) & & (1.16b) & \\
& & (1.1.33) & 
\end{align*}
\]
Only two examples of the direct reaction of geminal dihaloalkanes with neutral organometallic substrates are known. These two examples apply to the low oxidation state complexes $[\text{Pd}_2(dppm)_3]$ and $[\text{Au}_2(\text{CH}_2\text{PMe}_2\text{CH}_2)_2]$ (1.73). An alkylidene-bridged dipalladium A-frame complex (1.58), has been synthesized employing dihalomethanes as the carbene source (equation 1.1.23).\textsuperscript{88}

Methylene bridging of two gold atoms has been achieved via an oxidative addition of dihalomethanes to the cyclic ylide complex (1.73) to form the bridged bicyclic compounds (1.74) in 60-65% yield, virtually free of by-products (equation 1.1.34).\textsuperscript{96}

\begin{align*}
\text{(1.73)} & \quad \text{(1.74): } R=\text{Me, Ph; } X=X'=\text{Cl, Br, I} \\
\text{C-PR}_2\text{-C} &= (\text{CH}_2)_2\text{PR}_2 \\
R=\text{Ph; } X=\text{Cl, } X'=\text{Br, I} & \quad 1.1.34
\end{align*}

1.1.1.3 Syntheses from Wittig Reagents

Since the Ziegler group discovered that a bridging carbonyl ligand can be replaced by :CHR units originating from Wittig reagents, ylides have provided another carbene source as a synthetic approach to $\mu$-alkylidene complexes (equation 1.1.35). The availability of numerous ylides should give this third and final direct synthetic method general
The alkylidene-bridged species \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHR})]\) (1.76) has been prepared with a 3:1 ratio of the cis to trans isomers by heating \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2]\) (1.75) with \(\text{Ph}_3\text{P}=\text{CHR}\) in dioxane (equation 1.1.36)\(^8\), but an attempt to obtain the ruthenium analogues \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHR})]\) (1.11) from \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})_2]\) under the identical conditions proved unsuccessful.\(^9\)

\[
\begin{align*}
[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2] + \text{Ph}_3\text{P}=\text{CHR} & \xrightarrow{\Delta} [\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHR})] \\
(1.75) & \quad (1.76): R=H, \text{Me}, n-\text{Pr}
\end{align*}
\]

An important part in generating the alkylidene-bridged ruthenium dimers (1.11) is the reactivity of the precursor complex (1.9); (1.9) is formed from diphenylacetylene addition to \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})_2]\).\(^{19,34}\) While \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})_2]\) is unreactive, \([\text{Cp}_2\text{Ru}_2(\text{CO})(\mu-\text{CO})(\mu-\text{C}(\text{O})\text{C}_2\text{Ph}_2)]\) (1.9) readily reacts with ylides\(^9,35\), diazoalkanes\(^9\) (section 1.1.1.1.1) and allenenes\(^19\) (section 1.1.2.2).

Refluxing complex (1.9) with an ylide \(\text{Ph}_3\text{P}=\text{CHR}\) in toluene rapidly yields cis and trans isomers of the \(\mu\)-alkylidene complexes \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHR})]\) (1.11), shown by equation 1.1.37. The more sterically crowded \(\text{Ph}_3\text{P}=\text{CMe}_2\) produced only a negligible yield of the respective isomers.\(^9\)
The reaction of (1.9) with the ylide Ph₃P=CHCH=CH₂ generated the anticipated μ-alkylidene complex [Cp₂Ru₂(μ-μCO)(μ-CHCH=CH₂)] (1.11e) in only 13% yield, with an intramolecular rearrangement to form the cis,trans isomers in a 1.5:1 ratio, the major product being the substituted allyl complex (1.77). Complex (1.77) undergoes a Ru-Ru bond formation upon u.v. irradiation to generate (1.78), presumably via a sixteen-electron σ-allyl species, illustrated in equation 1.1.38.
1.1.2 Indirect Methods

1.1.2.1 The Carbene Path

Another source of $\mu$-alkylidene complexes is the modification of a mononuclear metal carbene complex by attack with nucleophilic, coordinatively unsaturated metal species M', according to equation 1.2.1.

$$
R_C-R' \\
M' + M=\stackrel{\text{C}}{\text{M}} \\ 
\rightarrow \\
\text{M} \\
\text{M} \\
1.2.1
$$

The dipolar character of the metal-carbon bond in the mononuclear metal-carbene complexes makes them susceptible to attack by low valent transition metal complexes. This encouraged an investigation centered on zero valent platinum complexes, which on reacting with mononuclear metal-carbene compounds, could produce dimetallacycloprenanes containing heteronuclear metal-metal bonds. Evidence for the carbene path was first provided by the synthesis of the diplatinum complex [Pt$_2$(COD)$_2$(μ-C(CF$_3$)$_2$)$_2$].

Experiments and subsequent X-ray crystallography studies confirmed the synthesis of asymmetric dinuclear $\mu$-alkylidene complexes by addition of [Pt(C$_2$H$_4$)(PMe$_3$)$_2$], generated in situ from [Pt(C$_2$H$_4$)$_3$], to the appropriate metal-carbene complex LM(CRR') (e.g., [W(CO)$_3$(C(OMe)R)]$^{1,5,18}$, [CpM(CO)$_2$(C(OMe)R)]$^{17}$ (M=Mn,Re; R=p-Me-Ph) illustrated by equation 1.2.2.

$$
\text{LM(CRR')} + \text{Pt(COD)}_2 \rightarrow \text{LM} \text{Pt(PMe}_3)_2 \\
\rightarrow 2\text{PMe}_3 \\
1.2.2
$$
Structural studies on the heteronuclear dimetallacyclopropanes have revealed that the geometry of the dimetallacyclopropane ring systems are susceptible to the nature of the ligands on the metal atoms.\textsuperscript{21} Hence the stability of these ring systems is enhanced as the metal becomes a better donor. For example, the $\mu$-C-W distance decreases for $[\text{LW}(\mu\text{-C(O\text{Me})Ph})\text{Pt(PMe}_3)_2]$ when $\text{L}=(\text{CO})_2$ (248(1) pm) is replaced by $\text{L}=(\text{CO})_2\text{PMe}_3$ (237(1) pm).

Homonuclear $\mu$-methylene complexes have also been synthesized with precursor Fischer-type carbenes. For the tungsten reaction (Scheme 1.10),\textsuperscript{89} the mechanism involves a rapid dimerization of the terminal alkylidene (1.80) and terminal vinylidene (1.81) products from the precursor $[\text{W(CO)}_5\text{(C(O\text{Me})Me)}]_2$ (1.79) to give a dimetallacyclobutane (1.82). The $\mu$-alkylidene product (1.83) stems from hydrogen migration in the dimetallacyclobutane.

Another example for the preparation of a homonuclear $\mu$-alkylidene complex via the carbene path is provided by initial treatment of either $\text{Re}_2(\text{CO})_{10}$ or the preformed-metal carbene $[\text{Re}_2(\text{CO})_9\text{(C(O\text{Me})R)}]_2$ (1.84) with excess organolithium reagent $\text{LiR}$.\textsuperscript{90} Subsequent alkylation by means of $\text{Me}_3\text{O}^+\text{BF}_4^-$ then generates the doubly bridged cis-$\mu$-(methoxy)(aryl)methylene system (1.85), illustrated in equation 1.2.3. This result, coupled with the former tungsten reaction mechanism, suggests the driving force for the homodinuclear $\mu$-alkylidene complex (1.83) and (1.85) formation is the low stability of the, transiently synthesized unsubstituted terminal alkylidene.
Scheme 1.10
1.1.2.2 The Acetylene Route

A simple rearrangement of a σ,η²-bonded vinyl ligand is the second indirect method leading to the alkylidene-bridged species (equation 1.2.4).

\[
\text{RC} = \text{CR}_2' + \text{H}^- \rightarrow \text{RC} = \text{CR}_2'H
\]

The acetylene path was first discovered by Knox et al.\textsuperscript{18} when their work succeeded in transforming an acetylene via a sequence of reactions initially involving the dimetallacycle \([\text{Cp}_2\text{Ru}_2(\text{CO})(\mu-\text{CO})-\text{(C} \equiv \text{C})\text{C}_2\text{H}_2]\) (1.86), into the \(\mu\)-ethyldene derivative \(\text{cis-[Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHCH}_3)]\) (1.11b). Thermolysis of (1.86) in refluxing toluene, formed from \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})_2]\) and acetylene and structurally analogous to the dimetallacycle \([\text{Cp}_2\text{Ru}_2(\text{CO})(\mu-\text{CO})-\text{(C} \equiv \text{C})\text{C}_2\text{Ph}_2]\) (1.9), generates a mixture of the cis and trans isomers of the corresponding \(\mu\)-vinylidene isomers (1.11f). Subsequent protonation of (1.11f) gives the \(\mu\)-ethyldyne complex \(\text{cis-[Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHCH}_3)]BF_4^-\) (1.87). Hydride attack (\(\text{NaBH}_4\)) yields the \(\mu\)-ethyldene complex \(\text{cis-[Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHCH}_3)]\) (1.11b).
This reaction sequence is illustrated in equations 1.2.5 and 1.2.6.

\[ \text{[Cp}_2\text{Ru}_2(\text{CO})(\mu-\text{CO})(\text{C}(\text{O})_2\text{H}_2)] \xrightarrow{110^\circ \text{C} \text{ toluene}} \text{[Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{C}==\text{CH}_2)] \]

\[ \text{(1.86)} \]

\[ \text{cis-}[\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHMe})] \]

\[ \text{(1.11f)} \]

An alternative synthetic route to this same \( \mu \)-ethylidene complex (1.11b) or its iron congener (1.76b) with the trans configuration involves a more complex rearrangement, shown in Scheme 1.11. The dimetallacycle (1.86) is irreversibly protonated with HBF\(_4\) to form the cationic \( \sigma,\eta^2 \)-vinyl derivative (1.88). A similar type of \( \sigma,\eta^2 \)-vinyl derivative was observed for the hydride-bridged tetraosmium olefin complex \([\text{Os}_4\text{H}_3(\text{CO})_1(\mu-\text{CR==CHR'})])\). Deuterium labelling studies have determined that the final \( \mu \)-ethylidene species cis-[Cp\(_2\)Ru\(_2\)(CO)\(_2\)(\mu-CO)-(\mu-C\text{HCH}_3)] (1.11b) and trans-[Cp\(_2\)Fe\(_2\)(CO)\(_2\)(\mu-CO)(\mu-C\text{HCH}_3)] (1.76b) stem from a hydride attack at the \( \beta \)-vinyllic carbon site; \( \alpha \)-hydride attack accounts for the small yield of the \( \eta^2 \)-ethylenic complex (1.89).
Both the cis and trans isomers (2:3) of the alkylidene-bridged ruthenium dimer \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHCH}_3)]\) \((1.91)\) have been synthesized employing an allene as an alkylidene source (equation 1.2.7).\textsuperscript{100} The initial allyl adduct \((1.9)\) is readily protonated to give a \(\sigma,\eta^2\)-vinyl complex \((1.90)\), analogous in structure to that illustrated for \((1.88)\), which on regiospecific hydride attack at the \(\beta\)-vinyllic carbon site produces the target complex \((1.91)\) in 60% overall yield (equation 1.2.7). All attempts to convert the vinyl-bridged cation \([\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu,\eta^2-\text{CHCH}_2)]^+\) to the respective dimetallacyclopropane proved inert upon treatment with identical or similar nucleophiles.\textsuperscript{101}
1.2 Bonding in Bridging Alkylidene Complexes

Theoretical descriptions of the bonding in bridging alkylidene complexes have centered on molecular orbital studies utilizing frontier orbital extended Hückel calculations. These calculations regard the methylene fragment, CRR', as a two-electron ligand, as opposed to a bridging four-electron donor, CRR²⁻. The general conclusion of the molecular calculations credits the stability of the alkylidene-bridge to an electron transfer from a metal-metal antibonding HOMO to the unfilled alkylidene p orbital. Four-electron bridging donor ligands are not capable of supporting this type of electron transfer, as evidenced by the absence of such species bridged between metals with higher d-electron counts. A comprehensive study into the bonding in Mn₄L₁₀ complexes suggested the μ-alkylidene fragment to be an excellent σ-donor and π-acceptor with respect to the isolobal μ-CO or μ-SO₂ fragments, supportive of the assignment as a two-electron donor ligand. Thus alkylidene-bridged species are further stabilized by electron-withdrawing methylene substituents.

The MO diagram of μ-methylene bis(dicarbonyl(η⁵-cyclopentadienyl)-manganese, [Cp₂Mn(η²-CX₄)}₄(μ-C₄H₈)] (1.92), was constructed from the methylene CH₂ orbitals and the hypothetical Cp₂Mn₄(CO)₄ dimer...
orbitals\textsuperscript{21,104}. A filled orbital of the methylene group acts as a sigma donor to the suitable LUMO of the dinuclear fragment. Similarly, the HOMO of the dinuclear framework donates electron density to the empty $p\pi$ orbital of the methylene fragment. Since the methylene was shown to be a better acceptor than donor in this system, the net result of these two interactions is the transfer of electron density from the metal-metal antibonding HOMO to an empty orbital predominantly comprised of carbon $p\pi$ character, producing a localization of electron density on the bridgehead carbon atom. These MO conclusions suggest that only asymmetric heterodimetallacyclop propane framework structures exist since any strengthening of a heterodimetallacyclop propane M-C bond is associated with the electron donor ability of the respective metal atom and hence correlated to the nature of the peripheral ligands.

The substantial localization of electron density on the bridgehead carbon atom in [CP$_2$Mn$_2$(CO)$_4$(μ-CH$_2$)] (1.92) has been confirmed by experimental studies on this alkyldiene-bridged species via an X-ray diffraction determination\textsuperscript{105} and two independent photoelectron studies.\textsuperscript{104,106}

A detailed extended Hückel molecular orbital analysis was also reported for [CP$_2$Rh$_2$(CO)$_4$(μ-CH$_2$)] (1.20).\textsuperscript{2} This methylene-bridged rhodium complex was envisioned to derive from the molecular overlap of the hypothetical CP$_2$Rh$_2$(CO)$_2$ dimer, containing a metal-metal double bond, with the CH$_2$ fragment; a qualitative description similar to the Walsh description of cyclopropane formation. The resultant dimetallacyclop propane is stabilized by an overall electron transfer from a Rh-Rh $\sigma$ bond, the HOMO in the CP$_2$Rh$_2$(CO)$_2$ fragment, into an empty orbital containing metal $\pi^*$ and carbon $p$ character.
Consequently the bridgehead methylene carbon becomes a nucleophilic center and the $^{13}$C($^4$H) NMR data reflect this greater electron density localized on the carbon bridge with respect to the carbene carbon of the electrophilic Fischer-type carbene complexes, $\text{L}_n\text{M}=$CRR$'$.\textsuperscript{21,23,24}

1.3 Geometry of the Alkylidene Bridge

The vast number of structurally characterized $\mu$-alkylidene complexes extensively reviewed by Herrmann\textsuperscript{21,23} has prompted several generalizations regarding the stability of these bridging alkylidene structures.

Most alkylidene-bridged species are air, thermally stable solids and appear at least as stable as the corresponding carbonyl-bridged complex in the absence of steric constraints imposed by the methylene carbon substituents.

The geometry of all known dimetallacyclop propane framework atoms is generally symmetric, described by an isosceles triangular array. However, the presence of semibridging carbonyls generally dictates an asymmetric methylene bridge, more characteristic of the heterodinuclear $\mu$-alkylidene complexes. Metal-metal distances for all alkylidene-bridged complexes are slightly longer (ca.15 pm) than the predicted values from consideration of the addition of Pauling covalent radii of the two respective single bonded metal atoms.

Figure 1.2 illustrates the internal $\text{M-C-M}$ angle $\alpha$ and the external R-C-R$'$ angle $\beta$. Throughout all the variations encompassing both the nature of the metal and the carbene substituents R and R$'$ in the characterized $\mu$-alkylidene complexes (Table 1.1), $\alpha$ remains virtually unchanged ($61\pm7^\circ$). The observed magnitude of $\alpha$ is consistent with
Figure 1.2: Geometry of the Alkylidene Bridge
Hoffmann's calculations\textsuperscript{103} which predict small internal angles about 80° for both \(\mu\)-alkylidene and \(\mu\)-carbonyl species. The magnitude of the metal-metal separation clearly determines the acuteness of the internal angle \(\alpha\) and thus this bimetallic bonding interaction is responsible for the acute angled deviation of \(\alpha\) from the anticipated tetrahedral result (109°28').

External angles \(\beta\) are typically in the 104-110° range (105±13°). The angle \(\beta\) lacks any correlation with either \(\alpha\) or the nature of the metals or peripheral ligands and furthermore, exhibits no predictable response to steric effects governed by the methylene substituents \(R\) and \(R'\).

1.4 Characterization of Bridging Alkylidene Complexes

1.4.1 \(^{13}\text{C}\{^{1}\text{H}\}\text{NMR}\)

Although the majority of \(\mu\)-alkylidene compounds have been characterized with X-ray crystallography, \(^{13}\text{C}\{^{1}\text{H}\}\text{NMR}\) is a useful spectroscopic technique to distinguish amongst bridging alkylidenes (M-CRR'-M), terminal alkylidenes (M=CRR') and alkanediyl derivatives (M-(CRR')\(_{2}\)-M). The nucleophilic metal carbene [\(\text{Cp}_{2}\text{TaN} (=\text{CH}_{3})(\text{CH}_{3})\)] [8 (\(\text{CH}_{3}\) at 228)] is one of the few mononuclear metalcarbenes which are close to the \(\mu\)-methylenic compounds in terms of their \(^{13}\text{C}\{^{1}\text{H}\}\text{NMR}\) chemical shifts. For example, the complex [\(\text{Cp}(\text{CO})_{2}\text{Mn}=\text{CMe}_{2}\)] exhibits a peak at 8 (\(\text{CMe}_{2}\) 372.75 ppm in its \(^{13}\text{C}\{^{1}\text{H}\}\text{NMR}\) spectrum. The resonance range for compounds in each of these three categories is listed in Figure 1.3\textsuperscript{21,22} and data from some relevant examples are tabulated in Table 1.2.

Alkylidene-bridged complexes exhibit carbon resonances which are
<table>
<thead>
<tr>
<th>Class</th>
<th>$\delta^{13}\text{C}; \text{ ppm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_M = \text{CRR'}$</td>
<td>240-370</td>
</tr>
<tr>
<td>$L_M \rightarrow \text{CRR'} \rightarrow \text{ML}_M$</td>
<td>60-210</td>
</tr>
<tr>
<td>$L_M \rightarrow (\text{CRR'})_n \rightarrow \text{ML}_M$</td>
<td>0-10</td>
</tr>
<tr>
<td>$M \rightarrow \text{CRR' R''}; R'' = \text{H, alkyl}$</td>
<td>-30.5</td>
</tr>
</tbody>
</table>

Figure 1.3: $^{13}\text{C}(^1\text{H})$ NMR Spectroscopic Diagnosis of the Alkylidene Bridge
considerably shielded with respect to the carbon resonances of their terminal alkyldiene counterparts. Bonding predictions based on Huckel-type MO calculations for dimetallacyclop propane complexes reflect this average upfield shift of 100-200 ppm for μ-alkyldiene complexes versus terminal carbene complexes due to the greater localized electron density on the bridgehead methylene carbon atom. The μ(α,ω)-alkanediyl complexes, represented by the general formula L2M-(CH2)n-ML2(2≤n≤10), are easily distinguished from metal alkyls since the chemical shift range of the latter is -30-5 ppm. Complex (1.66), the μ-methylene ruthenium dimer with no metal-metal bond, appears to be a unique case. In fact, it is the only μ-methylene complex not containing a metal-metal bond whose $^{13}$C($^1$H) NMR resonance has been determined.

1.4.2 $^1$H NMR

Herrmann$^{21,23}$ states that if an α-hydrogen(s) atom, a direct substituent of the methylene bridgehead carbon, exists then $^1$H NMR spectroscopy, although not diagnostic as compared to $^{13}$C($^1$H) NMR with differentiating between alkyldiene-bridged and mononuclear metal carbene complexes, can specify the existence of a metal-metal bond. Figure 1.4 reveals the resonance ranges of $^1$H NMR data for both the alkanediyl and metal alkyl complexes are significantly different than the corresponding $^1$H NMR resonance ranges for the alkyldiene-bridged or mononuclear metal carbene complexes. However, it appears that the chemical shift of the dimetallated methylene bridge protons is not diagnostic for the presence or absence of a metal-metal single bond since that observed for complex (1.59) in Table 1.3 is at significantly lower field than those observed in the related species where no
Class

M — CHR
M — CHR — M
M — (CHR)x — M
M — CHRR

6 CHR; ppm

9-11
5-11
1-3
-1-1

Figure 1.4: 1H NMR Spectroscopic Diagnosis of the Alkylidene Bridge
metal-metal bond is proposed, but lies within the range observed (5.97-10.68 ppm) in metal-metal bonded species.\textsuperscript{89}

The \(^1\)H NMR resonance parallels the respective \(^{13}\)C(\(^1\)H) NMR chemical shift in \(\mu\)-alkylidene complexes displaying an upfield shift from the corresponding metal carbene resonance, again attributed to the higher electron density localized on the bridgehead carbon atom (Table 1.2). This fact is reinforced by the presence of either an electron-donating peripheral ligand substituent or an electron-withdrawing methylene-bridged substituent in dimetallacyclop propane systems. A peripheral Cp ligand can provide valuable information as to the symmetry of the molecule.

No observable trends have emerged with respect to the magnitude of \(^1\)J(C,H) or \(^2\)J(H,H) from \(\mu\)-alkylidene or \(\mu\)-methylen complexes respectively.\textsuperscript{21,23}

1.4.3 \(^{31}\)P(\(^1\)H) NMR

The incorporation of phosphine ligands in \(\mu\)-alkylidene complexes can provide useful \(^{31}\)P(\(^1\)H) NMR data to determine the equivalence, or non-equivalence, of terminal or peripheral dimetallacyclop propane framework ligands. Equivalent phosphine ligands, like Cp ligands, can imply a symmetric structure and thus elucidate the presence of a single bridging alkylidene ligand rather than a terminal alkylidene.

1.4.4 Mossbauer Spectroscopy

The equivalence of two iron atoms supported a symmetric bridge in the Mossbauer spectrum of the complex \([\text{Fe}_2(\text{CO})_6(\mu-\text{CH}_2)]\) (1.61).\textsuperscript{8}
1.4.5 Mass Spectrometry

The disadvantage of using the MS technique with transition metal complexes is that the thermal decomposition of the complex on volatilization may prevent the detection of parent ion peaks. However, the fragmentation pattern can still yield valuable information concerning the structure of the complex. Terminal carbonyl ligands, successive losses of m/e 28, are generally lost prior to fragmentation of the three-membered frameworks of μ-alkylidene compounds. Subsequent rearrangement reactions of the dinuclear fragment ions L\textsubscript{2}M\textsubscript{2}(CH\textsubscript{2})\textsuperscript{+} depend strongly upon the nature of the metals.\textsuperscript{107} The direct elimination of the methylene unit has never been observed from the parent ion peak or from any fragment ion, yet methane is clearly fragmented from the pentamethylcyclopentadienyl derivative [(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Rh\textsubscript{2}(CO)\textsubscript{2}(μ-CH\textsubscript{2})] (1.29). Alternatively, the analogous cyclopentadienyl cobalt derivative eliminates C\textsubscript{8}H\textsubscript{8} from the key fragments Cp\textsubscript{2}CO\textsubscript{2}(CH\textsubscript{2})\textsuperscript{+}. The μ-alkylidene ligands can rearrange within the metal core and then eliminate olefins (e.g. C(=CH\textsubscript{3})CH\textsubscript{3} → C\textsubscript{2}H\textsubscript{4}).\textsuperscript{21}

The formation of carbido species L\textsubscript{2}M\textsubscript{2}C\textsuperscript{+} has occurred for some μ-alkylidene complexes.

1.4.6 Infrared Spectroscopy

IR techniques are useful in identifying the geometry of the other, nonalkylidene ligands. Since IR is extremely useful in distinguishing terminal or bridging carbonyls, the majority of the work discussed in this thesis employed IR techniques to monitor reaction progress for these dinuclear carbonyl systems by revealing an appropriate loss or gain of a bridging carbonyl(s) stretch. Table 1.4
lists the infrared carbonyl stretching frequencies for some representative μ-alkylidene complexes.
Table 1.1: Structural Data for Some μ-Alkylidene Transition Metal Complexes Belonging to the Dinuclear Type [μ-CRR']\[ML_y]_2

<table>
<thead>
<tr>
<th>Complex</th>
<th>d(M-M)/d(M-M') (pm)</th>
<th>d(M-CRR')/d(M'-CRR') (pm)</th>
<th>α (deg)</th>
<th>β (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Class I: Compounds with Metal-Metal Bonds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Cp}_2\text{Ru}(CO)_2(\mu-\text{CO})(\mu-\text{CH}_2)] (1.11a))</td>
<td>207.7(1)</td>
<td>207.7(6)</td>
<td>81.3(2)</td>
<td>126(5)</td>
<td>9</td>
</tr>
<tr>
<td>([\text{Cp}_2\text{Rh}_2(CO)_2(\mu-\text{CH}_2)] (1.20))</td>
<td>207.9(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\left[\eta^5-\text{C}_5\text{Me}_5\right]_2\text{Rh}_2(CO)_2(\mu-\text{CH}_2)] (1.29))</td>
<td>205.0(1)</td>
<td>202.6(8)</td>
<td>82.5(4)</td>
<td>109.4(10)</td>
<td>54</td>
</tr>
<tr>
<td>(\left[\eta^5-\text{C}_5\text{Me}_5\right]_2\text{Rh}_2(\mu-\text{CO})(\mu-C\text{Ph}_2)] (1.30))</td>
<td>209.4(6)</td>
<td>207.8(10)</td>
<td>75.3(2)</td>
<td>111.1(5)</td>
<td>54</td>
</tr>
<tr>
<td>([\text{Cp}_2\text{Co}_2(CO)<em>2(\mu-\text{CHO})</em>{2}\text{Et}]))</td>
<td>209.4(6)</td>
<td>207.8(10)</td>
<td>75.3(2)</td>
<td>111.1(5)</td>
<td></td>
</tr>
<tr>
<td>([\text{CO}]_2W(\mu-C(\text{OME})\text{Ph})\text{Pt}(\text{PMe}_3)_2])</td>
<td>204.1(1)[Pt]</td>
<td>207.8(10)</td>
<td>75.3(2)</td>
<td>111.1(5)</td>
<td>54</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BCO%7D">\text{PMe}_3</a>_2W(\mu-C(\text{OME})\text{Ph})\text{Pt}(\text{PMe}_3)_2])</td>
<td>203.1(1)[Pt]</td>
<td>207.8(10)</td>
<td>75.3(2)</td>
<td>111.1(5)</td>
<td>54</td>
</tr>
</tbody>
</table>

**Class II: Compounds without Metal-Metal Bonds**

<table>
<thead>
<tr>
<th>Complex</th>
<th>d(M-M)/d(M-M') (pm)</th>
<th>d(M-CRR')/d(M'-CRR') (pm)</th>
<th>α (deg)</th>
<th>β (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cp}_2\text{Ru}_2(CO)_4(\mu-\text{CH}_2)] (1.66))</td>
<td>360</td>
<td></td>
<td>123</td>
<td>NR</td>
<td>80</td>
</tr>
<tr>
<td>([\text{Rh}_2\text{Cl}_2(\mu-\text{CH}_2)(\mu-\text{HPB})(\mu-\text{dppm})_2]\ (1.59))</td>
<td>346.4(1)</td>
<td></td>
<td>114.5(5)</td>
<td>NR</td>
<td>89</td>
</tr>
<tr>
<td>([\text{Pt}_2\text{Cl}(\text{CH}_2\text{PR}_3)(\mu-\text{CH}_2)(\mu-\text{dppm})_2]]</td>
<td>311.5(1)</td>
<td></td>
<td>95.1(9)</td>
<td>NR</td>
<td>85</td>
</tr>
</tbody>
</table>

\* NR = not reported
### Table 1.2: $^{13}$C($^1$H) NMR Data of Some μ-Alkyldene Transition Metal Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>CRR'</th>
<th>δ_{CRR'}</th>
<th>δ_{CO}</th>
<th>δ(μ-CO)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class I: Compounds with metal-metal bonds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="1.1">Cp₂Fe₂(μ-Ch₂(μ-Cl)AlMe₂)</a></td>
<td>CH₂</td>
<td>188</td>
<td></td>
<td></td>
<td>C₆D₆</td>
<td>108</td>
</tr>
<tr>
<td><a href="1.21">Cp₂Fe₂(NO)₂(μ-Ch₂)</a></td>
<td>CH₂</td>
<td>(trans)127.38</td>
<td></td>
<td></td>
<td>THF-d₈</td>
<td>49</td>
</tr>
<tr>
<td><a href="1.76">Cp₂Fe₂(μ-CO)(μ-Ch₂)</a></td>
<td>CH₂</td>
<td>(cis)138.8</td>
<td>212.8</td>
<td>272.0</td>
<td>CDCl₃</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans)142.0</td>
<td>213.8</td>
<td>274.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="1.29">Cp₂Ru₂(μ-CO)(μ-Ch₂)</a></td>
<td>CH₂</td>
<td>102.3 b</td>
<td>193.6 c</td>
<td></td>
<td>toluene-d₈</td>
<td>29</td>
</tr>
<tr>
<td><a href="1.11a">Cp₂Ru₂(μ-CO)(μ-Ch₂)</a></td>
<td>CH₂</td>
<td>(cis)110.3</td>
<td></td>
<td></td>
<td>CDCl₃</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans)111.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Os₃(μ-CO)]₃(μ-Ch₂)](1.3)</td>
<td>CH₂</td>
<td>62.5</td>
<td>193.4</td>
<td>184.0</td>
<td>CD₂Cl₂</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>180.9</td>
<td>174.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>173.9</td>
<td>172.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cp₂Co₂(μ-CO)]₃(μ-Ch₂)](1.64)</td>
<td>CH₂</td>
<td>(cis) 85.2</td>
<td>207.8</td>
<td></td>
<td>C₆D₆</td>
<td>59,95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans) 86.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(η⁵-C₅Me₅)₂Co₂(μ-CO)]₃(μ-Ch₂)](1.36)</td>
<td>CH₂</td>
<td>116.06</td>
<td>220.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="1.35">(η⁵-C₅Me₅)₂Co₂(μ-CO)(μ-Ch₂)</a></td>
<td>CH₂</td>
<td>190.21</td>
<td>210.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cp₂Rh₂(μ-CO)]₃(μ-Ch₂)](1.20)</td>
<td>CH₂</td>
<td>102.3 b</td>
<td>193.6 c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(η⁵-C₅Me₅)₂Rh₂(μ-CO)]₃(μ-Ch₂)](1.29)</td>
<td>CH₂</td>
<td>111.36 d</td>
<td>196.64 e</td>
<td></td>
<td>CDCl₃</td>
<td>54,56</td>
</tr>
</tbody>
</table>
Table 1.2 (continued)

<table>
<thead>
<tr>
<th>Complex</th>
<th>CRR'</th>
<th>δCRR'</th>
<th>δCO</th>
<th>δ(μ-CO)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp₂Fe₂(CO)₄(μ-(CH₂)₃)]</td>
<td>(CH₂)₃</td>
<td>7.8</td>
<td></td>
<td></td>
<td>CDCl₃</td>
<td>109</td>
</tr>
<tr>
<td>[Cp₂Fe₂(CO)₄(μ-(CH₂)₄)]</td>
<td>(CH₂)₄</td>
<td>3.8</td>
<td></td>
<td></td>
<td>CDCl₃</td>
<td>109</td>
</tr>
<tr>
<td><a href="1.66">Cp₂Ru₂(CO)₄(μ-CH₂)</a></td>
<td>CH₂</td>
<td>-37.42</td>
<td>203.50</td>
<td></td>
<td>C₆D₆</td>
<td>80</td>
</tr>
</tbody>
</table>

a Spectra recorded at about 80°C unless otherwise noted; δ values [ppm] referenced against TMS; NR=not reported.

b t, ¹J(Rh,C) 28 Hz
c d, ¹J(Rh,C) 27 Hz
d t, ¹J(Rh,C) 29 Hz
e d, ¹J(Rh,C) 89.7 Hz
Table 1.3: $^1$H NMR Data of Some $\mu$-Alkylidene Transition Metal Complexes$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>CRR'</th>
<th>$\delta$ C (p.p.m.)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp$_2$Ti($\mu$-CH$_2$)(µ-Cl)AlMe$_2$] (1.1)</td>
<td>CH$_2$</td>
<td>8.49</td>
<td>C$_6$D$_6$</td>
<td>108</td>
</tr>
<tr>
<td>[Cp$_2$Fe$_2$(NO)$_2$(µ-CH$_2$)] (1.21)</td>
<td>CH$_2$</td>
<td>(trans) 8.09</td>
<td>THF-d$_8$</td>
<td>49</td>
</tr>
<tr>
<td>[Fe$_2$(CO)$_6$(µ-CH$_2$)] (1.61)</td>
<td>CH$_2$</td>
<td>5.5</td>
<td>(CD$_3$)$_2$CO</td>
<td>6</td>
</tr>
<tr>
<td>[Cp$_2$Fe$_2$(CO)$_2$(µ-Cl)(µ-CH$_2$)] (1.76)</td>
<td>CH$_2$</td>
<td>(cis) 0.43, 10.33</td>
<td>CDC$_3$</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans) 9.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cp$_2$Ru$_2$(CO)$_2$(µ-Cl)(µ-CH$_2$)] (1.11a)</td>
<td>CH$_2$</td>
<td>(cis) 7.52, 9.16</td>
<td>CDC$_3$</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans) 8.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cp$_2$Ru$_2$(CO)$_2$(µ-Cl)(µ-CHCO$_2$Et)] (1.10)</td>
<td>C(H)CO$_2$Et</td>
<td>(cis) 9.27</td>
<td>CDC$_3$</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans) 8.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Os$_2$(CO)$_6$(µ-CH$_2$)] (1.62)</td>
<td>CH$_2$</td>
<td>3.73</td>
<td>C$_6$D$_6$</td>
<td>94</td>
</tr>
<tr>
<td>[Cp$_2$CO$_2$(CO)$_2$(µ-CH$_2$)] (1.64)</td>
<td>CH$_2$</td>
<td>(cis) 7.80, 6.22</td>
<td>C$_6$D$_6$</td>
<td>59, 95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans) 6.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(η$^5$-C$_5$Me$_5$)$_2$CO$_2$(µ-Cl)(µ-CHCH$_3$)] (1.35)</td>
<td>C(H)CH$_3$</td>
<td>(trans) 5.05$^b$</td>
<td>CD$_2$Cl$_2$</td>
<td>58</td>
</tr>
<tr>
<td>[Cp(CO)Co(µ-CH$_2$)Rh(CO)Cp] (1.72)</td>
<td>CH$_2$</td>
<td>(cis) 7.70$^c$</td>
<td>(CD$_3$)$_2$CO</td>
<td>59, 95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.17$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans) 8.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(η$^5$-C$_5$Me$_5$)$_2$Rh$_2$(CO)$_2$(µ-CH$_2$)] (1.29)</td>
<td>CH$_2$</td>
<td>(trans) 5.97$^e$</td>
<td>CDC$_3$</td>
<td>54, 56</td>
</tr>
<tr>
<td>[(η$^5$-C$_5$Me$_5$)$_2$Rh$_2$(CO)$_2$(µ-CHCO$_2$Et)] (1.29)</td>
<td>C(H)CO$_2$Et</td>
<td>(trans) 5.78$^f$</td>
<td>CDC$_3$</td>
<td>54, 56</td>
</tr>
</tbody>
</table>
Table 1.3 (continued)

<table>
<thead>
<tr>
<th>Complex</th>
<th>CRR'</th>
<th>$\delta$CH(p.p.m.)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp₂Fe₂(CO)₄(μ-(CH₂)₃)]</td>
<td>(CH₂)₃</td>
<td>1.42</td>
<td>CDCl₃</td>
<td>109</td>
</tr>
<tr>
<td>[Cp₂Fe₂(CO)₄(μ-(CH₂)₄)]</td>
<td>(CH₂)₄</td>
<td>1.35</td>
<td>CDCl₃</td>
<td>109</td>
</tr>
<tr>
<td><a href="1.66">Cp₂Ru₂(CO)₄(μ-(CH₂)</a></td>
<td>CH₂</td>
<td>2.30</td>
<td>C₆D₆</td>
<td>80</td>
</tr>
<tr>
<td>[Rh₂Cl₂(μ-CH₂)(μ-HPB)(μ-dppm)₂] (1.59)</td>
<td>CH₂</td>
<td>6.07</td>
<td>NR</td>
<td>89</td>
</tr>
<tr>
<td>[Pt₄Cl₄(μ-CH₂)(μ-dppm)₂] (1.55)</td>
<td>CH₂</td>
<td>1.08</td>
<td>C₂D₂Cl₂</td>
<td>83</td>
</tr>
<tr>
<td>[MePt₂(CH₂PPh₃)(μ-CH₂)(μ-dppm)₂]PF₆ (1.56)</td>
<td>CH₂</td>
<td>1.50δ</td>
<td>NR</td>
<td>85</td>
</tr>
</tbody>
</table>

a. Spectra all recorded at about 30°C; δ values[ppm] referenced against TMS; NR = not reported.

b. q, J(H,H) 7.1 Hz
c. q, $^2$J(Rh₁H) 3.24 Hz, J(H,H) 0.34 Hz
d. q, $^2$J(Rh,H) 1.13 Hz, J(H,H) 0.34 Hz
e. t, $^2$J(Rh,H) 0.76 Hz
f. t, $^2$J(Rh,H) 1.7 Hz
g. $^3$J(P,H) 9.0 Hz, $^2$J(Pt,H) 50 Hz
### Table 1.4: Infrared Spectral Data of Some \(\mu\)-Alkylidene Transition Metal Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu(\text{CO})), cm(^{-1})</th>
<th>(\nu(\mu-\text{CO})), cm(^{-1})</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe}_2(\text{CO})_6(\mu-\text{CH}_2)]) (1.61)</td>
<td>2118(w), 2058(vs), 2028(vs), 2012(s)</td>
<td>1780(s)</td>
<td>(\text{C}<em>6\text{H}</em>{14})</td>
<td>6</td>
</tr>
<tr>
<td>([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CH}_2)]) (1.76)</td>
<td>1985(vs), 1940(s)</td>
<td>1780(s)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>8</td>
</tr>
<tr>
<td>([\text{Os}_2(\text{CO})_6(\mu-\text{CH}_2)]) (1.62)</td>
<td>2128(w), 2082(m), 2036(vs) 2022(m), 2004(m), 1966(m,sh)</td>
<td>1780(s)</td>
<td>(\text{C}<em>6\text{H}</em>{14})</td>
<td>94</td>
</tr>
<tr>
<td>([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CH}_2)]) (1.11a)</td>
<td>1985(s), 1941(m) 1781(m)</td>
<td>1782(m)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>9</td>
</tr>
<tr>
<td>([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHO}_2\text{Et})]) (1.10)</td>
<td>1994(s), 1959(m)</td>
<td>1792(m)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>9</td>
</tr>
<tr>
<td>([\text{Cp}_2\text{Co}_2(\text{CO})_2(\mu-\text{CH}_2)]) (1.64)</td>
<td>1966(w), 1957(br,s), 1924(w)</td>
<td>1770(s)</td>
<td>THF</td>
<td>59,95</td>
</tr>
<tr>
<td>([(\eta^5-\text{C}_3\text{Me}_5)_2\text{Co}_2(\mu-\text{CO})(\mu-\text{CH}_2)]) (1.35)</td>
<td></td>
<td>1770(s)</td>
<td>THF</td>
<td>58</td>
</tr>
<tr>
<td>([(\eta^5-\text{C}_3\text{Me}_5)_2\text{Rh}_2(\text{CO})_2(\mu-\text{CH}_2)]) (1.29)</td>
<td>1946(s)</td>
<td>1833(s)</td>
<td>(\text{C}<em>6\text{H}</em>{14})</td>
<td>54,56</td>
</tr>
<tr>
<td>([(\eta^5-\text{C}_3\text{Me}_5)_2\text{Rh}_2(\text{CO})_2(\mu-\text{CHO}_2\text{Et})]) (1.29)</td>
<td>1953(s)</td>
<td>1833(s)</td>
<td>THF</td>
<td>54,56</td>
</tr>
<tr>
<td>([(\eta^5-\text{C}_3\text{Me}_5)_2\text{Rh}_2(\mu-\text{CO})(\mu-\text{CPh}_2)(\mu-\text{CH}_2)]) (1.31)</td>
<td></td>
<td>1833(s)</td>
<td>THF</td>
<td>57</td>
</tr>
</tbody>
</table>
References


90. Reference 77; Scheme 5, p. 117 and references therein.


CHAPTER 2

FORMATION AND REACTIVITY OF THE NOVEL METALLACYCLE

\[ \text{[Mn}_2(\text{CO})_4(\mu-\text{C}(\text{O})\text{CHR}_{2})(\mu-\text{dppm})_2]} \ (R=\text{H, Me, CO}_{2}\text{Et}) \]

2.1 Transition Metal-Diazoalkane Complexes

The reactions of diazoalkanes with transition metal complexes have been the subject of intensive research over the past few years. Diazoalkanes have been used extensively in the preparation of \( \mu \)-alkyldene complexes. However, little is known concerning the reaction pathway leading to \( \mu \)-alkyldene metal complex formation from diazoalkanes but some stable diazoalkane complexes have been isolated and structurally characterized. In most instances focusing on the reaction of organometallics with diazoalkanes, the structurally intact diazo component is most likely initially attached to the metal center. Prior to the more common dinitrogen loss to generate an alkylidene unit, the heterocumulene systems RR'C=N\(_2\) possess several basic functions capable of coordination.

The following literature review describes results in which the reported molecules incorporate an entire diazoalkane unit without dinitrogen extrusion. Following this review, section 2.2 emphasizes the unusual structure and chemistry cited for the complex \([\text{Mn}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{dppm})_2]\), the exclusive species examined in this chapter with various diazoalkane additions.
2.1.1 Formation of Heterocumulene Systems

Attachment of the diazoalkane to the metal center as a monodentate ligand bonding via the terminal nitrogen atom has been observed in two cases: diethyl diazomalonate is strongly bonded in the carbonyl manganese complex (2.1) and is only displaced by carbon monoxide under high pressure, and the analogous mononuclear diazo complex (2.2) was characterized by X-ray analysis to incorporate tetrachlorodiazocyclopentadiene with a nonlinear skeleton replaceable by carbon monoxide or sulfur dioxide.³

\[ \text{(2.1)} \]

\[ \text{(2.2)} \]

Under extremely mild conditions, equation 2.1.1 illustrates the first example of the simultaneous stabilization of a cluster diazo compound (1.39) and the corresponding carbene in a transition metal \( \mu \)-alkyldene complex.⁴ Thermal conditions only generate the \( \mu \)-alkyldene derivative as previously described in Scheme 1.2.
The isolation of intact diazoalkane intermediates prepared from reaction of \([\text{Cp}_2\text{Mo}_2(\text{CO})_4]\) (1.40), containing a metal-metal triple bond, with various diazoalkanes (section 1.1.1.1.3) has perhaps proven most interesting from a mechanistic viewpoint. Thermal decomposition of the air-stable diazoalkane adducts (1.41) at 60° in benzene leads to dinitrogen extrusion and the resultant \(\mu\)-diarylcarbene complexes (1.42), as shown in Scheme 1.6. By contrast, the related dialkyldiazomethane complexes (1.45), derived from the similar triply bonded precursor (1.40°), exhibit unsymmetrically bridging diazo ligands. Heating the complexes (1.45) generally induces formation of a symmetrically bridged imine ligand and a terminal isocyanate ligand in the same complex (1.46), resulting from cleavage of the dinitrogen bond in (1.45), as shown in Scheme 1.8.
Another example of a 1:1 adduct for a diazoalkane complex was observed by Shapley and co-workers\textsuperscript{7} who described the reaction of a diazoalkane with the cluster $[\text{Os}_3(\text{CO})_6(\mu_2-\text{PhC} = \text{NPh})]$ as producing the thermally stable $\mu$-diazoalkane intermediate (2.3). Complex (2.3) can be photolyzed into the corresponding $\mu$-alkylidene complex (2.4), presumably proceeding through the dimetallapyrazolene intermediate structure displayed for (2.3) in equation 2.1.2.
The A-frame molecules $[\text{Rh}_2\text{(CO)}_2(\mu\text{-CRCO}_2\text{Et})\text{N}_2\text{(}\mu\text{-dppm})_2]$ (2.6),
which are based on the structure of the A-frame precursor complex $[\text{Rh}_2\text{(CO)}_2(\mu\text{-H})_2(\mu\text{-dppm})_2]$ (2.5), result from a reversible diazoalkane addition to (2.5). On photolysis or thermolysis, these adducts (2.6) do not eliminate dinitrogen but rather dissociate the intact diazoalkane molecule. The synthesis of the complexes (2.6) is represented by equation 2.1.3.
2.1.2 Diazalkane Insertion Reactions

Insertion of a carbene unit into a metal-hydrogen bond to form the alkyl complex (2.7) is accompanied by the nitrogeneous alkylazo product (2.8) containing a C-protonated diazalkane as a monodentate three-electron ligand. Both complexes (2.7) and (2.8) are shown in equation 2.1.4.

\[
\begin{align*}
\text{(2.7)} & \quad \text{M=Mo, W; R=R'=H, Me, Ph, SiMe}_3 \\
\text{(2.8)}
\end{align*}
\]

The insertion of diazomethane at 80°C with the weak acid HMn(CO)₅ was the first example of diazalkane coordination to metal centers via both nitrogen atoms¹⁰ (equation 2.1.5).
Diphenyldiazomethane reacts with \( \text{Cp}_2\text{ZrMe}_2 \) and \( \text{Cp}_2\text{ZrHCl} \) to produce nitrogen-carbon and nitrogen-hydrogen bond formation respectively by diazoalkane insertion into metal-carbon and metal-hydrogen bonds. Subsequent reaction is viewed in equation 2.1.6 as occurring through a preliminary step (2.9) in which the diazoalkane molecule coordinates to the electrophilic zirconium (IV) using the more basic terminal N atom, to which the methyl or hydride ligand can then inexplicably migrate.

\[
\begin{align*}
\text{Cp}_2\text{Zr} & \quad \text{N}_2\text{CPh}_2 \\
\text{R} & \quad \rightarrow \quad \text{R'} \\
\text{R} & \quad \rightarrow \quad \text{N}^+ = \text{N}^+ = \text{CPh}_2 \\
\text{R} & \quad \rightarrow \quad \text{Cp}_2\text{Zr} \quad \text{N}^- \quad \text{R} \\
\text{Ph} & \quad \rightarrow \quad \text{Ph} \\
\end{align*}
\]

\( R = R' = \text{Me}; R = H, R' = \text{Cl} \) (2.9) 2.1.6
2.2 Bidentate Phosphine Ligands

The electronic or steric effects of the bidentate phosphines \(X_2P(Y)_nPX_2\) are easily altered by variations in \(X, Y\) or \(n\). This complex yet convenient synthetic accessibility has led to an extensive chemistry of the bidentate phosphine ligands and some examples are listed in Table 2.1.\textsuperscript{12-19} The bidentate ligands are capable of bridging two metal centers with or without a metal bond, chelating to the same metal atom or alternatively "dangling" from one metal atom as an \(\eta^1\)-monodentate ligand. An example for each of these three bonding modes is provided by the dppm ligand in Table 2.1.

Binuclear systems incorporating bridging phosphine ligands utilize strong metal-phosphorus bonds to bind two metal centers in close proximity and hence promote bimetallic reactions involving either an activation or insertion of small molecules, or formation or cleavage of metal-metal bonds. The practicality of these bridged phosphine systems has been further demonstrated with the elucidation of mechanistic pathways in both homogeneous and heterogeneous catalysis.\textsuperscript{20}

2.2.1 Manganese Carbonyls with Bidentate Phosphine Ligands

Use of bidentate ligands, known to prevent dissociation of dimer to monomer, can ease the steric crowding on adjacent metals by promoting either bridging by other groups or allowing binuclear reactions involving formation and cleavage of metal-metal bonds.\textsuperscript{20} Thus compounds such as \(\text{[Mn_2(CO)_6(\mu-dppm)_2]}\) (2.10) have been prepared according to equation 2.2.1.\textsuperscript{21,23}
Table 2.1: Various Bidentate Phosphines and Representative Complexes

<table>
<thead>
<tr>
<th>Ligand((L_2))</th>
<th>Complex</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂PCH₂PMe₂</td>
<td>([\text{Pd}_2\text{Cl}_2(\mu-L_2)_2])</td>
<td>12</td>
</tr>
<tr>
<td>Ph₂PCH₂PPh₂</td>
<td>([\text{Pt}_2\text{Cl}_2(\mu-L_2)])</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>([\text{PtI}_2(L_2)])</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>([\text{Cr(CO)}_5(\eta^1-L_2)])</td>
<td>14</td>
</tr>
<tr>
<td>Ph₂P(CH₃)₂PPh₂</td>
<td>([\text{RhCl(CO)(L}_2])</td>
<td>15</td>
</tr>
<tr>
<td>F₂PN(Me)PP₂</td>
<td>([\text{Mo}_2\text{Cl}_2(\mu-L_2)₄])</td>
<td>16</td>
</tr>
<tr>
<td>(PhO)₂PN( Et )P(OPh)₂</td>
<td>([\text{Rh}_2\text{Cl}_2(\text{CO})(\mu-L_2)₂])</td>
<td>17</td>
</tr>
<tr>
<td>(EtO)₂POP(OEt)₂</td>
<td>([\text{Fe}_2\text{(CO)}₄(\mu-CO)(\mu-L_2)₂])</td>
<td>18</td>
</tr>
<tr>
<td>(CF₃)₂PSP(CF₃)₂</td>
<td>([\text{Ni}_2\text{(CO)}₂(\mu-CO)(\mu-L_2)₂])</td>
<td>19</td>
</tr>
</tbody>
</table>
Steric repulsions between the equatorial carbonyl groups and phenyl rings attached to the phosphorus atoms are significant and this leads to the result that a single carbonyl can easily be expelled (equation 2.2.2). The product of carbonyl loss, (2.11), achieves an 18-electron configuration at each metal by utilizing one carbonyl group in a unique fashion as a four-electron bridging carbonyl (4EBC) donor. Marked distortions must occur in (2.10) and formation of the bridging carbonyl group in (2.11) permits the dpmm ligands to adopt a configuration in which the contact distances are minimized.21,22,24

Since terminal carbonyl ligands absorb normally in the region 1900-2150 cm\(^{-1}\) and bridging carbonyl groups between 1850-1750 cm\(^{-1}\), the origin of the observed 1645 cm\(^{-1}\) band was not obvious and consequently complex (2.11) was confirmed by a crystal structure study.24 The novel 4EBC
bonds to one Mn atom, Mn(1), through a two-electron σ bond and to the other Mn atom, Mn(2), in a sideways, two-electron C=O π bond shown by I.

\[ \text{Mn(1)} \quad \text{Mn(2)} \]

(I)

A similar complex, (2.12), R=4-toly1, with a four-electron bridging isocyanide ligand is also known.\(^{25}\)

\[ \text{Subsequent reactions between } [\text{Mn}_2(\text{CO})_{10}] \text{ and depm (Et}_2\text{PCH}_2\text{PPh}_2) \text{ or dcpm ((C}_6\text{H}_11)_2\text{PCH}_2\text{PPh}_2) \text{ in refluxing decane gave binuclear complexes [Mn}_2(\text{CO})_8(\mu-\text{depm})_2] (2.13) \text{ and [Mn}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{dcpm})_2] (2.14) \text{ respectively.}^{26}\]

Complex (2.13) could be decarbonylated over a longer period to yield \([\text{Mn}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{depm})_2] (2.15)\). Decarbonylation solution studies indicate that each pentacarbonyl complex (2.14) and (2.15) contain a 4EBC ligand (1640 cm\(^{-1}\)) and are structurally related to (2.11). Furthermore, the steric demands override the electronic effects of the diphosphine ligands as the dominant factor responsible for the stabilization of the 4EBC in dimanganese pentacarbonyl
systems. Reaction of $[\text{Mn}_2(\text{CO})_{10}]$ with dmpm (Me$_2$PCH$_2$PMe$_2$), invoking the least bulky substituent of the bidentate phosphine ligands, produces only the hexacarbonyl $[\text{Mn}_2(\text{CO})_6(\mu\text{-dmpm})_2]$ (2.16) species, which along with (2.13), is structurally related to complex (2.10).

Subsequent reports of four-electron donor carbonyl bridges include $[\text{Cp}_2\text{NbMo}(\text{CO})_2\text{Cp}]^{30} \quad [\text{Cp}_2\text{Zr}(\text{CO})(\text{OCH}_3)\text{Mo(OCO)}\text{Cp}]^{29}$ and $[(\text{C}_5\text{Me}_5)_2\text{ZrCo(OCO)}\text{(Cp)}]^+.30$ A cluster-bound analogue$^{31}$ occurs in $[\text{HFe}_4(\text{CO})_{13}]^+$, where one of the carbonyl ligands donates a total of four electrons to all four iron atoms in $[\text{HFe}_4(\text{CO})_{13}]^+$. An extreme example of carbonyl Lewis basicity is found in $[\text{Cp}_3\text{Nb}(\text{CO})_3]$, where one carbonyl ligand lies obliquely over the Nb$_3$ triangle and donates via the carbon lone pair and both filled C=O $\pi$ orbitals.$^{32}$

It is interesting to note that a different geometry is assigned to compounds using the bidentate ligands bipy$^{33}$ and phen$^{33,34}$. Initial reactions of these ligands with $[\text{Mn}_2(\text{CO})_{10}]$ produce (2.17a), as in equation 2.2.1. These compounds are converted to (2.17b) (equation 2.2.4) under mild conditions.
2.2.2 Chemistry of $[\text{Mn}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{dppm})_2]$ 

Principal interest in the $\mu_2, \eta^2$-carbon monoxide ligand in electron-deficient systems, such as $[\text{Mn}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{dppm})_2]$ (2.11), stems from the unusual ligand-metal coordination that may resemble an intermediate state in the catalytic hydrogenation of small molecules such as carbon dioxide or dinitroglycerol on lightly loaded metal surfaces. This is exemplified by the proton induced carbonylation of (2.11) to afford $[\text{Mn}_2(\text{CO})_6(\mu-\text{H})(\mu-\text{dppm})_2]^+$ (2.18a) and its subsequent decarbonylation reactions. This protonation of the metal-metal bond in (2.11) greatly accelerates reactions with concurrent addition of another ligand, illustrated in equation 2.2.5.$^{35}$
Complex (2.11) may also serve as a model for an important mechanistic intermediate in the ligand substitution reactions of polynuclear organometallic compounds.

Despite tentative suggestions that the 4EBC mode might activate carbon monoxide towards nucleophilic attack, no example of this has been reported. In particular, this 4EBC mode for carbon monoxide does not seem to activate it towards reduction. Reactions of complex (2.11) and its derivatives suggest that small molecule addition to (2.11) leads to displacement of the carbonyl oxygen atom from the manganese coordination sphere, resulting in adducts containing only normal, two-electron donor carbonyl ligands. A report by Turney supports this general hypothesis. These authors concluded that coordination of a carbonyl ligand in the $\mu_2,\eta^2$-mode to relatively electron-rich manganese atoms does not confer any markedly increased activity upon either the carbon or oxygen atoms. Subsequent calculations indicate that the predominant component of the $\eta^2$-interaction is back-donation from the metal to the CO $\pi^*$ orbitals. This back-donation is necessitated by the extensive substitution at the manganese atoms by phosphorus donors so that the $\mu,\eta^2$-CO is deactivated.
toward nucleophilic attack. Consequently the idea of this carbonyl in
[Mn₂(CO)₄(μ-CO)(μ-dppm)]₂ \((2.11)\) acting as a four-electron donor can
only apply in a formal sense if at all.

2.3 Scope of the Chapter

With the aim of synthesizing complexes of the grouping Mn₂(μ-CR₂), a study of the reactions of various diazoalkanes N₂CRR' with Colton's complex \([Mn₂(CO)₄(μ-CO)(μ-dppm)]₂\) \((2.11)\), possessing an unusual 4EBC, was initiated. It was expected that locking the manganese atoms
together with μ-dppm ligands would aid in the isolation of reactive
formyl or methylene complex products, which are useful as models for
possible intermediates in the Fischer-Tropsch synthesis. For example,
the formally unsaturated compound \([Re₂H₂(CO)]₂\) readily breaks down to
\([ReH(CO)]₂(PPh₃)\) on reaction with triphenylphosphine above -30°C
whereas the use of the bridging diphosphine, Ph₂PCH₂PPh₂(dppm), allows
\([Re₂H(CO)]₂(μ-dppm)\) to react with different reagents with retention of
the binuclear framework. Each product from reaction of a particular
diazoalkane in excess with \((2.11)\) is shown to have a unique
metallacyclic unit formed by a novel coupling of the diazoalkane with a
carbonyl ligand without the liberation of dinitrogen. The synthesis,
structure and reactivity form the basis for this chapter.

2.4 Preparation of \([Mn₂(CO)₄(μ-C(0)CRR'N₂)](μ-dppm)]₂\) Complexes

Complex \((2.11)\), prepared by the literature method, reacted with
a series of diazoalkanes in dichloromethane under a dinitrogen
atmosphere. An excess of the particular diazoalkane was added to a
dichloromethane solution of \((2.11)\) in each case. The reaction progress
was monitored via solution cell IR spectroscopy since the loss of the 1645 cm\(^{-1}\) peak, corresponding to the 4EBC of (2.11), signified a complete reaction. Only one new species was isolated from each diazoalkane addition to (2.11) after a column chromatographic workup. Each product was recrystallized from a dichloromethane/n-pentane mixture to give an orange solid soluble only in polar chlorinated solvents. A high yield of the respective orange product was obtained in each case, with the notable exception of a small yield of red oil from reaction of (2.11) with isopropyldiazomethane (\(\text{N}_2\text{CMe}_2\)). The relatively electron-rich diphényldiazomethane (\(\text{N}_2\text{CPh}_2\)) failed to react with (2.11) under mild conditions. Subsequent work\(^{38}\) confirms this observation and reports the inactivity of \(\text{N}_2\text{CMePh}\) with Colton's complex (2.11).

The absence of the bridging carbonyl IR stretch at 1648 cm\(^{-1}\) in each product suggests that each product does not contain a 4EBC ligand, as in the precursor complex (2.11). If the alkylidene insertion had occurred as anticipated from the diazoalkane addition with concomitant dinitrogen loss, the reaction could be represented as in equation 2.4.1.

\[
\begin{align*}
\text{N}_2\text{CRR}' & \quad \to \quad \text{N}_2 \quad \to \quad (\text{CO})_2\text{Mn} & \\
(2.11) & \quad \text{+} & \quad \text{N}_2\text{CRR}' & \quad \text{25°C} & \quad (\text{CO})_2\text{Mn} & \quad \text{Mn(OCO)}_2
\end{align*}
\]

However, elemental analyses of these reaction products were consistent with the molecular formula \([\text{Mn}_2(\text{CO})_5(\text{N}_2\text{CRR}')\text{(dppm)}_2]\)

\((R=R'=\text{H}, \text{Me}; R=\text{H}, R'=\text{Me}, \text{CO}_2\text{Et})\), indicating diazoalkane addition without dinitrogen liberation. Full experimental details are given in section
2.5 Product Characterization

Since the structure of any orange product isolated from reaction of (2.11) with diazoalkanes could not be deduced from the spectroscopic data, a structure determination by X-ray methods was undertaken by Dr. G. Ferguson at the University of Guelph, Guelph, Ontario.

2.5.1 X-ray Structure Analysis

Recrystallization of complex (2.19), the product from reaction of complex (2.11) with a 6:1 molar excess of diazomethane, was obtained by slow diffusion of acetone into a dichloromethane solution of (2.19) over 21 days to afford large single crystals of what was later shown to be the bis(dichloromethane) solvate. Crystals of (2.19)·2CH₂Cl₂ were unstable in the absence of solvent, with decomposition being visually obvious after 12 minutes. A suitable crystal of (2.19) was coated with epoxy resin within seconds of it being removed from the mother liquor prior to data collection.

The X-ray crystal structure of (2.19) is identified as \([\text{Mn}_2(\text{CO})_4(\mu-\text{C}(\text{O})\text{CH}_2\text{N}_2)(\mu-\text{dpmm})_2]·2\text{CH}_2\text{Cl}_2\) and Figure 2.1 shows the molecular structure of the molecule revealing details of the manganese environment with principal bond lengths. The structure of (2.19) is very similar to that reported²⁴ for \([\text{Mn}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{dpmm})_2]\) (2.11) but with the additional unique feature of a diazomethane ligand that bridges asymmetrically via nitrogen the Mn atoms and also forms a C-C single bond to what had previously been a carbonyl carbon atom in (2.11). This unusual dimetallacycle formed by coupling with one of the
carbonyl ligands forms an equatorial plane set at an angle of 89.8° with the phosphine ligands, as in (2.11), occupying the trans axial sites. The stereochemistry at each Mn atom in (2.19) may be regarded as being derived from octahedral geometry with the addition of a Mn-Mn bond, 2.898(2)Å; a separation of the manganese atoms slightly shorter than that of (2.11) (2.934(6)Å)^24 and Mn₂(CO)₁₀ (2.923(3)Å)^41 indicating the presence of a metal-metal bond. In the Mn₂P₄ fragment of (2.19), the Mn-P distances are in the range 2.287-2.295(2)Å, mean 2.293(2)Å; in (2.11)^24, the Mn-P distances ranged between 2.234(9) and 2.311(9)Å.

The ORTEP drawing reveals the manganese atom Mn(1) forms two normal Mn-C bonds to terminal carbonyl groups (Mn(1)-C(1)=1.76(1)Å, Mn(1)-C(2)=1.83(1)Å), a Mn-N bond to the bridging diazo ligand (Mn-N=1.894(7)Å), and there is also a much weaker interaction to a semibridging equatorial carbonyl (Mn-C(4)=2.524(8)). The resulting trans effects are marked, with Mn-C(1) (trans to Mn...C(4)) shorter than Mn-C(2) (trans to N(1)).

The equatorial environment at Mn(2) differs from that at Mn(1). There is one terminal carbonyl (Mn(2)-C(3)=1.782(10)Å), the bridging carbonyl (Mn(2)-C(4)=1.826(9)Å), and the bridging diazomethane (Mn(2)-N(1)=1.967(7)Å), and the remaining carbonyl ligand has been incorporated into the five-membered MnC₂N₂ ring (Mn(2)-C(5)=2.001(9)Å). The Mn-N distances are significantly different with the shorter Mn-N bond being to Mn(1), the manganese atom with only a weak interaction to the bridging carbonyl C(4). In the five-membered MnC₂N₂ ring the N-N distance 1.238(9)Å is consistent with it being a double bond.
In (2.19), the bridging carbonyl group is much more asymmetric than was observed in (2.11) (compare Mn-C=1.826(9) and 2.584(8)\text{"A} and Mn(2)-C-O=159.9(7)° with the corresponding data for (2.11), 1.93(3) and 2.01(3)\text{"A} and 173(3)°), but the observed geometry for (2.19) indicates a significant Mn(1)...C(4) interaction.

The bridging carbon atoms C(7) and C(8) of the dppm ligands lie out of the Mn\textsubscript{2}P\textsubscript{4} plane (0.78 and 0.77\text{"A}) respectively on the same side as atom N(1) and remote from the bridging carbonyl C(4); an exactly similar situation was found in (2.11).

Steric crowding causes the phenyl rings to be bent away from the equatorial coordination plane; all the Mn-P-C angles are greater than tetrahedral (111.4-123.3(2)°), and the C-P-C angles are all less than tetrahedral (98.7-104.4(3)°). Other dimensions of the dppm ligand are as expected, e.g., average P-C=1.830(8)\text{"A}.

2.5.2 Elemental Analyses

Each adduct isolated from the incorporation of one entire diazoalkane molecule per mole of (2.11) provided a satisfactory elemental analysis consistent with the respective heterocumulene system. These elemental analyses are listed in Table 2.2 for both the observed and calculated values for the elements C, H and N only.

2.5.3 Mass Spectra

A mass spectral analysis was obtained for each of the 1:1 adducts. Although the parent ion (P) of the complexes (2.19) (m/e 1060), (2.20) (m/e 1074) and (2.21) (m/e 1132) was not observed in any case, the same mass spectral pattern was resolved from all three
Table 2.2: Elemental Analytical Data for $[\text{Mn}_2\text{(CO)}_4(\mu-\text{C(O)CRR'}\text{N}_2)(\mu-\text{dppm})_2]$}

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molecular Formula</th>
<th>Molecular Weight</th>
<th>Found (%)</th>
<th>Calculated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>$R=R'=H$ (2.19)</td>
<td>$C_{59}H_{48}Mn_2N_2O_3P_4$</td>
<td>1060</td>
<td>63.49</td>
<td>4.35</td>
</tr>
<tr>
<td>$R=H,R'=Me$ (2.20)</td>
<td>$C_{57}H_{48}Mn_2N_2O_3P_4$</td>
<td>1074</td>
<td>63.45</td>
<td>4.93</td>
</tr>
<tr>
<td>$R=H,R'=\text{CO}_2\text{Et}$ (2.21)</td>
<td>$C_{59}H_{50}Mn_2N_2O_3P_4$</td>
<td>1132</td>
<td>62.37</td>
<td>4.20</td>
</tr>
<tr>
<td>$R=R'=Me$ (2.22)</td>
<td>$C_{59}H_{50}Mn_2N_2O_3P_4$</td>
<td>1084</td>
<td>63.92</td>
<td>4.60</td>
</tr>
</tbody>
</table>
diazoalkane complexes. The assignment of each peak is as follows: m/e
assignment) 1018 (P-N xCRR'), 962 (P-N xCRR'-2CO), 934 (P-N xCRR'-3CO),
884 (P-N xCRR'-2CO·C 6H 6), 856 (P-N xCRR'-3CO·C 6H 6).

2.5.4 Infrared Spectroscopic Data

Given the molecular structure of (2.19), it is then possible to explain the spectroscopic data for the complexes \([\text{Mn}_x(\text{CO})_4] \)
\([\mu\cdot\text{C}(\text{O})\text{CRR}'\text{N}_2](\mu\cdot\text{dppm})_2\) and to understand the chemistry involved. Table 2.3 lists relevant IR spectroscopic data pertaining to and including the 1:1 adducts (2.19)-(2.21).

The IR spectra in the carbonyl region of complexes (2.11) and (2.19) are similar in many respects. However, the band in (2.11) at 1645 cm\(^{-1}\) is absent in (2.19), while new peaks arise at 1610 and 1820 cm\(^{-1}\) in dichloromethane. The semibridging carbonyl ligand is assigned to the 1820 cm\(^{-1}\) peak. Both the C=O and N=N stretching modes of the metallacyclic ring in (2.19) are assigned to the 1610 cm\(^{-1}\) peak.

The bonding in (2.19) is most readily described as shown in equation 2.5.1, and the formal oxidation states of Mn(1) and Mn(2) are then 0 and +2, respectively. This is a classic situation for a semibridging carbonyl to be present, since the weak Mn(1)...C(4)
interaction (Figure 2.1) allows excess electron density at Mn(1) to be delocalized onto the carbonyl ligand. A low \(\nu(\text{CO})\) of 1820 cm\(^{-1}\) results from this extra back-bonding. Therefore, since the structure of (2.19)
was established by X-ray crystallography, the interpretation of the IR data of (2.19) is of prime importance when assessing the structure of subsequent molecular systems \([\text{Mn}_x(\text{CO})_4(\mu\cdot\text{C}(\text{O})\text{CRR}'\text{N}_2)(\mu\cdot\text{dppm})_2]\) from their respective IR spectra.
Table 2.3: Infrared Data for \([\text{Mn}_2(\text{CO})_4(\mu-\text{C(O})\text{CHR}_2)(\mu-\text{dppm})_2]\) and Related Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu(\text{CO})), cm(^{-1})</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mn}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{dppm})_2]) (2.11)</td>
<td>1940(m), 1902(s), 1862(s), 1832(m), 1648(m)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
</tr>
<tr>
<td></td>
<td>1942(m), 1903(s), 1860(s), 1835(m), 1645(m)</td>
<td>(\text{Nujol})</td>
</tr>
<tr>
<td>R=H; (2.19)</td>
<td>1957(m), 1930(s), 1882(s), 1820(m), 1610(m)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
</tr>
<tr>
<td></td>
<td>1960(m), 1920(s), 1885(s), 1818(m), 1610(m)</td>
<td>(\text{Nujol})</td>
</tr>
<tr>
<td>R=Me; (2.20)</td>
<td>1957(m), 1930(s), 1882(s), 1820(m), 1610(m)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
</tr>
<tr>
<td></td>
<td>1960(m), 1920(s), 1885(s), 1805(m), 1610(m)</td>
<td>(\text{Nujol})</td>
</tr>
<tr>
<td>R=CO(_2\text{Et}); (2.21)</td>
<td>1955(s), 1935(m), 1882(s), 1835(m), 1740(m, br(^a)), 1615(m)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
</tr>
<tr>
<td></td>
<td>1950(s), 1935(s), 1882(s), 1835(m), 1740(m, br(^a)), 1615(m)</td>
<td>(\text{Nujol})</td>
</tr>
<tr>
<td>([\text{Mn}_2(\text{CO})_5(\text{N}_2\text{C(\text{CO}_2}\text{Et})_2)(\mu-\text{dppm})_2])(^c)</td>
<td>1937(s), 1867(s), 1850(m, sh), 1800(m), 1676(m)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{CO})_2(\mu-\text{N}_2\text{CHO}_2\text{Et})(\mu-\text{dppm})_2])(^d)</td>
<td>1955, 1940, 1610(^a), 1400(^b)</td>
<td>(\text{Nujol})</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{CO})_2(\mu-\text{N}_2\text{C(\text{CO}_2}\text{Et})_2)(\mu-\text{dppm})_2])(^d)</td>
<td>1955, 1940, 1670, 1570(^a), 1380(^b)</td>
<td>(\text{Nujol})</td>
</tr>
</tbody>
</table>

\(^a\) \(\nu(\text{CO}_2\text{Et})\)  \(^b\) \(\nu(\text{N}_2)\)  \(^c\) Reference 38  \(^d\) Reference 8
A similar assignment based on (2.19), as evidenced by the stretches in Table 2.3, is applied to complexes (2.20) and (2.21), each derived from the appropriate diazoalkane addition to (2.11). Consequently, the peaks at 1610 and 1615 cm\(^{-1}\) in (2.20) and (2.21) respectively are assigned, as in (2.19), to both \(\nu(C=O)\) and \(\nu(N=N)\) of their corresponding metallacyclic or MnC\(_2\)N\(_2\) equatorial rings, schematically represented in equation 2.5.1.

\[
[Mn_2(CO)_4(\mu-\cdot\cdot\cdot CO)(\mu-\cdot dppm)_2] \rightarrow [Mn_2(CO)_4(\mu-\cdot\cdot\cdot CO)(\mu-\cdot dppm)_2]
\]

(2.11)

(2.19): R=H
(2.20): R=Me
(2.21): R=CO\(_2\)Et

2.5.5 \(^1\)H and \(^{31}\)P\(^{\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
Table 2.4: NMR Spectral Data for the \([\text{Mn}_2(\text{CO})_4(\mu-\text{C}(\text{O})\text{CHR}N_2)(\mu-\text{dppm})_2] \) Complexes

<table>
<thead>
<tr>
<th>Complex (^a)</th>
<th>(^1\text{H} \text{NMR (100 MHz)})</th>
<th>(^{31}\text{P}(^{1}\text{H}) \text{NMR (40.5 MHz)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="2.11">\text{Mn}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{dppm})</a>)</td>
<td>(\delta(\text{ppm})) CHRN(_2)</td>
<td>(\delta(\text{ppm})) P(_2\text{CH}_2)</td>
</tr>
<tr>
<td>([\text{Mn}_2(\text{CO})_4(\mu-\text{C}(\text{O})\text{CHR}N_2)(\mu-\text{dppm})_2])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R=H; (2.19)(^c)</td>
<td>CH(_2): 4.81, br</td>
<td>3.51, br, 75.9(m), 59.5(m)(^b)</td>
</tr>
<tr>
<td>R=Me; (2.20)(^d)</td>
<td>CHCH(_3): 4.62, br CHCH(_3): 0.70, d, J(HH) 8Hz</td>
<td>2.76, br, 56.5(m), 53.7(m)(^b)</td>
</tr>
<tr>
<td>R=CO(_2\text{Et}); (2.21)(^d)</td>
<td>CHCO(_2\text{Et}): 4.20, br CO(_2\text{CH}_2\text{CH}_3): 4.46, q(br), J(HH) 6Hz</td>
<td>2.54, br, 57.5(m), 52.0(m)(^b)</td>
</tr>
<tr>
<td>\hspace{1cm}</td>
<td></td>
<td>CO(_2\text{CH}_2\text{CH}_3): 1.51, t(br), J(HH) 6Hz</td>
</tr>
</tbody>
</table>

\(^a\) dppm=Ph\(_2\text{PCH}_2\text{PPh}_2\) \hspace{1cm} \(^b\) AA'BB' multiplet \hspace{1cm} \(^c\) CD\(_2\text{Cl}_2\) \hspace{1cm} \(^d\) CDCl\(_3\)
Figure 2.2: $^{31}P(^1H)$ NMR Spectra of $[\text{Mn}_2(\text{CO})_4(\mu-C(O)\text{CH}_2\text{N}_2)(\mu\text{-dppm})_2](2.19)$ in $\text{CD}_2\text{Cl}_2$.

Simulation as an AA'BB' multiplet gives $\Delta \nu(A,B)$ 112 Hz at 40.5 MHz, 448 Hz at 162 MHz; $J(AB)$ 80 Hz, $J(AB')$ 32 Hz.
partially resolved $^{31}P$ coupling which was lost in the corresponding $^1H(\text{^{31}P})$ NMR spectrum. The broad singlet centered at $\delta$ 4.81 in the $^1H$ NMR spectrum of (2.19) is assigned to the $\text{CH}_2\text{N}_2$ protons attached to the unique metallacyclic $\text{MnC}_2\text{N}_2$ unit. In principle, two resonances are expected for the $\text{CH}_2\text{P}_2$ protons of the dpdm ligands since there is no plane of symmetry containing the PCP units in (2.19), but there is presumably accidental degeneracy of the $\text{CH}^8\text{H}^6\text{P}_2$ chemical shifts and only a single broad resonance centered at $\delta$ 2.76 (Figure 2.5) was observed. The spectrum showed no sign of sharpening at lower temperatures down to $-70^\circ\text{C}$. That the molecule (2.19) is not fluxional on the NMR time scale is shown by the $^{31}P(\text{^1H})$ NMR spectrum (Figure 2.2). At 40.5 MHz, this occurs as an AA'BB' multiplet as expected for structure (2.19). The spectrum is sharp at $-70^\circ\text{C}$ and the peaks broaden at room temperature, but no further broadening occurs up to $+60^\circ\text{C}$. This broadening is thus due to the presence of the quadrupolar manganese center ($I=5/2$) and not to the onset of a fluxional process.

The magnitude of the phosphorus-phosphorus coupling constants obtained from the first-order analysis were refined using the program LACGN III. Simulation as an AA'BB' multiplet gave $\Delta v(\text{A},\text{B})=112$ Hz at 40.5 MHz and 448 Hz at 162 MHz, $J(\text{AB})=80$ Hz, and $J(\text{AB'})=32$ Hz.

Unknown to us at this time, Turney$^{38}$ simultaneously isolated the same $[\text{Mn}_2(\text{CO})_6\text{(CH}_2\text{N}_2)(\text{dpdm})_2]$ adduct from the analogous reaction conditions. Although Turney confirms our spectroscopic data, particularly with regard to the absence of any observable PH coupling between the $\text{CH}_2\text{N}_2$ and $\text{CH}_2\text{P}_2$ protons of the dpdm ligands, he did not correctly deduce the structure of this 1:1 adduct (2.19). Turney favored a structure involving a terminal Mn-N=N-CH$_2$ unit, similar to
that reported for complexes (2.1) and (2.2).

The $^1$H NMR spectra of (2.20) and (2.21) contain broad resonances, as described in Table 2.4, in a 4:1 ratio indicative of the $\text{CH}_2\text{P}_2\text{CHR}$ protons. Furthermore, the protons of the substituent R in the 
\[\text{[Mn}_2(\text{CO})_4(\mu\cdot\text{C(O)CHR})_2(\mu\cdot\text{dppm})_2]\] complexes (2.20) and (2.21) display sharp peaks with well defined $^2J(\text{HH})$ values, and with the expected intensities. Figure 2.3 illustrates the $^1$H NMR spectrum of the diazoethane adduct (2.20), while that of the ethyl diazoacetate adduct (2.21) is shown in Figure 2.4.

The $^{31}$P($^1$H) NMR spectrum of the diazoethane derivative (2.20) exhibits a singlet in dichloromethane down to $-90^\circ\text{C}$, probably indicating fluxionality in this molecule. The alternative would require accidental degeneracy of all four $^{31}$P chemical shifts. However, the $^{31}$P($^1$H) NMR spectrum of (2.21) appears as a well-resolved AA'BB' multiplet at 20°C centered at 8 52.0, 57.5.

The mechanism of formation of these 1:1 adducts \[\text{[Mn}_2(\text{CO})_4(\mu\cdot\text{C(O)CHR})_2(\mu\cdot\text{dppm})_2]\] (R=H(2.19), Me(2.20), CO$_2$Et(2.21)) could reasonably involve initial coordination of the diazoalkane to (2.11) as a two-electron ligand replacing the Mn($\pi\cdot\text{CO}$) bond in the usual fashion to give II.

\[
\begin{array}{c}
\text{P} \\
\text{P} \\
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{P} \\
\text{P} \\
\text{Mn} \quad \text{Mn} \quad \text{Mn} \\
\text{P} \\
\text{P} \\
\text{(CO)}_3 \\
\text{(CO)}_3 \\
\end{array}
\]

(II)
Figure 2.3: $^1$H NMR Spectrum (100 MHz) of $[\text{Mn}_2(\text{CO})_4(\mu-C(\text{CHMeN}_2)(\mu-dppm)](2.20)$ in CDCl$_3$.
Figure 2.4: $^1$H NMR Spectrum (100 MHz) of \([\text{Mn}_2(\text{CO})_4(\mu-\text{C(0)CHCO}_2\text{EtN})_2(\mu-\text{dpmm})_2]^{2+}\) in CDCl$_3$. 
An example of particular relevance to the present work is the complex \([\text{CpMn(CO)}_2(\text{N}_2\text{C(CO}_2\text{Me})_2)]\) (2.1) in which the metal-diazoalkane bonding is of the form Mn-Nm-\(\cdot\)CR\(_2\). Turney\(^8\) favoured this same binding of diazomethane to a manganese atom for the adduct isolated from diazomethane addition to (2.11). Once II is produced, the formation of the metallacyclic ring in complexes (2.19)-(2.21) may derive from a nucleophilic attack of the carbonionic carbon of the diazoalkane in II on a terminal carbonyl ligand on the adjacent manganese atom.

It should also be noted that the 1:1 adducts obtained in equation 2.5.1 from reaction of excess diazoalkanes with (2.11) arise more rapidly at room temperature if acid catalysis (CF\(_3\)CO\(_2\)H) is employed. This accelerated reaction rate presumably proceeds through protonation of the metal-metal bond in (2.11) to give complex (2.18), as shown in equation 2.2.5,\(^{35}\) en route to each diazoalkane adduct.

2.6 Reactivity of the \([\text{Mn}_2(\text{CO})_4(\mu-\text{C(O)CHRN}_2)(\mu-\text{dpmm})_2]\) Complexes

2.6.1 Thermolysis and Photolysis Reactions

In order to induce the possible formation of an alkylidene bridged species by dinitrogen extrusion from the metallacyclic ring in the 1:1 adducts (2.19)-(2.21), each adduct was separately heated in benzene and also photolyzed in a dichloromethane solution. The diazoalkane adducts (1.41) were earlier reported to thermally decompose in benzene with dinitrogen loss to yield the corresponding \(\mu\)-diarylcarbene complexes (1.42)\(^9\) (Scheme 1.6). A similar dinitrogen elimination\(^7\) occurred when the \(\mu\)-diazoalkane intermediate osmium trimer (2.3) was photolyzed, producing the respective \(\mu\)-alkylidene trimer (2.4) shown in equation
2.1.2. However, for each 1:1 adduct (2.19)-(2.21), both the
thermolysis and photolysis reactions resulted in the dissociation of,
the intact diazoalkane unit and reformation of Colton's complex
(2.11). This reversible diazoalkane addition has also been reported for
the A-frame molecules [Rh₂(CO)₂(μ-CRCO₂EtN₂)(μ-dppm)₂] (2.6)
equation 2.11).

The X-ray structure of the diazomethane product [Mn₂(CO)₆-
[μ-C(0)CH₂N₂](μ-dppm)]·2CH₂Cl₂ (Figure 2.1) shows that the CH₂-C(0)
bond is long for a C-C single bond [C(5)-C(6)=1.560(13)Å, cf. 1.516(5)Å
in CH₃CHO]. It is therefore possible to rationalize the cleavage of
this bond on heating complex (2.19) in benzene or on photolysis of
(2.19) in dichloromethane solution. Both the diazoethane and ethyl
diazoacetate derivatives (2.20) and (2.21) respectively are anticipated
to exhibit similar, if not longer, CHR-C(0) bonds within their
metallacyclic units. It is not clear whether CH₂N₂ is a product of
pyrolysis of (2.19). The only organic product identified was ethane,
whereas diazomethane is expected to give ethylene or methane as
decomposition products. However, evidence for dissociation of the
intact diazoalkane moiety is provided by the thermolysis of the adduct
(2.21) in a vacuum sealed NMR tube. Although the ethyl diazoacetate
derivative (2.21) is the most thermally stable complex, a ¹H NMR
spectrum of these thermolysis reaction products detected the formation
of (2.11) [<50%] and liberation of free ethyl diazoacetate in near
quantitative yield.

The low yield of free ethyl diazoacetate in the photolysis
reaction of (2.21) is attributed to decomposition in a similar manner
to that reported in a control experiment in which a benzene solution
of ethyl diazoacetate was photolyzed in an evacuated vessel.

The easy formation and cleavage of carbon-carbon bonds is perhaps the most important general feature of the chemistry of transition metallacycles, and the above reactions provide a good example of this effect. In the present systems, the behaviour of these new bridged diazoalkane A-frame complexes parallels that reported for the similar A-frame complexes (2.6), yet differs markedly from that previously reported for other μ-diazoalkane complexes.\(^5\)\(^-\)\(^7\) It is possible that the stable nature of Colton's complex (2.11) outweighs the stability that would be gained by loss of dinitrogen and subsequent formation of μ-carbene complexes.

2.6.2 Protonation of \([\text{Mn}_2(\text{CO})_4(\mu-\text{C}(\text{O})\text{CH}_2\text{N}_2)(\mu-\text{dppm})_2]\)

The reactivity of the new diazoalkane adducts (2.19)-(2.21) was examined using protic reagents. All three adducts readily protonate to give deeply purple coloured solutions. When an excess of trifluoroacetic or aqueous perchloric acid is added to a dichloromethane solution of an individual complex (2.19)-(2.21), protonation is instant and is readily reversed by merely shaking each dichloromethane solution with diethyl ether. Attempts to isolate pure samples from these solutions invariably resulted in partial decomposition back to the starting materials, as was observed from a strong acid addition to a dichloromethane solution of \([\text{MnPdX(CO)}_3(\mu-\text{dppm})_2]\).\(^4\)\(^2\)

Spectral studies in solution reveal the formation of a cationic species in each case. Two basic sites were considered susceptible to protonation in these adducts. Both sites are adjacent skeletal atoms of the metallacyclic ring contained in the precursor complexes.
(2.19)-(2.21). If the α-carbon of the diazoalkane is protonated in each metallaacyclic unit, then the metallaacycle is expected to cleave and produce a cation \([\text{Mn}_2(\text{CO})_3(\text{CH}_2\text{RN}_2)(\mu-\text{dppm})_2]^+\) possessing a terminally bound \(\text{N}_2\text{CH}_2\text{R}\) ligand, shown by III. The ethyl diazoacetate adduct of (2.6) has been reported\(^8\) to be reversibly protonated at the α-carbon position of the bridged diazo group to form \([\text{Rh}_2(\text{CO})_2(\mu-\text{N}_2\text{CH}_2\text{CO}_2\text{Et})(\mu-\text{dppm})_2][\text{BF}_4^-]\). Turney\(^9\) suggests protonation of the diazoethane adduct \([\text{Mn}_2(\text{CO})_3(\text{CH}_2\text{N}_2)(\mu-\text{dppm})_2]\) (2.19), in which he favoured (2.19) involving a \(\text{Mn}-\text{N}==\text{CH}_2\) unit, with an excess of aqueous tetrafluoroboric acid (\(\text{HBF}_4\)) also reversibly protonates in a similar fashion to afford the purple \([\text{Mn}_2(\text{CO})_3(\text{N}_2\text{CH}_3)(\mu-\text{dppm})_2][\text{BF}_4^-]\) species containing a terminal \(\text{Mn}-\text{N}==\text{CH}_3\) unit. This assignment for the protonation of (2.19) reported by Turney is based on the observed IR spectrum (Table 2.5) and the AA'BB' spectral pattern in the \(^{31}\text{P}(^1\text{H})\) NMR spectrum. Generally, formation of a cationic complex is reflected in the IR data with \(\nu(\text{CO})\) frequencies shifted to higher energy.

\[
\begin{array}{c}
\text{P} \\
\bigg(\text{CO})_3\text{Mn} \\
\bigg(\text{CO})_2\text{Mn(}\text{N}_2\text{CH}_2\text{R)} \\
\text{P} \\
\end{array}
\]

(III)

However, our assignment favours formation of the alternative cationic complex in which protonation of the β-nitrogen atom of the metallaacyclic unit in (2.19)-(2.21) maintains the metallaacyclic unit intact. This assignment is evidenced from the IR data contained in
Table 2.5: Infrared Spectral Data for the \(\text{[Mn}_2(\text{CO})_4(\mu-\text{C(0)}\text{CHRHN})\mu-\text{dppm}]_2\)X Complexes in \(\text{CH}_2\text{Cl}_2\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu(\text{CO}), \text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{[Mn}_2(\text{CO})_5(\text{N}_2\text{CH}_3)(\mu-\text{dppm})_2][\text{BF}_4]^a]</td>
<td>1979(s),1959(vs),1911(s),1876(m)</td>
</tr>
<tr>
<td>[\text{[Mn}_2(\text{CO})_4(\mu-\text{C(0)}\text{CHRHN})(\mu-\text{dppm})_2]]X</td>
<td></td>
</tr>
<tr>
<td>(\text{R})</td>
<td>(\text{X})</td>
</tr>
<tr>
<td>H</td>
<td>(\text{ClO}_4^-)</td>
</tr>
<tr>
<td>H</td>
<td>(\text{CF}_3\text{COO}^-)</td>
</tr>
<tr>
<td>(\text{Me})</td>
<td>(\text{ClO}_4^-)</td>
</tr>
<tr>
<td>Me</td>
<td>(\text{CF}_3\text{COO}^-)</td>
</tr>
<tr>
<td>(\text{CO}_2\text{Et})</td>
<td>(\text{ClO}_4^-)</td>
</tr>
<tr>
<td>(\text{CO}_2\text{Et})</td>
<td>(\text{CF}_3\text{COO}^-)</td>
</tr>
</tbody>
</table>

\(^a^\text{Reference 38}\)
Table 2.5 since each of the protonated species (2.19)-(2.21) exhibit an IR peak (ca. 1610 cm⁻¹) indicative of the C=O stretching mode of the metallacyclic ring. These same IR spectral results also indicate higher ν(CO) frequencies for each cationic complex.

A ¹H NMR of the diazomethane adduct (2.19) in the presence of excess trifluoroacetic acid is illustrated in Figure 2.5. The broad singlet at 8 4.42 is assigned to the CH₄N₂ resonance, formerly at 8 4.81 in the initial diazomethane adduct (2.19). Two broad resonances of equal intensity in the protonated adduct of (2.19) [8 3.10, 8 2.88] are assigned to the two sets of chemically inequivalent CH₂P₂ protons, established by the absence of a plane of symmetry containing the PGO units. The single broad resonance centered at 8 2.76 (Figure 2.5) observed in (2.19) was attributed to an accidental degeneracy of the CH₄Hbpp resonances in this species. Each CH₄Hbpp resonance in the protonated (2.19) complex is also of equal intensity with the CH₂N₂ resonance. No metal hydride resonances were evident. Furthermore, no methyl resonance inferring formation of the protonated isomer III, as reported by Turney, was observed in solution to confirm the existence of a terminal Mn-N=N-CH₃ unit. Protonation of the rhodium dimer (2.6) to give [Rh₂(CO)₆(μ-N₂CH₂R)(μ-dppm)]⁺ (R=CO₂Et) was accompanied by ¹H NMR spectral changes in both the chemical shifts and the integrals of the protonated diazoalkane and the diphosphine methylene protons.

The ³¹P NMR of the protonated diazomethane adduct displays an AA'BB' spectral pattern centered at 8 51.3, 56.5, indicating that the manganese atoms are different and there is no plane of symmetry through Mn₂P₂C rings.

Unfortunately, the broadness of the ¹H NMR resonances of the
Figure 2.5: $^1$H NMR (200 MHz) in CD$_2$Cl$_2$ of: (a) [Mn$_2$(CO)$_4$(μ-C(0)CH$_2$N$_2$)-(μ-dppm)$_2$](2.19); (b) [Mn$_2$(CO)$_4$(μ-C(0)CH$_2$N$_2$)(μ-dppm)$_2$](2.19) in the presence of excess CF$_3$COOH. The + sign designates the CHDCl$_2$ impurity peak.
protonated complexes (2.20) and (2.21) hindered a precise assignment consistent with the proposed cationic structures. However, other than a broadening of both the CHRN₂ and CH₂P₂ resonances in these protonated samples, there were no spectral changes observed on comparison with the corresponding [Mn₂(CO)₄(μ-C(O)CHRN₂)(μ-dppm)] adducts (2.20) and (2.21). If cleavage of the metallacyclic Mn₂C₂ unit to produce a terminal Mn=MnCH₂R unit had occurred with excess acid addition, significant ¹H NMR spectral changes would be anticipated.

2.6.3 Iodomethane Addition

As was observed from their protonation reactions, the metallacycles (2.19)-(2.21) all produce deep reddish-purple solutions with excess iodomethane addition. The IR spectral data in Table 2.6 supports formation of a cationic species in each case. Repetitive attempts to obtain well-resolved ¹H NMR spectra for each iodomethane product were unsuccessful, yet revealed no significant spectral changes had occurred with iodomethane addition. The broadening of the CH₂P₂ signal resonances parallels that observed from protonation. This observation, when coupled with the IR data contained in Table 2.6, suggests a similar electrophilic addition occurs with iodomethane addition as was observed from protonation with strong acid addition. Excess iodoethane appeared to react similarly with complex (2.19), but the reaction was much slower (Table 2.6). Solvent removal produced solids which were identified as their respective metallacyclic precursor, again preventing suitable elemental analyses from being performed on the iodomethane products. Consequently, due to the chemical similarities of both the protonated and iodomethane products
<table>
<thead>
<tr>
<th>Complex</th>
<th>ν(CO), cm⁻¹</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=H, R'=Me</td>
<td>1980(m), 1960(s), 1910(s), 1860(m), 1610(w)</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>R=R'=Me</td>
<td>1980(m), 1960(s), 1910(s), 1870(m), 1610(w)</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>R=CO₂Et, R'=Me</td>
<td>1985(m), 1955(s), 1910(s), 1865(w), 1730(s, br), 1615(w)</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>R=H, R'=Et</td>
<td>1985(m), 1960(s), 1910(s), 1860(m), 1610(w)</td>
<td>CH₂Cl₂</td>
</tr>
</tbody>
</table>
of these metallacyclic adducts (2.19)-(2.21), the reaction of excess iodomethane addition to these forementioned precursors is also suspected to undergo electrophilic addition at the $\beta$-nitrogen site of each metallacyclic ring.

\[ \text{[Mn_2(CO)_4(\mu-C(O)CHR_N_2)(\mu-dppm)_2]} + \text{MeI} \xrightarrow{\text{CH}_2\text{Cl}_2 \atop 25^\circ\text{C}} \text{Mn}_2\text{(CO)}_2 \]

R=H(2.19), Me(2.20), CO_2Et(2.21)

2.7 Summary of the Chapter

Reaction of diazoalkanes CHRN_2(R=H, Me, CO_2Et) with [Mn_2(CO)_4(\mu-C(O)CH_2N_2)(\mu-dppm)_2] gives the simple adduct [Mn_2(CO)_4(\mu-C(O)CHR_N_2)(\mu-dppm)_2] rather than the expected \(\mu\)-alkylidene complex. The structure of the diazomethane adduct [Mn_2(CO)_4(\mu-C(O)CH_2N_2)(\mu-dppm)_2] was established by an X-ray analysis to possess a novel metallacycle derived from coupling of diazomethane and a carbonyl ligand. The spectroscopic data (IR, $^1$H and $^{31}$P($^1$H) NMR) are fully consistent with the determined structure. Each complex [Mn_2(CO)_4(\mu-C(O)CHR_N_2)(\mu-dppm)_2] (R=H, Me, CO_2Et) did not rearrange to the respective $\mu$-alkylidene complex on thermolysis or photolysis, but alternatively underwent dissociation of the diazoalkane instead to reform
[\text{Mn}_2(\text{CO})_5(\mu-\text{CO})(\mu-\text{dppm})].

The metallacycle is maintained in each case on reaction with electrophilic reagents, \text{CF}_3\text{CO}_2\text{H} or \text{CH}_3\text{I}, such that the resultant cationic species arise from an electrophilic addition to the \(\beta\)-nitrogen atom contained within the planar five-membered MnC\text{N}_2 ring.
References


CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF (µ-ALKYLDENE)DICOBALT COMPLEXES OF DPPM VIA DIAZOALKANE ADDITION

3.1 Introduction

Many µ-alkylidene complexes of the transition metals are known.\textsuperscript{1, 2} However, the chemistry of such complexes possessing more than one µ-alkylidene moiety per dinuclear metal center is limited. Surface-bound methylene groups figure predominantly in mechanistic proposals for reactions of hydrocarbons on metals.\textsuperscript{3-6} Consequently, interest in these bis(µ-alkylidene) complexes stems not only from their unique structural and chemical properties, but in their potential use as intermediates in several catalytic reactions. Generally carbenes are observed to prefer a bridging position as opposed to a terminal coordination site.\textsuperscript{3} This phenomenon has prompted the assessment that surface methylene species must be significant in certain catalytic reactions of carbon monoxide and hydrogen, notably the Fischer-Tropsch process.\textsuperscript{4-6} Furthermore olefin metathesis\textsuperscript{7} and Ziegler-Natta catalysis\textsuperscript{8} may proceed by mechanisms involving bridging alkylidene species.

3.1.1 Catalytic Implications of the Alkylidene Bridge

3.1.1.1 The Fischer-Tropsch Process

The Fischer-Tropsch synthesis,\textsuperscript{4-6} schematically represented in equation 3.1.1 as the reductive polymerization of carbon monoxide,
generates a wide range of hydrocarbon products. Converting coal into liquid fuels and chemical feedstocks has been achieved industrially by the Fischer-Tropsch synthesis in which synthesis gas - a mixture of carbon monoxide and hydrogen produced by burning coal in the presence of oxygen and steam - is passed over a catalyst to produce the "CHO" products. These "CHO" products are any organic molecules incorporating carbon, hydrogen, and oxygen which are stable under the reaction conditions employed in the synthesis. The distribution of the various products depends on both the type of catalyst and the reaction conditions employed. The nature of the intermediates and the mechanism of the Fischer-Tropsch synthesis are still in dispute. Consequently, numerous mechanistic schemes have been proposed for this metal-surface-catalyzed reduction of carbon monoxide.¹⁻¹⁴

\[
\text{CO} + \text{H}_2 \xrightarrow{\text{catalyst}} \Delta, P \quad \text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_n\text{CHCH}_2 = \text{CH} \quad 3.1.1
\]

Bridging methylene compounds were initially implicated as intermediates in the hydrogenation of carbon monoxide by Fischer and Tropsch in 1926.¹ These authors considered carbon monoxide hydrogenation as a "Polymerisation von Methylen-Gruppen" wherein a rapid dissociative chemisorption of carbon monoxide on Fischer-Tropsch catalysts generated disjoint surface carbide species, formulated as the pivotal precursors of the methylene groups, and metal oxide species. The surface carbides subsequently react with hydrogen to give oxygen-free \( \text{CH}_x \) intermediates \((x=1-3)\), and when \( x=2 \), polymerization of
neighbouring methylene groups was proposed to generate chain growth which desorb as saturated or unsaturated hydrocarbons (equation 3.1.2).

\[ \text{O} \xrightarrow{\text{H}_2} \text{H}_2\text{O} \text{ or } \text{CO}_2 \]

\[ \text{H}_2 \xrightarrow{\text{polymerize}} \text{CH}_3\text{CH}_3 \text{ etc.} \]

A current mechanistic proposal for Fischer-Tropsch catalysis is that originated by Pichler and Schultz\(^{11}\) in which chain growth is accomplished by direct insertion of an adsorbed carbon monoxide molecule into a metal-carbon bond produced by hydrogenation of a surface carbonyl. Reduction of the acyl group to an alkyl group and repetition of the insertion of carbon monoxide were proposed to lead to chain growth. This proposal\(^6,^{11,12}\) illustrated by equation 3.1.3, derived credibility from the well-established phenomenon in homogeneous organometallic systems of the insertion of carbon monoxide ligands into metal-alkyl bonds\(^{13}\), leading to metal-acyl derivatives. An insertion reaction is defined as one in which an atom or groups of atoms is inserted between two atoms initially bound together.

\[ \text{O} \xrightarrow{\text{H}_2} \text{CH}_3 \]

\[ \text{C} \xrightarrow{\text{H}_2} \text{CO} \]

\[ \text{CH}_3 \xrightarrow{\text{H}_2} \text{CH}_2 \text{CO} \text{ etc.} \]
However, the isolation and characterization of stable transition metal-methylene complexes with terminal and with bridging methylene functions rejuvenated interest in and prompted the design of elegant experiments for support of the earliest theory advanced by Fischer and Tropsch (equation 3.1.2). Furthermore, recent studies confirmed the dissociative chemisorption of carbon monoxide on some single-crystal metal surfaces and strongly implicate the role of this step in the hydrocarbon formation when hydrogen is present.

Elaborate work by Brady and Pettit utilized the dissociative chemisorption of diazomethane (CH₂N₂) to adsorbed CH₂ and free N₂ to provide metal-bound methylenes on active Ni, Pd, Fe, Co, Ru or Cu surfaces. These authors report gas-phase diazomethane, thermally decomposed (250–250°C) on these transition metal surfaces at 1 atm, to yield ethylene as the predominant product and minor amounts of xylene-soluble polymers. Therefore it appears that the principal gas-phase reaction of methylene fragments alone on transition metal surfaces is not polymerization, as suggested by Fischer and Tropsch (equation 3.1.2), but dimerization and elimination of ethylene from the surface as shown in equation 3.1.4. In the presence of hydrogen, higher hydrocarbons (up to C₁₆) were identified for the known Fischer-Tropsch catalysts Fe, Co and Rh, while on Ni or Pd surfaces hydrocarbons up to C₈ were recovered. Both olefin content and chain length decreased with increasing hydrogen partial pressure. Hence the metal hydride functionalities were concluded to initiate polymerization (equation 3.1.5). These results contrast those obtained from the gas-phase thermal decomposition of diazomethane (290–400°C) in the absence of any catalyst with or without the presence of excess
Similar labelling experiments employing diazomethane and $^{13}$C or the deposition of $^{13}$C carbide on transition metal catalysts supported the methylene-like mechanism when hydrocarbon product distribution revealed methylene groups as chain carriers in the catalytic hydrogenation of carbon monoxide. Additional support for this CO-dissociative route is provided by detailed surface science measurements and pulse-reactor studies over the metals Co, Ru and Ni.$^{14,16,20,21}$ In particular, a migratory insertion-type mechanism (equation 3.1.3) is ruled out by this data. Based on these results$^{3,14,17-21}$ concerning the dissociative chemisorption of carbon monoxide, a similar mechanism was postulated to account for the Fischer-Tropsch synthesis (equations 3.1.4 and 3.1.5), a mechanism in which the initial methylene is generated from hydrogenation of a carbonyl fragment by the metal-carbide reduction. This mechanism requires a facile exchange between methyne (CH), methylene (CH$_2$) and methyl (CH$_3$) fragments, as was observed for the [Os$_3$(CO)$_{10}$($\mu$·H)$_2($μ·CH$_2$)] cluster (1.25)$^{22}$ in equation 1.1.14.

\[ \text{CH}_2 \quad \text{CH}_2 \quad \rightarrow \quad \text{CH}_2 \quad \text{CH}_2 \quad \rightarrow \quad \text{C}_2\text{H}_4 \quad 3.1.4 \]

\[ \text{CH}_2 \quad \text{CH}_2 \quad \text{H} \quad \rightarrow \quad \text{CH}_2 \quad \text{CH}_3 \quad \rightarrow \quad \text{CH}_2 \quad \text{CH}_3 \quad 3.1.5 \quad \text{etc.} \]
3.1.1.2 Olefin Metathesis

Surface-bound alkylidene groups have also been implicated in competitive olefin metathesis.\textsuperscript{23, 24} The currently accepted mechanism of olefin metathesis was proposed by Herisson and Chauvin\textsuperscript{7} and involves a metallacyclobutane reaction intermediate (Scheme 3.1).\textsuperscript{7} Metallacyclobutanes have been proposed as key reaction intermediates in several catalytic and stoichiometric reactions involving transition metal complexes.\textsuperscript{25} This mechanism (Scheme 3.1) has now been generally accepted for the olefin metathesis reaction since there is substantial experimental support for this mechanism.\textsuperscript{23, 26} Confirmation for the validity of this Herisson-Chauvin mechanism is provided by the exchange of alkylidene (methylene) units catalyzed by a titanium carbene complex,\textsuperscript{27} depicted in equation 3.1.6, and by the isolation of a titanocyclobutane complex\textsuperscript{28} employing this same "CP₂TiCH₂" catalyst (equation 3.1.7) fragment. This "CP₂TiCH₂" fragment is derived from Tebbe's reagent [CP₂Ti(μ-CH₂)(μ-Cl)AlMe₂](1.1) with t-Bu-CH=CH₂ in the presence of Lewis bases (e.g., pyridine).\textsuperscript{28}

\[
\begin{align*}
\text{CH}_2 & + \text{H}_3\text{C} = \text{CMe}_2 \underset{\text{"CP₂TiCH₂"}}{\xrightarrow{\text{cat}}} \text{CH}_2 = \text{CMe}_2 \\
\text{"CP₂TiCH₂"} & + \text{t-BuCH} = \text{CH}_2 \longrightarrow \text{Cp₂Ti} - \text{tBu}
\end{align*}
\]

Substantial circumstantial evidence pointing toward the
Scheme 3.1: The Herisson-Chauvin Mechanism of Alkene metathesis.
involvement of bimetallic intermediates led Grubbs\textsuperscript{23} to propose an alternate mechanism, which includes a bridging alkylidene as an integral part of the reaction sequence (equation 3.1.8).

\[
\begin{align*}
\text{M} = & \text{Ti}\text{Cp}_2, \ M' = \text{AlMe}_2; \\
\text{M} + \text{CH}_2=\text{CH}_2 & \rightarrow \\
\text{M} + \text{CH}_2=\text{CHR} & \rightarrow
\end{align*}
\]

This mechanism also uses odd-carbon intermediates, as in equation 3.1.7, and is consistent with the mechanistic evidence available on olefin metathesis. Olefin addition to Tebbe's reagent is discussed to a greater extent in section 4.7.1.

3.1.2 Scope of the Chapter

It was the intent of this work to develop a bimetallic system containing bridging alkylidene ligands capable of modelling a "catalytic surface" similar to the classical Fischer-Tropsch systems. Several (cyclopentadienyl)-\(\mu\)-methylenedicobalt derivatives are known\textsuperscript{1,29,30} and their syntheses were reviewed in Chapter One. This work reports the first \(\mu\)-methylene derivatives based on cobalt.
carbonyl, \([\text{Co}_2(\text{CO})_6]\), although several fluoromethylene and carbon bridged complexes (3.1)\(^{31}\) and \(\gamma\)-lactone derivatives (representing the first examples of dinuclear bridged methylene-type complexes in the butyrolactone complexes) (3.2),\(^{32}\) have been reported.

\[
\begin{align*}
\text{(3.1a): } & R = R' = F, \text{CF}_3; R = F, R' = \text{CF}_3 \\
\text{(3.1b): } & R = R' = F; R = F, R' = \text{CF}_3
\end{align*}
\]

\[
\begin{align*}
\text{(3.2): }
\end{align*}
\]

<table>
<thead>
<tr>
<th>(R)</th>
<th>(R')</th>
<th>(R)</th>
<th>(R')</th>
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<td>Pr(^n)</td>
<td>Me</td>
<td>Pr(^n)</td>
</tr>
<tr>
<td>H</td>
<td>C(<em>6)H(</em>{11})(^n)</td>
<td>Me</td>
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</tr>
<tr>
<td>H</td>
<td>SiMe(_3)</td>
<td>Pr(^n)</td>
<td>Pr(^n)</td>
</tr>
</tbody>
</table>

The novel (\(\mu\)-methylenecubicobalt derivatives synthesized in this work exhibit strong evidence for a facile interconversion between terminal and bridging methylene sites in solution. Furthermore, the first bis(\(\mu\)-alkyldene) complexes were prepared, isolated and successfully characterized employing spectroscopic techniques.
3.2 The Preparative Route

The bridged alkylidene system \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2\eta(\mu-\text{CRR'})\eta(\mu-\text{dppm})]\) (n=1,2) was derived from the precursor \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]\) (3.4), containing a metal-metal bond bridged by the dppm ligand, by the room temperature displacement of one or both bridging carbonyls in (3.4) by isoelectronic bridging alkylidene functions, as shown in Scheme 3.2. This carbonyl exchange for bridging alkylidene units used diazoalkanes \(N_2\text{CRR'}\) as the carbene source with concomitant dinitrogen loss. No activation\(^1,^2\) via thermolysis or photolysis was required to induce carbonyl loss from (3.4), allowing the direct formation of the \((\mu\text{-methylene})\text{dicobalt products }[\text{Co}_2(\text{CO})_4(\mu-\text{C})(\mu-\text{CH}_2)(\mu-\text{dppm})]\) (3.5) and \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})]\) (3.6) from reaction of (3.4) with the parent diazomethane.

Although an initial dissociative loss of carbon monoxide is suspected to precede the simple coordination of the diazoalkane to the precursor (3.4), relatively little is known about the actual reaction pathway leading to \(\mu\)-alkylidene metal complex formation from diazoalkanes. In only a few instances have stable diazoalkane complexes been isolated and structurally characterized. Of the possible bonding modes of diazomethane in the reactive intermediate adduct (3.3) leading to (3.5) (Figure 3.1), symmetric arrangements such as (3.3a) are analogous to those found in \([\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu-N_2\text{CH}_2)]\) (1.41), \(^{33}\) \([\text{Cp}_3\text{Co}(\mu-\text{CO})(\mu-N_2\text{CH}_2)]\) (1.39), \(^{34}\) \([\text{Rh}_2(\text{CO})_2(\mu-N_2\text{CHCO}_2\text{Et})\cdot(\mu-\text{dppm})_2]\) (R=H,CO_2Et) (2.6), \(^{35}\) and \([\text{Os}_3(\text{CO})_8(\mu-2\text{CH}_2\text{Ph}_2)(\mu-N_2\text{CHR})]\) (2.3).\(^{36}\) Thermolysis of (1.41) at 60°C in benzene\(^33\) or photolysis of the trimer (2.3) converted each of these 1:1 adducts to the \(\mu\)-alkylidene complexes \([\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu-\text{CPh}_2)]\) (1.42) and
Scheme 3.2: Preparative Route to Formation of $\text{Co}_{2}(\text{CO})_{6}(\mu-\text{CO})_{2}(\mu-\text{dpdm})_{n}(\mu-\text{CRR})_{n}$ Complexes.
[Os₃(CO)₉(μ₂-η₂:C₃Ph₂)(μ-CHR)] (2.4) with dinitrogen extrusion, as shown in Scheme 1.6 and equation 2.1.2 respectively. Recently, Herrmann et al.¹⁷ have reported dialkyldiazomethane complexes [(η⁵-C₅Me₅)₂M₂(CO)₄-(μ(σ,π)-CR₂N₂)] (M=Mn(1.45), W(1.19)) containing an unsymmetrically bridging diazo ligand arrangement represented by (3.3b) in Figure 3.1. Both a 1,3-dipolar addition of diazomethane across the Co-Co bond in (3.4) to yield (3.3c), common in organic chemistry, or an arrangement like (3.3d) must also be considered as possible intermediates in the elimination of dinitrogen to form the mono-(μ-methylene)dicobalt complex (3.5), although transition metal adducts of diazo compounds with these bonding modes have yet to be isolated.

There is no precedent for a μ-CRR'N₂ transition metal complex with the diazo ligand in a bridging manner through the methylene carbon atom, but this arrangement (3.3e) may proceed via a one step dinitrogen elimination to form (3.5). Finally the configuration (3.3f), most recently observed for the [Mn₂(CO)₄(μ-C(O)CRR'N₂)(μ-dppm)₂] complexes (2.19) - (2.21), may also provide a feasible intermediate species prior to dinitrogen loss in the dicobalt system (3.4) with diazoalkane addition.

In a comparative study, Hoffmann et al.⁵⁸ deduced that the methylene bridge was more stable relative to the corresponding carbonyl bridge for dimers of the type M₂L₁₀. Calculations revealed that the carbonyl and methylene (CH₂) ligands were similar, except that the methylene ligand is both a better σ-donor and π-acceptor. Consequently, since a better donor metal strengthens the acceptor bridging, then for the d⁰-d⁰ system found in (3.4), the preference for the observed formation of (μ-alkylidene)dicobalt complexes (3.5)
Figure 3.1: Possible Bonding Modes of \( \text{N}_2\text{CRR}^\prime \) in the Reactive Binuclear Intermediate \([\text{Co}_{2}(\text{CO})_8(\text{N}_2\text{CRR}^\prime)(\text{u-dppm})]^{-}; M=\text{Co}(\text{CO})_2\).
(3.12) and not the $\mu$-carbonyl isomers is attributed to this phenomenon.

The parent (3.4) was synthesized according to equation 3.2.1 and was characterized via comparison with literature values listed for $^4\text{H}$ NMR and IR spectroscopies.\footnote{39}

\[
[\text{Co}_2(\text{CO})_6] + \text{dppm} \xrightarrow{25^\circ C} \frac{\text{C}_6\text{H}_6}{\text{C}_2\text{H}_4} [\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})] + 2\text{CO}
\]

(3.4)

Attempts to produce the complex $[\text{Co}_2(\text{CO})_4(\mu-\text{dppm})_2]$ by the following methods all gave no reaction under dinitrogen:

1. Thermolysis or photolysis of equimolar quantities of (3.4):dppm in benzene, or

2. Stirring equimolar amounts of (3.4):dppm in benzene in the presence of two equivalents of trimethylamine-N-oxide, a decarbonylating reagent, or

3. Replacement of two norbornadiene ligands from $[\text{Co}_2(\text{CO})_4(\text{nor}-\text{C}_9\text{H}_8)_2]$, IR $\nu(\text{CO})(\text{cm}^{-1}, \text{CH}_2\text{Cl}_2)$ 2015(s), 1810(m)\footnote{40} by two dppm molecules in refluxing cyclohexane.

The IR spectrum\footnote{39} of $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]$ (3.4) exhibits two types of carbonyl stretching frequencies and these carbonyl stretching frequencies of (3.4) are illustrated in Figure 3.2. The terminal carbonyl utilizes an sp hybrid to $\sigma$-bond with an empty cobalt d-orbital and further enhances this metal-carbon bond by acting as a $\pi$-acceptor ligand, receiving excess electron density from a filled cobalt t$_{2g}$d-orbital via backbonding. The resultant bond order between the terminal carbonyl atoms is reduced from three (as in free CO) but is still greater than two. Thus $\nu(\text{CO})$ for the terminal carbonyl ligand...
Figure 3.2: Infrared Spectrum in cyclohexane of: (a) $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})](3.4)$; (b) $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dppm})](3.5)$; (c) $[\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})](3.6)$. 
(2049, 2017 and 1991 cm⁻¹) is less than observed for carbon monoxide. The sp² hybridized bridging carboxyls display a carbonyl stretching frequency only slightly greater than the range of values found in ketones, indicative of an almost ketonic C/O interaction.

The spectroscopic data for all the (μ-alkylidene)dicobalt complexes synthesized in this chapter, specifically the IR, ¹H and ³¹P(¹H) NMR data tabulated in Tables 3.1, 3.2 and 3.3 respectively, were utilized to assign the preferred configuration of each μ-alkylidene species. These spectral data conform to those anticipated for a μ-alkylidene species as discussed in section 1.4. These tables are presented at the end of this chapter. All the elemental analyses appear in the appropriate experimental procedures discussed in Chapter 7.3. Furthermore, only the bis(μ-methylene) complex in this dicobalt series of μ-alkylidene complexes displayed a parent ion (m/e 642) in the mass spectrum.

3.3 Preparation and Characterization of [Co₂(CO)₄(μ-CO)-
(μ-CH₂)μ-dppm)] and [Co₂(CO)₄(μ-CH₂)₂(μ-dppm)]

3.3.1 Preparation
Reaction of [Co₂(CO)₄(μ-CO)₂(μ-dppm)] (3.4), prepared by the literature method,³⁹ and excess ethereal diazomethane in dichloromethane at room temperature produced a mixture of the μ-methylene derivatives [Co₂(CO)₄(μ-CO)(μ-CH₂)(μ-dppm)] (3.5) and [Co₂(CO)₄(μ-CH₂)₂(μ-dppm)] (3.6). Further reaction of the mono(μ-methylene) complex (3.5) with diazomethane resulted in the bis(μ-methylene) derivative (3.6) as illustrated in equation 3.3.1. However, since the diazomethane carbene addition was slow, the
liquid-phase decomposition of diazomethane to yield polymethylene under these reaction conditions was clearly evident. This liquid-phase decomposition of ethereal solutions of diazomethane has been noted over extended periods (8-24 h) on surfaces such as porcelain or on metals such as Cu or Au to lead to polymethylene formation. The analogous reaction with dicobalt octacarbonyl, the precursor to (3.4), did not yield \( \mu \)-methylene derivatives with excess diazomethane addition; only an unidentified, insoluble purple complex suspected to be decomposition products was obtained.

\[
\begin{align*}
(3.4) & \quad \text{CO}_2\text{Co} - \text{Co(CO)}_2 + \text{CH}_2\text{N}_2 \rightarrow \text{CO}_2\text{Co} - \text{Co(CO)}_2 - \text{CO}, \text{N}_2 \\
(3.5) & \quad \text{H}_2\text{O} \quad \text{CO}_2\text{Co} - \text{Co(CO)}_2 + \text{CH}_2\text{N}_2 \rightarrow \text{CO}_2\text{Co} - \text{Co(CO)}_2 - \text{CO}, \text{N}_2 \\
(3.6) & \quad \text{H}_2 \quad \text{CO}_2\text{Co} - \text{Co(CO)}_2 \\
& \quad \text{PP} = \text{Ph}_2\text{PCH}_2\text{PPPh}_2
\end{align*}
\]

The separation of the \((\mu\text{-methylene})\text{dicobalt products (3.5) and (3.6) from the reaction mixture initially involved column}

chromatography, with elution from the 100-200 mesh Florisil adsorbent with dichloromethane solvent. However, the complete separation of (3.5) from (3.6) required an alternative technique, since no suitable solvent mixture with the appropriate elution composition and concentration was discovered to completely separate each individual complex upon either a silica or Florisil adsorbent. The small yields of both μ-methylene complexes prevented the use of HPLC. Fortunately preparative TLC, on 20x20 cm² silica plates of 2000 microns thickness, with an elution solvent of 15% dichloromethane:hexanes by volume visibly separated the two yellow bands. Each band was easily extracted from the silica adsorbent with acetone and subsequently was identified by an IR analysis. Table 3.1 indicates that only terminal carbonyl stretching frequencies ν(CO) are observed in solution for the bis(μ-methylene) product (3.6) [Rf=.337] while IR evidence for the mono(μ-methylene) product (3.5) [Rf=0.5 Rf(3.6)=.167] is based on the observation of ν(μ-CO) at 1810 cm⁻¹, indicative of the single bridging carbonyl ligand in (3.5). Figure 3.2 shows the respective carbonyl bands in the IR spectrum of complexes (3.4), (3.5) and (3.6) in cyclohexane. Both μ-methylene products (3.5) and (3.6) were obtained as yellow solids after separation and solvent removal under vacuum, with the bis(μ-methylene) species (3.6) displaying the brighter yellow colour. Therefore this reaction (equation 3.3.1) was monitored by a colour change from the initially orange solution to a final dull yellow coloured solution. Furthermore, IR studies, while the reaction was in situ, also allowed the extent of μ-CO ligand displacement from (3.4) by the μ-CH₂ groups from diazomethane to be determined.

Both μ-methylene derivatives are extremely soluble in common
organic solvents such as dichloromethane and acetone. Solutions of (3.5) or (3.6) are air-sensitive and significant decomposition occurs over thirty minutes, yet the respective solids are air-stable at room temperature for up to four months.

3.3.2 Product Characterization

3.3.2.1 Mass Spectra

Due to the decomposition of the species (3.5) under the mass spectral conditions employed (70°C, 70 eV, 100 Hz filter), the mass spectrum of (3.5) revealed no parent ion peak (m/e 656). Only very weak peaks were observed above m/e 300 but these peaks were indistinguishable amidst the background noise.

These same conditions displayed a mass spectrum for the bis(µ-methylene) complex (3.6) exhibiting a parent ion peak (m/e 642) and successive carbonyl ligand losses, assigned as follows:

<table>
<thead>
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<th>m/e</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>642</td>
<td>P</td>
</tr>
<tr>
<td>586</td>
<td>P-2(CO)</td>
</tr>
<tr>
<td>572</td>
<td>P-2(CO)-(CH₂)</td>
</tr>
<tr>
<td>558</td>
<td>P-2(CO)-2(CH₂), P-3(CO).</td>
</tr>
<tr>
<td>530</td>
<td>P-3(CO)-2(CH₂), P-4(CO)</td>
</tr>
<tr>
<td>516</td>
<td>P-4(CO)-(CH₂)</td>
</tr>
<tr>
<td>502</td>
<td>P-4(CO)-2(CH₂)</td>
</tr>
</tbody>
</table>

3.3.2.2 ¹H and ³¹P(¹H) NMR Spectra

The ¹H NMR spectrum of the bis(µ-methylene) derivative (3.6) at room temperature in dichloromethane-d₂ solvent gave single resonances
in a 2:1 ratio for \((\text{CH}_2)_2\text{Co}_2\) \([8\ 4.90]\) and \(\text{CH}_2\text{P}_2\) protons respectively. The \(\text{CH}_2\text{P}_2\) resonance of the dppm ligand in (3.6) appeared as a broad triplet \([8\ 3.64, J(\text{PH}) 10.5 \text{ Hz}]\) at ambient temperatures (Figure 3.3), comparable to the AX\(_2\) pattern observed in (3.4) for the methylene protons of the dppm ligand \([8\ 3.41, J(\text{PH}) 10 \text{ Hz}]\).\(^{39}\) In the static structure of (3.6), the methylene protons, \(\text{CH}_6\text{H}\), of the dppm ligand are nonequivalent and, unless there exists an accidental degeneracy of the chemical shifts, should give rise to an AB quartet in the \(^1\text{H}\) NMR spectrum.\(^{42-44}\) The observation of only one methylene signal for the dppm ligand has been reported in some A-frame complexes and this generally results from a fluxional process leading to an inversion of the A-frame structure.\(^{44-45}\) At \(-80^\circ\text{C}\) the \((\text{CH}_2)_2\text{Co}_2\) resonance had split into four equal intensity peaks and the \(\text{CH}_2\text{P}_2\) resonance had split into two (Figure 3.3), as expected for the static structure shown in Newman projection down the Co-Co bond in Figure 3.3. One of the \((\text{CH}_2)_2\text{Co}_2\) resonances in Figure 3.3 occurred at anomalously low chemical shift \([8\ 3.65]\) and gave a large triplet coupling to phosphorus \([J(\text{PH}) 23.5 \text{ Hz}]\); this is assigned to \(\text{H}^8\) which lies over the diphosphine ligand and is presumably shielded by the diamagnetic influence of the phenyl substituents on the phosphorus atoms.

The \(^{31}\text{P}(^1\text{H})\) NMR spectrum of (3.6) exhibited a broad central singlet at \(8\ 40.8\) and, in the subsequent \(^1\text{H}(^{31}\text{P})\) NMR spectrum at \(-80^\circ\text{C}\), the triplet assigned to \(\text{H}^8\) collapsed to a broad singlet (Figure 3.3). The \(\text{CH}_2\text{P}_2\) protons, appearing as a partially masked multiplet in the \(^1\text{H}\) NMR at \(-80^\circ\text{C}\) for complex (3.6), reveal an AB pattern in the \(^1\text{H}(^{31}\text{P})\) NMR spectrum at \(-80^\circ\text{C}\) in Figure 3.3. Analysis of this AB pattern for the \(\text{CH}_2\text{P}_2\) protons gives the arbitrarily assigned chemical shifts of \(\text{H}^6\) \([8\ 7.30]\).
Figure 3.3: $^1$H NMR Spectra (100 MHz) of $[\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})](3.6)$ in $\text{CD}_2\text{Cl}_2$. The + peak is due to the CHDCl$_2$ impurity.

(a) 30°C  (b) -80°C  (c) -80°C with decoupling.
and $H^F$ at 4.32], and also $^2J(H^OH^F)$ of 14 Hz. This observation of the AB pattern for the C6·CH$_2$P$_2$ protons is consistent with the static structure for (3.6) depicted in Figure 3.3.

The protons of the phenyl substituents of the dppm ligand appear as a multiplet in a range between 8 7.0-7.8 for complex (3.6).

In contrast, the $^1$H NMR spectrum of the mono(μ-methylene) derivative (3.5) produced a resolved spectrum only at lower temperatures (Figure 3.4). The two bridging methylene protons $H^8$ and $H^9$, labelled in the Newman projection down the Co-Co bond of (3.5) in Figure 3.4, are expected to be chemically inequivalent and this inequivalence is supported by the $^1$H NMR spectrum of (3.5) at -40°C. $H^8$ is assigned to the methylene proton extending over the diphosphine ligand and the large PH coupling [8 3.66, $J$(PH) 23 Hz] defines the stereochemistry shown in the Newman projection of (3.5). Both $H^8$ and $H^9$ [8 4.50] exhibit geminal coupling [$^2J$(H$^8$H$^9$)] 2.75 Hz.

Complex (3.5) displayed a broad centered singlet at 8 57.5 in the $^31$P($^1$H) NMR spectrum, a significant difference from the $^31$P($^1$H) NMR resonance of the bis(μ-methylene) species (3.6) [8 40.8]. In the $^1$H($^31$P) NMR spectrum of (3.5) at -40°C (Figure 3.4), the triplet assigned to $H^8$ in the $^1$H NMR spectrum collapsed into a resonance of equal intensity with $H^9$. The geminal coupling $^2J$(H$^8$H$^9$) was 2.75 Hz. The CH$_2$CO$_2$ and CH$_2$P$_2$ resonances of (3.5) exhibit equal relative intensities of 1:1 in the $^1$H($^31$P) NMR spectrum.

An AB pattern is observed with appropriate relative intensities for the CH$_2$P$_2$ protons of the dppm ligand of (3.5), as anticipated from the static Newman projection shown in Figure 3.4. The chemically inequivalent dppm methylene protons $H^L$ and $H^J$ of complex (3.5) resonate
Figure 3.4: $^1$H NMR Spectra (100 MHz) of [Co$_2$(CO)$_4$(μ-CO)(μ-CH$_2$)(μ-dppm)]

(3.5) in CD$_2$Cl$_2$. 
in the $^1\text{H}(^{31}\text{P})$ NMR spectrum at $\delta$ 2.68 and $\delta$ 3.36 respectively, with $^2J(\text{H}^1\text{H}^1)$ of 15 Hz.

The phenyl substituent protons of the dppm ligand in (3.5) appear as a multiplet between the range $\delta$ 6.9-7.8.

3.3.2.3 $^{13}\text{C}$-labelling Study

The success of the preparative TLC technique described in section 3.3.1 to separate the ($\mu$-methylene)dicobalt complexes (3.5) and (3.6) enabled more elaborate experiments to be performed. In order to obtain a greater sensitivity of the carbon nuclei in the $^{13}\text{C}(^1\text{H})$ NMR spectrum of each ($\mu$-methylene)dicobalt complex, it was necessary to $^{13}\text{C}$-label (3.5) and (3.6) at both the carbonyl and $\mu$-methylene sites.

$^{13}\text{C}$-labelling of the carbonyl ligands in (3.5) and (3.6) was achieved by attaching a scaled glass bulb containing $^{13}\text{CO}$ (100 mL) via a hollow connecting tube (2 mm diameter) to a glass vessel (100 mL) equipped with a B-19 vacuum inlet and magnetic stir bar. The connecting tube was constricted near the vessel to prevent a floating iron bar from entering the vessel (Figure 7.1). A dichloromethane solution of $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]$ (3.4) (3.01 g, $4.5\times10^{-3}$ mol) and 10% Pd/charcoal (1.10x$10^{-1}$) was charged into the vacuum vessel. Then the solvent was degassed ($10^{-3}$ torr) and the vessel sealed to create an evacuated system. A magnet was then applied to the iron bar to break the seal of the bulb containing the $^{13}\text{CO}$ gas. After four hours in which the swirling dichloromethane solution had been exposed to the $^{13}\text{CO}$, the seal was opened and the solution gravity filtered to remove the 10% Pd/charcoal. The filtered solution was then column chromatographed with dichloromethane eluant through 100-200 mesh
Florisil. Subsequent solvent removal produced the orange $^{13}$C-labelled product (3.4) in 93% yield. The $^{13}$C enriched (3.4) was then treated with excess ethereal diazomethane to produce the products (3.5) and (3.6) (equation 3.3.1), which were $^{13}$C-labelled at the carbonyl sites only. Separation of the $\mu$-methylene products was performed as described in section 3.3.1.

The bridging methylene carbon(s) in (3.5) and (3.6) were $^{13}$C-labelled in a separate experiment. Diazald (1.935 g) was mixed with $^{13}$C-Diazald, 90% $^{13}$C (0.0215 g) to generate, on warming an ethereal solution in the presence of a potassium hydroxide base, a 9% $^{13}$C-enriched ethereal diazomethane solution. This $^{13}$C-labelled diazomethane was then added in excess to a dichloromethane solution of (3.4) under nitrogen (Equation 3.3.1) to produce $^{13}$C enriched (3.5) and (3.6) at the $\mu$-methylene sites. Separation of (3.5) from (3.6) was again performed as described in section 3.3.1.

3.3.2.4 $^{13}$C($^1$H) NMR Spectra

In the $^{13}$C($^1$H) NMR spectrum of the bis($\mu$-methylene) species (3.6) (100.6 MHz, $^{13}$C enriched at both CO and $\mu$-CH$_2$ sites) in dichloromethane-d$_2$, the broad resonances at room temperature due to the (CH$_2$)$_2$Co$_2$ and (CO)$_4$Co$_2$ carbons each split into two equal intensity peaks at low temperatures (Figure 3.5) due to non-equivalent carbons C$^a$, C$^b$, C$^c$ and C$^d$ shown in the Newman projection along the Co-Co bond in Figure 3.5. The terminal carbonyl resonances for C$^c$ and C$^d$ (Figure 3.5) appear as a broadened singlet centered at $\delta$ 205.8 at 30°C and clearly resolve into two signals with equal intensities at $\delta$ 207.0 and $\delta$ 204.7 at -50°C. The (CH$_2$)$_2$Co$_2$ carbon resonances are clearly resolved.
Figure 3.5: $^{13}\text{C}[^1\text{H}]$ NMR Spectra (100.6 MHz) of $[\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2-(\mu-\text{dppm})](3.6)$ in CD$_2$Cl$_2$.  

$30^\circ\text{C}$

$10^\circ\text{C}$

$-50^\circ\text{C}$

$\delta$ ppm
Figure 3.6: $^{13}{C}^1{H}$ NMR Spectra (100.6 MHz) of $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CH}_2)-(\mu-\text{dppm})](3.5)$ in $\text{CD}_2\text{Cl}_2$. 
at -50°C with the tentative assignments $C^a$ at 8 121.8 [J(PC) 28.6 Hz] and $C^b$ (trans to the diphosphine ligand) at slightly higher shielding with 8 111.0. Figure 3.5 also reveals that three of the four phenyl resonances [8 128-138] are split at -50°C. The methylene carbon of the dppm ligand in (3.6) resonates at 8 39.2 [J(FC) 21.0 Hz]; this compares to the methylene carbon of dppm in (3.4) resonating at 8 29.9 [J(FC) 24.5 Hz].

The corresponding $^{13}$C($^1$H) NMR spectrum for the complex

\[[\text{CO}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dppm})]\] (3.5) (Figure 3.6) revealed a coalescence of the carbonyl carbon peaks at 30°C; the resonance appearing at 8 216.7. However, at 10°C, both the terminal and bridging carbonyl resonances became visible. The $\mu$-CO carbon is assigned to the singlet at 8 247.6 with the two singlets of equivalent intensity at 8 207.1 and 8 204.6 assigned to the terminal carbonyls in the $^{13}$C($^1$H) NMR spectrum at -50°C (Figure 3.6). No PC coupling is observed for the bridging methylene carbon resonance [8 86.6] at -50°C. Resolution of all phenyl peaks [8 125-135] improved at lower temperatures. The methylene carbon of the dppm ligand in (3.5) at 8 27.6 did not exhibit resolved PC coupling at -50°C.

3.3.3 The Fluxional Methylene Bridge

There are three possible pathways to account for the fluxional process observed in bridging alkylidene systems, yet only one is consistent with (3.5) or (3.6) because of the presence of the bridging dppm ligand in these systems.

Mechanism I, initially considered to account for the cis-trans isomerization of the heteronuclear complex [\text{Cp}(\text{CO})\text{Co}(\mu-\text{CH}_2)\text{Rh}(\text{CO})\text{Cp}]_2
(1.72)^{30}, involves cleavage of a metal-metal bond and a subsequent pseudorotation process around a metal-carbon bond in which the bridging alkylidene groups remain intact. Reformation of the metal-metal bond accomplishes the isomerization (Scheme 3.3). However, this cis-trans isomerization of (1.72) was eventually assigned to Mechanism II^{30}, also illustrated in Scheme 3.3 for the cis-trans isomerization of (1.72).

Mechanism II incorporates a transition state or intermediate in which a metal-carbon bond is broken to generate nonbridging alkylidene groups behaving as carbenes, followed by rotation about the unbridged metal-metal bond and subsequent reclosure to produce the observed cis-trans isomerization. This rapid bridged-nonbridged-bridged interconversion is believed to occur quite commonly where bridging carbonyl groups are concerned. Convincing evidence and arguments have been presented for Mechanism II occurring generally in dinuclear, dibridged metal systems. This mechanistic route was first suggested by Knox for the cis-trans isomerization in \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CMe}_2)](1.91)^{48}\) and is shown in Scheme 3.4.

A third mechanistic pathway was proposed when the single methyl resonance in the $^1\text{H}$ NMR spectrum of the dicobalt compound \([\text{Co}_2(\text{CO})_6(\mu-\text{CMe}_2)_2]\), assigned to the dialkylgermylene bridges, split into two distinct methyl signals at $-42.5^\circ\text{C}$. This observed site exchange was rationalized by Mechanism III (Scheme 3.5) in which the initially distorted square-pyramidal coordination at either cobalt center rearranges to a trigonal bipyramidal intermediate or transition state without breaking the Co-Co bond. This latter configuration can then be interconverted in one step leading directly to the methyl group site exchange. The alternative pathway, where averaging of the methyl group
Scheme 3.3: Suggested Mechanisms for cis-trans isomerization of \([\text{Cp(CO)Co(\mu-\text{CH}_2)Rh(CO)\text{Cp}}]^{\dagger}\).
Scheme 3.4: Mechanistic Route for cis-trans isomerization of
\[\text{[Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CMe}_2)](1.91).\]
Scheme 3.5: Mechanism III as suggested for $[\text{Co}_2(\text{CO})_6(\mu-\text{GeMe}_2)_2]$.
environments occurs via bridge opening (Mechanism II), was ruled less likely because stable carbene-like R₂Ge groups had not yet been discovered (cf. \((\text{CO})_2\text{Cr} = /\text{GeX}_2, X=\text{Cl}, \text{Br}\); \((\text{CO})_2\text{Cr} = \text{Ge(Mes)}_2, \text{Mes}=\text{mesityl}\)).

The activation energy \(\Delta G^\ddagger\) was calculated to be 53±1 kJ mol\(^{-1}\) for the \(\text{bis(\(\mu\)-methylenec) complex (3.6)}\) from all \(^1\text{H}\) and \(^{13}\text{C}\) (including phenyl resonances of the dppm ligands) NMR coalescence points (Appendix 3.1), indicating that a single dynamic process was responsible in solution to account for the apparent equivalence of the \((\text{CH}_2)_2\text{CO}_2\) and \(\text{CH}_2\text{P}_2\) protons at room temperature. A modification of Mechanism II (Scheme 3.4) is favoured for complex (3.6) since the presence of the bridging phosphine ligand dppm prevents the alternative mechanisms. A reasonable mechanism is thus exhibited in equation 3.3.2, which involves a rate determining \(\mu\)-methylenic to terminal methylene transformation, followed by rapid pseudorotation of the \(\text{Co(\(\text{CO})_2(=\text{CH}_2)}\) units and reformation of (3.6).

\[
\begin{align*}
\text{(3.6)} & \quad \xrightarrow{\Delta G^\ddagger = 53\pm1 \text{kJ mol}^{-1}} \quad \text{equation 3.3.2}
\end{align*}
\]

The mono(\(\mu\)-methylenec) complex (3.5) shows very similar fluxional behaviour but with a higher activation energy (\(\Delta G^\ddagger = 62\pm1 \text{kJ mol}^{-1}\)) and the proposed mechanism for (3.5) includes terminal \(\text{CO}\) for bridging \(\text{CO}\) exchange. Similar dynamic behaviour of the related \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{GeMe}_2)]\) complex, specifically the cis \(\neq\) trans isomerization
and consequent averaging of Cp and Me environments, was also attributed to a facile, concerted bridge to terminal interconversion of both the bridging units, followed by a metal-metal bond rotation, and concerted bridge regeneration.\textsuperscript{50} This same mechanism was assigned by Knox\textsuperscript{48} for the [Cp$_2$Ru$_2$(CO)$_2$(μ-CO)(μ-OME)$_2$] complex (Scheme 3.4). Mechanism II is also favoured for the molecular dynamic behaviour of complex (3.5) for three additional reasons:

(i) The estimation of the free energy of activation of the process, from coalescence temperatures, provides a value of ca. 62 kJ mol$^{-1}$ (see appendix I). This barrier size discounts a mechanism for the facile interconversion of the bridging and terminal methylene groups in (3.5) which involves the carbene remaining as a bridge and the carbonyl alone exchanging bridge and terminal sites.\textsuperscript{48} In [Cp$_2$Rh$_2$(CO)(μ-CO)$\cdot$-\(\text{[P(OPh)$_3$]})$,\textsuperscript{51} isomerization by purely carbonyl migration faces a much lower barrier of nearly 37 kJ mol$^{-1}$. The parent [Co$_2$(CO)$_4$(μ-CO)$_2$-(μ-dppm)] (3.4) of (3.5) is fluxional at temperatures as low as -100°C,\textsuperscript{52} indicating a series of activation energies as (3.5) > (3.6) >> (3.4).

(ii) There is a precedent in [Re$_2$(CO)$_6$(C(OMe)C$_6$H$_4$Me)] (1.84), for the required transient terminal carbene complex proposed in the intermediate species for Mechanism II in Scheme 3.4, which on treatment with tolyl-lithium and [OMe$_2$][BF$_4$] yields [Re$_2$(CO)$_6$(μ-C(OMe)C$_6$H$_4$Me)$_2$] (1.85) (equation 1.2.3) to show that the terminal-to-bridge carbene transformation can occur.\textsuperscript{53} More recently the first Fischer-type carbene to exhibit fluxional behaviour has been assessed to occur via a bridging carbene species.\textsuperscript{54}

(iii) Thirdly, the reverse transfer of μ-alkylidene to a terminal site
has also been reported by Herrmann and Bauer, in the reaction of

\[ \{\eta^5-C_5Me_5\}_2Rh_2(CO)_2(\mu-CPh_2)\} \] (1.29) with sulfur dioxide to give

\[ \{\eta^5-C_5Me_5\}_2Rh_2(CO)(CPh_2)(\mu-\text{SO}_2)\} \] (4.16), shown by equation 4.6.3, and

by Messerle and Curtis in the preparation of \[ \{\text{Cp}_2\text{Mo}_2(CO)_3\

\{C(C_6H_4Me)_2\}N_2C(C_6H_4Me)_2\} \] (1.43) (Scheme 1.7).58

This preferred mechanism II suggests that the bridge-to-
terminal-to-bridge methylene exchange proposed for the molecular
dynamic behaviour of both (3.5) and (3.6) parallels carbon monoxide,
since this variable coordination mode provides a convenient route for
carbene mobility on metal surfaces and in complexes in catalysis.
Furthermore, this same phenomenon may account for the suspected
fluxional behaviour reported in the \(^{19}F\) NMR spectra for the dicobalt complexes \[ \{\text{Co}_2(CO)_4(\mu-\text{CO})(\mu-C(CF_3)R)\} \] \((R=\text{CF}_3)\).57

3.4 Preparation and Characterization of \[ \{\text{Co}_2(CO)_4(\mu-\text{CHMe})_2(\mu-dppm)\} \]

3.4.1 Preparation

A yellow solid of elemental composition \([\text{Co}_2(CO)_4(CHMe)_2(dppm)]\)
(3.9) was obtained from a preparative TLC workup \((R_f=.300)\) of a
solution from the reaction of (3.4) with excess ethereal diazoethane
\((\text{MeCN})_2\). This same organometal substrate (3.4) produced no reaction
with excess 2-diazopropane \((\text{Me}_2\text{CN})_2\) addition. An initial orange to
final dull yellow colour change assisted IR solution spectroscopic
studies in monitoring the extent of \(\mu-\text{CO}\) displacement in (3.4) by the
\(\mu\)-ethylidene groups to yield (3.9) (Table 3.1). A large amount of
polymeric material was suspended in the solution after four hours.41
Only a few milligrams of a paler yellow solid than (3.9) were isolated
from this reaction and a subsequent IR spectrum (Table 3.1) led to the
tentative identification of this species as the mono(μ-ethylidene)
complex \([\text{CO}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHMe})(\mu-\text{dppm})]\) (3.7). An insoluble green
band in moderate yield was noted, on preparative TLC workup \((R_f=0.150)\),
and was suspected to result from decomposition of the unstable product
(3.7).

This behaviour of the mono(μ-ethylidene) derivative (3.7) may
parallel that reported earlier for the (μ-alkyldiene)diiron
complexes,\(^{58}\) which also possess a β-hydrogen atom. These complexes are
unstable at room temperature in solution and readily decompose to give
\([\text{Fe}_3(\text{CO})_{12}]\) and the corresponding olefin. For example, the
μ-ethylidene complex \([\text{Fe}_2(\text{CO})_6(\mu-\text{CHMe})]\) decomposes in pentane solution
to yield \([\text{Fe}_3(\text{CO})_{12}]\) and ethylene. This decomposition has been
proposed to involve a dissociative carbonyl ligand loss to generate a
coordinatively unsaturated complex which then β-hydride eliminates to
produce the π complex capable of reductively eliminating ethylene
(equation 3.4.1).

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 \\
(\text{CO})_3\text{Fe} & \quad (\text{CO})_2\text{Fe} \\
\end{align*}
\]

The bis(μ-ethylidene) derivative (3.8) was sufficiently stable in
solution to be successfully characterized from this reaction (equation
3.4.2) by the corresponding \(^1\text{H}, \text{^13C}\) and \(^{31}\text{P}(^1\text{H})\) NMR spectral data
observed at room temperature. This is the first case in which a bis(μ-alkylidene) complex was prepared by the direct displacement of μ-CO groups from the precursor (3.4) at room temperature.

\[ \text{(3.4)} \quad \text{MeCHN}_2, \text{CO}, \text{N}_2 \rightarrow \text{(3.7)} \]

\[ \text{(3.7)} \quad \text{MeCHN}_2, \text{CO}, \text{N}_2 \rightarrow \text{(3.8)} \quad \text{(3.8)} \]

3.4.2 Product Characterization

The \( ^{31}P(\text{H}) \) NMR spectrum of (3.8) reveals a broad singlet at room temperature. This \( ^{31}P(\text{H}) \) resonance signal is very similar to that exhibited by the bis(μ-methylene) congener (3.6).

The \( ^1H \) NMR spectrum of (3.8) is well resolved at room temperature, and both the \( ^1H \) and corresponding \( ^1H(^{31}P) \) NMR spectrum for (3.8) are illustrated in Figure 3.7. A Newman projection along the Co-Co bond in (3.8) is also shown in Figure 3.7 to complement the respective NMR assignments.

The bridging ethylidene proton marked \( H^3 \) appears as a triplet of
Figure 3.7: $^1$H NMR Spectra (100 MHz) of [Co$_2$(CO)$_4$(u-CHMe)$_2$(u-dppm)](3.8) in CD$_2$Cl$_2$. 
quartets centered at 5.82, [J(HH) 8.0 Hz, J(PH) 26 Hz] and is assigned to the proton extending over the Co₂(dpmm) dimetallacycle in the ¹H NMR spectrum of complex (3.8). Proton H³ collapses on ³¹P(¹H) decoupling to yield a quartet [J(HH) 8.0 Hz] anticipated from coupling to the α-methyl substituent protons of Me⁴. Since the large magnitude of the PH coupling [J(PH) 26 Hz] for the triplet of quartets in the ¹H NMR spectrum of (3.8) is similar to the J(PH) exhibited by the most shielded μ-methylene proton in both complexes (3.5) and (3.6), H³ is assigned to the μ-ethylidene proton resonance which lies over the diphosphine ligand. The μ-ethylidene methyl substituent Me⁴ occurs as a doublet [J(HH) 8.0 Hz] with no observable PH coupling and with the appropriate 3:1 proton integration for Me⁴:H³. The doublet centered at 8 2.34 was assigned to Me⁴ based on selective homonuclear decoupling experiments. Selective homonuclear decoupling at 8 5.82 (H³) collapsed the doublet assigned to Me⁴ [8 2.34, J(HH) 8.0 Hz] into a singlet. Alternatively, proton decoupling centered on the doublet Me⁴ collapsed the triplet of quartets (H³) into a triplet [8 5.82, J(PH) 26 Hz].

The apparent quartet in the ¹H NMR spectrum of (3.8) centered at 8 2.76, with equal intensity to Me⁴, collapsed in the ¹H(³¹P) NMR spectrum into a doublet [J(HH) 8.0 Hz]. Although no peak was evident for the bridgehead ethylidene proton H³ shown in the respective Newman projection in Figure 3.7, the envisioned quartet [J(HH) 8.0 Hz] proton resonance for H³ was determined to be masked beneath the phenyl proton multiplet [8 7.46–8.16]. Thus, proton decoupling, focused on the center of the phenyl resonance region [ca. 8 7.81] collapsed the quartet [8 2.76, J(HH) 8.0 Hz] in the ¹H NMR spectrum into a triplet [8 2.76, J(PH) 8.0 Hz]. This triplet [8 2.76, J(PH) 8.0 Hz] results from
longer range coupling to the chemically equivalent phosphorus atoms of the dppe ligand as compared to H² [δ 5.82, J(PH) 26 Hz]. The resultant doublet [δ 2.76, J(HH) 8.0 Hz] in the ¹H(³¹P) NMR spectrum of complex (3.8) is assigned to Me⁴ based on proton coupling to H⁵. Therefore the apparent quartet (Me⁵) in the ¹H NMR spectrum derives from the superposition of a doublet of triplets.

The CH₃P₂ protons are evident as a doublet of triplets [J(PH) 10.0 Hz] in the ¹H NMR spectrum of (3.8) and appear as the simple AB pattern in the corresponding H¹(³¹P) NMR spectrum (Figure 3.7). Analysis of this AB pattern for the dppe methylene protons in (3.8) produces the chemical shifts tentatively assigned as H⁰ [δ 3.73] and H⁵ [δ 4.87], with ²J(H⁰H⁵) 14 Hz. This analysis for the chemically inequivalent CH₃P₂ protons is consistent with the static structure shown in Figure 3.7.

The spectral data of the bis(μ-ethylidene) complex [Co₂(CO)₄(μ-CH₂C≡C(μ-CH₂C≡CMe)₂(μ-dppe))] (3.8) are consistent with those observed from the analogous μ-methylene complexes (3.5) and (3.6), with regard to both the magnitude of J(PH) and the shielded chemical shifts of the phosphorus coupled μ-alkylidene bridgehead protons.

3.5 Preparation and Characterization of [Co₂(CO)₄(μ-CO)(μ-CHCO₂Et)-
(μ-dppe)]

3.5.1 Preparation

The complex [Co₂(CO)₄(μ-CO)(μ-CHCO₂Et)(μ-dppe)] (3.9) was prepared in situ from the cobalt carbonyl precursor (3.4) at room temperature. A red solution of complex (3.9) was obtained from a dichloromethane solution of (3.4) and a two fold molar excess of ethyl diazoacetate.
Ethyl diazoacetate produced only the monosubstituted derivative (3.9) and this reaction (equation 3.5.1) was monitored via IR spectroscopy in dichloromethane to indicate formation of (3.9) \[ \nu(\mu-\text{CO}) 1820 \text{ cm}^{-1} \] (Table 3.1). A large molar excess of the reagent diazoester did not induce formation of the bis(\(\mu\)-ester) product, presumably due to some form of steric repulsion introduced by a second alkylidene unit interacting with either the bulky ester substituent on the bridgehead alkylidene carbon or the phenyl groups of the dppm ligand in (3.9). Complex (3.9) crystallizes on solvent evaporation as a stable, red solid soluble only in polar chlorinated solvents.

![Chemical Structure](image)

3.5.2 Product Characterization

A clean broad singlet [6 53.5] was observed in dichloromethane-\(d_2\) solution down to \(-30^\circ\text{C}\) in the \(^{31}\text{P}(^{1}\text{H})\) NMR spectrum of complex (3.9). The chemical shift is similar to the chemical shift of the \(^{31}\text{P}(^{1}\text{H})\) signal recorded for the mono(\(\mu\)-methylene) species (3.5).

Figure 3.8 reveals that the \(^{1}\text{H}\) NMR spectrum of (3.9) was well resolved at probe temperature. The resolution sharpened with a 10\(^\circ\text{C}\) temperature increase. The stereochemistry of complex (3.9) is defined...
Figure 3.8: $^1$H NMR Spectra (100 MHz) of $[\text{Co}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{CHCO}_2\text{Et})(\mu-\text{dppm})](3:9)$ in CD$_2$Cl$_2$ (R=CO$_2$Et).
as drawn in the Newman projection (Figure 3.8). The bridging alkylidene proton H^2 in the \textsuperscript{1}H NMR spectrum of (3.9) appears as a triplet showing the diagnostic large PH coupling [\delta 4.64, J(PH) 21 Hz] from coupling to the two chemically equivalent phosphorus atoms of the dppm ligand. This triplet [\delta 4.64, J(PH) 21 Hz] collapses to a broad singlet in the \textsuperscript{1}H(\textsuperscript{31}P) NMR spectrum (Figure 3.8). The ethoxy moiety of the bridging substituent acetate ligand displays the characteristic quartet [\delta 4.04, J(HH) 7.0 Hz] and triplet [\delta 1.22, J(HH) 7.0 Hz] for the \textsuperscript{-}CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3} and \textsuperscript{-}CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3} protons respectively. The chemically inequivalent CH\textsubscript{2}P\textsubscript{2} protons form the simple AB pattern in the \textsuperscript{1}H(\textsuperscript{31}P) NMR spectrum with tentative assignments \textsuperscript{1}P\textsubscript{2}CH\textsuperscript{2}P\textsubscript{2} at \delta 2.67 and \delta 3.41 and \textsuperscript{3}J(H\textsuperscript{2}PP) 14.5 Hz. A clearly defined integration verified the proton assignments, including the appropriate integral for the phenyl proton multiplet resonance between \delta 7.2-7.8 with respect to the CHRCO\textsubscript{2}(R=CO\textsubscript{2}Et) and CH\textsubscript{2}P\textsubscript{2} resonance integrals.

3.6 Preparation and Characterization of [Co\textsubscript{2}(CO)\textsubscript{4}(\mu-CO)(\mu-CHPh)(\mu-dppm)]

3.6.1 Preparation

In order to investigate the steric restraints imposed by a carbene phenyl substituent, excess phenyldiazomethane (N\textsubscript{2}CHPh) was added under nitrogen to a dichloromethane solution of [Co\textsubscript{2}(CO)\textsubscript{4}(\mu-CO)\textsubscript{2}(\mu-dppm)] (3.4) at room temperature. A small yield of a red oil was identified by an IR analysis as the complex [Co\textsubscript{2}(CO)\textsubscript{4}(\mu-CO)(\mu-CHPh)(\mu-dppm)] (3.10), with ν(μ-CO) at 1805 cm\textsuperscript{-1} (Table 3.1). This red, oily product (3.10) appeared to decompose under nitrogen on standing at room temperature and during earlier separation via column chromatography.

When a large excess of diphenyldiazomethane (N\textsubscript{2}CPh\textsubscript{2}) was added in
portions over 2h at 0°C to a dichloromethane solution of (3.4) under nitrogen, an IR analysis revealed no reaction had occurred. This same result was obtained when the mixture was left to stir overnight at room temperature.

3.6.2 Product Characterization

3.6.2.1 $^1H$ and $^{31}P$($^1H$) NMR Spectra of $[\text{CO}_2(\text{CO})_4(\mu-C\text{OP})(\mu-C\text{HPh})(\mu-\text{dpmm})]$.

The $^{31}P$($^1H$) NMR resonance of (3.10) at 20°C was a clean singlet at 8 55.1. This value complies with the range of chemical shifts of the other mono($\mu$-alkylidenoc)dicobalt complexes in this system (Table 3.3), but a satisfactory elemental analysis of the appropriate composition for (3.10) could not be obtained.

Only cis-stilbene could be identified from the corresponding $^1H$ NMR spectrum of (3.10) at room temperature. Although a multiplet was evident for the phenyl protons in solution at 8 7.1-7.9, no large J(Ph) triplet resonance appeared in the spectrum. Only two broad singlets at 8 4.54 and 8 4.37, suspected to be unidentifiable organic products, were observed. No change occurred in the $^1H$($^{31}P$) NMR spectrum of (3.10). Since the IR and $^{31}P$($^1H$) NMR data suggest (3.10) is a mono($\mu$-alkylidene) species, there are three possible isomers applicable to this product (3.10).
The precedent for isomer (3.10a) has been established from characterization of (3.5) in section 3.3.2.2 and (3.9) in section 3.5.2, and thus (3.10b,c) appear less likely. An inversion of the methylene substituents in (3.10a) is probably restricted by steric interactions between the methylene phenyl substituent and the dppm phenyl substituents, but this is entirely speculative.

3.6.2.2 Reaction with Diazomethane

In an attempt to stabilize the preferred configuration of (3.10), excess ethereal diazomethane was added under nitrogen to a dichloromethane solution of freshly prepared (3.10) at 0°C. When the IR peak at 1805 cm\(^{-1}\) had diminished, the reaction was stopped and a yellow oil was obtained from solvent removal under vacuum. A subsequent \(^{31}\)P(\(^1\)H) NMR spectrum at 20°C revealed a peak at \(\delta\) 23.8, suspected to arise from some form of a thermal decomposition product. No identifiable peaks were observed in the \(^1\)H NMR spectrum except the same organic peaks at \(\delta\) 4.54 and \(\delta\) 4.37 previously noted in (3.10) in
different comparable intensities.

3.7 Preparation and Characterization of Mixed (μ-alkylidene)dicobalt Complexes \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)(\mu-\text{CHMe})(\mu-\text{dppm})]\) and \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)(\mu-\text{CHOEt})(\mu-\text{dppm})]\)

3.7.1 Preparation

The mixed bis(μ-alkylidene) complex \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)(\mu-\text{CHMe})(\mu-\text{dppm})]\) (3.11) was prepared by the addition of excess diazoethane to a dichloromethane solution of the mono(μ-methylene) species (3.5). Loss of ν(μ-CO) at 1810 cm\(^{-1}\) in (3.5) indicated complete conversion of (3.5) to the mixed alkylidene product (3.11); in this case there was no great colour change since both reagent (3.5) and product (3.11) were yellow coloured species (Table 3.1). Only a yellow oil could be isolated for the product (3.11) from this reaction route.

Unfortunately, the instability and insufficient yield of the mono(μ-ethylidene) complex (3.7) prevented the alternative synthetic route to generate complex (3.11), via diazomethane addition to (3.7), from being investigated.

Further reaction of the monosubstituted derivative (3.9) with diazomethane gave the mixed alkylidene derivative \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)(\mu-\text{CHOEt})(\mu-\text{dppm})]\) (3.12), but this complex (3.12) could not be prepared from the mono(μ-methylene) species (3.5) and an excess of ethyl diazoacetate, which produced no reaction. Table 3.1 illustrates this reaction was monitored via solution cell IR spectroscopy in dichloromethane, since loss of the ν(μ-CO) at 1820 cm\(^{-1}\) in (3.9) indicated complete reaction. Complex (3.12), the mixed bis-(μ-alkylidene) derivative, produced a red solid on solvent removal.
Both reaction equations are summarized by the following expression, referred to as equation 3.7.1.

\[
\begin{array}{ccc}
\text{(a)} & (3.5); R=H & (3.11); R=H, R' = \text{Me} \\
\text{(b)} & (3.9); R=\text{CO}_2\text{Et} & (3.12); R=\text{CO}_2\text{Et}, R' = \text{H}
\end{array}
\]

3.7.2 Product Characterization

3.7.2.1 $^1H$ and $^{31}P(\cdot H)$ NMR Spectra of $\text{[Co}_2(\text{CO})_6(\mu-\text{CH}_2)(\mu-\text{CCH}_2\text{Et})-(\mu-\text{dppm})]$:

Complex (3.12) displays a broad singlet at $8.41.8$ in dichloromethane-$d_2$ in the $^{31}P(\cdot H)$ NMR spectrum. This chemical shift for the singlet resonance conforms to the bis($\mu$-alkylidene) region observed for this particular dicobalt system containing two alkylidene bridges (Table 3.3).

Both the $^1H$ and $^1H(\cdot ^31P)$ NMR for complex (3.12) were resolved at room temperature. The stereochemistry of (3.12) is deduced from the chemical shift of the $\mu$-methylene group showing the large $PH$ coupling ($8.372$, $J(\text{PH}) = 22$ Hz). This $PH$ coupling compares to the corresponding data for compounds (3.5), (3.6), (3.8) and (3.9). The triplet ($8.372$, $J(\text{PH}) = 22$ Hz) is assigned to the $\mu$-methylene proton $H^a$ extending over the $\text{Co}_2(\text{dppm})$ ring since this triplet, particularly when $^{31}P$ decoupled to a singlet, exhibits a small geminal coupling with the broad singlet $H^b$ ($8.456$, $J(H^aH^b) = 2.5$ Hz) of equal intensity (Figure 3.9). The
Figure 3.9: $^1$H NMR Spectra of [Co$_2$(CO)$_4$(μ-CH$_2$)(μ-CHCO$_2$Et)(μ-dppm)](3.12): (a) at 200 MHz in CD$_2$Cl$_2$; (b) $^{31}$P decoupled at 100 MHz in CD$_2$Cl$_2$/CDCl$_3$. 
(Figure 3.9). The Newman projection for (3.12) in Figure 3.9 is drawn along the Co-Co bond to illustrate the defined isomer observed in solution. A broad singlet at 5.15 is assigned to H^c and integration of the signals assigned to H^a, H^b and H^c gave a 1:1:1 intensity ratio for these protons. The CO\_2CH\_2CH\_3 and CO\_2CH\_2CH\_3 protons appear as a quartet [6 4.10, J(\text{HH}) 7 Hz] and triplets [6 1.26, J(\text{HH}) 7 Hz] respectively with no observable PH coupling. Finally one half of the AB pattern at lower field is partially masked by the CO\_2CH\_2CH\_3 quartet and the H^a triplet [6 3.72, J(\text{PH}) 22 Hz] in the ^1H NMR spectrum of (3.12). However, on ^31P decoupling, the ^1H(^31P) NMR spectrum reveals a partially masked simple AB pattern with P\_2CH\_2OH\_0 shifts of 6 3.38 and 6 3.60, with J(\text{OH}) of 15 Hz.

The phenyl protons of the dppm ligand in (3.12) display a multiplet in the region 6 7.10-7.80.

### 3.7.2.2 ^1H and ^31P(^1H) NMR Spectra of [Co\_2(\text{CO})\_4(table:underline)(\mu-CH\_2)(\mu-CHMe)(\mu-dppm)]

Complex (3.11), assigned from IR data to be [Co\_2(\text{CO})\_4(table:underline)(\mu-CH\_2)(\mu-CHMe)(\mu-dppm)], revealed a broad singlet at 6 44.0 in dichloromethane-d\_2 which again is in the range of chemical shift values for ^31P(\text{^1H}) NMR resonances for the bis(\mu-alkylidene) complexes in the dicobalt system (Table 3.3).

Unfortunately, a well-resolved ^1H NMR spectrum of (3.11) could not be obtained between the temperature range -60°C to +30°C. The diagnostic large J(\text{PH}) of the comparatively shielded bridgehead alkylidene proton extending over the diphosphine ring was not defined in the spectrum at any temperature to identify which of the three possible isomers was preferred. Although a mixture of these three
isomers may exist, the assigned configuration of the mixed
bis(µ-alkylidene) species (3.11) suggests isomer (3.11a) is the least
probable conformation, as drawn along the Co-Co bond.

\[ \text{(3.11a)} \quad \text{(3.11b): } R=H, R'=\text{Me} \]
\[ \text{(3.11c): } R=\text{Me}, R'=H \]

The fact that (3.11) was only isolated as an unstable, oily product
suggests that the incorporation of a µ-ethylidene unit in (3.5) with
carbonyl loss to produce (3.11) may parallel the behaviour reported
earlier for the (µ-alkylidene)diiron complexes possessing a β-hydrogen
atom\(^{50}\) (equation 3.4.1) by inducing decomposition of (3.11) via a
β-hydride elimination to generate ethylene and unidentifiable
cobalt-containing products at room temperature.

3.8 Summary of the Chapter

Scheme 3.6 presents an overall view of the defined
stereochemistries from the characterized µ-alkylidene derivatives of
\[ [\text{Co}_2(\text{CO})_4(µ-\text{CO})_2(µ-\text{dppm})].(3.4); \] in each complex the Newmann projection
is drawn along the Co-Co bond. Only the µ-alkylidene complexes whose
stereochemistry was clearly defined by both a shielded chemical shift
of the proton exhibiting a large J(PH) value in the \(^1\text{H}\) NMR spectrum by
Scheme 3.6: Newmann Projections of Defined Stereochemistries for each Characterized
(μ-Alkylidene)dicobalt Derivative of $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]$ (3.4)
comparison to the other \( \mu \)-alkylidene proton resonances, and the
appropriate IR carbonyl stretching frequencies are illustrated in
Scheme 3.6. Unfortunately, suitable crystals for X-ray structural
analysis could not be obtained to confirm these assignments. In all
cases, there was no evidence for minor isomers in the NMR spectra, so
that alternative isomers must lie at considerably higher energy. Up to
+35°C, there is no evidence of fluxional behaviour of the alkylidenes
for complexes (3.8)-(3.12), unlike the \( \mu \)-methylene systems (3.5) and
(3.6). This suggests that any reversible, concerted opening of either
the mono- or di-\( \mu \)-carbene bridge in these complexes is a higher energy
process than for the simple \( \mu \)-methylene complexes.

It is interesting to note that for both the defined structures
(3.5) and (3.9) in Scheme 3.6, the mono-\( \mu \)-alkylidene ligand occupies a
position trans to a terminal carbonyl rather than trans to phosphorus,
presumably because the \( \pi \)-acceptor carbonyl can better remove excess
electron density donated by the \( \mu \)-CHR ligand in this configuration.
Significant deviations in the size of either angle \( \alpha \) (section 1.3), on
substitution of a carbonyl bridge by an alkylidene ligand, or angle \( \beta \)
(section 1.3) are not anticipated within this dicobalt system. This
suggests that steric interactions between the bridgehead carbon
substituents and the diphosphine phenyl substituents prevent product
formation in the preferred configuration, assigned to (3.5) and (3.9)
in Scheme 3.6, from the reaction of (3.4) with excess diphenyl-
diazomethane (\( \text{Ph}_2\text{CN}_2 \)) or 2-diazopropane (\( \text{Me}_2\text{CN}_2 \)) addition.
Consideration of molecular models illustrates this hypothesis.
Although the steric interactions are suspected to be weaker for the
isopropyl unit in this preferred configuration compared to the
diphenyl diazomethane carbene unit, any \( \mu \)-isopropylidene complex formed may readily decompose via a \( \beta \)-hydride elimination to eventually yield propylene (equation 3.4.1).

This work has succeeded in preparing the first series of dicobaltacyclopropane complexes based on cobalt carbonyl. Furthermore, this synthetic series provides the first example of an alkylidene-bridged complex in \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHR})(\mu-\text{dppm})]\) (\(R=\text{H}(3.5), \text{CO}_2\text{Et}(3.9)\)) obtained from \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]\) (3.4) and the appropriate diazoalkane. Excess diazoalkane addition results in formation of the bis\((\mu\)-alkylidene) complexes \([\text{Co}_2(\text{CO})_4(\mu-\text{CHR})_2(\mu-\text{dppm})]\) (\(R=\text{H}(3.6), \text{Me}(3.8)\)). Diazomethane reacts with (3.9) to yield a stable solid, identified as \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)(\mu-\text{CHCO}_2\text{Et})(\mu-\text{dppm})]\) (3.12). Only the two methylene-bridged complexes (3.5) and (3.6) are fluxional. This rearrangement is proposed to occur via reversible opening of the methylene bridges, a fluxional process first suggested by Knox\(^\text{40}\) to account for the cis-trans isomerization of \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CMe}_2)]\) (1.91).

The easy accessibility of the mixed bis\((\mu\)-alkylidene) dicobalt complexes from diazoalkane addition to (3.4) allows ideal binuclear models to be formulated as potential models for surface studies of bridged-alkylidene units. Consequently the chemistry of these \((\mu\)-alkylidene\) dicobalt complexes has been studied and will be described in the next chapter. Subsequent work in the remaining chapters will focus on alternative methods of producing these same \((\mu\)-alkylidenes\) dicobalt complexes and attempts to synthesize analogues of these same complexes with the less sterically hindered dppm ligand, \(\text{Me}_2\text{PCH}_2\text{PMe}_2\), in place of dppm.
Table 3.1: Infrared $\nu$(CO) Frequencies of (μ-alkylidene)dicobalt Complexes of dppm

<table>
<thead>
<tr>
<th>(Co₂(CO)₄(μ-R)(μ-R')(μ-dppm))</th>
<th>Terminal $\nu$(CO), cm⁻¹</th>
<th>Bridging $\nu$(CO), cm⁻¹</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=R'=CO; (3.4)</td>
<td>2049(s), 2017(s), 1991(s)</td>
<td>1842(m), 1793(m)</td>
<td>a³⁹</td>
</tr>
<tr>
<td></td>
<td>2040(s), 2010(s), 1995(s)</td>
<td>1825(m), 1795(m)</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>2047(s), 2005(s), 1985(s)</td>
<td>1810(s), 1799(s)</td>
<td>c³⁹</td>
</tr>
<tr>
<td>R=CO, R'=CH₂; (3.5)</td>
<td>2030(s), 2000(s), 1990(s)</td>
<td>1835(m)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>2035(s), 2000(s), 1990(s)</td>
<td>1810(m)</td>
<td>b</td>
</tr>
<tr>
<td>R=R'=CH₂; (3.6)</td>
<td>2030(m), 2000(s), 1990(s)</td>
<td></td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>2025(m), 2000(m), 1980(s)</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td>R=CO, R'=CH₄e; (3.7)</td>
<td>2030(m), 2010(s), 2000(s)</td>
<td>1810(m)</td>
<td>b</td>
</tr>
<tr>
<td>R=R'=CH₄e; (3.8)</td>
<td>2020(m), 2005(s), 1980(s)</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td>$[\text{Co}_2(\text{CO})_4(\mu-R)(\mu-R')(\mu-\text{dppm})]$</td>
<td>Terminal $\nu(\text{CO}), \text{cm}^{-1}$</td>
<td>Bridging $\nu(\text{CO}), \text{cm}^{-1}$</td>
<td>Medium</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-------</td>
</tr>
<tr>
<td>$R=\text{CO}, R'=\text{CHCO}_2\text{Et}; (3.9)$</td>
<td>2040(m), 2015(s), 1995(m), 1700(m)$^e$</td>
<td>1850(m)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>2040(s), 2010(s), 1990(s), 1695(m)$^e$</td>
<td>1820(m)</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>2040(s), 2010(s), 1995(s, br), 1695(w, br)$^e$</td>
<td>1820(s)</td>
<td>c</td>
</tr>
<tr>
<td>$R=\text{CO}, R'=\text{CHPh}; (3.10)$</td>
<td>2035(s), 2000(s), 1990(s, br)</td>
<td>1805(m)</td>
<td>b</td>
</tr>
<tr>
<td>$R=\text{CH}_2, R'=\text{CHMe}; (3.11)$</td>
<td>2030(s), 2000(s), 1990(s), 1980(s, br)</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>2040(s), 2010(s), 1990(s), 198(s, br)</td>
<td></td>
<td>d</td>
</tr>
<tr>
<td>$R=\text{CH}_2, R'=\text{CHCO}_2\text{Et}; (3.12)$</td>
<td>2035(m), 2010(s), 1985(m), 1690(m, br)$^e$</td>
<td></td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>2035(s), 2010(s), 1995(s), 1680(m)$^e$</td>
<td></td>
<td>b</td>
</tr>
</tbody>
</table>

a: cyclohexane  
b: dichloromethane  
c: nujol  
d: chloroform  
e: $\nu(\text{CO}_2\text{Et}), \text{cm}^{-1}$
The A-frame molecules $[\text{Rh}_2(\text{CO})_6(\mu-\text{CROCO}_2\text{EtN}_2)(\mu-\text{dppm})_2]$ (2.6), which are based on the structure of the A-frame precursor complex $[\text{Rh}_2(\text{CO})_6(\mu-\text{H})_2(\mu-\text{dppm})_2]$ (2.5), result from a reversible diazoalkane addition to (2.5). On photolysis or thermolysis, these adducts (2.6) do not eliminate dinitrogen but rather dissociate the intact diazoalkane molecule. The synthesis of the complexes (2.6) is represented by equation 2.1.3.
Table 3.2: $^1$H NMR Spectral Data for the \(\text{[u-alkylidene]dicobalt Complexes of dppm} \) at 100 MHz.\(^k\)

$$s(\text{ppm}) \text{ w.r.t. SiMe}_3$$

<table>
<thead>
<tr>
<th>Complex</th>
<th>(u)-CHR(^a)</th>
<th>(u)-CHR(^b)</th>
<th>(P_2\text{CH}_2) (^m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{[Co}_2\text{CO}_3\text{Cl}_2\text{]})</td>
<td>(3.91, t, J(\text{PH}) 10 \text{ Hz})</td>
<td>(3.41, t, J(\text{PH}) 10 \text{ Hz})</td>
<td>(P_2\text{CH}_2\text{H}^m) 2.68, m, (J(\text{H}^1\text{H}^2)) 15 Hz</td>
</tr>
<tr>
<td>(\text{[Co}_2\text{H}_3\text{]})</td>
<td>(3.36, m, J(\text{H}^1\text{H}^2)) 15 Hz</td>
<td>(3.64, t, J(\text{PH}) 10.5 \text{ Hz})</td>
<td>(P_2\text{CH}_2\text{H}^m) 3.10, m, (J(\text{H}^1\text{H}^2)) 14 Hz</td>
</tr>
<tr>
<td></td>
<td>(3.12, t, J(\text{PH}) 10.5 \text{ Hz})</td>
<td>(3.73, m, J(\text{H}^1\text{H}^2)) 14 Hz</td>
<td>(P_2\text{CH}_2\text{H}^m) 4.32, m, (J(\text{H}^1\text{H}^2)) 14 Hz</td>
</tr>
<tr>
<td>(\text{[Co}_2\text{H}_3\text{]})</td>
<td>(2.76, s, J(\text{H}^1\text{H}^2) 8 \text{ Hz})</td>
<td>(4.87, m, J(\text{H}^1\text{H}^2) 14 \text{ Hz})</td>
<td>(P_2\text{CH}_2\text{H}^m) 4.04, q, (J(\text{HH}) 7 \text{ Hz})</td>
</tr>
<tr>
<td>(\text{[Co}_2\text{H}_3\text{]})</td>
<td>(1.22, t, J(\text{HH}) 7 \text{ Hz})</td>
<td>(2.67, m, J(\text{H}^1\text{H}^2) 14.5 \text{ Hz})</td>
<td>(P_2\text{CH}_2\text{H}^m) 3.41, m, (J(\text{H}^1\text{H}^2)) 14.5 Hz</td>
</tr>
<tr>
<td>(\text{[Co}_2\text{H}_3\text{]})</td>
<td>(1.38, m, J(\text{H}^1\text{H}^2) 15 \text{ Hz})</td>
<td>(3.38, m, J(\text{H}^1\text{H}^2) 15 \text{ Hz})</td>
<td>(P_2\text{CH}_2\text{H}^m) 3.10, m, (J(\text{H}^1\text{H}^2)) 15 Hz</td>
</tr>
<tr>
<td>(\text{[Co}_2\text{H}_3\text{]})</td>
<td>(1.60, m, J(\text{H}^1\text{H}^2) 15 \text{ Hz})</td>
<td>(4.10, q, J(\text{HH}) 7 \text{ Hz})</td>
<td>(P_2\text{CH}_2\text{H}^m) 1.26, t, (J(\text{HH}) 7 \text{ Hz})</td>
</tr>
</tbody>
</table>

\(\text{dppm} = \text{Ph}_2\text{PCH}_2\text{Ph}_2\)\(^n\) \(\text{J(PH) = 10 Hz, unless otherwise stated n) -40°C o) -80°C}\)
Table 3.3: $^{31}$P($^1$H) NMR Spectral Data for the (μ-alkyldene)dicobalt Complexes of dppm at 40.5 mHza

<table>
<thead>
<tr>
<th>Complex</th>
<th>$8$(ppm) w.r.t. external (MeO)$_3$PO</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="3.4">Co$_2$(CO)$_4$(μ-μCO)$_2$(μ-dppm)</a></td>
<td>58.5</td>
</tr>
<tr>
<td>[Co$_2$(CO)$_4$(μ-μCO)(μ-R)(μ-dppm)]</td>
<td></td>
</tr>
<tr>
<td>R=CH$_2$; (3.5)</td>
<td>57.5</td>
</tr>
<tr>
<td>R=CHCO$_2$Et; (3.9)</td>
<td>53.5</td>
</tr>
<tr>
<td>R=CHPh; (3.10)</td>
<td>55.1</td>
</tr>
<tr>
<td>[Co$_2$(CO)$_4$(μ-R)(μ-R')(μ-dppm)]</td>
<td></td>
</tr>
<tr>
<td>R=R'=CH$_2$; (3.6)</td>
<td>40.8</td>
</tr>
<tr>
<td>R=R'=CHMe; (3.8)</td>
<td>42.8</td>
</tr>
<tr>
<td>R=CH$_2$, R=CHMe; (3.11)</td>
<td>44.0</td>
</tr>
<tr>
<td>R=CH$_2$, R=CHCO$_2$Et; (3.12)</td>
<td>41.8</td>
</tr>
</tbody>
</table>

a CD$_2$Cl$_2$

b dppm=Ph$_2$PCH$_2$PPh$_2$
APPENDIX 3.1

Calculation of the free energy for a fluxional process using NMR data and the Eyring equation

The inversion process of the \( \mu \)-methylene groups in \([\text{Co}_{2}(\text{CO})_{4}(\mu-\text{CH}_2)_{2}(\mu-\text{dpdm})]\) (3.6) was proposed to occur rapidly with respect to the NMR time scale at room temperature via a bridge/terminal methylene isomerization (equation 3.3.2). Figure 3.5 reveals that the two inequivalent \( \mu \)-methylene carbon atoms coalesce at approximately 30°C in the 400 MHz \(^{13}\text{C}(\text{^1H})\) NMR spectrum of (3.6). The separation of these two signals at the low exchange limit \( \Delta \nu \) is estimated using the Eyring equation (equation A.3.1).

\[
\Delta G = k_B T \ln \left( \frac{k_B T C \sqrt{2}}{\hbar \Delta \nu} \right) \tag{A.3.1}
\]

Only the two variables \( \Delta \nu \) and \( T_C \), the coalescence temperature (303K), are determined by experiment. The constants in the Eyring equation are: \( R \), the gas constant, \( 8.314 \text{ J mol}^{-1}\text{K}^{-1} \); \( k_B \), the Boltzmann constant, \( 1.381 \times 10^{-23} \text{ J K}^{-1} \); \( \hbar \), the Planck constant, \( 6.63 \times 10^{-34} \text{ J s} \). By substituting the experimental values into equation A.3.1, the estimated free energy \( \Delta G \) of this fluxional process for (3.6) is 54 kJ mol\(^{-1}\).
References

   (b) Tebbe, P.N.; Parshall, G.W. and Ovenall, D.W., Ibid. 101(1979)5074.


52. Hanson, B.E. and Mancini, J.S., Organometallics 2(1983)126.


CHAPTER 4

REACTIVITY OF (µ-ALKYLIDENE)DICOBALT COMPLEXES OF DPPM

4.1 Introduction

The introduction to the preceding chapter emphasized the controversy surrounding the mechanistic scheme for the Fischer-Tropsch synthesis. Several recent reports have emerged describing experimental results consistent with the carbon monoxide-dissociative route.\(^1\),\(^2\) According to this mechanism (equation 3.1.2), carbon monoxide is assumed to dissociate upon adsorption to give surface-bound carbon species which are subsequently hydrogenated to yield surface methylene and methyl fragments. These can then dimerize and add hydrogen to give hydrocarbon products. Although this mechanism has been called into question by some authors,\(^3\) particularly when experimental data did not support a carbon monoxide-dissociative mechanism,\(^4\) it is generally assumed that surface methylenes derive from hydrogenation of surface carbon generated via carbon monoxide dissociation.\(^5\) Consequently, the chemistry of methylene-bridged transition-metal compounds is under active investigation to determine the possible relevance of these observations to carbon monoxide reduction on metal surfaces.

The reactivity of the novel (µ-alkylidene)dicobalt complexes prepared and spectroscopically characterized in Chapter 3 was investigated with small molecule additions in order to assess their potential catalytic behaviour. The relationship of these reactions to
catalytic activity will be discussed for these (μ-alkylidene)dicobalt complexes and related systems.

4.1.1 Scope of the Chapter

This work reports the first example of hydrogenolysis of a d1(μ-methylene) transition metal complex to give ethane and some remarkably easy methylene coupling reactions to give ethylene. The reactions are significant as models for the proposed steps in the Fischer-Tropsch synthesis using transition metal catalysts such as cobalt shown in equation 3.1.5, and with respect to the related reaction of equation 3.1.4. In an attempt to determine the thermally induced coupling mechanism, a deuterium labelling study was conducted for the bis(μ-methylene) complex [Co₂(μ-CH₂)₂(μ-dppm)] (3.6). Reaction of the bis or mono(μ-methylene) species with ethylene resulted in propylene.

An interesting feature from the reaction of these (μ-alkylidene) dicobalt complexes with the small molecules carbon monoxide, sulfur dioxide and alkynes ROCR (R=Ph,CF₃) is the formation of ketene or a ketene derivative by coupling of the organic μ-alkylidene molecule with a carbonyl group. This insertion of a coordinated carbonyl ligand into a cobalt-μ-alkylidene bond is proposed to occur via an unstable bridging ketene complex. Although the respective μ₆-bridged ketene derivatives postulated as intermediates in these reactions could not be isolated, the ketene derivatives were trapped in the presence of methanol·d₄ as the respective esters in high yield and characterized via ¹H NMR spectroscopy. The possibility that methanol·d₄ attacks coordinated rather than free ketene cannot be ruled out, although free
ketene could be detected by g.c. when reactions were carried out in the absence of alcohol.

4.2 Thermal Decomposition Reactions

4.2.1 Thermolysis of Bridging Alkyldiene Complexes

The limited thermolysis chemistry of dimetallacyclop propane has revealed carbon-carbon coupling processes occurring on these metal surfaces, indicating a possible connection to Fischer-Tropsch and carbon monoxide reduction chemistry.

Coupling of substituted alkyldiene groups to yield 2-methyl-2-butene [ca. 70%] has been observed on pyrolysis of the complex [Cp2Ru2(O)2(μ-CMe2)(μ-CHMe)] (6.1), containing the Ru2(μ-CMe2)(μ-CHMe) unit, at 200°C.6 Minor volatile products observed were ethylene (ex. μ-CHMe) and propylene (ex. μ-CMe2) suggesting that alkyldiene recombination, or carbon-carbon coupling reactions, can effectively compete with hydrogen abstraction. The absence of 2-butenes or 2,4-dimethyl-2-butene indicates that the 2-methyl-2-butene observed is formed intramolecularly. This fact has been interpreted by Knox et al.6 to support the viability of carbene combination at a dinuclear metal center in catalytic processes, such as Fischer-Tropsch synthesis (equation 3.1.4).

Thermolysis of internal or disubstituted alkyldiene complexes (1.69a), (1.69b) and (1.69c) (Scheme 4.1) produces a novel rearrangement in which the dicobalt moiety migrates to the end of the alkyldiene carbon chain, generating terminal alkyldiene complexes having the same number of carbon atoms.7 For example, when a benzene d6 solution of the saturated 2-propyldiene complex (1.69a) was
Scheme 4.1

60°C; R = R' = Et

(1.69b)

Cp(OC)Co + Co(OC)Cp → H n-Bu

(1.68c)

60°C

Cp(OC)Co + Co(OC)Cp + pentenes

(1.68c)

60°C

Cp(OC)Co + Co(OC)Cp + CH₃CH=CH₂

(1.68b)

60°C; R = R' = Me

(1.69a)
heated at 80°C for 10 h, loss of one carbonyl ligand to give the
corresponding doubly bonded complex was observed and soon subsequent
decomposition produced propylene [79%] and the unbranched 1-propylidene
complex (1.68b) [7%] during the course of the reaction. No reverse
isomerization was observed on heating (1.68b) or (1.68c) in Scheme 4.1;
only olefin and intractable organometallic products were formed.
Deuterium labelling studies revealed the mechanism of rearrangement
for the complete conversion of a labelled 3-pentylidene complex
(1.69b)-d₄ to the 1-pentylidene isomer (1.68c)-d₄ (equation 4.2.1)
utilizes both sequential 1,2-metal shift (leading to olefin π
complexes) and allylic C-H activation (leading to π-allyl complexes) in
accomplishing this rearrangement of olefin isomerization. This work
demonstrates the conversion of olefin into μ-alkylidene ligands is a
viable process.

\[
\begin{align*}
&\text{CH}_3\text{CD}_2 \quad \text{CD}_2\text{CH}_3 \\
Cp(\text{CO})\text{Co} & \quad \text{Co(}\text{CO})\text{Cp} \\
(1.69b)\cdot d_4 & \quad \text{60°C} \quad \text{C}_2\text{D}_8 \\
& \quad \text{Cp(}\text{CO})\text{Co} \quad \text{Co(}\text{CO})\text{Cp} \\
& \quad (1.68c)\cdot d_4
\end{align*}
\]

4.2.1

The pyrolysis of the complex cis\-\(\{\eta^5\text{-C}_5\text{Me}_5\}\text{Rh}_2\text{Me}_2(\mu\text{-}\text{CH}_2)_2\} \) (4.2)
at 350°C produces a product composition of methane [48%], ethylene
[20%], ethane [2%], and propylene [30%]. Only trace amounts of
propane and C₄ hydrocarbons were observed, but no cyclopropane. By
contrast, the corresponding trans isomer was more difficult to pyrolyze
and revealed only one-tenth the yield of the identical mixture of
gaseous products. A suggested mechanism proposed by Maitlis and
co-workers to account for the methane and propylene product formation is outlined in equation 4.2.2 to involve a linking of one methyl and two methylene ligands in an oxidized form of the complex to give a C₃ ligand, which β-eliminates propylene. The product of propylene rather than propane in the pyrolysis also agrees with the general view that the initial products of Fischer-Tropsch reactions are α-olefins. This work appears to be an excellent model for equation 3.1.5 and subsequent steps.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{M} & \quad \text{M} \\
\text{CH}_3 & \quad \text{H} \\
\text{M} & \quad \text{CH} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[M = \text{Rh(n}^5\text{-C}_9\text{H}_{13})\]

This form of polymerization reaction illustrates the ability of the alkylidyne groups to couple on metal surfaces and furthermore, the more readily pyrolyzed cis-isomer emphasizes the importance of specific geometric requirements on transition metal surfaces to induce this polymerization reaction.

Since the thermal decompositions of the dicobaltacyclop propane complexes discussed in the preceding chapter were suspected to involve carbon-carbon coupling processes, these dicobalt complexes were subjected to mild pyrolysis experiments and the results are presented in section 4.2.2. Gaseous thermolysis products were characterized via gas chromatographic (g.c.) techniques, as described in the experimental section 7.4.1.
4.2.2 Thermolysis of Novel Dicobaltacyclopropane Complexes

Pyrolysis of the bis(μ-methylene) complex \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)\text{-}(\mu-\text{dppm})]\) (3.6) occurred readily at 80-90°C in decalin to give ethylene, identified by g.c. analysis. No other hydrocarbon products were observed in the gas phase. However, the \(C_2\)-oxygenated product ketene \((\text{CH}_2=\text{C}=\text{O})\) was also formed. Ketene was prepared in a separate experiment by pyrolysis of diketene and had an identical g.c. retention time to that observed using the porapak Q column. The retention time is the same as that of carbon dioxide, and final confirmation of ketene formation was obtained by trapping experiments which are described later. These results suggest that a competition exists between a carbon-carbon coupling of the simple methylene units to generate ethylene and the formation of ketene. An insertion of a carbonyl ligand into a cobalt-μ-methylene bond is suggested to produce an unstable ketene complex, which subsequently generates the ketene product. Two moles of ketene or one mole of ethylene could be formed per mole of (3.6) decomposed. The yield of ketene was difficult to estimate by g.c. because the ketene peak was superimposed on the carbon dioxide peak in the g.c. spectrum, but, qualitatively, more ketene was formed and this suggests that ketene production is the more favourable carbon-carbon coupling process at these temperatures.

The methylene coupling reaction to produce ethylene was suspected to be intramolecular, as determined for the 2-methyl-2-butenone formation from pyrolysis of (4.1), when the similar pyrolysis of the mono(μ-methylene) complex (3.5) or the complex \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)\text{-}(\mu-\text{CHOOC}_2\text{Et})(\mu-\text{dppm})]\) (3.12) in decalin failed to produce ethylene; only the ketene product was detected. No carbon-carbon coupling reaction to
generate the unsaturated diethyl fumarate or diethyl maleate products were observed from a similar pyrolysis of \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHCO}_2\text{Et})](\mu-\text{dppm})\) (3.9)(see section 7.4.1).

In addition, pyrolysis in decalin between 80-85°C of \([\text{Co}_2(\text{CO})_4(\mu-\text{CHMe})_2(\mu-\text{dppm})]\) (3.8) gave ethylene only (no butenes) and pyrolysis of \([\text{CO}_2(\text{CO})_4(\mu-\text{CH}_2)(\mu-\text{CHMe})(\mu-\text{dppm})]\) (3.11) gave ethylene and propylene, with the ethylene presumably being formed by \(\beta\)-elimination from the \(\mu\)-CHMe moiety. This same phenomenon was earlier observed on pyrolysis at 200°C of \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CHMe})(\mu-\text{CHMe}_2)]\) (4.1) to generate both ethylene (ex. \(\mu\)-CHMe) and propylene (ex. \(\mu\)-CHMe). Similar diiron complexes \([\text{Fe}_2(\text{CO})_6(\mu-\text{CRR'})}\) (1.61), where either or both methylene bridgehead substituents \(R\) and \(R'\) contain a \(\beta\)-hydrogen atom, were reported to readily undergo \(\beta\)-hydride elimination prior to reductively eliminating the appropriate olefin and \([\text{Fe}_3(\text{CO})_{12}]\) at room temperature in solution (equation 3.4.1). The coupling of the substituted alkylidene groups in (3.11) to yield propylene indicates, as was deduced from pyrolysis of the ruthenium dimer (4.1) at 200°C, that the carbon-carbon coupling reactions producing propylene compete with hydrogen abstraction in (3.11). Furthermore, the observation of no butene products from pyrolysis of (3.11) is consistent with the occurrence of only intramolecular carbon-carbon coupling reactions for these dicoalt systems. Only ketene was detected from pyrolysis of (3.11) on g.c. analysis.

This discovery that the \(\mu\)-methylene groups are mobile in the dicoalt system (3.6), and that the smaller \(\mu\)-alkylidene ligands can couple on the small clusters (3.6) and (3.11), is consistent with suggestions that similar coupling reactions of alkylidene groups may
also occur on heterogeneous catalysts.

4.2.3 Deuterium Labelling Study

In order to confirm the apparent intramolecular coupling mechanism suspected for the ethylene formation from pyrolysis of the bis(μ-methylene) species (3.6), a deuterium labelling study was conducted. Reaction of an excess ethereal diazomethane-d₂ solution with [Co₂(CO)₄(μ-CO)₂(μ-dppm)] (3.4) produced a mixture of the deuterated products [Co₂(CO)₄(μ-CO)(μ-CD₂)(μ-dppm)] (4.3) and [Co₂(CO)₄(μ-CD₂)₂(μ-dppm)] (4.4), analogous to equation 3.3.1. The separation of these deuterated μ-methylene derivatives (4.3) and (4.4) was performed as described in section 3.3.1.

Three separate, evacuated reaction flasks, each containing an equimolar amount of either (3.6), (4.4) or a 1:1 mixture of (3.6) and (4.4), were pyrolyzed for 8 hours in degassed decalin (3.0 mL) at 80-85°C. A second trial was repeated for each case in an identical manner without the solvent decalin, permitting a solid sample pyrolysis as shown by equations 4.2.3 - 4.2.5.

\[
[\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})] \quad \overset{\Delta}{\longrightarrow} \quad \text{C}_2\text{H}_4 \quad (\text{m/e} \ 28) \quad 4.2.3
\]

\[
[\text{Co}_2(\text{CO})_4(\mu-\text{CD}_2)_2(\mu-\text{dppm})] \quad \overset{\Delta}{\longrightarrow} \quad \text{C}_2\text{D}_4 \quad (\text{m/e} \ 32) \quad 4.2.4
\]

\[
(3.6) \quad + \quad (4.4) \quad \overset{\Delta}{\longrightarrow} \quad \text{C}_2\text{H}_4 \quad + \quad \text{C}_2\text{D}_4 \quad \text{or} \quad \text{C}_2\text{H}_4 \quad + \quad \text{C}_2\text{H}_2\text{D}_2 \quad (\text{m/e} \ 30) \quad + \quad \text{C}_2\text{D}_4 \quad 4.2.5
\]
If indeed the carbon-carbon coupling reaction to give ethylene
\((C_2H_4)\) from pyrolysis of \((3.6)\) is intramolecular, then a similar
pyrolysis of the 1:1 mixture of \((3.6)\) and \((4.4)\) should evolve \(C_2H_4\) (m/e
28) and \(C_2D_4\) (m/e 32) only, with no \(C_2H_2D_2\) (m/e 30) being formed
(equation 4.2.5). However, \(C_2H_2D_2\) will be observed if an
intermolecular coupling process of the methylene bridges is dominant.
The gas produced from the pyrolysis of each experiment can be analyzed
by mass spectrometry. The pyrolyses of \((3.6)\) (equation 4.2.3) and
\((4.4)\) (equation 4.2.4) were conducted in separate chambers to act as
controls to determine their individual experimental fragmentation
patterns, particularly with regard to the magnitude of the peak at m/e
30 \((C_2H_2D_2)\).

There are four basic assumptions or criteria which were necessary
for these mass spectral results to elicit meaningful information:

1. Equimolar quantities of \((3.6)\) and \((4.4)\) must be employed for all
three experiments.

2. Sample \((4.4)\) must be completely deuterated; the initial ethereal
diazomethane-\(d_2\) was actually 97% deuterated.

3. Pyrolysis is total for each experiment.

4. The background/solvent mass spectral intensity must be calibrated
for each of the three individual experiments by comparison with a
blank experiment.

In order to determine a ratio of the abundance of each ethylene
product \(C_2H_4;C_2H_2D_2;C_2D_4\) obtained from reaction 4.2.5, the following
mass spectral calculations were conducted using the results of
reactions 4.2.3 to 4.2.5 listed in Table 4.1. Each recorded peak
intensity contained in Table 4.1 has been corrected for
Table 4.1: Mass Spectral Data from Reactions 4.2.3 to 4.2.5

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative peak intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.2.3</td>
</tr>
<tr>
<td>28</td>
<td>13.6</td>
</tr>
<tr>
<td>30</td>
<td>0.27</td>
</tr>
<tr>
<td>32</td>
<td>0</td>
</tr>
</tbody>
</table>
background/solvent intensity such that the relative peak intensities in Table 4.1 are considered directly proportional to the abundance of that particular ion in the gas phase.

The peak intensity at m/e 30 displayed from reaction 4.2.3 is very small and thus is considered to create a negligible contribution at m/e 30, as is observed for this same reaction at m/e 32. However, the intensity of the peaks in Table 4.1 for both reactions 4.2.4 and 4.2.5 require some calibration to eliminate any contribution to peaks m/e 28 and m/e 30 originating from fragmentation of the C₂D₄ species, and the peak m/e 28 from the fragmentation of the C₂H₂D₂ species formed from reaction 4.2.5. Since equimolar quantities of the tetradueterated complex (4.4) were employed in both equations 4.2.4 and 4.2.5, a direct comparison of their respective peak intensities is achieved via normalization of the peak at m/e 32. Thus each peak intensity for equation 4.2.4 requires a division by 5.2 to produce the normalized peak intensities shown in Table 4.1 as 4.2.4*. If the intensity values of 4.2.4* are then subtracted from those of 4.2.5, the resultant peak intensities represent the peak intensity contributions due to the mixed C₂H₂D₂ species formed exclusively from equation 4.2.5. These difference values, listed in Table 4.1 under (4.25-4.24*), eliminate any additional intensity at peaks m/e 28 and m/e 30 contributed via fragmentation of the C₂D₄ species. However, in order to estimate the peak intensity of C₂H₄ (m/e 28) produced solely via an intramolecular carbon-carbon coupling process in equation 4.2.5, the m/e 28 peak must be corrected for the fragmentation of the intermolecularly coupled C₂H₂D₂ product. A C₂H₂D₂ product will add intensity to the peak m/e 28 if one deuterium (C₂H₂D⁺) or two hydrogen atoms (C₂D₂⁺) are lost from
the base peak (m/e 30). Depending on the specific C₂H₂D₂ species formed from equation 4.2.5, the fragmentation peak at m/e 28 from 1,1-dideuteroethylene, trans-1,2-dideutero and cis-1,2-dideuteroethylene is 40%, 42% and 43% respectively as compared to their base peak (m/e 30). It is assumed for the purpose of the calculation that their is an equal probability of forming all three C₂H₂D₂ isomers, and hence the fragmentation pattern of the C₂H₂D₂ product peak at m/e 28 is estimated to be 41.7% of the base peak (m/e 30) intensity, or .417x8.48=3.54. Consequently, 41.7% of the peak intensity at m/e 30 for (4.2.5-4.2.4⁻¹) will result from fragmentation of the C₂H₂D₂ species at m/e 28, while the remaining peak intensity at m/e 28 is attributed to the C₂H₄ species formed from equation 4.2.5. Therefore, at m/e 28, the corrected peak intensity due to C₂H₄ formed exclusively from equation 4.2.5 is 13.06-3.54=9.52.

Analysis of the combined mass spectral data obtained from these experiments, with or without pyrolysis in decalin, indicate that the carbon-carbon coupling process in (3.6) is not a trivial intramolecular phenomenon. The ratio of C₂H₄:C₂H₂D₂:C₂D₄ observed from equation 4.2.5 is approximately 9.5:8.5:1.0, suggesting that the ethylene formation from the pyrolysis of (3.6) is an intermolecular coupling process and proceeds via a complex mechanistic route incorporating a large isotope effect.

4.2.4 The Mechanism of the Carbon-Carbon Coupling

The mass spectral results in section 4.2.3 indicate that the ethylene formation from pyrolysis of (3.6) is more complex than the direct coupling of methylene units (equation 3.1.4), which has been
implicated to proceed through a dimetallocyclobutane intermediate.

This mass spectral data lends support to the theoretical interpretations of Hoffmann et al.,\textsuperscript{10} which claim that the simple coupling of two \( \mu \)-methylene groups in a binuclear complex is an unlikely process due to orientational problems acute in both the reactant and product. These authors propose that two factors account for the reluctance of the bis(\( \mu \)-methylene) complexes to form ethylene:\textsuperscript{10}

(1) Although binuclear acetylene complexes exhibit a "perpendicular" type of bonding (4.5), no binuclear ethylene complexes are known with this bonding configuration. Only "parallel" bonding modes (4.6) exist for these ethylene complexes.

(2) All known complexes containing two or more bridging substituted methylenes possess a rotated conformation (4.8) of the locally tetrahedral methylene carbons, not the least motion coupling orientation (4.7). Hoffmann et al.\textsuperscript{10} predict that there is no simple motion which can convert the favoured conformation (4.8) to the normal coordinated ethylene geometry (4.6).

The observation of ethylene and propylene from pyrolysis of (3.6)
and (3.11) respectively emphasize that some more complex carbon-carbon coupling mechanism, in accordance with the mass spectral results and Hoffmann's theoretical arguments, exists for this olefin synthesis from the bis(μ-alkylidene) units in these dicobalt systems. Hoffmann's hypothesis suggests that the size of the energy barrier controlling an intramolecular carbon-carbon coupling process of bis(μ-alkylidene) groups increases with bulkier bridgehead substituents, if in the rotated orientation (4.8). Although an X-ray structural analysis could not be obtained, the preferred configuration assigned to the dicobalt complexes (3.6), (3.9) and (3.12) from their 1H NMR data (section 3.3.2.2, 3.4.2.1 and 3.7.2.1) signifies that these dicobalt complexes adopt the rotated conformation. This assumption may account for the absence of the intramolecular coupled products 2-buten-1 and ethyl acrylate from pyrolysis of (3.8) and (3.12) respectively.

The observation of ethylene from pyrolysis of the bis(μ-methylene) complex (3.6) may be dependent on the presence of the fluxional methylene bridges (equation 3.3.2). Similarly, propylene creation from (3.11) may also extend from a coupling mechanism incorporating a fluxional methylene bridge. Since the mass spectral data indicate a high deuterium isotope effect in the carbon-carbon coupling reaction to form ethylene from pyrolysis of (3.6), an intermediate or activated complex in which partial or total rupture of a carbon-hydrogen bond has occurred is strongly suggested. Since the carbon-hydrogen bond has a greater (ca. 1.2 kcal mol⁻¹) zero-point energy than the corresponding carbon-deuterium bond, an isotope effect is expected if the carbon-hydrogen or carbon-deuterium bond is broken or stretched in the rate-determining step. Consequently, although speculative, this
system may traverse through an activated methyne-type complex (equation 4.2.6), which may establish a coupling phenomenon invoking a methylene bridge and a terminal carbene, accessible via a fluxional methylene bridge. If, indeed this carbon-carbon coupling process proceeds by a route employing formation of a methyne-type species, a kinetic isotope effect may explain the observed mass spectral results.

![Chemical Diagram](image-url)

However, the intramolecular reaction sequence proposed in equation 4.2.6 does not account for the mixed C₄H₂D₂ species. The formation of C₄H₂D₂ must derive from an intermolecular carbon-carbon coupling mechanism, although g.c. and ¹H NMR evidence contradicts any butene production from pyrolysis of (3.11) or ethylene formation from pyrolysis of (3.5) or (3.12). One possible mechanistic pathway incorporating both a large isotope effect and the apparent intermolecular carbon-carbon coupling process may involve a tetranuclear activated complex which, when subsequently formed from thermolysis of equimolar amounts of (3.6) and (4.4), could permit C₄H₂D₂ formation and also the observed low C₄D₄ product yield.

Regardless of the tentative mechanistic proposals, this deuterium labelling study confirms that the olefin production observed from the pyrolysis of (3.6) and possibly (3.11) is a more complex phenomenon than the supposed direct methylene coupling action (equation 3.1.4).
Unfortunately, the specific mode of this coupling procedure cannot be conclusively elucidated from this experimental study.

4.3 Thermal Decomposition Reactions in the Presence of Hydrogen

4.3.1 Thermolysis of Bridging Alkyldene Complexes under Hydrogen

Pyrolysis of \([\text{Os}_3\text{(CO)}_{11}(\mu-\text{CH}_2)](1.3)\) leads to the decarbonylated cluster \([\text{Os}_3\text{(CO)}_{10}(\mu-\text{CH}_2)](4.9)\).\(^\text{12}\) When (4.9) was heated to 70-80°C under a hydrogen atmosphere, methane (20%) was evolved. Only methane-d\(_2\) resulted from thermolysis of (4.9) in a deuterium atmosphere. The analogous trimer \([\text{Os}_3\text{(CO)}_8(\text{NCMe})(\mu-\text{CO})(\mu-\text{CH}_2)]\) adds hydrogen to give a mixture of tautomers \([\text{H}_2\text{Os}_3\text{(CO)}_{10}(\mu-\text{CH}_2)](1.25)\) and \([\text{HOS}_3\text{(CO)}_{10}(\mu-\text{CH}_3)](1.24)\), which on further hydrogenation releases methane.\(^\text{13}\) This fact suggests that these tautomers are intermediates in the hydrogenation of (4.9). In addition to demonstrating the stepwise reduction of carbon monoxide to methane on a cluster face, these results support the idea that hydrogenation of surface bound carbenes is a reasonable path for hydrocarbon production.

The addition of hydrogen (200 psi) at 60°C to a benzene solution of \([\text{Fe}_3\text{(CO)}_8(\mu-\text{CH}_2)](1.61)\) produces methane (81%), acetaldehyde (5%), and \([\text{Fe}_3\text{(CO)}_{12}]\).\(^\text{14}\) Since this reaction was inhibited by carbon monoxide addition,\(^\text{14}\) these authors proposed a mechanism involving an initial carbon monoxide dissociation step (Scheme 4.2).

It is not known how methane is eliminated from (4.10) in Scheme 4.2, whether directly or from hydrogen migration to the iron atom bearing the methyl group and then elimination, but an intramolecular insertion of carbon monoxide in the Fe-CH\(_3\) bond of (4.10) followed by reductive elimination was suggested to produce acetaldehyde. This
behaviour is consistent with that postulated for methylene groups bound to a metal surface by Pichler and Schulz (equation 3.1.3).

This same mechanism, suggested in Scheme 4.2 to account for methane formation from (1.61),\(^\text{14}\) is also forwarded to describe the dimethyl ether produced in equation 4.3.1 from treatment of the methoxymethylene complex (4.11), containing an oxygenated methylene ligand, with hydrogen at 125°C in heptane.\(^\text{9}\) The formation of (4.12) is presumably due to the reaction of coordinatively unsaturated iron carbonyl species with (4.11). This trinuclear hydride (4.12) was obtained in good yield by treatment of (4.11) with Fe\(_2\)(CO)\(_6\).\(^\text{9}\)

\[
\begin{align*}
[\text{Fe}_2\text{(CO)}_6(\mu-\text{CHOCH}_3)] + H_2 & \xrightarrow{125^\circ C} [\text{Fe}_4\text{(CO)}_4(\mu-H) + \text{CH}_3OOCH] \\
(4.11) & \quad (4.12)
\end{align*}
\]

When bis(η\(^5\)-cyclopentadienyl)-μ-(methoxymethylene)-tricarbonyldiiron (4.13) is treated with hydrogen (270 psi) in THF at 150°C, the gaseous products are methane [5%] and dimethyl ether [15%] while the liquid phase contained [Cp\(_2\)Fe\(_2\)(CO)\(_2\)(μ-CO)]\(_2\) (1.75). Under identical conditions the μ-methylene derivative [Cp\(_2\)Fe\(_2\)(CO)\(_2\)(μ-CO)(μ-CH\(_2\))] (1.76a) produced methane [50%] and complex (1.75) [60%]. The corresponding μ-ethylidene derivative (1.76b) afforded only ethane and (1.75) when pyrolyzed at 165°C in p-xylene in the presence of hydrogen. All three hydrogenation reactions\(^\text{15}\) are proposed to occur by
\[ \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{C}(\text{H})\text{OME})] \text{CO} \rightarrow \text{CpFe} \rightarrow \text{Fe(CO)Cp} \rightarrow \text{CpFe} \rightarrow \text{Fe(CO)Cp} \rightarrow \text{H}_3\text{C} \to \text{O} \to \text{CH}_3 \rightarrow \text{CpFe} \rightarrow \text{Fe(CO)Cp} \]

(4.13)

Scheme 4.3
the same mechanism forwarded earlier for the hydrogenation of the iron dimer \((1.61)^{14}\) (Scheme 4.2). The suggested mechanistic pathway for the dimethyl ether formation from the hydrogenation reaction of the \(\mu\)-methoxymethylene derivative \((4.13)\) is illustrated by Scheme 4.3.

When \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHMe})]\) \((1.76b)\) was allowed to react with carbon monoxide and hydrogen \((1:1; 600 \text{ psi})\) and heated at 165°C in p-dioxane, a GC-MS analysis exposed ethane [trace] and propanal \([10\%]\) in the solution phase.\(^{15}\) The mechanism of propanal formation is also envisioned to parallel the acetaldehyde formation from pyrolysis of \([\text{Fe}_2(\text{CO})_6(\mu-\text{CH}_2)]\) \((1.61)\) under hydrogen\(^{14}\) (Scheme 4.2).

4.3.2 Thermoysis of the Novel Dicobaltacyclopropane Complexes Under Hydrogen

The pyrolysis of the bis(\(\mu\)-methylene) complex \((3.6)\) in decalin at 85°C under hydrogen \((14.7 \text{ psi})\) formed only traces of ethylene \([0.4\%]\), the major hydrocarbon product being ethane \([55\%]\). Formation of ethane is suggested to occur by oxidative addition of hydrogen to an unsaturated complex, followed by the reactions depicted in equation 3.1.5, and reductive elimination of ethane. An overall scheme to account for ethane formation from the pyrolysis of \((3.6)\) in the presence of hydrogen is illustrated in Scheme 4.4.

Note that the mechanism outlined by Scheme 4.4 involves an initial thermal dissociation of carbon monoxide to create a coordinatively unsaturated complex, first postulated by Pettit et al.\(^{14}\) for their hydrogenation of the \(\mu\)-methylene diiron complex \((1.61)\) shown in Scheme 4.2. An alternate route to the coordinatively unsaturated species could invoke cleavage of the cobalt-cobalt metal bond prior to
SCHEME 4.4: Suggested Mechanism for Ethene Formation from Pyrolysis of $[\text{Co}_2(\text{CO})_6(\mu-\text{CH}_2)_2(\mu-\text{dppm})](3.6)$ in the Presence of Hydrogen.
the oxidative addition of hydrogen. However, the activation of molecular hydrogen with [Co₂(CO)₆] (equation 4.3.2) requires ligand dissociation from the binuclear carbonyl, which precedes the rate-determining oxidative addition of hydrogen with the coordinatively unsaturated [Co₂(CO)₇]. Therefore, by comparison, the former pathway involving a carbonyl ligand dissociation from (3.6) appears to be the more probable preliminary step in Scheme 4.4.

\[
\begin{align*}
[\text{Co}_2(\text{CO})_6] & \xrightarrow{K} [\text{Co}_2(\text{CO})_7] + \text{CO} \xrightarrow{k} 2[\text{HCo(CO)}_4] \\
\text{H}_2 \text{rds}
\end{align*}
\]

Pyrolysis of [Co₂(CO)₄(μ-CO)(μ-CH₂)(μ-dppm)] (3.5) under hydrogen at 85°C gives methane but no ethane, again suggesting an intramolecular carbon-carbon coupling reaction for (3.6). Similarly this thermal decomposition pathway of (3.5) under a hydrogen atmosphere is envisioned to parallel the bis(μ-methylene) congener's decomposition pathway (Scheme 4.4) on exposure to the same reaction conditions.

The bis(μ-ethyldene) complex (3.8), which gave only ethylene via β-elimination from pyrolysis in decaline, produced ethylene [9%] and ethane [36%] under hydrogen and similar decomposition conditions. Complex [Co₂(CO)₄(μ-CH₂)(μ-CHMe)(μ-dppm)] (3.11) under hydrogen evolved ethylene [10%], ethane [53%], propylene [20%] and propane [4%]. Therefore, under hydrogen, both (3.8) and (3.11) gave considerably higher ethylene:ethane ratios than did (3.6). Since the pyrolysis products from (3.6), (3.8) and (3.11) are apparently the same black insoluble solids, a mechanism of ethane formation from (3.6) by catalytic hydrogenation of initially formed ethylene is very
improbable. This system therefore provides a useful model for the first and second steps of the proposed catalytic reaction of equation 3.1.5. An excellent model for the second and subsequent steps for this same equation 3.1.5 has been developed by Maitlis et al., described by equation 4.2.2. Hence the formation of ethane by the thermal decomposition under hydrogen of both (3.8) and (3.11), and propane by this same pyrolysis of (3.11), are proposed to originate from generation of the respective coordinatively unsaturated species, an oxidative addition of hydrogen to the unsaturated cobalt atom, the subsequent reactions of equation 3.1.5 followed by the reductive elimination of the respective alkane. This decomposition mode is represented by Scheme 4.4, which demonstrates ethane evolution from (3.6).

4.4 Reaction with Small Molecules

This section focuses on reactions of the bridged alkyridene dicobalt complexes (3.5), (3.6), (3.8), (3.9), (3.11) and (3.12) with either carbon monoxide, sulfur dioxide or unsaturated hydrocarbons. The reaction of small molecules with binuclear metal complexes and the subsequent coordination modes of these molecules are of considerable interest owing to the implications regarding homogeneous catalysis by metal systems. The limited chemistry of alkyridene-bridged compounds studied to date with small molecules generally reveals an insertion of these small molecules into the metal-alkylidene bond. No mechanistic details are implied by the term insertion; insertion merely refers to the structural result of cleavage of a metal-carbon bond with the interposition of the small molecule between the metal and the
alylidene. A literature survey precedes each separate reaction series
of the novel (μ-alkylidene)dicobalt complexes with an individual small
molecule addition. Some of these reactions are pertinent to
catalysis. Only the complexes [Pd₂X₂(μ-CHR)(μ-dppm)] (1.58) have been
reported unreactive toward these small molecules. ①⁷

4.5 Carbon Monoxide Reactions

4.5.1 Carbon Monoxide Addition to Alkylidene-Bridged Complexes

The catalytic literature reports analogies supporting the initial
Fischer-Tropsch synthesis mechanism proposal¹ describing the
hydrocarbon synthesis to occur through oligomerization of surface
methylene and methyl groups, such that carbon monoxide insertion is not
required. However, the formation of C₂-oxygenated products has been
suggested to evolve from an alternative mechanism; ⑧ one in which
surface methylenes initiate chain growth but the chain growth is
propagated by carbon monoxide addition. This conclusion was confirmed
from experiments studying ¹⁴C-labelled ketene dissociation over
Fischer-Tropsch catalysts during CO/H₂ reduction. ⑨ Hence a class of
compounds derived from insertion of carbon monoxide into a
metal-methylene bond to give a surface ketene ligand may be of
potential relevance to carbon monoxide reduction chemistry over
heterogeneous catalysts. This insertion of carbon monoxide into a
metal-methylene bond could account for chain growth via ketene
intermediates (equation 4.5.1).
This type of reaction has been suggested by Ichikawa et al.\textsuperscript{20} to be of prime importance when assigning a mechanism for the selective formation of ethanol from CO/H\textsubscript{2} over certain Rh/ZrO\textsubscript{2}/SiO\textsubscript{2} and Rh/TiO\textsubscript{2}/SiO\textsubscript{2} catalysts, shown in equation 4.5.2. This same reaction step has been invoked to explain recent isotopic tracer results for the rhodium catalyzed reduction of carbon monoxide to ethanol.\textsuperscript{21}

\[
\begin{align*}
\text{CH}_2 & \quad \text{+CO} \rightarrow \text{CH}_2=\text{C}=\text{O} \\
\text{[H]} & \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CHO}
\end{align*}
\]

Although a few mononuclear carbene complexes have been reported to insert or add carbon monoxide to produce complexes incorporating ketene ligands,\textsuperscript{22} there is growing evidence for similar reactions with polynuclear \(\mu\)-alkylidene complexes.

Initially Curtis and Messerle noted diphenylketene (Ph\textsubscript{2}C=\text{C}=\text{O}) from the room temperature reaction of \([\text{Cp}_2\text{Mo}_{2}(\text{CO})_4(\mu-\text{CPh}_2)]\) (1.42) with carbon monoxide,\textsuperscript{23} a reaction which may proceed via a bridging diphenylketene complex. Evidence indicating that carbon monoxide insertion into a metal-methylene bond proceeds through an unstable bridging ketene complex was later forwarded by Keim et al.\textsuperscript{24} when \([\text{Fe}_2(\text{CO})_6(\mu-\text{CH}_2)]\) (1.61) reacted with methanol and ethanol in the presence of carbon monoxide to yield the corresponding acetates (equation 4.5.3). Ketene itself reacts with nucleophiles such as water.
and methanol to give acetic acid and methyl acetate.²⁵

\[
(1.61) + \text{CO} \rightarrow \text{CH}_2=\text{CO} \rightarrow 2[\text{Fe(CO)}_3] + \text{CH}_3\text{COOR}
\]

4.5.3

In contrast, Pettit et al.⁹ reported that the reaction of (1.61) with nucleophiles leads to products containing an acetyl group (equation 4.5.4) but does not necessarily proceed via a ketene-type intermediate prior to nucleophilic attack. The rate of the reaction of (1.61) with nucleophiles was qualitatively observed to be enhanced by the presence of iodide.

\[
[\text{Fe}_2(\text{CO})_6(\mu-\text{CH}_2)] + \text{R-Z-H} \rightarrow \text{H}_2\text{CC(=O)-Z-R}
\]

4.5.4

(1.61)\quad \text{Z=O, NH}

These authors⁹ suggest that the treatment of (1.61) with water at room temperature in acetone (equation 4.5.5) produces organic products consistent with the ability of a carbonyl ligand to undergo nucleophilic attack to generate a metal hydride, as in the water gas shift reaction. The fate of the iron carbonyl is still undetermined.

\[
(1.61) + \text{H}_2\text{O} \rightarrow \text{Fe} \begin{array}{c}
\text{H} \\
\text{CH}_2
\end{array} \begin{array}{c}
\text{O} \\
\text{Fe} \\
\text{C} \\
\text{OH}
\end{array} \rightarrow \text{Fe} \begin{array}{c}
\text{H} \\
\text{CH}_2
\end{array} \begin{array}{c}
\text{O} \\
\text{Fe} \\
\text{C} \\
\text{OH}
\end{array} \rightarrow \text{Fe} \begin{array}{c}
\text{H} \\
\text{CH}_2
\end{array} \begin{array}{c}
\text{O} \\
\text{Fe} \\
\text{C} \\
\text{OH}
\end{array} \rightarrow \text{Fe} \begin{array}{c}
\text{H} \\
\text{CH}_2
\end{array} \begin{array}{c}
\text{O} \\
\text{Fe} \\
\text{C} \\
\text{OH}
\end{array}
\]

4.5.5

\[
\text{CH}_3\text{CO}_2\text{H} \quad \text{CH}_4 + \text{CH}_3\text{CHO}
\]
Lin et al. recently reported that carbon monoxide inserts into the ruthenium-methylene bond of \([\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\cdot\text{CH}_2)]\) (1.66), in which no Ru-Ru bond exists, to produce the spectroscopically but not structurally characterized ketene complex in equation 4.5.6.

\[
\begin{align*}
\text{M} & \quad \text{CH}_2 \quad \text{M} + \text{CO} \quad \longrightarrow \quad \text{M} \quad \text{CH}_2 \quad \text{C} \quad \text{O} \\
\text{(1.66)}
\end{align*}
\]

\[\text{M} = \text{CpRu(\text{CO})}_2\]

The only polynuclear \(\mu\)-ketene complex of any type to be fully characterized by a single crystal X-ray diffraction study was \([\text{Os}_3(\text{CO})_{12}(\eta^2-(\text{C},\text{C}),\mu_2\cdot\text{CH}_2\text{CO})]\) (4.14), abbreviated as \([\text{Os}_3(\text{CO})_{12}(\mu\cdot\text{CH}_2\text{CO})]\). A similar \(\mu\)-ketene cluster exhibited a 10\(^2\) accelerating effect of the halide ligands on the carbon monoxide insertion into metal-(\(\mu\)-methylene) bonds to give \(\text{PPN}[\text{Os}_3(\text{CO})_{10}(\mu\cdot\text{CH}_2\text{CO})(\mu\cdot\text{X})]\) (4.15), where \(\text{X}=\text{Cl}, \text{Br}, \text{I}\) and \(\text{NO}_2\). Both the clusters (4.14) and (4.15) derive from the precursor \([\text{Os}_3(\text{CO})_{11}(\mu\cdot\text{CH}_2)]\) (1.3) and these reactions are illustrated in equations 4.5.7 and 4.5.8 respectively.

\[
\begin{align*}
\text{Os}(\text{CO})_4 + 2\text{CO} & \quad \longrightarrow \quad (\text{CO})_4\text{Os} \quad \text{Os}(\text{CO})_4 \\
\text{(4.14)}
\end{align*}
\]
\[ \text{(1.3) + [PPN]}X \quad \text{25°C} \quad \text{PPN(Os}_2(\text{CO})_{10}(\mu-\text{CH}_2)(\mu-X)) + \text{CO} \quad \text{25°C} \]

\[
\begin{array}{c}
\text{Os} \\
\text{CH}_2 \\
\text{CO}
\end{array}
\quad \begin{array}{c}
\text{Os} \\
\text{X}
\end{array}
\quad \begin{array}{c}
\text{Os(\text{CO})}_3
\end{array}
\quad \begin{array}{c}
\text{(CO)}_4
\end{array}
\]

(4.15)

4.5.2 Carbon Monoxide Addition to Novel Dicobaltacyclopropane Complexes

Separate 5 mm NMR tubes were charged with an individual
\((\mu\text{-alkylidene})\text{dicobalt complex (Table 4.2), an equimolar volume of}
\)
dichloromethane and methanol-\text{d}_4 [50 \mu\text{L}] in chloroform-\text{d}[1.5 \text{ mL}]. The
solution was then degassed [ca. \(10^{-3}\) torr] prior to sealing the tube
with carbon monoxide. A complete reaction at room temperature,
monitored by \(^{31}\text{P}\text{(H)}\) NMR spectroscopy (Table 3.3), resulted in the
formation of the \(\mu\text{-alkylidene precursor} \{\text{Co}_2(\text{CO})_4 (\mu-\text{CO})_2(\mu-\text{dppm})\}
(3.4) and specific alkyl acetates in each case. Table 4.2 lists the
individual organometal substrate reagents and their respective products
and yields for both the alkyl acetates and (3.4). Identification of
each of the acetate species was determined via \(^1\text{H}\) NMR spectroscopy and
verified from spectroscopic comparison with authentic samples. Because
the \(^1\text{H}\) NMR signals were broad from the final reaction mixture, the
yields of the acetates were determined by a vacuum transfer of the
Volatile products into another 5 mm NMR tube, which was then sealed. Integration with dichloromethane as the internal reference revealed the recorded yields (Table 4.2) of the respective alkyl acetates based on the amount of the (μ-alkylidene)dicobalt substrate reagent consumed. $^1$H NMR integrations showed all of the reactions to be essentially quantitative.

A g.c. sample analysis from each reaction mixture containing a dicobalt substrate incorporating a μ-methylene ligand revealed traces of ketene; earlier deduced to exhibit the same retention time as carbon dioxide (section 4.2.2), implying that acetate formation arises from a ketene-type intermediate prior to nucleophilic attack by methanol $d_4$. Therefore the insertion of a coordinated carbon monoxide molecule into a cobalt-alkylidene bond to produce the unstable bridged ketene intermediate is anticipated for each reaction studied prior to ketene trapping to generate the acetate formation (equation 4.5.1).

Furthermore, the g.c. analyses gave no evidence for direct coupling of the μ-alkylidene groups from either an intramolecular or intermolecular coupling process, perhaps supporting the theoretical arguments of Hoffmann et al. that such couplings will be difficult, particularly when considering these observations in lieu of the bis(μ-alkylidene)-dicobalt complexes (3.6), (3.11) and (3.12). It is interesting to note that, based on $^{13}$C-labelling experiments, it has been deduced that the ketene carbonyl ligand in (4.14) and (4.15) derives from one of the original cluster carbonyls and not from exogenous carbon monoxide. Carbon monoxide insertion into a carbon-metal bond is an intramolecular process, and often reversible,
Table 4.2: Percentage Yield of Products from Reactions of \([\text{Co}_2(\text{CO})_4(\mu-\text{R})(\mu-\text{R'})(\mu-\text{dppm})]\) with CO
in the presence of CD$_3$OD

<table>
<thead>
<tr>
<th>([\text{Co}_2(\text{CO})_4(\mu-\text{R})(\mu-\text{R'})(\mu-\text{dppm})])</th>
<th>(3.4)</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3.5); (R=\text{CH}_2), R' = CO</td>
<td>70</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.6); (R=R'=\text{CH}_2)</td>
<td>80</td>
<td>95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.8); (R=R'=\text{CHMe})</td>
<td>80</td>
<td></td>
<td></td>
<td>85</td>
</tr>
<tr>
<td>(3.9); (R=\text{CHCO}_2\text{Et}, R'=\text{CO})</td>
<td>70</td>
<td></td>
<td></td>
<td>85</td>
</tr>
<tr>
<td>(3.11); (R=\text{CH}_2, R'=\text{CHMe})</td>
<td>70</td>
<td>85</td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>(3.12); (R=\text{CH}_2, R'=\text{CHCO}_2\text{Et})</td>
<td>90</td>
<td>95</td>
<td></td>
<td>90</td>
</tr>
</tbody>
</table>

(3.4) = \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]\) : $\delta$(CH$_2$P$_2$) 3.06, $\delta$($^3$J(PH)) 10 Hz; $\delta$($^3$P) 58.5 w.r.t. PO(OMe)$_3$

\(a\) = methyl acetate-$d_4$:

\[
\begin{align*}
H_2\text{CD} & \quad \overset{\text{O}}{\sim} \\
\text{OCD}_3
\end{align*}
\]

\(b\) = ethylacetoxycetate-$d_4$:

\[
\begin{align*}
\text{H}_3\text{CH}_2\text{C} & \quad \overset{\text{O}}{\sim} \\
\text{C} & \quad \overset{\text{CHD}}{\sim} \\
\text{C} & \quad \overset{\text{O}}{\sim} \\
\text{OCD}_3
\end{align*}
\]

\(c\) = methyl propionate-$d_4$:

\[
\begin{align*}
\text{H}_3\text{CCHD} & \quad \overset{\text{O}}{\sim} \\
\text{C} & \quad \overset{\text{O}}{\sim} \\
\text{OCD}_3
\end{align*}
\]
where L is any ligand including carbon monoxide. The reaction has been well documented.\textsuperscript{29,30}

Three different acetate products were isolated and characterized from reaction of the ($\mu$-alkylidene)dicobalt complexes surveyed with carbon monoxide. The simplest alkylidene unit, the methylene bridge, must couple with a coordinated carbonyl to eliminate gaseous ketene (CH$_2$=CO) which subsequently forms methyl acetate-$d_4$[DCH$_2$COOCOCH$_3$;$\delta$(CHD)=2.06, s] when trapped by methanol-$d_4$. Consequently, each dicobalt complex in Table 4.2 theoretically produces one molecule of methyl acetate-$d_4$ per methylene unit. Similarly the bis($\mu$-ethylidene) complex [Co$_2$(CO)$_4$($\mu$-CHMe)$_2$($\mu$-dppm)] (3.8) creates two moles of methyl propionate-$d_4$[CH$_3$COOCH$_2$CD$_3$;$\delta$(CHD)=2.32, q,$J$(HH) 7 Hz; $\delta$(CH$_3$)=1.14, d, $J$(HH) 7 Hz] per mole of (3.8), paralleling the methyl acetate-$d_4$ formation from [Co$_2$(CO)$_4$($\mu$-CH)$_2$($\mu$-dppm)] (3.6). The complexes (3.9) and (3.12), each containing one $\mu$-CHCO$_2$Et group, should produce equimolar amounts of the methanol-$d_4$ trapped product ethyl acetoxyacetate-$d_4$

[CH$_3$CH$_2$OCOCH$_2$COCD$_3$;$\delta$(CHD)=1.46, s; $\delta$(CH$_3$)=4.12, q,$J$(HH) 7 Hz; $\delta$(CH$_3$)=1.20, t,$J$(HH) 7 Hz]. However the ethyl acetoxyacetate-$d_4$ species was prone to transesterification by the excess methanol-$d_4$ in solution and subsequent ethanol-$d_1$[CH$_3$CH$_2$OD;$\delta$(CH$_2$)=3.59, q,$J$(HH)= 8 Hz; $\delta$(CH$_3$)=1.15 t, $J$(HH)= 8 Hz] formation (equation 4.5.9). Therefore the total yield of the trapped carboethoxyketene species was calculated by a direct comparison of the combined ethanol-$d$ and ethyl acetoxyacetate-$d_4$ integrals versus the reference dichloromethane integration.
\[ \text{CH}_3\text{CH}_2\text{-CH} = \text{O} \quad \text{CD}_3\text{OD} \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{-CHD} = \text{CH-CD}_3\text{OD} \quad \text{CD}_3\text{OD} \quad \rightarrow \]

\[ \text{CD}_3\text{O} = \text{CD}_2\text{-CHD-CD}_2\text{OCD}_3 \quad \text{CH}_3\text{CH}_2\text{OD} \]

Regardless of the controversy concerning the role of surface methylenes during carbon monoxide reduction, this work emphasizes the organometallic precedent for carbon monoxide insertion into metal-μ-alkylidene bonds to give ketene ligands and implicates these reactions as important mechanistic steps in discussions of carbon monoxide reduction chemistry. Under these conditions, the coupling of two μ-alkylidene groups to give alkenes is not competitive with the alkylidene-CO coupling.

4.6 Sulfur Dioxide Reactions

4.6.1 Sulfur Dioxide Insertion Reactions

Extensive reviews have appeared in the literature surveying the insertion of sulfur dioxide into metal-carbon σ-bonds.\(^{31-35}\) Initially suspected to be analogous to the carbon monoxide insertion reaction, more recent work\(^{32}\) disproved this hypothesis. The sulfur dioxide insertion reaction, first noted by Bibler and Wojcicki,\(^ {31}\) is depicted by equation 4.6.1, where M is a transition metal and R is either an alkyl or aryl group.

\[ \text{M-R} + \text{SO}_2 \quad \rightarrow \quad \text{M-(SO}_2\text{)R} \quad \text{4.6.1} \]

The product from a sulfur dioxide insertion reaction can possess several bonding possibilities, since binding of the sulfur dioxide
ligand, considered electrophilic in nature, to the metal has been observed through either the sulfur or oxygen atom. However, the S-sulfinate(I) insertion product is the most common structural form reported for the interposition of the sulfur dioxide between the metal-carbon bond. Studies have shown that sulfur dioxide insertion into optically active mononuclear complexes progresses with inversion of configuration at carbon but retention at the metal.

\[
\begin{array}{cccc}
\begin{array}{c}
\text{O} \\
\text{M-S-R}
\end{array} & \begin{array}{c}
\text{O} \\
\text{M-S-O-R}
\end{array} & \begin{array}{c}
\text{O} \\
\text{M-O-S-R}
\end{array} & \begin{array}{c}
\text{O} \\
\text{M-O-S-R}
\end{array}
\end{array}
\]

\[\text{S-sulfinate} \quad \text{O-alkyl-S-sulfonate} \quad \text{O-sulfinate} \quad \text{O,\text{O}'-sulfinate}\]

Considerable interest has been directed towards the coordination chemistry of sulfur dioxide in cluster compounds. Earlier X-ray structure determinations report complexes, such as \([\text{Rh}_2\text{Cl}_2(\mu-\text{SO}_2)\text{-}(-\text{dppm})_2]\)\(^{38}\) and \([\text{Pd}_3(\mu-\text{SO}_2)_2(\text{Bu^3NC})_3]\)\(^{39}\), possessing one or more bridging sulfur dioxide ligands in a \(\mu_2,\eta^1\)-bridging manner (V). Other binuclear examples containing \(\mu_2,\eta^1\)-bridging sulfur dioxide ligands include the complexes \([\text{M}_2\text{Cl}_2(\mu-\text{SO}_2)(\mu-\text{dppm})_2]\) \((\text{M}=\text{Pd}^{4+},\text{Pt}^{4+})\), \([\text{Mn}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{SO}_2)(\mu-\text{dppm})_2]\)\(^{42}\) and \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{SO}_2)]\)\(^{43}\). However, the significant differences in the electronic characteristics of these ligands together with their very different steric requirements suggested that the reactions of sulfur dioxide with polynuclear metal complexes might lead to the isolation of cluster ligands with unusual geometries and reactivities.

Novel bridging geometries were determined by X-ray structures to
reveal both sulfur dioxide ligands in \([\text{Mo}_2(\text{CO})_4(\text{PPh}_3)_2(\text{C}_5\text{H}_4\text{N})_2(\mu-\text{SO}_2)_2]\) to be bridging two Mo atoms by bonding to one metal atom through an \(\eta^2\cdot\text{S}=\text{O}\) linkage and the second through the remaining oxygen atom (VI),\(^{44}\) while each sulfur dioxide ligand in the butterfly cluster \([\text{Rh}_4(\mu-\text{CO})_4(\mu-\text{SO}_2)_3[\text{P}(\text{OPh})_3]_4]\) was shown to be bridging two metal atoms through the sulfur atom and a third metal atom through one of the oxygen atoms.\(^{45}\) These latter two examples suggest that sulfur dioxide may prove to be a very flexible ligand in the context of cluster chemistry.

The reaction of sulfur dioxide, considered a good \(\pi\)-acceptor ligand (section 1.2), with transition metal \(\mu\)-alkylidene complexes is relatively limited. It is generally restricted to facile sulfur dioxide additions to metal-metal double bonds, exclusively dinuclear organorhodium- and -cobalt complexes, with the formation of stable 1:1 adducts exhibiting \(\mu_2,\eta^1\)-bridging sulfur dioxide ligands,\(^{46}\) as shown in Figure 4.1. Only in equation 4.6.3 does the coordination mode of the former \(\mu-\text{CPh}_2\) ligand convert to a terminal carbene with the novel \(\mu-\text{SO}_2\) complex formation.\(^{47,48}\) The presence of the \(\mu,\eta^1\)-bridged sulfur dioxide product (4.16) in equation 4.6.3 is attributed to the high \(\pi\)-acceptor capability of sulfur dioxide that retains this ligand in the bridging position. Low temperature IR measurements (-80°C) indicate
Figure 4.1: Dinuclear $\nu$-Alkylidene Complexes Containing a $\nu_2, n^1$-bridging $\text{SO}_2$ Ligand.
that formation of (4.16) proceeds through an initial sulfur dioxide addition to the Rh=Rh double bond of the precursor complex, with a bridge opening process above -40°C. This is consistent with product (4.17) in equation 4.6.4 where no ring opening was observed, emphasizing the higher stability of triply-bridged cobalt complexes compared to their rhodium congeners.  

The first recorded $\mu$-(thioformaldehyde $S,S$-dioxide-C$_2$S) complexes (4.18), in equation 4.6.5, were prepared via clean electrophilic ring expansion reactions when sulfur dioxide inserted into a metal-$\mu$-alkylidene bond, similar to that described earlier in section 4.5.1 for the isoelectronic carbonyl ligand.

The following sections 4.6.2-4.6.7 are centered on the insertion reactions of sulfur dioxide into a metal-$\mu$-alkylidene bond of the forementioned ($\mu$-alkylidene)dicobalt complexes discussed in Chapter 3.

4.6.2 Preparation and Characterization of $\text{[Co}_2\text{(CO)}_4(\mu:\text{SO}_2)(\mu:\text{CH}_2)}$ ($\mu$-dppm)

4.6.2.1 Preparation

When sulfur dioxide is bubbled through a dichloromethane solution of the bis($\mu$-methylenic) complex (3.6) for five minutes at room temperature, the solution gradually darkens in colour from the initial light yellow coloured mixture over the next twenty minutes. An orange precipitate (4.20) was suction filtered from the reaction mixture and a subsequent IR spectrum (Table 4.3) and elemental analysis led to the formulation of (4.20) as $\text{[Co}_2\text{(CO)}_4(\mu:\text{SO}_2)_2(\mu$-dppm)$]$, in 10% yield. Complex (4.20) was soluble in methanol yet only sparingly soluble in polar chlorinated solvents.
Table 4.3: Infrared Spectral Data for Some Binuclear $\mu$-$SO_2$ Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$(CO), cm$^{-1}$</th>
<th>$\nu$(SO$_2$), cm$^{-1}$</th>
<th>Medium</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>free $SO_2^a$</td>
<td></td>
<td>1340($\nu$(SO$<em>2$)$</em>{as}$), 1150($\nu$(SO$<em>2$)$</em>{s}$), 524(8 SO$_2$)</td>
<td>CH$_3$CN</td>
<td></td>
</tr>
<tr>
<td>trans-$[(n^3-C_3Me_3)_2M_2(CO)_2(\mu-SO_2)]$</td>
<td>1980(vs)</td>
<td>1377(s), 1188(vs), 1064(w), 1043(vs), 517(s)</td>
<td>KBr</td>
<td>46</td>
</tr>
<tr>
<td>M=Rh</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M=Co</td>
<td>1973(vs), 1938(w)</td>
<td>1379(s), 1177(vs), 1033(vs), 508(s)</td>
<td>KBr</td>
<td>46</td>
</tr>
<tr>
<td>[M$_2$Cl$_2$(\mu-SO$_2$)(\mu-dppm)$_2$]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M=Pt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M=Pd$^b$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn$_2$(CO)$_4$(\mu-CO)(\mu-SO$_2$)(\mu-dppm)$_2$]</td>
<td>2025(s), 1967(s), 1926(s), 1889(s), 1848(m)</td>
<td>1144, 1015</td>
<td>nujol</td>
<td>42</td>
</tr>
<tr>
<td>[CO$_2$(CO)$_4$(\mu-R)(\mu-R')(\mu-dppm)]</td>
<td>2040(s), 2020(s), 1995(s)</td>
<td>1150(m), 1040(s)</td>
<td>CH$_2$Cl$_2$</td>
<td></td>
</tr>
<tr>
<td>R=CH$_2$, R'=SO$_2$i(3.19)</td>
<td>2050(s), 2020(s), 2005(s)</td>
<td>1370(s), 1165(s,br), 1035(s)</td>
<td>nujol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2070(s), 2050(s), 2030(s), 1380(s), 1050(s), 1030(m)</td>
<td></td>
<td>nujol</td>
<td></td>
</tr>
<tr>
<td>R=R'=SO$_2$i(3.20)</td>
<td>2015(s,sh)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---


$b$  The doubling up of reported SO$_2$ bonds being presumably due to the presence of two slightly different molecules of the complex [Pd$_2$Cl$_2$(\mu-SO$_2$)(\mu-dppm)$_2$] in the unit cell.

NR = not reported
The filtrate was column chromatographed on 100-200 mesh florisil adsorbant and removal of the methanol eluant produced a yellow solid (4.19). Complex (4.19) was extremely soluble in dichloromethane and chloroform and the IR data were consistent with only terminal carbonyl and bridging sulfur dioxide stretching frequencies. Table 4.3 presents the comparative IR data for both the carbonyl and sulfur dioxide ligands in complexes (4.19) and (4.20), as well as related binuclear $\mu$-alkylidene compounds. An elemental analysis, along with the IR data, was consistent with the formulation of (4.19) as $\text{Co}_2(\text{CO})_4(\text{CH}_2)(\text{SO}_2)(\text{dppm})$, formed in 68% yield. However, the specific bridging mode of the sulfur dioxide ligand is not absolutely defined by these data.

4.6.2.2 Product Characterization

Complex (4.20), although only slightly soluble in chloroform-d, displays a $^{31}\text{P}[^1\text{H}]$ NMR resonance at δ 32.9. This broad singlet is complemented in the corresponding $^1\text{H}$ NMR spectrum by a triplet [δ 4.01, 2J(\text{PH}) 14 Hz] for the $\text{CH}_2\text{P}_2$ methylene protons and a multiplet [δ 7.1-7.8] for the phenyl protons of the diphosphine ligand in (4.20).

A $^{31}\text{P}[^1\text{H}]$ NMR spectrum of (4.19) in chloroform-d revealed only one broad singlet centred at δ 60.2. The $^1\text{H}$ and $^1\text{H}[^3\text{P}]$ NMR spectrum of (4.19), both illustrated in Figure 4.2, suggests (4.19) is $[\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dppm})]$, containing a bridging sulfur dioxide ligand in the $\mu_2,\eta^1$-bridging mode (V). The AX-spin system for the bridging methylene protons in (4.19) displayed a singlet [δ 5.18], assigned to $\text{H}^5$ in Figure 4.2, and a triplet [δ 4.28, J(\text{PH}) 20 Hz] for $\text{H}^3$ with each methylene resonance exhibiting a geminal coupling [J($\text{H}^3\text{H}^2$) 4 Hz] and equivalent integrals. This triplet resonance [δ 4.28, J(\text{PH})]
Figure 4.2: $^1$H NMR Spectra of $[\text{Co}_2(\text{CO})_4(\mu-SO_2)(\mu-\text{CH}_2)(\mu-dppm)](4.19)$ in CDC$_3$. 
20 Hz, J(H^aH^b) 4 Hz] is considered diagnostic of the methylene proton H^a extending over the diphosphone ring. The large J(PH) value and the diamagnetic shielding of H^a with respect to H^b, induced by the electronic circulations within the \pi-electron cloud of the diphosphone phenyl substituents, established a precedent in the preceding chapter for interpreting \(^1\)H NMR spectra of (\mu-alkylidene)dicobalt complexes in this system. The corresponding \(^1\)H(\(^{31}\)P) NMR spectrum of (4.19) collapses this triplet (H^a) into a singlet [\(8 4.28, J(H^aH^b) 4 \text{ Hz}\) with equal intensity to the \(^{31}\)P uncoupled H^b proton resonance [\(8 5.18, J(H^aH^b) 4 \text{ Hz}\)]. A simple AB pattern of the appropriate integrated intensity appears for the \(P_2CH^2H^b\) chemically inequivalent protons of the diphosphone bridge in the \(^1\)H(\(^{31}\)P) NMR spectrum of (4.19) [\(8(H^a) 3.41, 8(H^b) 2.93; J(H^aH^b) 15 \text{ Hz}\)]. The phenyl protons of the dppe ligand resonate as a multiplet between \(8 6.90-7.90\). Figure 4.2 portrays a Newman projection of (4.19) drawn along the Co-Co bond representing the preferred configuration of \([\text{Co}_2(\text{CO})_6(\mu-\text{SO}_2)(\mu-\text{CH}_2)-\mu-\text{dppe}]\) (4.19).

Therefore the reaction sequence leading to complex (4.20) from sulfur dioxide addition to (3.6) is summarized pictorially by equation 4.6.6.
4.6.3 Pyrolysis of $[\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dpmm})]$}

Sulfenes are molecules of the formula RR'\text{C}=\text{SO}_2 and may be regarded either as the sulfonyl analogue of ketenes or as derivatives of sulfur trioxide formally obtained by replacement of one oxygen atom by a RR' group. Methanolsysis of sulfene (\text{CH}_2\text{SO}_2) serves as a convenient sulfene trap to give methyl methanesulfonate (b.p. 202-203°C) in a manner similar to the trapping of ketene to generate esters.\textsuperscript{50}

In an attempt to induce sulfene formation from (4.19), a sealed, evacuated vessel containing a degassed chloroform-d solution of (4.19) and methanol-d\textsubscript{4} (30 \mu L) was warmed at 60°C. After three days, the resultant brown solution was g.c. analyzed prior to filtering into a 5 mm NMR tube containing a fixed molar quantity of reference dichloromethane solvent. The g.c. sample showed only a trace of ketene with no ethylene or sulfur dioxide being evident. A $^1$H NMR spectrum indicated that the only organic entity in solution was the tetradecuterated methyl acetate product DCH$_2$COOCD$_3$ [65\%] with no
identifiable organometallic species. Only this same DCH₂COOCD₃ [60%] species was also formed under the identical reaction conditions in the presence of catalytic amounts of triethylamine. No sulfene appeared to be trapped by methanolysis under these reaction conditions in the form of D₃COSO₂CH₂D [δ(CH₂D) 3.02, s], leaving the fate of the μ,η¹-bridged sulfur dioxide ligand undetermined. To date no evidence to suggest sulfene formation has been reported from any μ-alkylidene complex incorporating a sulfur dioxide ligand. One possible source of producing sulfene might derive from pyrolysis of (4.18), possessing a μ,η²-bridged sulfur dioxide ligand (VI),¹⁰ in much the same manner as the ketene eliminations via the proposed μ,η²-bridged ketene intermediates discussed in sections 4.5.1 and 4.5.2.

The DCH₂COOCD₃ formation stems from the methanol·d₄ entrapment of ketene (CH₂CO) from (4.19), whereby the ketene results from an intramolecular insertion of a carbonyl ligand into a cobalt-methylene bond of (4.19). This intramolecular type of insertion reaction must also apply, as suspected, to ketene formation from carbon monoxide addition to the (μ-alkylidene)dicobalt complexes in section 4.5.2.

4.6.4 Sulfur Dioxide Addition to the Novel Dicobaltacyclop propane Complexes

In order to determine the fate of the carbene ligand exiled from the bis(μ-methylene) complex (3.6) by sulfur dioxide addition, the (μ-alkylidene)dicobalt complexes cited in Table 4.4, including (3.6), were individually sealed in an evacuated vessel with sulfur dioxide (100 torr). The experimental procedure for these experiments parallels that described earlier for these same (μ-alkylidene)dicobalt complexes.
interacting with carbon monoxide (section 4.5.2), with the exception of
a specially designed glassware system in which the reaction vessel and
a clean 5 mm NMR test tube are contained within the same evacuated
system. This facilitates a vacuum distillation transfer of the organic
products on reaction completion from the insoluble organometallic
species, suspected to be primarily decomposition products, to ensure a
well resolved $^1$H NMR spectrum. A complete reaction, generally within
two days, was assessed by a decline in the production of an apparently
insoluble, orange precipitate, later identified via $^1$H [6 4.01, $^2$J(HP)
14 Hz] and $^{31}$P [$^1$H] [6 32.9] NMR spectroscopy as \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)_2
(\mu-\text{dpdm})]\) (4.20) in each case.

On reaction completion, the organic products formed were
transferred along with the chloroform-d solution via vacuum
distillation into the 5 mm NMR tube. Table 4.4 lists the yields of
each organic product identified in solution for each respective sulfur
dioxide addition reaction obtained via integration versus an internal
dichloromethane reference. The data recorded in Table 4.4 features the
identical alkyl acetates produced in each case as observed previously
with the corresponding carbon monoxide addition reactions (Table 4.2).
These products arise from methanalysis of the appropriate ketene
species ejected from the (μ-alkylidene)dicobalt complex during the
reaction. However, no sulfene analogues were trapped by the
methanol-d₄ solvent in either the initial reaction vessel, comprising
principally the organometallic product \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)_2(\mu-\text{dpdm})]\)
(4.20), or the vacuum distilled organic solution. The low yield of
(4.20) observed from the $^1$H NMR spectrum in each experiment is
attributed to the poor solubility of (4.20) in chloroform-d (Table
Table 4.4: Percentage Yield of Products from Reaction of [{\text{Co}_2(\text{CO})_4(\mu-R)(\mu-R')(\mu-dppm)}] with SO_2 in the presence of CD_3OD.

<table>
<thead>
<tr>
<th>[{\text{Co}_2(\text{CO})_4(\mu-R)(\mu-R')(\mu-dppm)}]</th>
<th>[{\text{Co}_2(\text{CO})_4(\mu-SO_2)(\mu-dppm)}]</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3.5); R=CH_2, R'=CO</td>
<td>20</td>
<td>65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(3.6); R=R'=CH_2</td>
<td>70</td>
<td>-</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>(3.8); R=R'=CHMe</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>(3.9); R=CHO_2Et, R'=CO</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>55</td>
</tr>
<tr>
<td>(3.11); R=CH_2, R'=CHMe</td>
<td>25</td>
<td>25</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>(3.12); R=CH_2, R'=CHO_2Et</td>
<td>15</td>
<td>60</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>(4.19); R=CH_2, R'=SO_2</td>
<td>35</td>
<td>-</td>
<td>60</td>
<td>-</td>
</tr>
</tbody>
</table>

[Co_2(CO)_4(\mu-SO_2)(\mu-dppm)](4.20): 8(CH_2P_2) \( \delta, \gamma \text{J(PH)} 14 \text{ Hz} \)

\[ a = \text{methyl acetate} \cdot d_4; \quad H_2\text{CD} - C - OCD_3 \]
Table 4.4 (continued)

b = ethylacetoxacetate-d₄; H₃CCH₂CO

c = methyl propionate-d₄; H₃CCHCD₃
4.4). Although each g.c. analysis revealed traces of ketene with each 
μ-methylene complex, only the bis(μ-methylene) complex (3.6) showed a 
trace of ethylene from carbon-carbon coupling of the two methylene ligands in addition to the ketene presence in the g.c spectrum.

The elimination of ketene from (3.6) via an unstable two-electron 
μ,η²-bridged donor ketene ligand is suspected to create the vacant site 
renabling the, initial formation of (4.19) (equation 4.6.7). An 
alternative route, less likely to apply to the bis(μ-methylene) complex 
(3.6), involves an initial expulsion of a carbonyl ligand to generate 
the coordinatively unsaturated intermediate prior to the external 
sulfur dioxide two-electron donor ligand uptake in the site vacated by 
the carbonyl ligand loss. The insertion of a carbon monoxide ligand 
between a metal-alkylidene bond would follow the sulfur dioxide 
coordination. In either case, incorporation of external carbon 
monoxide molecules to form the preliminary product (4.19) must 
originate from decomposition of the starting (μ-alkylidene)dicobalt complex (3.6).
Support for an intramolecular carbon monoxide insertion into a metal-alkylidene bond has surfaced in recent literature.\textsuperscript{28-29} This same type of insertion reaction was earlier suggested to account for the observed alkyl acetates in Table 4.2, arising from the unstable \(\mu,\eta^2\)-bridged ketene intermediates speculated to be formed from carbon monoxide addition to the various (\(\mu\)-alkylidene)dicobalt complexes (section 4.5.2). Carbonylation of the methyl manganese complex (4.21) with \(^{13}\text{C}\)-labelled carbon monoxide gives \(^{13}\text{C}\)-labelled carbon monoxide incorporation solely in a vacated position cis to the acyl group in (4.22), demonstrating an intramolecular insertion process of a carbon monoxide ligand between the metal atom and alkyl group.\textsuperscript{81} Although two plausible reversible processes, methyl migratory insertion and carbonyl insertion, may apply to equation 4.6.8, the former pathway has been experimentally established.
Furthermore, alkyl manganese pentacarbonyl complexes (4.23) rearrange in the presence of ligands (L) such as carbon monoxide, a tertiary phosphine, an amine, or a halide ion, affording the acyl complexes (4.24), as shown in equation 4.6.9.

This work suggests that the tetradeuterated esters recorded in Table 4.4, analogous to those presented in Table 4.2, are also derived from a ketene intermediate, formed from the initial (μ-alkylidene)dicobalt complex by an intramolecular carbon monoxide insertion into a cobalt-alkylidene bond.

Some clarification with regard to the nature of the carbonyl insertion reactions into the cobalt-alkylidene bond, namely whether insertion occurs before the coordinatively unsaturated intermediate takes up the external ligand in the site vacated by the migrating carbonyl group or, alternatively, after a dissociative carbonyl loss, is provided by the following observations. When the reaction of [Co₂(CO)₈(μ-CO)(μ-CHCO₂Et)(μ-dppm)] (3.9) with sulfur dioxide was terminated after four hours at room temperature, allowing insufficient
time for the complete reaction to exclusively produce the products (4.20) and ethyl acetoxyacetate-d₄ (Table 4.4), a new species (4.25) was detected in solution. If the organic products are vacuum distilled into a separate container from the initial reaction mixture, the ¹H NMR spectrum of the remaining organometallic species displays resonances indicative of (3.9) (section 3.5.2) and the novel (4.25), assigned as the complex \([\text{Co}_2(\text{CO})_6(\mu-SO_2)(\mu-\text{CHO}_{2}\text{Et})(\mu-dppm)]\). Complex (4.25) is characterized by the triplet [δ 4.56, J(HP) 22 Hz] displaying the diagnostic large J(HP) value, implying the configuration of (4.25) shown in the Newman projection of (4.25) drawn along the Co-Co bond.

\[
\begin{align*}
\text{R} & \quad \text{O} \quad \text{O} \\
\text{H} & \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{P} \quad \text{C} \quad \text{O}
\end{align*}
\]

(4.25); \(R = \text{CO}_2\text{Et}\)

The protons of the ester substituent resonate simply as a predicted quartet [δ 4.01, J(HH) 7 Hz] and triplet [δ 1.20, J(HH) 7 Hz]. Although this ¹H NMR spectrum was not ³¹P(¹H)-decoupled, an AB multiplet for the methylene protons of the dppm ligand in (4.25) is centered at δ 3.40 and 6.2.66. These chemical shifts observed for the protons of (4.25) are very similar to those shifts reported earlier for the complex (3.9) in Table 3.2.

Under the identical conditions, \([\text{Co}_2(\text{CO})_6(\mu-\text{CH}_2)(\mu-\text{CHO}_{2}\text{Et})](\mu-dppm)]\) (3.12) also produces (4.25) with the ketene elimination from the methylene ligand trapped as methyl acetate-d₄. Formation of (4.25) [δ(³¹P) 54.6] from reaction of sulfur dioxide with (3.12) illustrates
the preference for the formation of (4.25), since there was no evidence for the alternative species \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dppm})]\) (4.19) in solution from either the \(^1\text{H}\) or \(^{31}\text{P}(^1\text{H})\) NMR spectrum to complement the small yield of ethyl acetoxycetate-\(d_4\) observed from methanalysis of the respective ketene in the corresponding \(^1\text{H}\) NMR spectrum. This result indicates a greater reactivity of the \(\mu-\text{CH}_2\) group compared to the \(\mu-\text{CHO}_2\text{Et}\) group towards coupling with CO. Observation of (4.20) [5 4.01, t, \(J(\text{PH}) 14 \text{ Hz}\)] in the \(^1\text{H}\) NMR spectrum of the reaction mixture was obscured by the ethoxy quartet [6 4.01, \(J(\text{HH}) 7 \text{ Hz}\)] of (4.25).

These spectral results suggest that an initial dissociative carbonyl loss from the mono(\(\mu\)-alkylidene) complexes creates the vacant site for the sulfur dioxide uptake prior to the carbonyl insertion to form the \(\mu,\eta^6\)-bridged ketene intermediate species. This mechanistic proposal is based on the observation of (4.25) during the reaction progress of (3.9) with sulfur dioxide. In contrast, this same observation of (4.25) from sulfur dioxide addition to (3.12) under the identical conditions supports an intramolecular carbonyl insertion into a cobalt-alkylidene bond of a bis(\(\mu\)-alkylidene) complex in order to generate the coordinatively unsaturated intermediate species required for the sulfur dioxide uptake. These two proposals may also apply for carbon monoxide addition to these same respective complexes discussed in section 4.5.2.

Consequently, because of the presence of the trapped alkyl esters recorded in Table 4.4, the observed yields of the final product \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)_2(\mu-\text{dppm})]\) (4.20), also in Table 4.4, are reported as a direct percentage versus the maximum molar amount of (4.20) obtainable from each separate reaction. Therefore, since two moles of ketene
products are ejected per mole of each bis(µ-alkylidene)dicobalt complex in Table 4.4, the maximum yield of (4.20) will be 50% per mole of the initial bis(µ-alkylidene)dicobalt precursor complex. The additional molecules of carbon monoxide required to form (4.20) are suspected to arise from decomposition of the precursor complex. Similarly, formation of the product (4.20) from any mono(µ-alkylidene)dicobalt complex featured in Table 4.4 requires insertion of only one carbonyl ligand into a cobalt-alkylidene bond to eliminate a ketene group. Thus the single respective ketene loss overall from each mono(µ-alkylidene)dicobalt complex leaves the resultant sulfur dioxide complex void of only one carbonyl ligand. Hence the maximum yield of (4.20) anticipated per mole of a specific mono(µ-alkylidene)dicobalt precursor is 75%.

4.6.5 Diazoalkane \(\text{CHR}_2\text{N}_2(R=\text{H}, \text{CO}_2\text{Et})\) Addition to \([\text{CO}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_3)\cdot (\mu-\text{dppm})]\)

In order to determine the reversibility of equation 4.6.6, a 1.1% solution of ethereal diazomethane was repetitively administered in small volumes every thirty minutes to a dichloromethane solution of (4.19), at room temperature, over a four hour period. Polymethylene formation from diazomethane decomposition increased substantially over this four hour period. A subsequent \(^{31}\text{P}(^{1}\text{H})\) NMR spectrum in chloroform-d of the reaction mixture, one hour after the final ethereal diazomethane addition, revealed only a small yield of the desired bis(µ-methylene) complex (3.6) \([\delta(^{31}\text{P}) 40.8,8]\) arising from sulfur dioxide displacement by the methylene bridge. The majority of the initial (4.19) \([\delta(^{31}\text{P}) 60.2]\) was still evident in solution along with
very minor, unidentifiable peaks \(8(31^p) 21,23\), suspected to be decomposition products from this reaction. Hence it was concluded that diazomethane addition to (4.19) with concomitant dinitrogen loss is extremely slow at room temperature, resulting in the high polymethylene yield.

Ethyl diazoacetate, \(N_2\text{CHO}_2\text{Et}\), considerably more stable at room temperature than the corresponding parent diazomethane, was introduced in a 3:1 molar excess to a degassed dichloromethane solution of (4.19) contained in a vacuum vessel equipped with a stopcock adapter. The vessel was then evacuated and sealed, leaving the vessel's contents to react at room temperature. Displacement of the sulfur dioxide ligand was expected to generate the bis(\(\mu\)-alkylidene) complex \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)(\mu-\text{CHO}_2\text{Et})(\mu-\text{dppm})]\) (3.12) \(8(31^p) 41.8\) and this conversion could conveniently be monitored qualitatively by the appropriate colour change from initially yellow to an orange solution. Although this characteristic colour change emerged after two days, the vessel remained sealed for six days to ensure a complete reaction. A preliminary g.c. analysis revealed only ketene in the spectrum with no evidence for sulfur dioxide expulsion. The \(31^p(1^H)\) NMR spectrum of this reaction mixture indicated a disappearance of the resonance peak for (4.19) \(8(31^p) 60.2\) in solution but no broad singlet resonance at \(8 41.8\). Only broad singlet resonances characteristic of \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CHO}_2\text{Et})(\mu-\text{dppm})]\) (4.25) \(8(31^p) 54.6\) and \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)_2(\mu-\text{dppm})]\) (4.20) \(8 32.9\) were evident in solution from the reaction of (4.19) with excess ethyl diazoacetate. This observation illustrates the resistance to displacement of the \(\mu,\eta^4\)-bridged sulfur dioxide ligand from this dicobalt system (4.19) by alkylidene units at
4.6.6 Reaction of $[\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dpmm})]$ with Carbon Monoxide

When a degassed chloroform-d solution of (4.19) is sealed under carbon monoxide (80.6 torr) in the presence of methanol-d$_4$(30µL), in an analogous manner to that described earlier in section 4.5.2, a complete reaction at room temperature occurred after seven days when a $^{31}\text{P}^{(1\text{H})}$ NMR analysis revealed no trace of (4.19) [δ 60.2]. Only broad singlets at δ 58.5 and δ 50.2, identified as $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{dpmm})]$ (3.4) and $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{SO}_2)(\mu-\text{dpmm})]$ (4.26) respectively, were detected in solution. Prior to a vacuum distillation transfer of the organic products to a separate 5 mm NMR tube, a sample from the sealed environment was g.c. analyzed on the porapak Q column. Only a trace of ketene was discovered with no ethylene or sulfur dioxide, indicating that the methanol-d$_4$ had trapped the anticipated ketene and possibly sulfone products. However, a $^1\text{H}$ NMR spectrum of the volatile organic products revealed only methyl acetate-d$_4$ (DCH$_2$COOCD$_3$, δ 2.06, s) in 65% yield with respect to the internal dichloromethane reference. The high boiling point of the sulfone trapped species methyl methane sulfonate-d$_4$ (D$_3$COSO$_2$CH$_2$D, δ 3.02, s), if formed, required the corresponding $^1\text{H}$ NMR spectrum of the organometallics from this reaction to be determined in the event that D$_3$COSO$_2$CH$_2$D was not transferred as a volatile organic product via vacuum distillation (10$^{-3}$ torr). Although the D$_3$COSO$_2$CH$_2$D resonance signal was not observed, the complex (3.4) [δ(CH$_2$P$_2$) 3.06, t, $^3$J(PP) 10 Hz] and (4.26) [δ(CH$_2$P$_2$) 3.25, t, $^2$J(PP) 10 Hz] were formed in 35% and 25% yield respectively. Partially chloroform soluble, green decomposition products visible in the initial
reaction mixture, which necessitated the vacuum distillation transfer of the volatile organic products, are postulated to account for the low yields of these reaction products as compared with the quantitative product formations from similar reactions in Table 4.4. The presence of (4.26) emphasizes the stability of the bridged sulfur dioxide \( \mu, \eta^1 \)-ligands in this dicobalt system with respect to the bridged alkylidene ligands.

4.6.7 Summary of Sulfur Dioxide Addition Reactions

The addition of sulfur dioxide to this (\( \mu \)-alkylidene)dicobalt system has succeeded in paralleling that observed from carbon monoxide addition to this same system. The formation of \( \mu, \eta^1 \)-bridged sulfur dioxide ligand complexes in this dicobalt system is suggested to occur via intramolecular carbonyl insertion into a cobalt-alkylidene bond to form ketene or a ketene derivative. This insertion reaction was evidenced by the elimination of alkyl acetates derived by trapping the ejected ketene moiety with methanol-d\(_4\). Thus the CHR-CO coupling to give ketene occurs more readily than CHR-SO\(_2\) coupling to give sulfene in these complexes. Furthermore, the \( \mu, \eta^1 \)-bridged bonding mode of the sulfur dioxide ligand appears to bind more strongly between the two cobalt atoms than the isoelectronic carbonyl and alkylidene bridge within the same system.

4.7 Olefin Addition Reactions

4.7.1 Olefin Addition to Bridging Alkylidene Complexes

Metallocyclobutane rings are considered established intermediates in the transition metal catalyzed metathesis of olefins and it has been
suggested that they are involved in the carbon chain growth of the
Fischer-Tropsch synthesis. The possibility that a dimetallacyclo-
pentane takes part in these important processes has also been
considered.

Generally the treatment of alkylidene-bridged dimers with
aliphatic olefinic hydrocarbons results in a one carbon homologation of
the olefin. For example, Pettit et al.\textsuperscript{14} observed the formation of
propylene [90\%] from the reaction of \([\text{Fe}_2(\text{CO})_6(\mu-\text{CH}_2)]\) (1.61) with
ethylene (400 psi) at 55°C, in a reaction which is inhibited by carbon
monoxide addition. Similar treatment of (1.61) with propylene gave
isobutylene together with lesser amounts of \(n\)-butylenes. These authors
proposed that propylene derived from a diferracyclopentane intermediate
which \(\beta\)-eliminates to form an olefin \(n\)-complex. Reductive elimination
then gives propylene, as shown in Scheme 4.5.

The \(\mu\)-ethylidene complex \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHMe})]\) (1.76b)
reacts with ethylene to produce methane [trace], propylene [3.6\%], and
\(\text{C}_4\) hydrocarbons [2.2\%] consisting of 1-butene, 2-butenes and
isobutylene.\textsuperscript{13} Both propylene and all the \(\text{C}_4\) hydrocarbons are
explicable by a binuclear olefin metathesis involving an intermediate
branched dimetallacyclopentane (Scheme 4.6), as first suggested by
Pettit and coworkers.\textsuperscript{14}

A dimetallacyclopentane was also invoked to explain the formation
of propylene when the \(\mu\)-methylené complexes (1.62) and (1.64) are
treated with ethylene\textsuperscript{53,54} (equation 4.7.1). The complex (4.28),
isolated as a stable entity via equation 6.1.1, does evolve
propylene:cyclopropane in a 4:1 ratio at 80°C.\textsuperscript{55}
Scheme 4.5
\[ \text{[Cp}_2\text{Fe}_2\mu_2\text{(CO)}(\mu-\text{CHMe})] + \text{C}_2\text{H}_4 \rightarrow \text{Cp(CO)Fe} - \text{FeCp} \leftrightarrow \text{Cp(CO)Fe} - \text{FeCp} + \text{CH}_3\text{CH} = \text{CH}_2 \]

\[ \text{CH}_2 = \text{CHCH}_2\text{CH}_3 \]

\[ \text{CH}_3\text{CH} = \text{CHCH}_3(\text{cis} + \text{trans}) \]

\[ \text{CH}_2 = \text{C(CH}_3)_2 \]

\text{SCHEME 4.6}
Direct confirmation for a dimetallacyclopentane intermediate directly synthesized from a (μ-methylene)-ethylene ring expansion was obtained when (1.62) interacted with ethylene to provide the isolated, air-stable dioxamacyclopentane complex (4.27) (equation 4.7.1). Propylene results from decomposition of (4.27), as required in a model for Fischer-Tropsch carbon chain growth, but ethylene was also liberated and (1.62) regenerated, modelling an olefin metathesis step at a dinuclear metal center\textsuperscript{53} (equation 4.7.2).

\[(\text{4.27}) \xrightarrow{130^\circ C} (1.62) + \text{CH}_4 + \text{C}_2\text{H}_4 + \text{CH}_3\text{CH}≡\text{CH}_2 \quad \text{4.7.2}\]

A modified version of the Pettit proposal\textsuperscript{14} was forwarded by Theopold and Bergman\textsuperscript{7,54} to account for propylene formation from heating (1.64) in the presence of ethylene (equation 4.7.3), although the mechanism still incorporates a transient dimetallacyclopentane intermediate.

\[
\begin{align*}
\text{[Cp}_2\text{Co}_2(\text{CO})_2(\mu-\text{CH}_2)] + \text{C}_2\text{H}_4 & \xrightarrow{61^\circ C} \text{CpCo(CO)(C}_2\text{H}_4)[95\%] \quad + \\
(1.64) & \quad \text{CH}_4[3\%] + \text{CH}_3\text{CH}≡\text{CH}_2[65\%] 
\end{align*}
\quad \text{4.7.3}\]
Whereas the inhibited rate of conversion of (1.64) to propylene by carbon monoxide was interpreted by Pettit et al.\textsuperscript{14} to imply an initial dissociative loss of carbon monoxide, Theopold and Bergman\textsuperscript{7,54} proposed an autocatalytic pathway (Scheme 4.7) involving a metal-assisted carbon monoxide dissociation by the coordinatively unsaturated CpCo(C\textsubscript{2}H\textsubscript{4}) catalyst to explain this same phenomenon, and also the inhibiting effect of other ligands (e.g., C\textsubscript{2}F\textsubscript{4}) on the rate of the reaction of equation 4.7.3. This same autocatalytic mechanism may also apply to the related iron system (Scheme 4.5).

Knox et al.\textsuperscript{56} have determined that the thermal and photochemical decompositions of the complexes \([\text{Cp(}CO\text{)}\text{2}(\mu-(CH\textsubscript{2})\text{3})\text{M'}(CO)\text{2}Cp])\) (M=M'=Fe,Ru; M=Fe, M'=Ru), which contain no metal-metal bonds, yield cyclopropane and propylene in a ratio strongly dependent upon the identity of the metal atoms and the reaction conditions. These factors are rationalized by the proposed mechanism interpreted in terms of a transient dimetallacyclopentane, induced from a carbonyl ligand loss, which undergoes decomposition via \(\beta\)-elimination and reductive elimination processes. This work provides strong evidence for the intermediacy of a dimetallacyclopropane in the production of hydrocarbons.

Finally, Tebbe's reagent \([\text{Cp}_{2}\text{Ti}(\mu-CH\textsubscript{2})(\mu-Cl)\text{AlMe}_{2})]\) (1.1) is a good selective catalyst for terminal methylene exchange (equation 4.7.4). This reagent has also been noted for the transfer of a carbene to ethylene or to propylene to give propylene or isobutylene respectively.\textsuperscript{57} Deuterium labelling studies\textsuperscript{57} verified that the \(\mu\)-methylene and not the alkyl aluminum group is transferred, supporting both the proposed cyclic intermediate in equation 4.7.4 and the
\[ \text{[CP}_2\text{Co}_2(\mu-\text{CO})_2] + \text{C}_2\text{H}_4 \rightarrow \text{CpCo(C}_2\text{H}_4)_2 \quad \quad \text{CpCo(C}_2\text{H}_4) + \text{C}_2\text{H}_4 \]

\[ \text{CpCo(C}_2\text{H}_4) + \text{[CP}_2\text{Co}_2(\text{CO})_2(\mu-\text{CH}_2)] \rightarrow \text{CpCo(\text{CO})(C}_2\text{H}_4) + \text{Cp(\text{CO})Co} \quad \quad \text{Cp(\text{CO})Co} \rightarrow \text{CpCo(C}_2\text{H}_4) + \text{C}_2\text{H}_4 \]

(1.64)

\[ \text{CP}_2\text{Co}_2(\text{CO}) + \text{CH}_3\text{CH} = \text{CH}_2 \rightarrow \text{Cp(\text{CO})Co} \quad \quad \text{Cp(\text{CO})Co} \rightarrow \text{CpCo(C}_2\text{H}_4) + \text{C}_2\text{H}_4 \]

SCHEME 4.7
preceding olefin isomerization mechanisms for the formentioned transition metal systems; notably ethylene addition to \([\text{Fe}_2(\text{CO})_8(\mu-\text{CH}_2)]^+ (1.61)\).

\[
\begin{align*}
\text{CD}_2 + \text{CD}_2 & \rightarrow \begin{array}{c}
\begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{Cl}
\end{array}
\end{array} \\
& \rightarrow \begin{array}{c}
\begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{Cl}
\end{array}
\end{array} \\
& \rightarrow \begin{array}{c}
\begin{array}{c}
\text{CD}_3\text{CD}=\text{CH}_2 \\
\text{CD}_2=\text{CDCH}_2\text{D}
\end{array}
\end{array}
\end{align*}
\]

4.7.4

The titanocyclobutane formed on reaction of (1.1) with terminal olefins produces the dimer \([\text{Cp}_4\text{Ti}_2(\mu-\text{CH}_2)_2] (4.29)\) on warming\(^{58}\) (equation 4.7.5); a useful source of the "\text{Cp}_2\text{TiCH}_2" fragment (equations 3.16 and 3.17),

\[
(1.1) + \begin{array}{c}
\begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{Cl}
\end{array}
\end{array} \rightarrow \begin{array}{c}
\begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{Cl}
\end{array}
\end{array} \rightarrow 5(4.29)
\]

4.7.5

4.7.2 Ethylene Addition to the Novel Dicobaltacyclop propane Complexes

The reaction of the \((\mu\text{-methylene})\text{dicobalt complexes (3.5) or (3.6) under tetrafluoroethylene produced no reaction, while these same substrates under ethylene (0.5 psi) at room temperature gave propylene, [CO_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})] (3.4) and other unidentifiable cobalt-containing products. No butenes were detected in either case, indicating that ethylene couples with only one \(\mu\text{-methylene group of (3.6). Although the origin of the carbon monoxide ligand dissociation from (3.5) or (3.6) to generate a coordinatively unsaturated dicobalt}

\[
\begin{array}{c}
\begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{Cl}
\end{array}
\end{array} \rightarrow \begin{array}{c}
\begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{Cl}
\end{array}
\end{array} \rightarrow 5(4.29)
\]

4.7.5
Scheme 4.8: Suggested Mechanism for Propylene Formation from Ethylene Addition to
\[ \text{[Co}_{2}(\mu-\text{CO})_{4}(\mu-\text{C}_{2}H_{2})(\mu-\text{dppm})] } \]

\[ (3.5) \]

\[ \text{+C}_{2}H_{4} \]

\[ \text{[Co}_{2}(\mu-\text{CO})_{4}(\mu-\text{C}_{2}H_{2})(\mu-\text{dppm})] \]

\[ (3.4) \]

\[ \text{+CO} \]

\[ \text{CH}_{2}=\text{CH}_{2} \]
species is unknown, a transient dicobaltacyclopentane intermediate is postulated to describe the propylene formation from interaction of (3.5) or (3.6) with ethylene. A suggested mechanism, paralleling Pettit's proposal, requires ethylene addition to the coordinatively unsaturated organodimetal substrate, followed by cobalt-centered ethylene-methylene combination to yield a dicobaltacyclopentane frame. Subsequent β-hydride elimination from the metallacycle and reductive elimination of propylene are thought to account for the final outcome of this reaction; no cyclopropane was detected from g.c. analysis. An outline of the preceding discussion is given by Scheme 4.8 for reaction of the mono(µ-methylene) species (3.5) with ethylene.

The identification of the (µ-methylene)dicobalt precursor (3.4) was obtained from the 1H NMR spectrum in chloroform-d of the sealed 5 mm NMR tube containing the reaction mixture under ethylene. No evidence of any olefin products were visible in solution. Formation of (3.4) in Scheme 4.8 requires scavenging of external carbon monoxide molecules most likely arising from decomposition of the precursor complex (3.5).

4.8 Alkyne Addition Reactions

Recent reports emphasize a possible connection between stable dimetallacycles and catalysis processes occurring on metal surfaces. These dimetallacycles have been demonstrated to derive from an intramolecular carbon-carbon bond formation in which an alkylidene unit migrates to a coordinated alkyne. Consequently, this type of carbon chain growth, combining an alkylidene carbon with an alkyne carbon at binuclear centers, has prompted mechanistic proposals to support both
alkyne oligomerization and polymerization initiated by \( \mu \)-alkylidene transition metal complexes.

The literature contains a number of examples of reactions between alkylidene units and alkynes, where one of these reactants is initially coordinated to a dinuclear transition metal center. In most of these cases, a \( \mu \)-alkylidene complex is treated with an alkyne; a few discussed in section 4.8.3 involve the addition of a diazoalkane to an alkyne-metal complex.

### 4.8.1 Alkyne Addition to Alkylidene-Bridged Complexes

Tebbe’s reagent (1.1) has proven highly reactive towards alkyne addition, forming a stable titanocyclobutene species (4.30). This titanocyclobutene species (4.30) is much more stable than the non-isolable metallacyclobutane intermediate\(^{29}\) (equations 3.16-3.18).

\[
[\text{CpTi}(\mu-\text{CH}_2)(\mu-\text{Cl})\text{AlMe}_2] \xrightarrow{\text{RCCR}} \text{Cp}_2\text{Ti} \quad \begin{array}{c}
\text{CH}_2 \\
\text{R} \\
\text{C} \\
\text{CR} \\
\end{array} \\
(1.1)
\]

\[
\begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{CH}_2 \\
\text{R} \\
\text{C} \\
\text{CR} \\
\end{array} \quad \xrightarrow{-\text{CH}_2=\text{CMe}_2} \quad \begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{CH}_2=\text{CMe}_2 \\
\text{R} \\
\end{array} \\
(4.30)
\]

\[
\begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{CH}_2 \\
\text{R} \\
\text{C} \\
\text{CR} \\
\end{array} \quad \xrightarrow{-\text{CH}_2=\text{CMe}_2} \quad \begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{CH}_2=\text{CMe}_2 \\
\text{R} \\
\end{array} \\
(4.30)
\]

\[
\begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{CH}_2 \\
\text{R} \\
\text{C} \\
\text{CR} \\
\end{array} \quad \xrightarrow{-\text{CH}_2=\text{CMe}_2} \quad \begin{array}{c}
\text{Cp}_2\text{Ti} \\
\text{CH}_2=\text{CMe}_2 \\
\text{R} \\
\end{array} \\
(4.30)
\]
Reaction of alkynes with the binuclear \( \mu \)-alkylidene complex \([W_2(CO)_{10}(\mu-\text{CMe}_2)]\) (4.31) gives polymers in a metathetical reaction\(^60,61\) (equation 4.8.1). The product (4.32) of the initial insertion of 2-butyne into one of the original 2-methylidene metal-carbon bonds of (4.31) was determined via X-ray structural analysis. This \( \mu \)-alkylidene complex \([W_2(CO)_6(C_2H_5)]\) (4.32) inserts another molecule of the monomer 2-butyne into a metal-alkylidene bond to yield the structurally characterized nine-carbon alkylidene complex (4.33).\(^60\)

While the reaction with 2-butyne is slow, (4.31) reacts with terminal alkynes rapidly to generate polyalkynes with molecular weights between 800 and 16,500 in good yield.\(^61\) This is one of the few catalytically active systems for which possible intermediates are structurally defined.
The formation of a new carbon-carbon bond was also observed from insertion of alkynes into a iron-methylene bond of $[\text{Fe}_{2}(\text{CO})_{6}(\mu-\text{CH}_2)]$ (1.61). These alkyne insertion products of (1.61) are shown in Scheme 4.9, as determined on the basis of IR, $^1$H and $^{13}$C($^1$H) NMR data. Reaction of (1.61) with acetylene produces the $\sigma,\pi$-allyl complex (4.34) along with the ferrole (4.35). Insertion of an alkyne molecule into the iron-allyl $\sigma$ bond gives the diinsertion product (4.36). Treatment of (1.61) with propyne or phenylacetylene results in the formation of only a ferrole (4.37) or $\sigma,\pi$-allyl product (4.38) respectively. When 2-butyne reacts with (1.61), the products (4.39) and (4.40) are isolated. Complex (4.39) is suggested to form via a $\sigma,\pi$-allyl complex which rapidly reacts with 2-butyne. A hydrogen atom originally bound to the methylene ligand in (1.61) has migrated to the terminal olefinic carbon in both (4.34) and (4.38), yet the migration mechanism of this methylenic hydrogen atom remains unclear.

Knox et al. have observed that mono($\mu$-alkylidene)diruthenium complexes and the ($\mu$-ethylidene)diiron complex (1.76b) displayed an insertion-polymerization reaction of alkynes in which, under photochemical conditions, the alkyne ligand stereospecifically inserts into the original metal-carbon bridge to form a three carbon $\sigma,\pi$-allyl bridging complex (4.41) (equation 4.8.2). The mono($\mu$-alkylidene) complexes $[\text{Cp}_2\text{Ru}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{CR}_2)]$ (R=H(1.11a); Me(1.91)) undergo a double insertion with dimethyl acetylenedicarboxylate and acetylene respectively to yield five-carbon chain products (4.42) and (4.43) of differing stereochemistry as deduced from X-ray diffraction studies (equations 4.83 and 4.84). This linking of alkynes with a specific stereochemistry is attributed to the different steric demands of the
Scheme 4.9: Alkyne addition to $[\text{Fe}_2(\text{CO})_8(\mu-\text{CH}_2)](\text{1.61})$
carbene substituents.

\[
\begin{align*}
\text{(a) } & \quad M=\text{Fe}; R=R^1=H, R^2=\text{Me} \\
\text{(b) } & \quad M=\text{Fe}; R=\text{CO}_2\text{Me}, R^1=H, R^2=\text{Me} \\
\text{(c) } & \quad M=\text{Ru}; R=R^1=H, R^2=\text{Me} \\
\text{(d) } & \quad M=\text{Ru}; R=H, R^1=R^2=\text{Me} \\
\text{(e) } & \quad M=\text{Ru}; R=\text{CO}_2\text{Me}, R^1=R^2=H \\
\text{(f) } & \quad M=\text{Ru}; R=\text{Me}, R^1=R^2=H
\end{align*}
\]
In contrast, whereas acetylene inserts into a ruthenium-carbene bond of mono(μ-alkylidene) complexes,\textsuperscript{62} acetylene addition to the bis(μ-alkylidene) complex \([\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CHMe})(\mu-\text{CMe}_2)](\text{4.1})\) under the same photochemical conditions ejects both carbenes to form the acetylene-bridged species \([\text{Cp}_2\text{Ru}_2(\mu-\text{CO})(\mu-\text{C}_2\text{H}_2)](\text{4.44})\), containing a ruthenium-ruthenium double bond. The fate of the ejected carbenes is unknown.\textsuperscript{8}

*The heteronuclear μ-alkylidene complex (4.45) was reported\textsuperscript{64} to insert 2-butyne in a mechanistic manner similar to that proposed earlier by Knox et al.\textsuperscript{62} to form the σ,π-allyl product (4.46), shown by equation 4.8.5.

\[
\begin{align*}
\text{[CpW(CO)]}_2(\mu-\eta^1,\eta^3-\text{CHC}_6\text{H}_4\text{Me}-\text{p})\text{Co(CO)}(\eta^3-\text{C}_6\text{Me}_3)\text{BF}_4 & \xrightarrow{\text{CH}_3\text{CCH}_3} & \text{[CpW(CO)]}(\mu-\eta^1,\eta^3-\text{C}(\text{C}_6\text{H}_4\text{Me}-\text{p})\text{CMe=CHMe})(\mu-\text{CO})\text{Co(\eta^3-C}_6\text{Me}_3)\text{BF}_4
\end{align*}
\]

(4.45)

There is also a report of a bis(π-allyl)dicobalt complex (4.48) synthesized from the dimerization of the cobaltacyclobut-2-enes (4.47). The low yield of (4.48) is suspected to derive
from the steric interaction between the alkoxycarbonyl groups and the 
cobalt atoms.83

Bis(η⁶-cyclooctadiene-μ-methylenearidium), [(η⁶-COD)₂Ir₂(μ-CH₂)₂], 
reacts with alkynes to yield various products.84 Reaction of the 
bis(μ-methylene)diiridium complex with diphenylacetylene produces two 
compounds, both of which were isolated and identified as 1:1 adducts; 
(4.49) containing a μ-η¹-η²-1,2-diphenylallyl ligand, as determined by 
an X-ray structural analysis, and the other product as a 
1,2,4,5-tetraphenyl benzene.

We have studied the alkyne addition reactions with some novel 
coordinatively saturated (μ-alkylidene)dicobalt complexes prepared in 
Chapter 3, and the results are discussed in the next section 4.8.2.
4.8.2 Reaction of CF<sub>3</sub>COCF<sub>3</sub> with the Novel Dicobaltacyclopropane Complexes

All the (μ-alkylidene)dicobalt complexes studied proved highly reactive with the alkyne hexafluoro-2-butyne (CF<sub>3</sub>COCF<sub>3</sub>) at room temperature. In each case, a (μ-alkylidene)dicobalt species listed in Table 4.5 was dissolved in a solvent mixture containing chloroform-d (1.5 mL), methanol-d<sub>4</sub> (50 µL) and an equimolar volume of dichloromethane, to serve as an internal reference. This solution was then degassed in an evacuated 5 mm NMR tube prior to sealing with hexafluoro-2-butyne (~0.5 psi). Each closed reaction was monitored via a decrease in the <sup>31</sup>P(1H) NMR resonance of that particular (μ-alkylidene)dicobalt complex (Table 3.3). A complete reaction in each case was indicated by a single <sup>31</sup>P(1H) NMR resonance signal at 8 36.6, characteristic for the alkyne-bridged complex [Co<sub>2</sub>(CO)<sub>4</sub>(μ-CF<sub>3</sub>COCF<sub>3</sub>)(μ-dppm)] (4.50), prepared separately by an equimolar addition of hexafluoro-2-butyne to [Co<sub>2</sub>(CO)<sub>4</sub>(μ-CO)<sub>2</sub>(μ-dppm)] (3.4).

\[\text{}\]

\[\text{}\]

A <sup>1</sup>H NMR spectrum for the products in each sealed tube revealed a triplet [δ 3.43, J(PP)=10 Hz] assigned to the alkyne-bridged complex (4.50) for each reaction and the corresponding organic resonance.
indicative of the respective methanol-\textsubscript{d\textsubscript{4}} trapped alkyl acetate species, previously described from reaction of these same dicobalt complexes with carbon monoxide (Table 4.2) and sulfur dioxide (Table 4.4). Traces of ketene superimposed on the carbon dioxide peak in the g.c spectrum were observed for samples from all the dicobalt complexes incorporating a \(\mu\)-methylene ligand studied with hexafluoro-2-butyne addition. These spectral results combine to suggest that the acetate products derive from an unstable ketene-bridged complex, originating from the coupling of the organic \(\mu\)-alkylidene ligand with a carbonyl group (equation 4.5.1). Therefore the alkyl acetates are formed from an electrophilic addition of the methanol-\textsubscript{d\textsubscript{4}} (CD\textsubscript{3}-\textsubscript{8}O-\textsubscript{6}D) to the various ketene products. Table 4.5 lists each (\(\mu\)-alkylidene)dicobalt reagent studied with hexafluoro-2-butyne addition and identifies their corresponding alkyl acetate products. The yields of both the alkyl acetate products and (4.50) for each reaction are also presented in Table 4.5, invoking integration with respect to the internal dichloromethane reference to estimate these values. An impurity in the alkyn reagent inhibited an exact integral for the product (4.50) from being calculated; only an approximation is found for these values in Table 4.5. It is interesting to note that the complex [Co\textsubscript{2}(CO)\textsubscript{4}-(\(\mu\)-SO\textsubscript{2})(\(\mu\)-CH\textsubscript{2})(\(\mu\)-dpdm)] (4.19) produces only (4.50) and methyl acetate [DCH\textsubscript{2}COOCD\textsubscript{3}, 8(CH\textsubscript{2}D)=2.06, s] after reaction with hexafluoro-2-butyne (Table 4.5). No evidence exists in the \textsuperscript{1}H NMR spectrum of (4.19) to suggest the formation of sulfene (CH\textsubscript{2}=SO\textsubscript{2}), which would have been detected in solution as methyl methanesulfonate [CD\textsubscript{3}OSO\textsubscript{2}CH\textsubscript{2}D, 8(CH\textsubscript{2}D)=3.02, s] using \textsubscript{d\textsubscript{4}}-methanol as a sulfene trap.\textsuperscript{50} This observation of the trapped alkyl acetates from (4.19) and all the other
Table 4.5: Percentage Yield of Products from Reactions of \([\text{Co}_2(\text{CO})_4(\mu-R)(\mu-R')(\mu-\text{dppm})]\) with \(R^2\text{OCR}^2\) in the presence of \(\text{CD}_3\text{OD}\)

<table>
<thead>
<tr>
<th>([\text{Co}_2(\text{CO})_4(\mu-R)(\mu-R')(\mu-\text{dppm})])</th>
<th>(R^2)</th>
<th>([\text{Co}_2(\text{CO})_4(\mu-R^2\text{CCR}^2)(\mu-\text{dppm})])</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3.5); (R=\text{CH}_2, R'=\text{CO})</td>
<td>(\text{CF}_3)</td>
<td>&gt;50</td>
<td>85</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(3.5); (R=\text{CH}_2, R'=\text{CO})</td>
<td>(\text{Ph})</td>
<td>95</td>
<td>95</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(3.6); (R=R'=\text{CH}_2)</td>
<td>(\text{CF}_3)</td>
<td>&gt;50</td>
<td>80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(3.6); (R=R'=\text{CH}_2)</td>
<td>(\text{Ph})</td>
<td>90</td>
<td>90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(3.8); (R=R'=\text{CHMe})</td>
<td>(\text{CF}_3)</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>45</td>
</tr>
<tr>
<td>(3.9); (R=\text{CHCO}_2\text{Et}, R'=\text{CO})</td>
<td>(\text{CF}_3)</td>
<td>&gt;50</td>
<td>-</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>(3.11); (R=\text{CH}_2, R'=\text{CHMe})</td>
<td>(\text{CF}_3)</td>
<td>50</td>
<td>35</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>(3.12); (R=\text{CH}_2, R'=\text{CHCO}_2\text{Et})</td>
<td>(\text{CF}_3)</td>
<td>&gt;50</td>
<td>95</td>
<td>95</td>
<td>-</td>
</tr>
<tr>
<td>(4.19); (R=\text{CH}_2, R'=\text{SO}_2)</td>
<td>(\text{CF}_3)</td>
<td>55</td>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\((4.50) = [\text{Co}_2(\text{CO})_4(\mu-\text{CF}_3\text{CCCP}_3)(\mu-\text{dppm})]; 6(\text{CH}_2\text{P}_2) 3.45 \text{ Hz} ; 6(^{31}\text{P}) 36.6 \text{ from PO(OMe)}_3\)  
\((4.51) = [\text{Co}_2(\text{CO})_4(\mu-\text{PhCCPh})(\mu-\text{dppm})]; 6(\text{CH}_2\text{P}_2) 3.30 \text{ Hz} ; 6(^{31}\text{P}) 34.9 \text{ from PO(OMe)}_3\)
Table 4.5 (continued)

\[ a = \text{methyl acetate-}d_4: \quad \text{H}_2\text{CD} - \text{C}^{\text{OCD}_3} \]

\[ b = \text{ethylacetoxyacetate-}d_4: \quad \text{H}_3\text{CH}_2\text{CO} - \text{CHD} - \text{C}^{\text{OCD}_3} \]

\[ c = \text{methyl propionate-}d_4: \quad \text{H}_3\text{CHCD} - \text{C}^{\text{OCD}_3} \]
(µ-alkylidene)dicobalt complexes contained in Table 4.5, resulting from reaction with hexafluoro-2-butyne, reveals that the ketene formation occurs via an intramolecular coupling of a carbonyl ligand and an alkylidene moiety. A g.c. sample analysis from the sealed tube reaction of (4.19) with hexafluoro-2-butyne did not show any sign for the eliminated sulfur dioxide unit, particularly when comparing with the reference free sulfur dioxide peak position.

When calculating the yield of (4.50) formed in Table 4.5, since an alkyne molecule did not insert into a metal-alkylidene bond, the addition of the four-electron donor alkyne ligand requires an overall equivalent four-electron donor loss from the initial (µ-alkylidene)-dicobalt substrate, in order to maintain the 18-electron rule. The presence of the alkyl acetates suggest that the carbenes from either a mono- or bis(µ-alkylidene) complex are ejected after an intramolecular coupling with a carbonyl ligand creating a total loss of four electrons per carbene ejected. This carbonyl migratory insertion reaction is suspected to create the coordinatively unsaturated intermediate required for the initial alkyne addition. Since (4.50) is the only organometallic product formed from alkyne addition to the bis(µ-alkylidene)dicobalt complexes (3.6), (3.11) and (3.12), this implies after their respective ketene eliminations involving both alkylidene units, the maximum yield of (4.50) produced is 50% per mole of that particular bis(µ-alkylidene)dicobalt precursor. The additional molecules of carbon monoxide required to generate (4.50) are most likely scavenged from some decomposition of the bis(µ-alkylidene)-dicobalt precursor. Thus the recorded yields of (4.50) are the percentage values of the maximum (4.50) obtainable from each reaction.
in Table 4.5. The corresponding alkyl acetate yields from each ketene trapped are calculated on a comparative equimolar basis with the reagent (μ-alkylidene)dicobalt substrate. This type of alkyne addition observed for this (μ-alkylidene)dicobalt system parallels that reported earlier under photochemical conditions to produce the acetylene-bridged species [Cp₂Ru₂(μ-CO)(μ-H₂C₃)] (4.44), although the fate of the ejected carbenes from [Cp₂Ru₂(CO)₂(μ-C₃H₅)(μ-CHMe)] (4.1) is unknown.⁶

It should be noted that under identical experimental conditions, both the mono- and bis(μ-methylene) complexes (3.5) and (3.6) respectively reacted slowly with alkynes RCCR (equation 4.8.6) at room temperature to give [Co₂(CO)₄(μ-RCCR)(μ-dppm)] (R=CF₃(4.50), Ph(4.51)) and the methyl acetate-d₄ product DCH₂COOCO₂ (Table 4.5) from the 1:1 stoichiometric reaction of ketene with methanol-d₄. However, only alkyne reaction with the bis(μ-methylene) complex (3.6) evolved ethylene [ca. 3%], identified by g.c., again suggesting an intramolecular carbon-carbon coupling process. Ethylene formation from equation 4.8.6 is only the second example of the room temperature coupling of simple methylene units to give ethylene. The previous example involved the decomposition of trans-[(η⁵-C₅Me₅)₂Rh₂Me₂(μ-CH₂)₂] (4.2) in the presence of 1-electron oxidizers at 20°C to give methane, ethylene and propylene by coupling reactions of the C₃ ligands.⁷

Propylene formation is envisioned to proceed by a linking of one methyl and two methylene ligands to produce an oxidized C₃ ligand, which β-eliminates propylene (equation 4.8.7).
It should also be noted that a trace of ethylene was also observed from sulfur dioxide addition to (3.6) to give \([\text{Co}_2(\text{CO})_4(\mu-SO_2)_2(\mu-dppm)]\) (4.20) in section 4.6.4. This formation of ethylene from equation 4.6.6 supports an intermolecular carbon-carbon coupling process deduced from the mass spectral results discussed in section 4.2.3.

4.8.3 Alkylidene Addition to Alkyne-Bridged Complexes

Sequential methylene addition to an alkyne coordinated at a diruthenium centre was reported by Knox et al.\textsuperscript{66} when diazomethane
addition at 0°C to \( [\text{Cp}_2\text{Ru}_2(\mu\text{-CO})(\mu\text{-C}_2\text{Ph}_2)] \) (4.52) yielded \( [\text{Cp}_2\text{Ru}_2(\text{CO})(\mu\text{-CH}_2)(\mu\text{-C(Ph)C(Ph)CH}_2)] \) (4.53), in which an X-ray diffraction established that two methylene units were incorporated in the structure of (4.53). A second carbon-carbon bond formation (equation 4.5.8) occurred to link the methylene groups in (4.53) to give the \( \sigma,\pi \)-allyl complex (4.54) on refluxing a xylene solution of (4.53)\(^{88}\), (4.54) was also obtained by insertion of diphenylacetylene into the \( \mu \)-ethyldiene complex \( [\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CHMe})] \)\(^{82}\).

\[
\begin{align*}
\text{Ph} & \quad \text{C} \quad \text{C} \quad \text{CH}_2 \\
\text{OC} & \quad \text{Ru} \quad \text{Ru} \\
\text{Cp} & \quad \\
\text{H} & \quad \\
\end{align*}
\quad 140°C
\begin{align*}
\text{Ph} & \quad \text{C} \quad \text{C} \quad \text{C(H)Me} \\
\text{OC} & \quad \text{Ru} \quad \text{Ru} \\
\text{Cp} & \quad \\
\text{H} & \quad \\
\end{align*}
\]

(4.53)

(4.54)

The complex \( [\text{Os}_3(\text{CO})_6(\mu\text{-CH}_2)(\mu_3\text{-C}_2\text{Ph}_2)] \) (4.55) also undergoes carbon-carbon bond formation on heating to link the hydrocarbon ligands and yield (4.56). This reaction 4.8.9 is proposed to proceed via a \( \sigma,\pi \)-allyl intermediate which subsequently rearranges to \( [\text{HOS}_3(\text{CO})_6(\mu_3,\eta^3\text{-C}_2\text{Ph}_2H)] \) (4.56) following oxidative addition of a methylene C-H bond to the cluster\(^{89}\).

\[
\begin{align*}
[\text{Os}_3(\text{CO})_6(\mu\text{-CH}_2)(\mu_3\text{-C}_2\text{Ph}_2)] & \quad \text{135°C} \\
\end{align*}
\]

(4.55)

(4.56); \( M=\text{Os}(\text{CO})_3 \)
A similar binuclear σ,π-allyl complex (4.59) results when the complex \([\text{Cp}_2\text{Rh}_2(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{CF}_3\text{CCCF}_3)]\) (4.58), isolated from equation 4.8.10, undergoes an intramolecular migration of the \(\mu\)-methylen group to the coordinated alkyne at room temperature in solution (Scheme 4.10). In contrast, an X-ray structural determination revealed that the \(\mu\)-alkylidene complex \([\text{Cp}_2\text{Rh}_2(\mu-\text{CO})(\mu-\text{C(CO}_2\text{Et})_2)(\mu-\text{CF}_3\text{CCCF}_3)]\) (4.60) displays a similar alkylidene migration to form a new carbon-oxygen bond in (4.61) involving the carbonyl oxygen atom of an ester substituent, as opposed to the carbon-carbon bond formation in (4.59) (Scheme 4.10).

\[
\begin{align*}
0^\circ\text{C} & \quad [\text{Cp}_2\text{Rh}_2(\mu-\text{CO})(\mu-\text{CF}_3\text{CCCF}_3)] + \text{N}_2\text{CR}_2 \rightarrow [\text{Cp}_2\text{Rh}_2(\mu-\text{CO})(\mu-\text{CR}_2)(\mu-\text{CF}_3\text{CCCF}_3)] \\
& \quad (4.58); \ R=\text{H} \\
& \quad (4.60); \ R=\text{CO}_2\text{Et}
\end{align*}
\]

These reports suggest that the linking of coordinated olefinic and methylene groups at these binuclear centers may be correlated to carbon homologation in the Fischer-Tropsch synthesis, where such combinations are proposed to occur on metal surfaces.

By an adaptation of the preceding literature precedents, treatment of both the alkyne-bridged complexes \([\text{Co}_2(\text{CO})_4(\mu-\text{RCRR})(\mu-\text{dppm})]\) \((R=\text{CF}_3(4.50), \text{Ph}(4.51))\) with an ethereal solution of diazomethane at 0°C in dichloromethane produced no reaction, as verified by IR and \(^{31}\text{P}(^1\text{H})\) NMR spectral studies. This work emphasizes the stability of these alkyne-bridged dicobalt complexes.
Scheme 4.10: Alkylidene migration in the complexes \([\text{Cp}_2\text{Rh}_2(\mu-\text{CO})(\mu-\text{CR}_2)\mu-\text{CF}_3\text{CCC}F_3]\). The Cp and CO ligands are omitted in the pictorial representation of (4.61) for clarity.
4.9 Summary of the Chapter

This work has determined that only the simplest bis(μ-alkylidene)-
dicobalt complexes [Co₂(CO)₄(μ-CH₂)₂(μ-dppm)] (3.6) and [Co₂(CO)₄-
(μ-CH₂)(μ-CH₂Me)(μ-dppm)] (3.11) are thermally decomposed under mild
conditions to produce olefin products derived from a coupling of their
μ-alkylidene units. Deuterium labelling studies suggest that olefin
formation proceeds via a complex intermolecular carbon-carbon coupling
process as opposed to a direct intramolecular coupling of the
μ-alkylidene groups. This behaviour might require a fluxional
methylen bridge. These same pyrolysis reactions in the presence of
hydrogen produced the corresponding alkane (ethane from (3.6); propane
from (3.11)), interpreted to arise from an oxidative addition of
hydrogen to the substrate prior to reductive elimination of the
respective alkane.

Reaction of the mono- or bis(μ-methylene) species (3.5) and (3.6)
respectively with ethylene generated propylene, suggesting the
formation of a transient dimetallacyclopentane complex.

It appears to be a general phenomenon in this system that small
molecule addition, specifically CO, SO₂ or alkynes RCR (R=Ph, CF₃), to
these coordinatively saturated (μ-alkylidene)dicobalt complexes creates
an unstable intermediate following an intramolecular carbonyl insertion
into a cobalt-alkylidene bond. This unstable intermediate species is
suspected to release ketene or a ketene derivative. Evidence for this
insertion reaction was obtained by identification of the alkyl
acetate(s) in solution when the corresponding ketene moiety was trapped
with methanol·d₄. The combined results of Tables 4.2, 4.4 and 4.5
suggest that coupling of μ-CHR and CO groups is a reasonable step.
during catalysis of the Fischer-Tropsch synthesis by cobalt catalysis.
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CHAPTER 5

SYNTHESIS AND CHARACTERIZATION OF (μ-ALKYLIDENE)DICOBALT COMPLEXES OF

DMPM VIA DIAZOALKANE ADDITION

5.1 Introduction

Current interest in small bite bidentate trivalent phosphorus ligands has focused on their ability to stabilize polynuclear as well as mononuclear transition metal complexes through the formation of five- and four-membered chelate rings respectively, as shown by (5.1) and (5.2). The ligand dmpm, which is considered the simplest possible ditertiary phosphine, is of particular interest in being highly basic and sterically undemanding. Recent evidence consistent with these proposals has been documented. When the bulkiness of the phenyl substituents of dppm was suspected to hinder the accessibility of the platinum center toward oxidative addition, subsequent work by Puddephatt et al. provided results for dmpm which indicate that the smaller steric effect of methyl substituents can lead to different, and in some ways enhanced, reactivity compared to similar dppm complexes. Furthermore, from a systematic study of platinum complexes with diphosphine ligands R_2PCH_2PR_2 (R=Me,Et,OEt,Ph), it was deduced that the structures and reactivities of these platinum diphosphine complexes are principally governed by steric effects.
5.1.1 A Survey of bis(dimethylphosphino)methane Cobalt Complexes

Studies involving dmpm metal complexes are relatively limited as compared to other bidentate diphosphine ligands such as dpdm. The few reported cobalt complexes incorporating at least one dmpm ligand are illustrated in Figure 5.1 and provide suitable examples pertaining to the five-membered (5.1) and four-membered (5.2) chelate ring complexes. Two complexes in Figure 5.1, [Co(PMe₃)(dmpm)]⁺ (5.3b) and [Co(PMe₃)₂(dmpm)]⁺ (5.4b), have been prepared with chlorides as counterions.⁴,⁵ These complexes are monomers with dmpm in the cis-chelated form. Studies focused on the series of isoelectronic complexes [M(PMe₃)(dmpm)]⁺ (5.3) and [M(PMe₃)₂(dmpm)]⁺ (5.4), where M=Fe, n=0 (5.3a, 5.4a); M=Co, n=1 (5.3b, 5.4b); M=Ni, n=2 (5.3c, 5.4c), have revealed that complexes possessing two chelating dmpm ligands are less stable than the corresponding complexes containing only one dmpm ligand. It was also noted that the stabilities of these same complexes decrease in the order Fe>Co>Ni. For example, the cobalt(I) complex (5.3b) disproportionates slowly in tetrahydrofuran at room temperature to yield the cobalt(III) complex [CoCl₂(PMe₃)(dmpm)] and the neutral dmpm bridged dimer (5.5) shown in Figure 5.1, cis,cis-[Co₂(μ-PMe₂)₋(PMe₃)₂(μ-dmpm)]₂.

A methylcobalt complex of dmpm (5.6) has also been prepared
(5.3a) \( M=Fe, n=0 \)
(5.3b) \( M=Co, n=1 \)
(5.3c) \( M=N_1, n=2 \)

(5.4a) \( M=Fe, n=0 \)
(5.4b) \( M=Co, n=1 \)
(5.4c) \( M=N_1, n=2 \)

Figure 5.1: Some examples of metal complexes with the ligand \( \text{bis(dimethylphosphino)methane (P,P)} \).
5.1.2 Bridging Alkylidene Complexes of bis(dimethylphosphino)methane

The limited literature precedents describing transition metal complexes incorporating a chelating dmpm ligand are reflected in the report of only one such complex also possessing a $\mu$-alkylidene ligand, namely $[N(PPh_3)_2]_2[ReW(\mu-CHR)(CO)_7(\mu-dmpm)]$ (5.8), where $R=4-MeC_8H_4$. This heteronuclear dimeric $\mu$-alkylidene complex (5.8), synthesized from the alkylidyne complex $[ReW(\mu-CHR)(CO)_8]$ (5.7), is a characterized intermediate species en route to complex (5.9) (Scheme 5.1). The asymmetrically bridging p-xylyl group, $\mu$-CH$_2$R, in (5.9) acts as a normal $\sigma$-donor to rhenium, but also functions as a two-electron donor via interaction of a C-H bond with tungsten, thus forming a three-center two-electron bond. This stepwise conversion of an alkylidyne unit to an alkyl unit illustrated in Scheme 5.1 serves as an important model for several catalytic reactions, such as the Fischer-Tropsch reaction.

5.1.3 Scope of the Chapter

It was the purpose of this work to develop a ($\mu$-alkylidene)-
dicobalt carbonyl system of dmpm complexes, ideally originating from
Scheme 5.1: Stepwise conversion of an alkyldyne ligand to an asymmetrically bridging alkyl group.
diazokane addition to [Co₂(CO)₆(μ-CO)₂(μ-dpm)] (5.10). In order to investigate any chemical differences compared with the analogous dicobalt carbonyl complexes stabilized by the dpmm ligand studied earlier. Literature reports⁸,¹⁰ reveal metal carbonyl complexes of dpmn appear to be significantly more air-sensitive than analogous metal carbonyl complexes of most other tertiary phosphines. The increased air-sensitivity of metal carbonyl complexes of dpmm is attributed to the sterically unencumbered and relatively electron-rich metal atoms in these metal carbonyl complexes compared with analogous metal carbonyl complexes of other trivalent phosphorus ligands (e.g., dpmm). This fact predominates despite the tendency of these metal carbonyls to favour an 18-electron rare gas electronic configuration and the presence of several π-accepting carbonyl ligands to remove excess metal electron density. Consequently, all solvents were rigorously dried where possible and an inert atmosphere was required at all times when handling any dicobalt carbonyl complex of dpmm.

The reaction of diazoalkanes with the dicobalt carbonyl complex [Co₂(CO)₆(μ-CO)₂(μ-dpm)] (5.10) bridged by the small bite ditertiary phosphine (CH₃)₂PCH₂P(CH₃)₂, dpmm, leads in some instances to the formation of air-sensitive, electron-rich μ-alkylidene complexes, similar in structure to the analogous dpmm derivatives (Chapter 3). However, an attempt to generate a mixed bis(μ-alkylidene)dicobalt complex incorporating a bridging dpmm ligand resulted in the synthesis of a novel trinuclear cluster [Co₃(CO)₆(μ₂-CO₂Et)(μ-dpm)]. The instability of these electron-rich (μ-alkylidene)dicobalt dpmm complexes prevented any comparison between the chemistry observed in the preceding chapter for the dpmm complexes and their dpmm analogues.
5.2 Preparation and Characterization of \([\text{Co}_2(\text{CO})_6(\mu-\text{CO})_2(\mu-\text{dmpm})]\)

Despite a tentative report that reactions of \text{dmpm} with \([\text{Co}_2(\text{CO})_6]\) and with \([\text{CpCo(\text{CO})_3}]\) (1.16b) gave products too air-sensitive for a definitive identification and full characterization,\(^{10}\) the complex \([\text{Co}_2(\text{CO})_6(\mu-\text{CO})_2(\mu-\text{dmpm})]\) (5.10) was prepared by equation 5.2.1, in a similar manner to its \text{dppm} congener (equation 3.2.1).

\[
\begin{align*}
\text{[Co}_2(\text{CO})_6] + \text{dmpm} & \xrightarrow{25^\circ\text{C}} \text{[Co}_2(\text{CO})_6(\mu-\text{CO})_2(\mu-\text{dmpm})] + 2\text{CO} \\
\text{THF} & & & \text{5.2.1}
\end{align*}
\]

The reaction is complete within 30 minutes, as evidenced by solution IR studies. Solvent removal produces a black solid, which is actually a deep red colour in solution.

Although the air-sensitive complex (5.10), possessing two bridging carbonyl ligands, displays an IR spectrum similar to its \text{dppm} analogue (3.4) (Table 5.1), a higher basicity of \text{dmpm} relative to \text{dppm} is reflected in the \(\nu(\text{CO})\) frequencies of the analogous dicobalt carbonyl complexes of these two ligands. This observation of lower \(\nu(\text{CO})\) frequencies for the \text{dmpm} derivative (5.10) as compared to the corresponding \text{dppm} complex (3.4) is also evident on comparison of other analogous metal carbonyl complexes incorporating these same two diphosphine ligands. Representative examples illustrating the higher basicity of \text{dmpm} relative to \text{dppm}, as inferred from their respective IR data, are listed in Table 5.1. The higher basicity and lower \(\pi\)-acceptor strength of the \text{dmpm} ligand relative to \text{dppm}, as implied by the IR data in Table 5.1, emphasize a higher electron density on the metal atom of the corresponding \text{dmpm} complex. Consequently, an
Table 5.1: Infrared ν(CO) Frequencies of Metal Carbonyl Complexes of bis(dimethylphosphino)methane and Related Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Terminal ν(CO) cm⁻¹</th>
<th>Bridge ν(CO) cm⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mn}_2(\text{CO})_6(\mu-\text{dpm})])</td>
<td>a</td>
<td>2054(m), 1984(s), 1961(s), 1937(m), 1912(m)</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>([\text{Mn}_2(\text{CO})_6(\mu-\text{dppm})])</td>
<td>b</td>
<td>2060(s), 2000(m), 1997(s), 1952(m), 1925(s)</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>([\text{Mn}_2(\text{CO})_6(\mu-\text{dpm})_2])</td>
<td>a</td>
<td>1980((\tilde{\text{w}})), 1906(s), 1874(s), 1850(m)</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>([\text{Mn}_2(\text{CO})_6(\mu-\text{dppm})_2])</td>
<td>a</td>
<td>1994((\tilde{\text{w}})), 1923(sh), 1912(s), 1866(m)</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>([\text{Fe}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{dpm})])</td>
<td>a</td>
<td>2044(s), 1988(s), 1972(s), 1937(s)</td>
<td>1745(m)</td>
<td>10</td>
</tr>
<tr>
<td>([\text{Fe}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{dppm})])</td>
<td>c</td>
<td>2050(s), 2005(s), 1992(s), 1965(s), 1950(s), 1935(m)</td>
<td>1770(m)</td>
<td>12</td>
</tr>
<tr>
<td>([\text{Co}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{dpm})]) ((5.10))</td>
<td>d</td>
<td>2045(m), 2010(s), 1990(s)</td>
<td>1840(m), 1780(m)</td>
<td></td>
</tr>
<tr>
<td>([\text{Co}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{dppm})]) ((3.4))</td>
<td>d</td>
<td>2049(m), 2017(s), 1991(s)</td>
<td>1842(m), 1793(m)</td>
<td></td>
</tr>
</tbody>
</table>

a) dichloromethane

b) hexane

c) methylcyclohexane

d) cyclohexane
increase in the $d_{π}−π^{*}$ back-bonding to carbonyl groups in the dmpm metal carbonyl complexes accounts for the lowering of the $ν(\text{CO})$ frequencies in metal carbonyl complexes of dmpm compared with analogous metal carbonyl complexes of dppm.$^{10}$

The availability of both the methylene and methyl groups as proton NMR probes in $(\text{CH}_{3})_{2}\text{PCH}_{2}\text{P(CH}_{3})_{2}$, dmpm, render complexes containing this diphosphine ligand more amenable to NMR characterization than analogous complexes of $\text{Ph}_{2}\text{PCH}_{2}\text{PPh}_{2}$, dppm. Figure 5.2 illustrates the $^1\text{H}$ NMR spectrum of $[\text{Co}_{2}(\text{CO})_{4}(μ-\text{CO})_{2}(μ-\text{dmpm})]$ (5.10) exhibiting both the $\text{PCH}_{2}$ $[δ 2.01, \text{t, } J(\text{PH}) 10 \text{ Hz}]$ and $\text{PCH}_{3}$ $[δ 1.66, \text{t, } J(\text{PH}) 4 \text{ Hz}]$ resonances. A broad $^{31}\text{P}(^1\text{H})$ NMR resonance for (5.10) was observed in acetone-$d_6$ at $δ 39.0$.

The low molecular weight of the dmpm ligand results in all the mononuclear metal carbonyl complexes and some binuclear metal carbonyl complexes (e.g., $[\text{Mn}_{2}(\text{CO})_{10−2n}(μ-\text{dmpm})_{n}] (n=1,2)$) being sufficiently volatile to obtain the mass spectrum.$^{10}$ Generally, a stepwise loss of carbonyl groups from their parent molecular ions is observed$^{13}$ for these metal carbonyl derivatives, and complex (5.10) is no exception. Other types of fragmentation processes do not appear to compete effectively with this carbonyl loss.

The identification and characterization of the electron-rich (5.10) provides a potentially convenient precursor to a $μ$-alkylidene system via carbonyl loss induced from diazoalkane addition to (5.10), similar to that developed for $[\text{Co}_{2}(\text{CO})_{4}(μ-\text{CO})_{2}(μ-\text{dmpm})]$ (3.4) in Chapter 3, but with the advantage of the less hindered diphosphine dmpm ligand.
Figure 5.2: $^1$H NMR Spectrum (200 MHz) of $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dmpm})](5.10)$ in $(\text{CD}_3)_2\text{CO}$ at $-35^\circ\text{C}$. 
5.3 Preparation and Characterization of \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})]\)

5.3.1 Preparation

Modelling the syntheses of the (\(\mu\)-methylene)dicobalt complexes of dppm (3.5) and (3.6), as shown in equation 3.3.1, an excess of ethereal diazomethane was added to a solution of \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]\) (5.10) at room temperature under a nitrogen atmosphere. After 10 hours, the initially red-coloured solution had turned green with a large yield of polymethylene clearly evident under these reaction conditions. Schlenk ware was utilized to separate the polymer from the green solution under nitrogen. Solvent removal under vacuum and a subsequent column chromatograph produced a green oily solid whose cyclohexane solution IR spectrum, although contaminated with (5.10), revealed no novel \(\nu(\mu-\text{CO})\) bands with terminal \(\nu(\text{CO})\) frequencies tentatively assigned in \(\text{cm}^{-1}\) as 2040s, 2000s, 1970m, 1950m.

5.3.2 Product Characterization

A \(^1\text{H} \text{NMR}\) spectrum of the green oil in acetone-\(d_6\) revealed only broad resonance signals at 25°C. Particularly of interest at this temperature were the broad resonances in the characteristic \(\mu\)-methylene region, notably 5.3-6. Low temperature \(^1\text{H} \text{NMR}\) spectroscopy revealed a sharpening of these broad resonances at 0°C with the best definition of the spectrum at -35°C (Figure 5.3). It is evident at -35°C that the complex \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})]\) (5.11) exists in solution, exhibiting a similar \(^1\text{H} \text{NMR}\) spectrum to that observed for the analogous dppm bis(\(\mu\)-methylene) derivative (3.6).

Four equal intensity peaks are observed at -35°C in Figure 5.3 to represent the chemical inequivalence of the four \((\text{CH}_2)_2\text{Co}_4\) protons.
One of these \((\text{CH}_2)_2\text{CO}_2\) protons in Figure 5.3 centered at 8 3.54 exhibits a large triplet coupling to phosphorus \([J(\text{PH}) 22 \text{ Hz}]\), diagnostic of the assigned proton \(H^4\) lying over the dmpm ligand in the static structure for (5.11), shown in the Newman projection drawn along the Co-Co bond in Figure 5.3. Although the size of the triplets' \(J(\text{PH})\) values are similar for both the dmpm bis(\(\mu\)-methylene) complex (5.11) \([J(\text{PH}) 22 \text{ Hz}]\) and its dppm analogue (3.6) \([J(\text{PH}) 23.5 \text{ Hz}]\), only the triplet observed in (3.6) (Figure 3.3) displays the lowest chemical shift (5 3.65) of the chemically inequivalent \(\mu\)-methylene protons in that complex. This anomalously low chemical shift (5 3.65) in (3.6) was attributed to the diamagnetic influence of the phenyl substituents on the phosphorus atoms of dppm. This postulate is supported by the more deshielded chemical shift of \(H^4\) (8 3.54) with respect to the other \(\mu\)-methylene protons in the dmpm analogue (5.11) (Figure 5.3) since both these chelating diphosphine bis(\(\mu\)-methylene) derivatives (3.6) and (5.11) are assumed to possess the same static structure in solution.

An \(AB\) spectral pattern is observed and analyzed for the \(\text{CH}_2\text{P}_2\) protons of the dmpm ligand in (5.11) at 35°C, consistent with the chemical inequivalence of these protons in the static Newman projection. In Figure 5.3, \(\text{CH}_2^2\text{H}^2\text{P}_2\) is visible as an apparent quartet at 8(H^2) 1.74 \([J(\text{PH}) 10 \text{ Hz}], J(\text{HH}) 14 \text{ Hz}]\) while H^2 (8 2.54; J(\text{PH}) 10 Hz, J(\text{HH}) 14 Hz) is partially masked by an impurity peak assumed to be the \(\text{PCH}_2\) 8 1.66 resonance of the unreacted \([\text{Co}_{2}(\text{CO})_6(\mu-\text{CO})_2(\mu-\text{dmpm})]\) (5.10) complex in solution. Evidence for the complex (5.10) in the sample is provided by both the \(^{31}\text{P} \text{NMR and IR spectra.}\)

The broadening of the methylene \(^1\text{H} \text{NMR signals on warming the sample (5.11) to 25°C (Figure 5.3)}\) suggests a possible interconversion,
Figure 5.3: $^1$H NMR Spectrum (200 MHz) of [Co$_2$(CO)$_4$(μ-CH$_2$)$_2$(μ-dmpm)](5.11) in (CD$_3$)$_2$CO. The + sign indicates the (CD$_3$)$_2$CO impurity peak, while the asterisked peaks represent residual amounts of (5.10).
apparently via a bridge/terminal methylene isomerization. By warming the sample above 25°C, the coalescence temperature for the $\mu$-methylene protons of the $[\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dmpm})]$ (5.11) system was determined to be 50.3°C. Since the diphosphine methylene protons ($\text{P}_2\text{CH}_2$) in (5.11) coalesce at approximately 55°C, the activation energy $\Delta G^\ddagger$ was estimated from these $\text{P}_2\text{CH}_2$ protons using the Eyring equation ($\Delta v=160$ at 200 MHz, $T_c=328$ K) to be 64.6 kJ mol$^{-1}$ for this fluxional behavior. It appears this system (5.11) is governed by the same single dynamic process in solution to account for the apparent inequivalence of the ($\text{CH}_2$)$_2\text{Co}$ and $\text{CH}_2\text{P}_2$ protons as was previously deemed responsible for this same phenomenon in the analogous dppm bis$(\mu$-methylene) system (3.6) (equation 3.3.2). Hence the $^1\text{H}$ NMR evidence in Figure 5.3 suggests a facile bridge/terminal interconversion of the methylene protons in the dmpm bis$(\mu$-methylene) species (5.11).

No definitive explanation can account for the higher activation energy estimated for the dmpm bis$(\mu$-methylene) system ($\Delta G^\ddagger=64.6$ kJ mol$^{-1}$) as compared to the barrier estimated for the analogous dppm system (3.6) ($\Delta G^\ddagger=53.1$ kJ mol$^{-1}$). Steric factors alone might predict the opposite trend. However, perhaps the observed trend may indicate the preference of the bulkier dppm system's cobalt atoms to attain a lower coordination number, achieved via the terminal carbene formation (equation 3.3.2), with respect to the cobalt atoms in the dmpm system.

5.3.3 Summary

Due to the extreme air-sensitivity of the bis$(\mu$-methylene) complex (5.11), a subsequent $^1\text{H}[^{31}\text{P}]$ and $^{31}\text{P}[^1\text{H}]$ NMR spectra of (5.11) revealed only unidentifiable decomposition products. Attempts to reproduce
(5.11) from equations 5.3.1 and 5.3.2 resulted only in the same green
decomposition products. No sign in solution from either NMR or IR
spectroscopy was evident to support the presence of the
mono(μ-methylene)dicobalt complex of dmpm, [Co₂(CO)₄(μ-μCO)(μ-CH₂)-
(μ-dmpm)]. This fact may relate to that earlier observed for the
Corresponding dpdm μ-methylene derivative when the mono(μ-methylene)
species (3.6) was found to be less stable in solution than the
bis(μ-methylene) congener (3.6).

The instability of the bis(μ-methylene) complex (5.11) of dmpm in
solution prevented any chemistry of this complex from being
investigated. It appears that the increased electron density on the
cobalt atoms resulting from the more basic dpdm ligand relative to dpdm
in this metal carbonyl system is predominantly a destabilizing factor.

\[ [\text{Co}_x(\text{CO})_y(\mu-\text{CO})_z(\mu-\text{dmpm})] \xrightarrow{\text{CH}_2\text{N}_2} [\text{Co}_x(\text{CO})_y(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dmpm})] \]

\[ \text{CO}_1, \text{N}_2 \]

(5.10)

\[ [\text{Co}_x(\text{CO})_y(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dmpm})] \xrightarrow{\text{CH}_2\text{N}_2} [\text{Co}_x(\text{CO})_y(\mu-\text{CH}_2)_2(\mu-\text{dmpm})] \]

\[ \text{CO}_1, \text{N}_2 \]

(5.11)

5.4 Reaction of [Coₓ(CO)ᵧ(μ-μCO)z(μ-dmpm)] with Diazoethane

Reaction of (5.10) with excess ethereal diazoethane under the same
reaction conditions as for equations 5.3.1 and 5.3.2 produced a similar
green oil after separation from the polymeric material. No
identifiable species aside from the precursor (5.10) could be detected in solution, particularly with regard to a $\mu$-ethylidene complex of dmpm. This failure to observe a $\mu$-ethylidene complex derived from an ethylidene replacement of a bridging carbonyl ligand in (5.10) may reflect on the instability introduced by the increased $\sigma$-donor strength of the $\mu$-ethylidene unit with respect to a $\mu$-methylene group and/or the tendency of a ($\mu$-ethylidene)dicobalt complex to readily $\beta$-eliminate.

5.5 Preparation and Characterization of $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHCO}_2\text{Et})(\mu-\text{dmpm})]$ 

5.5.1 Preparation

Both the chelating diphosphine systems $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dmpm})]$ (5.10) and the dppm congener (3.4) do not react with diphenyl-diazomethane ($N_2\text{CPh}_2$), presumably due to instability introduced by the bulkiness of the phenyl substituents of the incoming diphenylcarbene unit. The complex $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHCO}_2\text{Et})(\mu-\text{dmpm})]$ (5.12), the analogue of the dppm derivative (3.9), was isolated as a red, air-sensitive oil from the addition of excess ethyl diazoacetate to a dichloromethane solution of the cobalt carbonyl precursor (5.10) at room temperature under nitrogen (equation 5.5.1). However, the less bulky methyl substituents of dmpm did not allow formation of a bis($\mu$-alkylidene) species, thereby paralleling the similar dppm reaction cited by equation 3.5.1. Equation 5.5.1, incorporating the chelating dmpm ligand, was conveniently monitored by solution IR spectroscopy since the product (5.12) contains only one bridging carbonyl ligand ($\nu(\mu-\text{CO})$ 1790 cm$^{-1}$).
\[
\text{[Co_2(CO)_4(\mu-\text{CO})_2(\mu-\text{dmpm})]} \xrightarrow{\text{xs,N}_2\text{CHO}_2\text{Et}} [\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHO}_2\text{Et})-\text{CO},N_2] (5.10)
\]

\[
[\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHO}_2\text{Et})-\text{CO},N_2] \xrightarrow{\text{xs,N}_2\text{CHO}_2\text{Et}} [\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHO}_2\text{Et})-\text{CO},N_2] (5.12)
\]

5.5.2 Product Characterization

The air-sensitive product (5.12) exhibited a broad singlet in acetone-d_8 at 8 33.7 in the ^31P(^1H) NMR spectrum at probe temperature. Both the ^31P(^1H) NMR chemical shifts of (5.12) and its precursor complex (5.10) are shielded by approximately 20 ppm with respect to their dppm congeners' ^31P(^1H) NMR chemical shift (Table 5.2).

Figure 5.4 reveals the ^1H NMR spectrum of (5.12) at -35°C in acetone-d_8. The sharpest definition of the broad resonance peaks of the ethoxy protons in (5.12) occurred at -35°C, yet aside from these specific proton resonances [8 3.49, 8 0.74], the remaining peaks appeared the same at 20°C. The stereochemistry of complex (5.12) is defined by the Newman projection shown in Figure 5.4 shown along the Co-Co bond. The bridging alkylidene proton is evident as a triplet [8 3.90, J(PH) 21 Hz] from coupling to the two chemically equivalent phosphorus atoms of the dmpm ligand. This large J(PH) value of 21 Hz [8 3.90, t] is diagnostic of the assigned stereochemistry in the Newman projection. The ethoxy moiety of the bridging substituent acetate ligand appears only as broad resonances [-CO_2CH_2CH_3, 8 3.49; -CO_2CH_2CH_3, 8 0.74] of the appropriate integration in Figure 5.4 exhibiting an observable geminal coupling [J(HH) 8 Hz]. Variable
Figure 5.4: $^1$H NMR Spectrum (200 MHz) of [Co$_2$(CO)$_4$(μ-CO)(μ-CHCO$_2$Et)(μ-dmpy)](5.12) in (CD$_3$)$_2$CO at
-35°C. The CH$_{α_1}H_{α_2}$ resonance is superimposed on the (CD$_3$)$_2$CO impurity peak.
Table 5.2: NMR Spectral Frequencies for the \( (u\text{-alkylidene})\text{dicobalt Complexes of dmpe}\).\(^b\)

<table>
<thead>
<tr>
<th>Complex(^c)</th>
<th>(^1^H\text{NMR (200 MHz)})</th>
<th>(^{31^P(H)}\text{NMR (81 MHz)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co}_2(\text{CO})_4(u-R)(u-R')(u-dmpe)])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R=R'=\text{CO} (5.10)</td>
<td>u-CHR(^*) 2.01, t, (^2J(\text{PH})10\text{ Hz}) 1.66, t, (^2J(\text{PH})4\text{ Hz})</td>
<td>-CO(_2\text{Et}) -CO(_2\text{Et}) 36.0</td>
</tr>
<tr>
<td>R=R'=\text{CH}_2 (5.11)</td>
<td>u-\text{CH}_2(^*) 4.85, s; 4.05, s; P(_2\text{CH}_2\text{H}_3)^(^2); 1.74, m, (^2J(\text{PH})10\text{ Hz}); (^2J(\text{PH})14\text{ Hz}) 1.15, s(br); 1.35(br) 3.54, t, (^3J(\text{PH})22\text{ Hz}); P(_2\text{CH}_2\text{H}_3)^(^2); 2.54, m, (^2J(\text{PH})10\text{ Hz}); (^2J(\text{PH})14\text{ Hz}) 3.40, s</td>
<td></td>
</tr>
<tr>
<td>R=CO,R'=\text{CHCO}_2\text{Et} (5.12)</td>
<td>u-\text{CH}CO(_2\text{Et})^(^2); 3.90, t, (^2J(\text{PH})12\text{ Hz}) P(_2\text{CH}_2\text{H}_3)^(^2); 2.10, m, (^2J(\text{PH})12\text{ Hz}); (^2J(\text{PH})14\text{ Hz}) 1.15, s(br); 1.35(br) -CO(_2\text{CH}_3). 3.49, m(br) 33 7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(b\) (CO\(_2\))\(_2\text{CO}\), -35°C

\(c\) dmpe = \((\text{CH}_3)_2\text{PCH}_2\text{P(\text{CH}_3)}_2\)
temperature $^1$H NMR studies could not induce the characteristic quartet and triplet anticipated for these CO$_2$CH$_2$CH$_3$ proton resonances respectively.

The chemically inequivalent CH$_2$P$_2$ protons of the dmpm ligand in (5.12) reveal the anticipated AB spectral pattern in Figure 5.4 as an apparent multiplet centered at $\delta$ 2.14. This multiplet results from a superposition of the two sets of the diphosphine’s methylene proton resonances at $\delta$(H) 2.10 [J(PH) 12 Hz, $^2$J(HH) 14 Hz] and $\delta$(H) 2.19 [J(PH) 12 Hz, $^2$J(HH) 14 Hz]. This observation of the AB pattern for the CH$_2$H$_2$P$_2$ protons in (5.12) is consistent with the static structure depicted in Figure 5.4 for (5.12).

5.6 Preparation and Characterization of [Co$_3$(CO)$_4$(μ$_3$-CO$_2$Et)(μ-dmpm)]

In an attempt to produce the mixed bis(μ-alkylidene)dicobalt species [Co$_2$(CO)$_4$(μ-CH$_2$)(μ-CHCO$_2$Et)(μ-dmpm)], the analogue of the dpdm derivative (3.12), complex (5.12) was treated under nitrogen with excess ethereal diazomethane. It was suspected that the introduction of a second μ-alkylidene unit into (5.12) with carbonyl loss might further stabilize the resultant binuclear species. This desired bis(μ-alkylidene) product might provide insight into a comparative study between the alkylidene coupling reaction chemistry of the dmpm derivative [Co$_2$(CO)$_4$(μ-CH$_2$)(μ-CHCO$_2$Et)(μ-dmpm)] (5.12) and its dpdm analogue (3.12).

Reaction of a dichloromethane solution of (5.12) with excess ethereal diazomethane at room temperature converted the initially red coloured solution to a violet colour. Solvent removal produced a purple oil, complex (5.13), which readily decomposes in air to produce
an unidentifiable green species exhibiting no carbonyl stretches in its IR spectrum. The absence of a bridging carbonyl ligand in (5.13), consistent with formation of a bis(μ-alkyldene) system, is confirmed by the absence of absorption around 1800 cm⁻¹ in the IR spectrum [CHCl₃, ν(CO), cm⁻¹: 2050s, 2010s, 1995sh, 1980sh, 1650m]. A ³¹P(¹H) NMR spectrum of (5.13) in dichloromethane-d₂ indicates only a single broad resonance centered at 8 11.9. However, when a well-resolved ¹H NMR spectrum of (5.13) (Figure 5.5) did not reveal any μ-alkyldiene proton resonance; specifically a μ-CH₂ or a μ-CHO₂Et proton resonance with or without a diagnostic triplet possessing the large J(ΦH) value, it was apparent that (5.13) did not contain a μ-alkyldene ligand.

This fact was verified when low temperature ¹H NMR spectroscopy of (5.13) revealed only a finer splitting of the PCH₃ protons, indicating an absence of a coalescence for any μ-CH₂ proton resonance.

Furthermore, no hydride resonances were observed in solution. The ¹H NMR spectrum of (5.13) (Figure 5.5) illustrates the P₂CH₂ protons [δ(¹H) 2.26, δ(¹H) 2.99] are inequivalent with the resultant AB spectral pattern [J(ΦH) 14 Hz, ²J(ΦH) 14 Hz]. All the PCH₃ (δ 1.52, t, J(ΦH) 12 Hz) and COCH₂CH₃ [CH₂: 8 4.28, q; CH₃: 8 1.34, t, J(HH) 8 Hz)] proton resonances are clearly resolved at 20°C in Figure 5.5, yielding an integration of the COCH₂CH₃:COCH₂CH₃:P₂CH₂:PCH₃ proton peaks in the ratio 2:3:2:12.

The identity of (5.13) was confirmed as [Co₃(CO)₇(μ₃-CO₂Et): (μ-dmpm)] [(M⁺) m/z 594] from its fragmentation pattern (Table 5.3) in the mass spectrum (equation 5.6.1). This assignment of (5.13) as the trinuclear cluster [Co₃(CO)₇(μ₃-CO₂Et):(μ-dmpm)] was verified by reacting [(μ₃-CO₂Et)Co₃(CO)₉], prepared by the literature method,¹⁵
Figure 5.5: $^1$H NMR Spectra (200 MHz) of [Co$_3$(CO)$_7$(μ$_3$-CCO$_2$Et)(μ-dmpm)] (5.13) in CO$_2$Cl$_2$/CDCl$_3$. The asterisked peak is impurity. The + sign designates the CHDCl$_2$ impurity.
Table 5.3: Mass Spectral Data for $[\text{Co}_3(\text{CO})_6(\mu_2:\text{CO}_2\text{Et})(\mu: \text{dmpm})]$ (5.13)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>594</td>
<td>P</td>
</tr>
<tr>
<td>566</td>
<td>P-CO</td>
</tr>
<tr>
<td>538</td>
<td>P-2CO</td>
</tr>
<tr>
<td>510</td>
<td>P-3CO</td>
</tr>
<tr>
<td>482</td>
<td>P-4CO</td>
</tr>
<tr>
<td>466</td>
<td>P-4CO-O, P-4CO-CH₄</td>
</tr>
<tr>
<td>454</td>
<td>P-5CO</td>
</tr>
<tr>
<td>438</td>
<td>P-5CO-O, P-5CO-CH₄</td>
</tr>
<tr>
<td>426</td>
<td>P-6CO</td>
</tr>
<tr>
<td>410</td>
<td>P-6CO-O, P-6CO-CH₄</td>
</tr>
<tr>
<td>398</td>
<td>P-7CO</td>
</tr>
<tr>
<td>382</td>
<td>P-7CO-O, P-7CO-CH₄</td>
</tr>
</tbody>
</table>

$P$ = Molecular ion

$m/e(P)$ at 60°C, 70 eV, 100 Hz Filter
with one equivalent of dmpm in benzene at room temperature to afford 
the same spectroscopically characterized cluster (5.13). This product 
(5.13) results from the replacement of two carbonyls by the dmpm ligand 
(equation 5.6.2).

![Diagram]

(5.12)

\[ [\text{CO}_2(\text{CO})_4(\mu_{-}\text{CO})(\mu_{-}\text{CHR})(\mu_{-}\text{dmpm})] \xrightarrow{x_\text{N}_2.\text{CH}_2\text{N}_2} \text{(CO)}_3\text{Co} \xrightarrow{25^\circ\text{C}} \text{(CO)}_2\text{Co} \xrightarrow{\text{Me}_2} \text{(CO)}_2\text{Co} \xrightarrow{\text{Me}_2} \text{(CO)}_2\text{Me}_2 \]

(5.13), \text{R=CO}_2\text{Et}

5.6.1

![Diagram]

(5.13), \text{R=CO}_2\text{Et}

5.6.2

Support for the proposed structure of (5.13) is provided by a more 
recent report\textsuperscript{10} concerning the reaction of \([\text{[\(\mu_3\)-CCH\(_3\)]Co}_3(\text{CO})_6]\) (5.14) 
with dppm to give the cluster \([\text{Co}_2(\text{CO})_7(\mu_3\)-CCH\(_3\)](\mu_{-}\text{dppm})]\) (5.15), as 
shown in equation 5.6.3.
The crystal molecular structure of (5.15) was determined at 
\(-160 ^\circ C\) to possess a dpdm ligand bridging one of the three metal-metal 
edges in the equatorial plane to give a five-membered ring, which 
adopts an envelope conformation. The observation of an absence of a 
bridging carbonyl ligand and the two inequivalent methylene dpdm 
protons in the IR and \(^1H\) NMR spectra of (5.15) respectively are in good 
agreement with the equatorial coordination of the dpdm ligand as 
revealed by the crystal structure.\(^{15}\)

Formation of the trinuclear cobalt cluster (5.13) in equation 
5.6.1 is suspected to arise from an initial deprotonation of the 
\(\alpha\)-hydrogen of the \(\mu\)-alkylidene ligand in \([\text{CO}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHCO}_2\text{Et})\text{(dpdm)}])\) (5.12). The carbene generated from diazomethane with 
dinitrogen loss is speculated to act as a base in deprotonating this 
\(\alpha\)-hydrogen atom in (5.12). A subsequent intermolecular attack of the 
anionic bridgehead carbon atom on unreacted (5.12) or some form of 
decomposition derived from (5.12) is tentatively suggested to account 
for incorporation of the appropriate cobalt carbonyl fragment to 
produce the observed cluster (5.13). Synthetic attempts designed to 
form the more stable dpdm analogue of the trinuclear cobalt cluster 
(5.13) from deprotonation of the \(\alpha\)-hydrogen of the \(\mu\)-alkylidene ligand
in \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHCO}_2\text{Et})(\mu-\text{dppm})]\) (3.9) proved unsuccessful.
Since diazomethane addition to (3.9) produces the bis(\mu-alkylidene) complex (3.12) (equation 3.7.1), excess amounts of powdered sodium hydroxide, powdered potassium hydroxide, or triethylamine proved inert as a source of base to induce formation of the target \([\text{Co}_2(\text{CO})_4(\mu_3-\text{COCO}_2\text{Et})(\mu-\text{dppm})]\) complex from the binuclear precursor (3.9) and \([\text{Co}_2(\text{CO})_6]\) (equation 5.6.4).

\[
[\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHCO}_2\text{Et})(\mu-\text{dppm})] + [\text{Co}_2(\text{CO})_6] + \text{xs. NaOH/KOH/Et}_3\text{N} \rightarrow \text{THF} \rightarrow \text{N.R.}
\] (3.9) 5.6.4

Interest in complexes such as (5.13) or (5.15) stems from the ligating atom's ability to inhibit complete dissociation of the cluster. An obstacle to the development of a mechanistic interpretation as to how clusters function as catalysts is the reversible or complete fragmentation of metal clusters under catalytic conditions. Although the clusters \([((\mu_3-\text{CR})\text{Co}_3(\text{CO})_9)]\) are known for their catalytic activity in hydroformylation and hydrosilylation reactions,\(^{17,18}\) the incorporation of a dppm ligand in (5.14) (equation 5.6.3) increases the rate of the hydroformylation reaction and seems to suppress or completely eliminate cluster fragmentation.\(^{18}\) Both the synthetic approaches described by equations 5.6.1 and 5.6.2 provide a tetrahedral-type chiral cluster in which the asymmetry introduced by the dissymmetric bridging diphosphine dppm is a basic skeletal property of the cluster (5.13).
5.7 Summary of the Chapter

Evidently the stability of \(\mu\)-alkylidene complexes prepared from diazoalkane addition to the novel system \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dmpm})]\) (5.10) is hindered by the higher basicity and smaller steric constraints imposed by the coordinated diphosphine bridge dmpm. By contrast, the identical diazoalkane addition to the analogous dppm system gave stable \(\mu\)-alkylidene complexes. Formation of the bis(\(\mu\)-methylene) complex \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dmpm})]\) (5.11) was confirmed by \(^{1}H\) NMR and the complex was found to undergo a fluxional rearrangement of the methylene protons. This rearrangement was proposed to occur via reversible opening of the methylene bridges as earlier deduced for the bis(\(\mu\)-methylene)dicobalt dppm congener (3.6). An attempt to induce formation of the mixed bis(\(\mu\)-alkylidene)dicobalt complex \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)(\mu-\text{CHO})_2\text{Et}(\mu-\text{dmpm})]\), from the same method employed to produce its dppm congener, resulted in the first example of a cluster incorporating a bridging dmpm ligand, notably \([\text{Co}_3(\text{CO})_7(\mu_3-\text{CO}_2\text{Et})(\mu-\text{dmpm})]\) (5.13).
References


CHAPTER 6
DIIODOMETHANE AND α,ω-DIHALOGENOALKANE
ADDITION TO \([CO_2(CO)_6(\mu-L)]^2^-(L=DPPM, DMPE)\)

6.1 Introduction

The introduction to Chapter Three centered on the original suggestion of Fischer and Tropsch that the polymerization of methylene groups on a transition metal surface may account for the formation of the observed products in the Fischer-Tropsch reaction.\(^1\),\(^2\) Aside from methylene or alkylidene bridged binuclear complexes, there is also considerable interest in alkanediyl bridged binuclear complexes. These binuclear complexes containing polymethylene groups may serve as useful models for intermediates in the Fischer-Tropsch synthesis which involves the growth of methylene chains on a catalyst surface. A possible route to such polymethylene complexes utilizes the difunctionality of α,ω-dihalogenoalkanes.

Section 1.1.1.2 concentrated on the preparation of dinuclear \(\mu\)-alkylidene complexes from methylene dihalides. Although diazoalkanes remain probably the most versatile precursors for the direct synthesis of \(\mu\)-alkylidene complexes,\(^3\) the geminal dihaloalkane route is of growing interest in their reactions with anionic dimetallic species. The present survey will focus on binuclear complexes possessing a polymethylene bridge which were synthesized from the reaction of α,ω-dihalogenoalkanes with the appropriate binuclear transition metal
complex. Recently three comprehensive reviews have appeared\textsuperscript{3-5} dealing with these bridged dinuclear transition metal complexes.

6.1.1 Literature Precedents

There exists an abundance of complexes in which two metal centers are bridged by a hydrocarbyl ligand.\textsuperscript{3-5} (1,n)-Alkanediy1 bridged complexes are known, either with a metal-metal bond (I) or without a metal-metal bond (II), where \( n > 1 \).

\[
\begin{align*}
(I) & \quad \begin{aligned}
\overset{C}{\text{M}} & \quad \overset{n}{\text{M}} \\
\end{aligned} \\
(II) & \quad \begin{aligned}
\overset{C}{\text{M}} & \quad \overset{n}{\text{M}} \\
\end{aligned}
\end{align*}
\]

6.1.1.1 Complexes of Class I

For compounds of type I, few examples are known at present and none with \( n > 4 \) have been reported to date.\textsuperscript{3-5} A very general method for the preparation of polymethylene bridged complexes is the reaction of dimetallic carbonyl anions with \( \sigma, \omega \)-dihalogenoalkanes.

Bergman et al.\textsuperscript{6,7} succeeded in synthesizing compounds of type I from reaction of the radical anion \( [\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2]^+ \) with (1,n)-dihaloalkanes \( (n=3,4) \) as shown by equation 6.1.1. Treatment of the dinuclear radical anion \( [\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2]^+ \) with 1,2-diiodoethane did not result in the formation of the expected four-membered dimetallacycle since the target complex was suspected to readily decompose to ethylene and unsaturated cobalt fragments.
\[ \text{Na}[\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2]^+ + I(\text{CH}_2)_nI \rightarrow [\text{Cp}(\text{CO})_2\text{Co}(\mu-(\text{CH}_2)_n)\text{Co}(\text{CO})\text{Cp}] \]
\[ (n=3, 4) \]

6.1.1

The first benzodimetallacycloclohexane, a six-membered metallacycle containing two metals in the ring, was reported from alkylation of \([\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2]^+\) with \(\alpha,\alpha'\)-dibromo-\(\alpha\)-xylene (equation 6.1.2).

\[ \text{Na}[\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2]^+ + \alpha\text{-C}_6\text{H}_4(\text{CH}_2\text{Br})_2 \rightarrow \text{analogous structure} \]

6.1.2

At room temperature in benzene, this benzodimetallacycloclohexane decomposes to \([\text{CpCo}(\text{CO})_2]_2\) (1.16b) and a novel mononuclear complex \([\text{CpCo}(\alpha\text{-xylene})]\) by a process proposed to involve an initial reversible binuclear elimination with the formation of \(\alpha\)-xylene and \([\text{Cp}_2\text{Co}_2(\mu-\text{CO})_2]^+\).

Anderson and coworkers reported the first 1,2-dimetallacyclobutane along with other metal-metal bonded \(\mu\)-alkanediyl complexes (equation 6.1.3).

\[ \text{Na}_2[\text{Os}_2(\text{CO})_6] + X(\text{CH}_2)_nX \rightarrow [(\text{CO})_4\text{Os}(\mu-(\text{CH}_2)_n)\text{Os}(\text{CO})_4] \]
\[ X=I, OTs \]
\[ n=2, 3 \]

6.1.3

Thermal and photochemical decomposition of complexes such as \([\text{Cp}(\text{CO})_2\text{Fe}(\mu-(\text{CH}_2)_n)\text{Fe}(\text{CO})_2\text{Cp}] (n=3, 5)\) are believed to proceed via
transient dimetallacycles \([\text{Cp}(\text{CO})\text{Fe}(\mu-(\text{CH}_2)_n)(\mu-\text{CO})\text{Fe}(\text{CO})\text{Cp}]\) containing a metal-metal single bond.\(^{10}\)

6.1.1.2 Complexes of Class II

Typical members of class II have been reported for 2<n<12 but there is no reason to assume that the chain length has an upper limit.\(^{3}\)

An early prediction\(^{11}\) claimed that the ethylene bridge (n=2) was inherently unstable. However, Sinn et al.,\(^{12}\) in contrast to this view, produced a series of \(\mu-(\text{C}_2\text{H}_4)\) organometals, e.g. \((\mu-\text{C}_2\text{H}_4)\) \([\text{Cp}_2\text{Zr} \cdot \text{Cl} \cdot \text{AlEt}_3]\) (6.1). The complex (6.1) was determined to possess a carbon-carbon bond distance in the \(\mu-(\text{C}_2\text{H}_4)\) group of 15.5 pm, typical of a single bond, but with no metal-metal bond present. By comparison, Beck\(^{13}\) reports that the rhenium compound \([(\text{CO})_5\text{Re}(\mu-(\text{C}_2\text{H}_4))\text{Re}(\text{CO})_5]\) reveals a shorter carbon-carbon distance in the ethylene bridge. These complexes were envisioned to be more ethane-derived organometals rather than ethylene-bridged systems. An interesting feature of Beck's work was the synthetic route involving a nucleophilic attack of metal carbonyl anions on coordinated ethylene in cationic complexes (equation 6.1.4).

\[
[\text{Cp}M(\text{CO})_3(\pi-\text{C}_2\text{H}_4)]^+ + [\text{Re}(\text{CO})_5]^- \rightarrow [\text{Cp}(\text{CO})_3\text{M}(\mu-(\text{CH}_2)_x)\text{Re}(\text{CO})_5]
\]

\(M=\text{W, Mo}\)

6.1.4

The first type II alkanediyl bridged compounds prepared were the binuclear iron compounds \([\text{Cp}(\text{CO})_2\text{Fe}(\mu-(\text{CH}_2)_n)\text{Fe}(\text{CO})_2\text{Cp}]\) (n=3-6).\(^{14}\) An
extension of these \(\mu(1,n)\)-alkanediyl binuclear iron complexes (\(n=7-12\))
was recently performed\(^5\) by essentially the same method as that
reported for the earlier members of the series (equation 6.1.5).

\[
2\text{Na}[\text{CpFe(CO)}_2] + \text{Br(CH}_2)_n\text{Br} \xrightarrow{\text{THF}} \text{[Cp(CO)}_2\text{Fe(\mu-(CH}_2)_n\text{Fe(CO)}_2\text{Cp}]}
\]

\(n=3-12\)

6.1.5

Different products from those in equation 6.1.5 were isolated for this
same reaction with the anion \([\text{Mn(CO)}_5]^-\).

The dimeric ruthenium complexes \([\text{Cp(CO)}_2\text{Ru(\mu-(CH}_2)_n\text{Ru(CO)}_2\text{Cp}]\)
\((n=2,4)\) have been prepared\(^6\) according to equation 6.1.6.

\[
\text{Na[CpRu(CO)}_2] + X(CH}_2)_nX \xrightarrow{} \text{[Cp(CO)}_2\text{Ru(\mu-(CH}_2)_n\text{Ru(CO)}_2\text{Cp}]}
\]

\(X=\text{Cl}; n=2\)

\(X=\text{Br, I}; n=3,4\)

6.1.6

In order to synthesize mixed \(\mu\)-alkanediyl complexes, Moss\(^7\) has
employed the strategy of reacting a haloalkyl complex of one metal with
the anionic carbonyl complex of another (equation 6.1.7).

\[
[\text{CpFe(CO)}_2((\text{CH}_2)_3\text{Br})] + [\text{CpMo(CO)}_3]^- \rightarrow [\text{Cp(CO)}_2\text{Fe(\mu-(CH}_2)_3\text{Mo(CO)}_3\text{Cp}]}
\]

6.1.7

This same general method has also produced the heteronuclear
dimeric \([\text{Cp(CO)}_2\text{Fe(\mu-(CH}_2)_3\text{Ru(CO)}_2\text{Cp}]\) complex\(^8\) (equation 6.1.8)
Winter's group has recently published a series of papers on the reactions of iron, tungsten and molybdenum complexes with $X(CH_2)_3X$ ($X=\text{Br}, \text{I}$). Both halomethyl and $\mu$-alkanediyl products were isolated.

The most recent documented compounds of type II, exhibiting no metal-metal bond, include $[(\text{phen})I(\text{Me})_2\text{Pt}(\mu-(CH_2)_n)\text{Pt}(\text{Me})_2I(\text{phen})]$ (phen=1,10-phenanthroline; $n=2\cdot5$), $((\text{bipy})I(\text{Me})_2\text{Pt}(\mu-(CH_2)_n)\text{Pt}(\text{Me})_2I(\text{bipy}))$ (bipy=2,2'-bipyridine; $n=3\cdot5$) and $[\text{Me}_2\text{Pt}(\mu-\text{bipy})I(\text{Me})_2\text{Pt}(\mu-(CH_2)_3)\text{Pt}(\text{Me})_2I(\mu-\text{bipy})\text{PtMe}_2]$. 

Collman has studied a series of alkyl halides with respect to their reactivity with a macrocyclic rhodium (I) complex (equation 6.1.9). The only product resulting from equation with $\text{Br}(CH_2)_n\text{Br}$ ($n=2\cdot4\cdot6$) addition was the binuclear rhodium (III) complex. It is thought that the reaction goes via a bromoalkyl intermediate and that the second oxidative addition is much faster than the first due to a neighbouring group effect.

$$\text{Rh}^I + \text{Br}(CH_2)_n\text{Br} \rightarrow \text{Br-Rh}^\text{III}-(CH_2)_n\text{-Rh}^\text{III}-\text{Br}$$

$$\text{Rh}^I = \begin{array}{c}
\begin{array}{c}
N \\
\text{R}
\end{array} \\
\begin{array}{c}
N \\
\text{Y}
\end{array} \\
\begin{array}{c}
\text{R} \\
\text{Y}
\end{array}
\end{array}$$

$R=\text{Et}, Y=\text{BF}_2$
6.1.2 Scope of the Chapter

It was the intent of this work, by analogy to the preceding literature, to investigate the preparation of the methylene-bridged complexes $[\text{Co}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dppm})]$ (3.5) and its dmpm analogue $[\text{Co}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dmpm})]$ from reaction of the respective anionic dimetallic species $[\text{Co}_2(\text{CO})_6(\mu-\text{L})]^2-$ ($\text{L}=\text{dppm}, \text{dmpm}$) with diiodomethane. In addition, the reaction of various $\alpha,\omega$-diiodoalkanes was also observed with these same anionic dicobalt precursors in an effort to obtain dicobaltacycles of differing ring sizes. In this study, however, no dicobaltacycles were isolated.

6.2 Reduction of $[\text{Co}_2(\text{CO})_6(\mu-\text{CO})_2(\mu-\text{L})].(L=\text{dmpm}(5.10), \text{dppm}(3.4))$

The reduction of transition metal carbonyl complexes provides access to a number of interesting anionic organometallic species. Monoanions have proven convenient synthetic routes in the preparation of compounds with metal-metal and metal-carbon bonds (equation 6.2.1).

\[
\begin{align*}
\text{Na} \cdot \text{Hg} & \quad \xrightarrow{\text{Na} \cdot \text{Hg}} \quad \text{Fe(\text{CO})}_5 \\
[\text{Co}_2(\text{CO})_6] & \quad \xrightarrow{\text{Na} \cdot \text{Hg}} \quad 2[\text{Co}(\text{CO})_4]^- \quad \text{eqn} \text{ 6.2.1} \\
& \quad \xrightarrow{42e^-} \quad \text{Fe(\text{CO})}_5 \\
& \quad \xrightarrow{\text{R} \cdot \text{X}} \quad [\text{R} \cdot \text{Co}(\text{CO})_4] 
\end{align*}
\]

The conventional method for the preparation of monometal carbonyl anions employs sodium-mercury amalgam to reductively cleave the corresponding metal-metal dimers. This method is handicapped by the necessity to remove relatively large quantities of mercury from the system. Furthermore, contamination of the metal carbonylate product...
through the formation of mercury derivatives is possible. For example, the reduction of $[\text{Co}_2(\text{CO})_6]$ with sodium amalgam gives $\text{Na}[\text{Co}(\text{CO})_4]$, but the reaction does not always go to completion and the product is contaminated with $\text{Hg}[\text{Co}(\text{CO})_4]$.

The reaction between sodium amalgam and $[\text{Co}_2(\text{CO})_6(\mu-\text{CO})_2(\mu-\text{dpmm})]$ (3.4) was conducted in THF at room temperature under air- and water-free conditions to afford $\text{Na}_2[\text{Co}_2(\text{CO})_6(\mu-\text{dpmm})]$ over a 12 hour period (equation 6.2.2).

\[
2\text{Na} + [\text{Co}_2(\text{CO})_6(\mu-\text{CO})_2(\mu-\text{dpmm})] \xrightarrow{25^\circ \text{C, THF}} 2\text{Na}^+ + [\text{Co}_2(\text{CO})_6(\mu-\text{dpmm})]^2^-
\]

Formation of the reduced product $[\text{Co}_2(\text{CO})_6(\mu-\text{dpmm})]^2^-$ in equation 6.2.2 was monitored via an absence of the IR carbonyl stretching frequencies for (3.4) and replacement by a new absorption at 1910 cm$^{-1}$. This strong, broad absorption at 1910 cm$^{-1}$ indicates a product with only terminal carbonyl ligands in solution. A similar behaviour of only a single carbonyl absorption was also observed in solution from a detailed IR spectral analysis for the sodium salts of $[\text{Cp}_2\text{Co}_2(\text{CO})_2]^2^-$ [1890 cm$^{-1}$]$^{2^5}$ and $[\text{Co}(\text{CO})_4]^-$ [1887 cm$^{-1}$]$^{2^6}$.

An alternative route to producing the same dianionic complex $[\text{Co}_2(\text{CO})_6(\mu-\text{dpmm})]^2^-$ was achieved by utilizing the method of Edgell and Lyford$^{2^7}$ for the preparation of $\text{M}[\text{Co}(\text{CO})_4]$ ($\text{M}=\text{Li, Na, K}$) from $[\text{Co}_2(\text{CO})_6]$. This synthetic route required the stirring of a dried THF
solution of \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})] \) (3.4) with powdered sodium hydroxide or potassium hydroxide to generate \(\text{Na}_2[\text{Co}_2(\text{CO})_6(\mu-\text{dppm})] \) or \(\text{K}_2[\text{Co}_2(\text{CO})_6(\mu-\text{dppm})] \) respectively. However, although the reduction occurred more readily employing these alkali metal hydroxides as opposed to sodium amalgam, the intensity of the resultant brown solutions containing the soluble anionic product \([\text{Co}_2(\text{CO})_6(\mu-\text{dppm})]^2^- \) was considerably lower, indicating a lower yield of the dianion.

The reduction of the dmpm congenor \([\text{Co}_2(\text{CO})_6(\mu-\text{CO})_2(\mu-\text{dmpm})] \) (5.10) to yield \([\text{Co}_2(\text{CO})_6(\mu-\text{dmpm})]^2^- \) \(\nu(\text{CO})=1830 \text{ cm}^{-1} \) paralleled those results described for the preparation of \([\text{Co}_2(\text{CO})_6(\mu-\text{dppm})]^2^- \). A higher basicity of the dmpm ligand with respect to dppm is reflected by the comparative IR spectral data for the dianionic dicobalt complexes.

The subsequent sections describe the observations obtained from the reaction of each dianionic dicobalt derivative \([\text{Co}_2(\text{CO})_6(\mu-\text{L})]^2^- \) \((\text{L}=\text{dmpm}, \text{dppm}) \) with some or all of the diiodoalkanes \(\text{I}(\text{CH}_2)_n\text{I} \) \((n=1,3-5) \). The anionic material used throughout the following experiments was the crude, filtered THF solution from the reduction of \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{L})] \) \((\text{L}=\text{dmpm}(5.10), \text{dmpm}(3.4)) \). It should be noted that both the sodium and potassium salts of \([\text{Co}_2(\text{CO})_6(\mu-\text{L})]^2^- \) \((\text{L}=\text{dmpm}, \text{dppm}) \) produced identical reaction products when exposed to the same diiodoalkane reagent.

6.3 Reaction of \(\text{Na}_2[\text{Co}_2(\text{CO})_6(\mu-\text{dmpm})] \) with \(\text{I}(\text{CH}_2)_n\text{I} \), \(n=1,3 \)

By an adaptation of the literature methods outlined in sections 1.1.1.2 and 6.1.1, diiodomethane was added in excess to a filtered THF solution of \(\text{Na}_2[\text{Co}_2(\text{CO})_6(\mu-\text{dmpm})] \) at room temperature in a dry box. Although no immediate colour change occurred from the initial dark red
solution of the dianion, the strong, broad IR carbonyl stretching frequency $\nu(\text{CO})=1830 \text{ cm}^{-1}$ of the dianion was replaced by new absorptions exhibiting both terminal and bridging carbonyl peaks after 60 minutes. Column chromatography on Florisil under nitrogen yielded the first fraction, $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dmpm})]$ (5.10), and a second crimson red fraction of a new material (6.2) in a very small yield. An IR spectroscopic characterization of (6.2) revealed no carbonyl stretching frequencies exist in solution for this material. On solvent removal, the red oil obtained for (6.2) readily decomposed on exposure to air to form unidentified green oxidation products.

Literature precedents might predict this reaction should yield the $\mu$-methylene complex $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dmpm})]$ as one reaction product. However, the absence of carbonyl peaks in the IR spectrum of (6.2) verifies this species is not present in solution. Most surprising was the $^1$H NMR spectrum for this new material (6.2). Two broad singlets with no observable phosphorus couplings were observed in dichloromethane-$d_2$ at $8$ 4.34 and $8$ 2.14 in a 1:6 integrated ratio. These proton resonances were subsequently identified as the $\text{CH}_2\text{P}_2$ (8 4.34) and $\text{PCH}_3$ (8 2.14) protons of the diphosphine ligand in (6.2). The red material (6.2) was identified by its mass spectral fragmentation pattern (Table 6.1) as $[\text{Co}_2\text{I}_4(\mu-\text{dmpm})_2]$ [M$^+$:m/e 898]. An accurate mass measurement verified this assignment as $[\text{Co}_2\text{I}_4(\mu-\text{dmpm})_2]$ (HRMS calc. for $C_{10}H_{20}O_2\text{Co}_2\text{I}_4\text{P}_4$:m/e 897.5984. Found:m/e 897.6020.)

This assignment of (6.2) as $[\text{Co}_2\text{I}_4(\mu-\text{dmpm})_2]$ accounts for the observed $^1$H NMR data, which indicated that the $\text{CH}_2$ group of diiododimethane was absent in the final reaction product (6.2). Further confirmation of this result was obtained when the dianion $\text{Na}_2[\text{Co}_2(\text{CO})_6]$
<table>
<thead>
<tr>
<th>m/e</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>898</td>
<td>P</td>
</tr>
<tr>
<td>771</td>
<td>P - I</td>
</tr>
<tr>
<td>761</td>
<td>P - dmpm</td>
</tr>
<tr>
<td>635</td>
<td>P - I - dmpm</td>
</tr>
<tr>
<td>508</td>
<td>P - 2I - dmpm</td>
</tr>
<tr>
<td>498</td>
<td>P - I - 2(dmpm)</td>
</tr>
<tr>
<td>458</td>
<td>P - Co - 3I</td>
</tr>
<tr>
<td>322</td>
<td>P - Co - 3I - dmpm</td>
</tr>
</tbody>
</table>

P = Molecular ion

m/e(P) at 130°C, 70 eV, 100 Hz Filter

High-resolution MS calc. for \( \text{C}_{10}\text{H}_{26}\text{Co}_4\text{I}_4\text{P}_4 \): m/e 897.5984.

Found: m/e 897.6020.
(\(\mu\)-dmpm)) was exposed to excess 1,3-diiodopropane in THF under similar reaction conditions. The same red complex \([\text{Co}_2\text{I}_4(\mu\text{-dmpm})_2]\) (6.2) was formed, again in small yield, instead of the target dimetallacyclopentane complex \([\text{Co}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-}(\text{CH}_2)_3)(\mu\text{-dmpm})]\). The expected paramagnetic character of the Co(II) atoms in (6.2) is considered responsible for the poorly resolved \(^1\text{H}\) NMR spectral data recorded for this same species.

\[
\begin{align*}
2\text{Na} + [\text{Co}_2(\text{CO})_6(\mu\text{-CO})_2(\mu\text{-dmpm})] & \quad \xrightarrow{25^\circ\text{C}} \xrightarrow{\text{THF}} \quad 2\text{Na}^+ + [\text{Co}_2(\text{CO})_6(\mu\text{-dmpm})]^2^- \\
(5.10) & & 6.3.1
\end{align*}
\]

\[
\begin{align*}
[\text{Co}_2(\text{CO})_6(\mu\text{-dmpm})]^2^- + \text{I}(\text{CH}_2)_n\text{I} & \quad \xrightarrow{25^\circ\text{C}} \xrightarrow{\text{THF}} \quad (5.10) + \\
& \quad \text{n}=1,3 \\
(6.2) & & 6.3.2
\end{align*}
\]

Although a single crystal X-ray structure was not obtained for (6.2), formation of the tentative cobalt-cobalt single bond in (6.2) shown in equation 6.3.2 may result due to the presence of the two trans bridging diphosphine ligands holding the two cobalt atoms in close proximity. An alternative structure for (6.2), containing no metal-metal bond, might require a pseudo-tetrahedral arrangement of the ligands about each cobalt center as reported\(^2\) for the paramagnetic \([\text{Co(dppm)}X_2]\) (X=Cl, Br, I) complexes in solution.
6.4 Reaction of Na₂[Co₂(CO)₆(μ-dppm)] with I(CH₂)ₙI, n=1,3-5, or RI, R=Me,Et

Whereas addition of diiodomethane to a THF solution of the dianion [Co₂(CO)₆(μ-dppm)]²⁻ might be expected to yield the dimetallacyclopropane complex [Co₂(CO)₄(μ-CO)(μ-CH₂)(μ-dppm)] (3.5), the reaction products reveal, as observed for the dmpm congener in section 6.3, that this is not the case (equation 6.4.1). The characteristic IR carbonyl stretching frequency of the dianion [ν(CO)=1910 cm⁻¹] was replaced after 30 minutes by new absorptions indicative of both terminal and bridging carbonyl frequencies. A column chromatograph under nitrogen of this reaction mixture on Florisil produced a dark brown band, subsequently identified as the oxidized product [Co₂(CO)₄(μ-CO)₂(μ-dppm)] (3.4). A second band, crimson red in colour, provided an air-stable red oil, complex (6.3), on solvent removal, exhibiting carbonyl stretches at 1970(s) and 1820(w) cm⁻¹ in dichloromethane. This IR data shows that (6.3) is not the dppm congener of (6.2), [Co₂I₄(μ-dmpm)₂].

Complex (6.3) displays a very sharp ³¹P(¹H) NMR singlet at 8 9.9 in dichloromethane-d₂. It was apparent from the ¹H NMR spectrum of (6.3) that this product had not incorporated the organic methylene moiety, a phenomenon earlier described from the reaction of diiodomethane with [Co₂(CO)₆(μ-dmpm)]²⁻ in section 6.3. Confirmation of this
observation was provided from reaction of $[\text{Co}_2(\text{CO})_6(\mu-\text{dppm})]^2-$ with $\text{I}(\text{CH}_2)_n\text{I}$ ($n=3$-5) which produced these same products (3.4), (6.3) and an unidentified complex (6.4) in low yield in approximately the same yields (equation 6.4.1). No evidence for any dimetallacycle was detected in any case. Furthermore, both iodomethane and iodoethane react with the dianion $[\text{Co}_2(\text{CO})_6(\mu-\text{dppm})]^2-$ in a similar manner to generate these three identical products (equation 6.4.2).

The methylene protons of the diphosphine ligand in complex (6.3) exhibit a $^1$H NMR resonance at 8.4.28 as an apparent symmetrical 1:4:6:4:1 quintet [$J(\text{PH}) 4$ Hz], reminiscent of the virtual coupling phenomenon observed for complexes involving trans phosphine units (e.g., $[\text{Pd}_2\text{X}_4-n(\mu-\text{dppm})_2]^n$; $n=0,1$, $\text{X}=$Cl,Br,I). As a result, the methylene protons CH$_2$P$_2$ appear to be coupled to four equivalent nuclei. These NMR parameters suggest that complex (6.3) has a symmetrically bridged, dimeric structure with trans dppm ligands. An elemental analysis supports the molecular formula of (6.3) as $C_{52}H_{44}O_{14}I_2P_4$. The cumulative chemical data for (6.3) suggests its formulation as trans-$[\text{Co}_2\text{I}_2(\text{CO})_2(\mu-\text{CO})_2(\mu-\text{dppm})_2]$, containing no metal-metal bond.

![Diagram of complex (6.3)](image)
The identity of complex (6.4) is unknown. When repetitive attempts to produce complex (6.3) from excess diiodomethane addition to [Co₂(CO)₆(μ-dppm)]²⁻ also generated NMR data consistent with complex (6.4); previously observed from similar reactions with excess α,ω-diiodoalkane (equation 6.4.1) or excess iodoalkane (equation 6.4.2), it was evident that complex (6.4) had not incorporated any organic group. The red oil containing the mixture of (6.3) and (6.4) exhibited the same dichloromethane IR spectrum observed for the pure compound (6.3). Complex (6.4) also displays a sharp phosphorus resonance at δ 31.5. A triplet [δ 4.48, 2J(3H) 13 Hz] due to coupling of the methylene protons to two equivalent phosphorus atoms is observed for the CH₂P₂ protons in the ¹H NMR spectrum of (6.4). The failure to isolate (6.4) from (6.3) prevents a definitive assignment for (6.4); although these NMR parameters suggest a symmetrical molecule incorporating only one μ-dppm ligand. A suitable solvent mixture was not found to separate the two complexes (6.3) and (6.4) in the oily, red mixture via preparative TLC.

\[ [\text{Co}_2(\text{CO})_6(\mu-\text{dppm})]^2^- + \text{I}(\text{CH}_2)_n\text{I} \quad \begin{array}{c} \text{THF} \end{array} \quad \begin{array}{c} \text{25°C} \end{array} \quad [\text{Co}_2(\text{CO})_6(\mu-\text{CO})_2(\mu-\text{dppm})] \quad \begin{array}{c} \text{n=1,3-5} \end{array} \]

\[ + \text{trans-}[\text{Co}_2\text{I}_2(\text{CO})_2(\mu-\text{CO})_2(\mu-\text{dppm})_2] \]

\[ \text{eq} (6.3) \quad 6.2.1 \]

\[ [\text{Co}_2(\text{CO})_6(\mu-\text{dppm})]^2^- + \text{RI} \quad \begin{array}{c} \text{THF} \end{array} \quad \begin{array}{c} \text{25°C} \end{array} \quad (3.4) + (6.3) + (6.4) \quad \begin{array}{c} \text{R=Me,Et} \end{array} \]

\[ 6.4.2 \]
6.5 Discussion

When no reaction was observed from addition of any of the diiodoalkane reagents to the neutral dimer $[\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})]$ (3.4) under these same or photolysis (Xe lamp, pyrex filter) reaction conditions, it became evident that the products observed in equations 6.3.2, 6.4.1 and 6.4.2 are dependent on their respective dianion species. This criterion, coupled with the absence of the diiodoalkane organic entity in the reaction products, suggests that these products may derive from an initial electron transfer from the respective dianionic binuclear complex to the diiodoalkane in an outer sphere mechanism, followed by abstraction of the anionic halogen.\textsuperscript{30} Reduction of alkyl halides is known to occur by a dissociative electron capture, proceeding by successive one-equivalent changes (equation 6.5.1). Equation 6.5.2 describes radical formation by subsequent fragmentation of the radical anion.

$$\begin{align*}
\text{L}_n\text{M} + \text{RX} & \rightarrow [\text{L}_n\text{M}]^+[(\text{RX})^-] \\
[\text{L}_n\text{M}]^+ + \text{R}^- & \rightarrow \text{R} + \text{X}^-
\end{align*}$$

6.5.1

6.5.2

If an electron transfer pathway exists en route to the assigned $[\text{Co}_2\text{I}_4(\mu-\text{dppm})]$ (6.2) and trans-$[\text{Co}_2\text{I}_2(\text{CO})_2(\mu-\text{CO})_2(\mu-\text{dppm})]$ (6.3) products from equation 6.3.2, 6.4.1 and 6.4.2 respectively, one tentative pathway may proceed via the following scheme ($\text{M} = \text{Co(CO)}_3$); this proposal is speculative.
In addition, the mechanistic scheme must also incorporate some form of fragmentation to lead to the observed bis(μ-diphosphine) complexes (6.2) and (6.3); both these complexes contain trans diphosphine ligands. Formation of these final bis(μ-diphosphine) products (6.2) and (6.3) is suspected to arise from decomposition of an earlier diphosphine product. Consequently, the maximum yield of each species is expected to be 50% per mole of the respective dianionic dicobalt carbonyl complex. However, competition between production of (6.3) and (6.4) in equation 6.4.1 will further reduce the maximum yield of the bis(μ-dppm) complex (6.3). A decomposition pathway could
account for the low yields observed from equations 6.3.2, 6.4.1 and 6.4.2, and the considerable extent of insoluble decomposition matter visible in each case.

6.6 Summary of the Chapter

These results show that treatment of the dianionic species \([\text{Co}_2(\text{CO})_8(\mu \cdot \text{L})]^2^- (\text{L}=\text{dpm}, \text{dppm})\) with iodoalkanes \(\text{I}(\text{CH}_2)_n\text{I}\) \((n=1, 3, 5, \text{L}=\text{dpm}; n=1, 3, 5, \text{L}=\text{dppm})\) does not yield dicobaltacycles. When \(\text{L}=\text{dpm},\) the dinuclear complex \([\text{Co}_2\text{I}_4(\mu \cdot \text{dpm})_2]\) \((6.2)\) was formed in each case along with the oxidized complex \([\text{Co}_2(\text{CO})_4(\mu \cdot \text{CO})_2(\mu \cdot \text{dpm})]\) \((5.10)\). However, when \(\text{L}=\text{dppm},\) \([\text{Co}_2(\text{CO})_4(\mu \cdot \text{CO})_2(\mu \cdot \text{dppm})]\) \((3.4)\) is produced along with a complex tentatively identified as the novel \(\text{trans-}[\text{Co}_2\text{I}_4(\text{CO})_2(\mu \cdot \text{CO})_2(\mu \cdot \text{dppm})_2]\) \((6.3)\), containing no metal-metal bond, and an unidentified product \((6.4)\), suspected to contain only one dppm ligand. These same dppm products were obtained from treatment of \([\text{Co}_2(\text{CO})_8(\mu \cdot \text{dppm})]^2^-\) with iodoalkanes \(\text{RI}(\text{R}=\text{Me, Et})\).

The two symmetrical dimers \((6.2)\) and \((6.3)\), possessing trans diphosphine ligands, may arise from an initial electron transfer from the dianionic, dinuclear precursor complex to the iodoalkane reagent followed by halogen abstraction from more iodoalkane.
References


GLOBAL SUMMARY

The objective of this research was to synthesize novel \( \mu \)-alkylidene complexes of dimanganese and dicobalt, and to study the chemical properties of such complexes. This work also involved characterizing reaction products and examining their reactivity. Interest concerning the structural and chemical properties of \( \mu \)-alkylidene complexes is directed towards their potential as models for proposed intermediates in the Fischer-Tropsch synthesis.

Diazoalkane addition to \([\text{Mn}_2(\text{CO})_5(\mu\text{-dppm})_2]\) forms a unique metallacyclic unit via coupling of \( \text{N}_2\text{CHR}(\text{R}=\text{H, Me, CO}_2\text{Et}) \) with a carbonyl ligand. By contrast, diazoalkane addition to \([\text{Co}_2(\text{CO})_8(\mu\text{-dppm})]\) under identical reaction conditions provides \( \mu \)-alkylidene dicobalt complexes.

Since dimetallacyclopropanes are of special interest for the mechanistic explanation of the Fischer-Tropsch synthesis, reactivity studies were concentrated on reactions of the \( \mu \)-alkylidene dicobalt complexes with hydrogen, carbon monoxide, sulfur dioxide and unsaturated hydrocarbons. The results of these experiments suggest alkylidene-bridged species may be significant in certain catalytic reactions.

The carbon-carbon coupling reactions of \( \text{CO}_2(\mu\text{-CH}_3)_2 \) groups on pyrolysis of \([\text{Co}_2(\text{CO})_4(\mu\text{-CH}_2)_2(\mu\text{-dppm})]\) to give \( \text{C}_2\text{H}_6 \), or \( \text{C}_2\text{H}_8 \) in the presence of hydrogen, serve as models for hydrocarbon formation on transition metal catalysts by the Fischer-Tropsch synthesis.

The observed interaction of an alkylidene dicobalt bridge with a terminal carbonyl ligand to give a ketene derivative may model the reactions which lead to oxygen-containing products in the
Fischer-Tropsch synthesis. This alkylidene-carbonyl coupling reaction is not limited to μ-CH₂ groups but also occurs in high yield for μ-CHMe and μ-CHO₂Et groups. Thus, when oxygenated products are formed, the coupling of a μ-CHR and CO groups is a reasonable step during catalysis by cobalt catalysts of the Fischer-Tropsch synthesis. Under the conditions studied, the carbon-carbon coupling of two μ-alkylidene groups to yield alkenes is not competitive with the alkylidene-carbonyl coupling in this dicobalt system.

This work illustrates how the development of simple molecules to mimic two-fold sites on a transition metal surface can provide insight into the mechanisms of homogeneous and heterogeneous catalysis. The design of homogeneous catalysts for the Fischer-Tropsch synthesis is a longer term objective. This work shows how carbon-carbon bond formation may occur, but the reduction of carbon monoxide by hydrogen must await the development of more reactive complexes.
CHAPTER 7
EXPERIMENTAL

7.1 General

7.1.1 NMR spectroscopy

\(^1\text{H} \) NMR spectra were recorded using a Varian T-60, a Varian XL-100, a Varian XL-200, or a Bruker WH-400 NMR spectrometer. \(^{13}\text{C} (\text{\textsuperscript{1}\text{H}}) \) NMR spectra were recorded using a Varian XL-200 NMR spectrometer at 50.3 MHz, or a Bruker WH-400 NMR spectrometer operating at 100.6 MHz. \(^{31}\text{P} (\text{\textsuperscript{1}\text{H}}) \) NMR spectra were recorded using a Varian XL-100, a Varian XL-200 or a Varian XL-300 NMR spectrometer.

Both the \(^1\text{H} \) and \(^{13}\text{C} (\text{\textsuperscript{1}\text{H}}) \) NMR spectroscopic chemical shifts are reported relative to tetramethylsilane, Me\(_4\)Si. The \(^{31}\text{P} (\text{\textsuperscript{1}\text{H}}) \) NMR spectroscopic reference was trimethyl phosphate, (MeO)\(_3\)PO.

7.1.2 Infrared Spectroscopy

Infrared spectra of solid samples were recorded on a Beckman 4250 infrared spectrometer as Nujol mulls with NaCl or CsI plates. Similarly, the same Beckman 4250 infrared spectrometer recorded all solution infrared spectra using NaCl solution cells.

7.1.3 Mass Spectrometry

Mass spectra were obtained using a Varian MAT 311A instrument.
7.1.4 Elemental Analysis

All elemental analyses were performed by the Guelph Chemical Laboratories, Guelph, Ontario, Canada.

7.1.5 Gas Chromatography

Gaseous and liquid samples were examined using a Varian 1400 instrument equipped with a porapak Q 80/100 and a 10% SE-30 on 68/80 diatoport columns (6'x1/8''). respectively. The flow rate was about 30 mL/min. Usually the column temperature was maintained at 55°C for liquid samples and at 25°C for gaseous samples.

7.1.6 Sources of Chemicals

Solvents were obtained from Aldrich, Baker or Fischer and were used without purification except when the experiment required oxygen and moisture-free conditions. In order to remove oxygen and moisture, solvents were refluxed over finely divided Na(Benzene), CaH₂(THF) or Mg turnings(alkohols) for one hour prior to distillation, always maintaining an N₂ atmosphere throughout each operation. All deuterated solvents were obtained from MSD Isotopes.

Chemicals were supplied by Aldrich, BDH or Fisher. Only the ligand dmpm was obtained from Strom Chemicals Inc., and was used without further purification. Carbon monoxide, ethylene, hexafluoro-2-butyne (HFB) and sulfur dioxide were all secured from Linde. All ¹³C-labelled reagents, specifically ¹³C-Diazaald and ¹³CO, were supplied by MSD Isotopes.
7.1.7 Preparation of Diazocompounds

7.1.7.1 Diazomethane (\( \text{CH}_2\text{N}_2 \))

The reaction of Diazald (\( N\)-methyl-\( N\)-nitroso-\( p\)-toluenesulfonamide) with base (equation 7.1.1) was used to generate diazomethane.\(^1\)

\( ^{13}\text{C}\)-Diazald, 90%, was mixed with Diazald to generate \( ^{13}\text{C}\)-labelled diazomethane (~9%) in the same manner. An estimation of the diazomethane content of the undried ethereal solution was determined by the titration technique of Marshall and Acree.\(^2\)

\[
\begin{align*}
\text{p-CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{N(NO)}\text{CH}_3 + \text{KOH} & \xrightarrow{\text{EtOH}} \text{CH}_2\text{N}_2 \\
\text{Et}_2\text{O} & \xrightarrow{\text{EtOH}} \text{CH}_2\text{N}_2
\end{align*}
\]

7.1.7.2 Diazomethane-\( d_2 \) (\( \text{CD}_2\text{N}_2 \))

2-(2-Ethoxyethoxy)ethanol (10 g) and anhydrous ether (10 mL) were added to a solution of 30% sodium deuteroxide in \( \text{D}_2\text{O} \) (10 g). A solution of Diazald in anhydrous ether (2.5 g in 25 mL) was added dropwise to this \( \text{D}_2\text{O} \) mixture as described by de Boer and Bucker\(^1\) for the preparation of diazomethane (equation 7.1.1). The ethereal distillate contained about 12 \( \text{mmol} \) of \( \text{CD}_2\text{N}_2 \), 97%.

7.1.7.3 Diazothane (\( \text{CH}_3\text{CH}_2\text{N}_2 \))

Diazothane was either directly prepared from \( N\)-ethyl-\( N\)’-nitro-\( N\)’-nitrosoguanidine (equation 7.1.2)\(^3\) or synthesized from a modification\(^4\) of the procedure of Arndt\(^5\) and Werner.\(^6\) The latter preparation (equation 7.1.5)\(^4\) required synthesis of the precursor \( N\)-ethyl-\( N\)-nitrosourea (52% yield)\(^5\) shown by equations 7.1.3 and 7.1.4.
Concentration of the ethereal diazomethane solution was determined via the method of Marshall and Acree.²

\[
\text{O}_2\text{NNHC(NH)}_2\text{(NO)}_\text{CH}_2\text{CH}_3 + \text{KOH} \xrightarrow{\text{Et}_2\text{O}} \text{CH}_3\text{CHN}_2
\]

7.1.2

\[
\text{CH}_3\text{CH}_2\text{NH}_2\text{Cl} + \text{H}_2\text{NCONH}_2 \xrightarrow{} \text{CH}_3\text{CH}_2\text{NHCONH}_2 + \text{NH}_4\text{Cl}
\]

7.1.3

\[
\text{CH}_3\text{CH}_2\text{NHCONH}_2 + \text{HNO}_2 \xrightarrow{} \text{CH}_3\text{CH}_2\text{N(NO)}\text{CONH}_2 + \text{H}_2\text{O}
\]

7.1.4

\[
\text{H}_2\text{NCON(NO)}_\text{CH}_2\text{CH}_3 + \text{KOH} \xrightarrow{\text{Et}_2\text{O}} \text{CH}_3\text{CHN}_2
\]

7.1.5

7.1.7.4 2-Diazopropane ((CH₃)₂CN₂)

The preparation⁷ of 2-diazopropane is derived from the precursor acetone hydrazone under reduced pressure (equation 7.1.6) at -78°C. Spectrometry from the visible absorption band at 500 µ (which has ε=2, was used to estimate the yield of 2-diazopropane generated.

\[
(\text{CH}_3)_2\text{CNNH}_2 \xrightarrow{\text{HgO}} (\text{CH}_3)_2\text{CN}_2
\]

7.1.6

7.1.7.5 Ethyl Diazooacetate (N₂CHOO₂Et)

Ethyl Diazooacetate was either directly obtained from Aldrich or synthesized⁶ from the precursor glycine ethyl ester hydrochloride (equation 7.1.7). The dichloromethane solution of ethyl diazoacetate obtained from equation 7.1.7 was initially determined by ¹H NMR spectroscopy to be 31% by weight ethyl diazoacetate.
HCl·NH₂CH₂CO₂Et + NaNO₂ → N₂CHCO₂Et + NaCl + 2H₂O  

7.1.7.6 Phenyl diazomethane (N₂CHPh)

A convenient synthesis⁹ of phenyl diazomethane was derived from the precursor N-nitroso-N-benzyl-p-toluenesulfonamide (equation 7.1.8). An 81% yield of the N-nitroso-N-benzyl-p-toluenesulfonamide reagent was achieved following a general procedure¹⁰ evolving from N-benzyl-p-toluenesulfonamide, which itself was prepared according to the procedure of Holmes and Ingold.¹¹

p-CH₃·C₆H₄·SO₂N(NO)CH₂Ph + CH₂ONa → N₂CHPh
Et₂O

7.1.7.7 Diphenyl diazomethane (N₂CPh₂)

Diphenyl diazomethane was prepared in a similar manner¹² to 2-diazopropane and is shown by equation 7.1.9.

Ph₂CNNH₂ + HgO → N₂CPh₂
KOH
7.2 Experimental Details for Chapter Two

7.2.1 Preparation of \([\text{Mn}_2(\text{CO})_5(\mu-\text{dppm})_2]\) (2.11)

\([\text{Mn}_2(\text{CO})_5(\mu-\text{dppm})_2]\) (2.11) was prepared by the literature method\(^{13}\) and purified by chromatography on Florisil (100-200 mesh) eluting with \(\text{CH}_2\text{Cl}_2\); mp 228-234°C dec; IR \(\nu(\text{CO})\) (cm\(^{-1}\), Nujol) 1942 (m), 1930 (s), 1860 (s), 1835 (m), 1645 (m); NMR (CD\(_2\)Cl\(_2\)) \(\delta\) (P\(_2\)CH\(_2\)) 3.51, 8 (\(^{31}\)P) 75.9, 59.5.

7.2.2 Reaction of \([\text{Mn}_2(\text{CO})_5(\mu-\text{dppm})_2]\) with Diazoalkanes

7.2.2.1 \([\text{Mn}_2(\text{CO})_5(\mu-\text{C}(\text{O})\text{CH}_2\text{N}_2)(\mu-\text{dppm})_2]\) (2.19)

This was prepared by reaction of complex (2.11) (2.515 g, 2.471 \times 10\(^{-3}\) mol) stirring in \(\text{CH}_2\text{Cl}_2\) (100 mL) with dropwise addition of ethereal \(\text{CH}_2\text{N}_2\) (105 mL of 0.60% solution, 1.482 \times 10\(^{-2}\) mol) over 1 h at 0°C. After addition was completed, the colour of the solution slowly changed from red to yellow-orange over a period of 24 h at room temperature. The mixture was purified by chromatography on Florisil (100-200 mesh). Elution with \(\text{CH}_2\text{Cl}_2\) gave complex (2.11) (0.2279 g, 2.232 \times 10\(^{-4}\) mol, 90%) and then with 20% \(\text{CH}_3\text{OH/CH}_2\text{Cl}_2\) gave complex (2.19) (1.9448 g, 1.835 \times 10\(^{-3}\) mol, ~75%), recovered as an orange solid, which was recrystallized from \(\text{CH}_2\text{Cl}_2\)/pentane. The initially formed solvated crystals lost \(\text{CH}_2\text{Cl}_2\) rapidly to give the product as an orange powder: mp 197.5-199.5°C. Anal. Calc. for \(\text{C}_5\text{H}_4\text{aMn}_2\text{N}_2\text{O}_5\text{P}_4\): C, 63.41; H, 4.34; N, 2.64. Found: C, 63.49; H, 4.35; N, 2.63. IR and NMR data are listed in Tables 2.3 and 2.4 respectively. MS: parent ion (m/e 1060) not observed, m/e (assignment) 1018 (P-\(\text{CH}_2\text{N}_2\)), 962 (P-\(\text{CH}_2\text{N}_2\)-2CO), 934 (P-\(\text{CH}_2\text{N}_2\)-3CO), 884 (P-\(\text{CH}_2\text{N}_2\)-2CO-C\(_6\)H\(_6\)), 856 (P-\(\text{CH}_2\text{N}_2\)-3CO-C\(_6\)H\(_6\)).
7.2.2.2 \([\text{Mn}_2(\text{CO})_4(\mu-\text{C}(\text{O})\text{CHMeN}_2)(\mu-\text{dppm})_2)]\) (2.20)

In an analogous manner to that described in section 7.2.2.1, the diazoethane adduct (2.20) was prepared from reaction of (2.11) (2.020 g, 1.984x10^{-3} mol) in CH$_2$Cl$_2$ (100 mL) with ethereal CH$_3$CHN$_2$ (43 mL of a 1.6% solution, 1.190x10^{-2} mol). Complex (2.20) was recrystallized after a column chromatograph from a CH$_2$Cl$_2$/pentane mixture. These crystals lost CH$_2$Cl$_2$ rapidly to yield the product as an orange powder (1.45 g, 68%): mp 140-144°C. Anal. Calc. for C$_8$H$_{10}$Mn$_2$N$_2$O$_5$P$_2$: C, 63.69; H, 4.47; N, 2.61. Found: C, 63.45; H, 4.91; N, 2.65. IR and NMR data are listed in Tables 2.3 and 2.4 respectively. MS: parent ion (m/e 1074) not observed, m/e (assignment) 1018 (P-CH$_3$CHN$_2$), 962 (P-CH$_3$CHN$_2$-2CO), 934 (P-CH$_3$CHN$_2$-3CO), 884 (P-CH$_3$CHN$_2$-2CO-C$_8$H$_8$), 856 (P-CH$_3$CHN$_2$-3CO-C$_8$H$_8$).

7.2.2.3 \([\text{Mn}_2(\text{CO})_4(\mu-\text{C}(\text{O})\text{CHCOO}_{2}\text{EtN}_2)(\mu-\text{dppm})_2)]\) (2.21)

A solution consisting of (2.11) (.252 g, 2.68x10^{-4} mol) and N$_2$CHR$\equiv$CO$_2$Et (130 mL, 1.24x10^{-3} mol) in CH$_2$Cl$_2$ (50 mL) was stirred for 24 h at room temperature. No significant colour change occurred after this time but an IR analysis revealed an absence of the IR peak at 1645 cm$^{-1}$ indicative of (2.11). Purification by chromatography on Florisil (100-200 mesh) produced complex (2.21) with 50% CH$_3$OH/CH$_2$Cl$_2$ elution. Solvent removal and recrystallization from CH$_2$Cl$_2$/pentane produced an orange powder (.171 g, 61%) mp 147-149°C. Anal. Calc. for C$_{56}$H$_{50}$Mn$_2$N$_2$O$_{17}$P$_4$: C, 62.54; H, 4.42; N, 2.47. Found: C, 63.37; H, 4.20; N, 2.69. IR and NMR data are listed in Tables 2.3 and 2.4 respectively. MS: parent ion (m/e 1132) not observed, m/e (assignment) 1018 (P-CHR), 962 (P-CHR-2CO), 934 (P-CHR-3CO), 884 (P-CHR-2CO-C$_8$H$_8$),
7.2.2.4 Reaction of $[\text{Mn}_2(\text{CO})_5(\mu\text{-dppm})_2]$ with 2-diazopropane

A dichloromethane solution of $[\text{Mn}_2(\text{CO})_5(\mu\text{-dppm})]_2$ (2.11) (1.00 g, $9.82 \times 10^{-4}$ mol) was cooled to -78°C prior to addition of 2-diazopropane, $\text{N}_2\text{C(CH}_3)_2$ (15.7 mL of 5.25% solution, $1.14 \times 10^{-2}$ mol). No colour change was evident after 1 h stirring at -78°C. The solution was allowed to stir an additional 15 h at room temperature during which time a crimson solution was obtained. Solvent removal and subsequent chromatography on Florisil (100-200 mesh) of the red oil on a column equipped with a water-cooled jacket yielded two visible bands. Elution with dichloromethane produced a yellow-orange coloured band, the major product, subsequently identified via IR and $^1\text{H}$ NMR spectroscopies as (2.11). However, a red band of very small yield was eluted with 5% CH$_3$OH/CH$_2$Cl$_2$ solution. Solvent removal under high vacuum produced a red oil (~20 mg) which could not be recrystallized from CH$_2$Cl$_2$/pentane at -78°C. The red oil appeared unstable on standing at room temperature (yellow-orange oil) over 2 h and was consequently stored at -10°C. The decomposition product was identified as the precursor $[\text{Mn}_2(\text{CO})_5(\mu\text{-dppm})_2]$ (2.11) via IR analysis. Red oil: Anal. Calc. for C$_3$H$_5$Mn$_2$N$_2$O$_3$P$_4$: C, 63.97; H, 4.60; N, 2.57. Found: C, 63.92; H, 4.60; N, 2.36.

7.2.3 Reactions of 1:1 Adducts (2.19)-(2.21)

7.2.3.1 Thermal and Photochemical Decomposition Reactions

In a typical thermolysis experiment, one of the three 1:1 adducts (2.19)-(2.21) was dissolved in C$_6$H$_6$ (15 mL) and degassed in a closed
vessel fitted with a vacuum tap and a serum cap prior to heating at 80°C for 24 h. Analysis of any major volatile organic product was identified by g.c. Each residue was chromatographed on Florisil (100-200 mesh) to separate the product mixture. Identification of each sample was determined by spectroscopic comparison with authentic samples.

Complex (2.19) (0.047 g) gave a mixture of (2.19) (0.01 g) and (2.11) (0.03 g) with ethane evolution. Similarly, thermolysis of a solution of the diazoethane adduct (2.20) (0.051 g) gave ethane as the gas phase product and (2.11) (0.021 g) and unidentifiable decomposition products. Complex (2.21) (0.040 g) was determined by 1H NMR spectroscopy to produce (2.11) (~0.17 g), (2.20) (0.01 g) and N₂CHCO₂Et (58%) using an internal dichloromethane reference. In all cases, heating in an open vessel gave more rapid conversion to (2.11).

In a typical photolysis reaction, a dichloromethane solution of each adduct was similarly prepared for photolysis (Xe lamp, Pyrex filter) over a 24 h period. All three adducts generate complex (2.11) in comparable yields to their respective thermolysis reactions. Both adducts (2.19) and (2.20) produced ethane, while complex (2.21) gives a very low yield of N₂CHCO₂Et (see section 2.6.1).

7.2.3.2 With Strong Acids CF₃COOH, HClO₄

To a saturated CH₂Cl₂ solution of each adduct (2.19)-(2.21) (ca. 0.03 g in 5 mL) was added an excess amount of acid (50 µL). Each solution instantly darkened from red to a deep purple. Protonation is reversible with a diethyl ether wash. Only the starting materials were regenerated when isolating solids. A CH₂Cl₂ solution IR spectrum
(Table 2.5) revealed a new product in each case. Characterization of products was based on dissolution of the diazomethane adduct (2.19) in CDCl₃ (25 mg in 0.5 mL) in a 5 mm NMR tube. An initial spectra was taken before CF₃COOH (50 µL) was added. Resultant cationic species identified as \([\text{Mn}_2(\text{CO})_4(\mu-C(\text{O})\text{CH}_2\text{NHN})\{\mu-\text{dppm}\}_2]^+\); \(\delta(^{31}\text{P}(^1\text{H}), \text{AA'-BB'})\) 51.3, 56.5; \(\delta(\text{CH}_2\text{N}) 4.42\); \(\delta(\text{CH}_2\text{P}) 3.10, 2.88\) (Figure 2.5).

7.2.3.3 With Iodomethane

As described in section 7.2.3.2, excess CH₃I (200 µL) was added to a dichloromethane solution of each adduct (2.19)-(2.21) (50 mg in 5 mL). Each solution darkened to produce a deep red-purple solution up to 30 min after initial CH₃I addition. Only the starting materials were regenerated when isolating solids. Solution IR studies (Table 2.6) revealed formation of a cationic species in each case. Addition of CH₃CH₂I to the complex (2.19) in dichloromethane (35 mg in 5 mL) produced a similar colour change after 15 min whereas CH₃I addition to (2.19) required only 5 min to generate colour change.
7.3 Experimental Data for Chapter Three

7.3.1 \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-\text{dppm})] (3.4)\)

In a modification of the literature preparation, the ligand dppm (2.834 g, 7.382x10^{-3} mol) was added in three separate portions every 20 min to a stirring benzene solution of \([\text{Co}_2(\text{CO})_6] (2.523 \text{ g}, 7.382x10^{-3} \text{ mol in 50 mL}) while an \(N_2\) atmosphere was maintained throughout. After stirring for an additional 3 h at room temperature, the solution was chromatographed under nitrogen on Florisil (100-200 mesh) to yield the orange product \([\text{Co}_2(\text{CO})_6(\mu-\text{dppm})] (3.4)\) with \(\text{CH}_2\text{Cl}_2\) elution. Solvent removal and recrystallization from \(\text{CH}_2\text{Cl}_2/\text{hexanes}\) gave an orange powder (2.505 g, 3.74x10^{-3} mol, 50.7%). The product (3.4) was characterized by comparison of the \(^1\text{H}\) NMR and IR spectra with the literature values listed in Tables 3.2 and 3.1. \(^{31}\text{P} (\text{H})\) NMR (CDCl\(_3\)): δ 58.5.

7.3.2 \([\text{Co}_2(\text{CO})_6(\mu-\text{dppm})] (3.4)\)

\([\text{Co}_2(\text{CO})_6(\mu-\text{dppm})] (3.4) (1.357 \text{ g}, 2.02x10^{-3} \text{ mol}), powdered 10\% \text{Pd/charcoal (110 mg) and CH}_2\text{Cl}_2 (30 mL) were placed in the reaction vessel illustrated in Figure 7.1. The solution was degassed and the vessel evacuated (10^{-3} \text{ torr} prior to sealing the vacuum tap. When the solution had warmed to room temperature, the seal to the \(^{13}\text{CO} (100 \text{ mL, ~4.5 mmol}) was opened via the magnetic bar to allow the reaction contents to interact at room temperature for 4 h. After 4 h, the vacuum seal was opened and the resultant black solution gravity filtered through fluted qualitative filter paper (7 cm, medium porosity). The filtered solution was then column chromatographed on Florisil (100-200 mesh). An orange band was eluted with \(\text{CH}_2\text{Cl}_2\) and recrystallized from \(\text{CH}_2\text{Cl}_2/\text{hexane after solvent removal. Yield:}\)
Figure 7.1: Experimental Apparatus for Preparation of $[\text{Co}_2(^{13}\text{CO})_4-(\pi-^{13}\text{CO})_2(u-dppm)]$. 
$[\text{Co}_2(1^{3}\text{CO})_6(\mu\text{-dppm})]$ (1.26 g, 92%).

7.3.3 $[\text{Co}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-CH}_2)(\mu\text{-dppm})]$ (3.5) and $[\text{Co}_2(\text{CO})_4(\mu\text{-CH}_2)_2(\mu\text{-dppm})]$ (3.6).

Excess ethereal diazomethane (28 mL of a 1.1% solution, 2.69x10^{-3} mol) was added dropwise under $N_2$ to a stirring solution of $[\text{Co}_2(\text{CO})_4(\mu\text{-dppm})]$ (0.300 g, 4.48x10^{-4} mol) in $\text{CH}_2\text{Cl}_2$ (20 mL) over 20 min at 0°C. After $\text{CH}_2\text{N}_2$ addition was complete, the solution was allowed to stir at room temperature for 4 h under $N_2$. After 1 h, the initially orange colored solution lightened to eventually yield a yellow solution. The solution appeared to darken to a yellowish-gray colour with polymethylene formation after 3 h. After 4 h stirring, a bright yellow solution was collected via filtration through a sintered glass crucible to remove the insoluble polymeric material. This filtered solution was concentrated and chromatographed on Florisil (100-200 mesh) with $\text{CH}_2\text{Cl}_2$ elution. Solvent removal yielded a yellow solid. Preparative TLC (ANALTECH silica plates) with 15% $\text{CH}_2\text{Cl}_2$/hexanes separated the bis($\mu$-methylene) complex (3.6) ($R_f=0.333$) and the mono($\mu$-methylene) complex (3.5) ($R_f=0.167$), which were subsequently extracted with acetone. Each complex produced a yellow solid on solvent removal and recrystallized from a $\text{CH}_2\text{Cl}_2$/hexanes mixture. Both products were characterized by $^1\text{H}/^1\text{H}(^{31}\text{P})$, $^{31}\text{P}(^1\text{H})$ NMR and IR spectroscopies presented in Tables 3.2, 3.3 and 3.1 respectively. $[\text{Co}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-CH}_2)(\mu\text{-dppm})]$ (3.5): Yield 53 mg, 18%, decomp. 133°C. Anal. Calc. for C$_{24}$H$_{24}$Co$_2$O$_8$P$_2$: C, 56.72; H, 3.66.

Found: C, 56.78; H, 3.87; N, 0.00.

$[\text{Co}_2(\text{CO})_4(\mu\text{-CH}_2)_2(\mu\text{-dppm})]$ (3.6): Yield 106 mg, 37%, decomp.
139-142°C. Anal. Calc. for C₃₂H₂₈O₉P₂: C, 57.96; H, 4.05. Found: C, 57.84; H, 4.23. MS: m/e (assignment) 642 (P), 586 (P-2CO), 572 (P-2CO-CH₂), 558 (P-2CO-2CH₂, P-3CO), 530 (P-3CO-2CH₂, P-4CO), 516 (P-4CO-CH₂), 502 (P-4CO-2GH₂).

7.3.4 [Co₂(CO)₆(μ-CO)(μ-¹³CH₂)(μ-dppm)] and [Co₂(CO)₆(μ-¹³CH₂)₂(μ-dppm)]

¹³C-Diazald, 90% (0.215 g) was mixed with Diazald, 99% (1.935 g) to generate an estimated 1:1% ethereal solution of 9% ¹³C-labelled diazomethane. This ¹³C-labelled diazomethane (20 mL) was added to a CH₂Cl₂ (25 mL) solution of [Co₂(CO)₆(μ-dppm)] (3.4) (0.573 g, 8.55x10⁻⁴ mol) as described in sections 7.3.3. Separation of the ¹³C-labelled μ-methylene products (3.5) and (3.6) was also performed as outlined in section 7.3.3. Yields: [Co₂(CO)₆(μ-CO)(μ-¹³CH₂)(μ-dppm)] (88 g, 15.7%); [Co₂(CO)₆(μ-¹³CH₂)₂(μ-dppm)] (41 mg, 7.5%).

7.3.5 [Co₂(CO)₆(μ-CO)(μ-CD₂)(μ-dppm)] (4.3) and [Co₂(CO)₆(μ-CD₂)₂(μ-dppm)] (4.4)

An ethereal solution of deuto-diazomethane, 97% (25 mL of unknown concentration) was introduced to a CH₂Cl₂ (15 mL) solution of [Co₂(CO)₆(μ-dppm)] (3.4) (0.275 g, 4.10x10⁻⁴ mol) as described in section 7.3.3. After 4 h stirring, the yellow solution was worked-up as described in section 7.3.3 to separate the [Co₂(CO)₆(μ-CO)-(μ-CD₂)(μ-dppm)] (4.3) and [Co₂(CO)₆(μ-CD₂)₂(μ-dppm)] (4.4) products. Preparative TLC analysis revealed unreacted [Co₂(CO)₆(μ-dppm)] (3.4) was evident in solution. Yields: [Co₂(CO)₆(μ-CO)(μ-CD₂)(μ-dppm)] (4.3) (51 mg, 18.9%); [Co₂(CO)₆(μ-CD₂)₂(μ-dppm)] (4.4) (97 mg, 36.6%).
7.3.6 Reaction of \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dpmm})]\) (3.5) with Excess Diazomethane

Excess ethereal diazomethane (15 mL of a 0.9% solution) was added dropwise under \(N_2\) to a stirring solution of \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dpmm})]\) (3.5) (30 mg, 4.57\times 10^{-3}\) mol) in \(\text{CH}_2\text{Cl}_2\) (10 mL) at 0°C over 10 min. After diazomethane addition was complete, the reaction was warmed to room temperature and left to stir. The reaction was monitored by solution IR spectroscopy and the absence of the \(\nu(\mu-\text{CO})\) peak in (3.5) at 1810 cm\(^{-1}\) after 1.5 h indicated a complete conversion to the product (3.6). The bis(\(\mu\)-methylene) complex (3.6) was identified by its IR and \(^{31}\text{P}(\text{H})\) NMR spectra (Tables 3.1 and 3.3). Yield 22 mg, 75.0%.

7.3.7 \([\text{Co}_2(\text{CO})_4(\mu-\text{CHMe})_2(\mu-\text{dpmm})]\) (3.8)

In a similar manner to that described in section 7.3.3, a solution of \([\text{Co}_2(\text{CO})_6(\mu-\text{dpmm})]\) (3.4) (330 mg, 4.92\times 10^{-4}\) mol) was dissolved in \(\text{CH}_2\text{Cl}_2\) (20 mL) under \(N_2\) at 0-5°C. Excess ethereal diazomethane (11 mL of a 1.5% solution) was added dropwise to this solution over 25 min. The reaction was left to stir overnight at room temperature since no colour change occurred after 1 h stirring. After 16 h, the insoluble polymeric material was separated from the green coloured solution to give a green oil on solvent removal. Elution from a Florisil (100-200 mesh) column chromatograph produced a green solid (165 mg) with solvent removal and recrystallization from \(\text{CH}_2\text{Cl}_2/\text{hexanes}\). Preparative TLC (silica) with the solvent mixture 15% \(\text{CH}_2\text{Cl}_2/\text{hexanes}\) produced three bands; the yellow band (\(R_f=0.300\)), the green band (\(R_f=0.155\)) and an orange band (\(R_f=0.050\)) were identified as \([\text{Co}_2(\text{CO})_4(\mu-\text{CHMe})_2(\mu-\text{dpmm})]\) (3.8), \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CHMe})(\mu-\text{dpmm})]\) (3.7) and (3.4) (ca. 30 mg).
respectively from an IR analysis and/or subsequent $^1$H/$^1$H($^{31}$P) and
$^{31}$P($^1$H) NMR spectra given in Tables 3.1, 3.2 and 3.3 respectively. A
yellow solid was obtained for the bis($\mu$-ethyldiene) complex (3.8) (68
mg, 22.7%) decom. <150°C. Anal. Calc. for C$_{34}$H$_{40}$Co$_2$O$_4$P$_2$: C, 59.1; H,
4.5. Found: C, 58.6; H, 4.1.

7.3.8 [Co$_2$(CO)$_4$(\(\mu\)-CO)(\(\mu\)-CHO$_2$Et)(\(\mu\)-dpmm)] (3.9)

Ethyl diazoacetate (55 \(\mu\)L, 5.22x10$^{-4}$ mol) was diluted in CH$_2$Cl$_2$
(5 mL) and added dropwise under N$_2$ to a solution of [Co$_2$(CO)$_6$($\mu$-dpmm)]
(3.4) (175 mg, 2.61x10$^{-4}$ mol) in CH$_2$Cl$_2$ (15 mL) at room temperature.
After stirring 12 h, the solution was column chromatographed through
Florisil (100-200 mesh) with CH$_2$Cl$_2$ elution. Solvent removal and
recrystallization from CH$_2$Cl$_2$/hexanes yielded a reddish-orange solid
(3.9) (152 mg, 80%) decom. 147-150°C. Anal. Calc. for C$_{34}$H$_{40}$Co$_2$O$_4$P$_2$:
C, 56.05; H, 3.85. Found: C, 56.06; H, 3.96; N,0.00. IR and NMR data
are listed in Tables 3.1 and 3.2, 3.3 respectively.

7.3.9 Reaction of [Co$_2$(CO)$_6$($\mu$-dpmm)] (3.4) with excess
phenyl diazomethane ($\text{N}_2\text{CHPh}$)

This preparation was conducted as described in section 7.3.3
employing a solution of [Co$_2$(CO)$_6$($\mu$-dpmm)] (3.4) (329 mg, 4.91x10$^{-4}$
mol) in CH$_2$Cl$_2$ (12 mL). When no colour or IR spectral changes appeared
evident after 12 h stirring, the solution was refluxed for 12 h. A red
oil (3.10) was isolated from a column chromatograph on Florisil
(100-200 mesh) with CH$_2$Cl$_2$ eluant. Yield ~20 mg. IR and $^{31}$P($^1$H) NMR
data are listed in Tables 3.1 and 3.3 respectively.
7.3.10 Reaction of $\text{[Co}_2(\text{CO})_8(\mu\text{-dppm})] \ (3.4)$ with excess $\text{N}_2\text{CPh}_2$ and $\text{N}_2\text{CMe}_2$.

Both the diazoalkanes 2-diazopropane ($\text{N}_2\text{CMe}_2$) and diphenyl-
diazomethane ($\text{N}_2\text{CPh}_2$) did not react with complex (3.4) at 0°C (1 h) and
subsequent room temperature stirring (6 h) under the same conditions
described in section 7.3.3. Each diazoalkane was initially added to
(3.4) in a five molar excess, with an additional five molar excess
supplement up to 2 h later when no reaction had been observed.
Monitoring was by IR spectroscopy of reaction solutions.

7.3.11 $\text{[Co}_2(\text{CO})_4(\mu\text{-CH}_2)(\mu\text{-CHMe})(\mu\text{-dppm})] \ (3.11)$

Under an $\text{N}_2$ atmosphere, $\text{[Co}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-CH}_2)(\mu\text{-dppm})] \ (3.5) \ (120$
mg, 1.83x10^{-4} mol) in $\text{CH}_2\text{Cl}_2$ (10 mL) at 0°C was introduced dropwise to
excess ethereal diazoethane (10 mL of a 1.1% solution) over a 10-12
min. period. No colour change occurred after 4 h from the initial
yellow but the absence of the $\nu(\mu\text{-CO})$ frequency in (3.5) at 1810 cm$^{-1}$
indicated a complete reaction. Since analytical TLC (15%
$\text{CH}_2\text{Cl}_2$/hexanes) revealed only one reaction product, the reaction
mixture was chromatographed on Florisil (100-200 mesh) to yield a
yellow oily solid (38 mg, ~31.7%) which could not be induced to
crystallize. IR and $^{31}\text{P}[{^1}\text{H}]$ NMR data are listed in Tables 3.1 and 3.3
respectively.

7.3.12 $\text{[Co}_2(\text{CO})_4(\mu\text{-CH}_2)(\mu\text{-CHCO}_2\text{Et})(\mu\text{-dppm})] \ (3.12)$

Excess ethereal diazomethane (5 mL of a 1.1% solution) was added
dropwise over 10 min under $\text{N}_2$ to a solution of $\text{[Co}_2(\text{CO})_4(\mu\text{-CO})-$
$(\mu\text{-CHCO}_2\text{Et})(\mu\text{-dppm})] \ (3.9) \ (47.5 \text{ mg}, 6.53x10^{-5} \text{ mol})$ in $\text{CH}_2\text{Cl}_2$ (12 mL)
at 0°C. No colour change occurred during the initial diazomethane addition. The reaction was best monitored by IR spectroscopy with the loss of the $\nu(\mu\text{-CO})$ peak in (3.9) at 1820 cm$^{-1}$. After stirring for 6 h at room temperature, the red solution was chromatographed on Florisil (100-200 mesh) to yield a reddish-orange powdered solid (27.5 mg, 59.0%) on solvent removal and recrystallization from CH$_2$Cl$_2$/petroleum ether (low boiling). Decomp. 141-143°C. Anal. Calc. for C$_{34}$H$_{30}$Co$_2$O$_7$P$_2$: C, 57.16; H, 4.20. Found: C, 57.22; H, 4.37. IR and NMR data are listed in Tables 3.1, 3.2 and 3.3.
7.4 Experimental Details for Chapter Four

For all the reactions discussed in this section, all solutions were degassed by three freeze-pump-thaw cycles, pumping each time to a residual pressure of $10^{-3}$ torr at 77 K prior to sealing the reaction system. All vacuum distillations were conducted at $10^{-3}$ torr pressure. All gas samples (0.05 mL) were removed from the closed reaction system via a serum cap by a gas tight syringe and injected into the g.c. (porapak Q column). All gas-phase products were identified by identical retention times with authentic samples under the same gas chromatograph conditions.

7.4.1 Pyrolysis Reactions of (μ-alkylidene)dicobalt Complexes

Each (μ-alkylidene)dicobalt complex was degassed in decalin (3.0 mL) prior to sealing the reaction vessel with a vacuum tap. After each pyrolysis reaction at 80-90°C was deemed complete (usually > 4 h), a gas chromatograph sample was obtained via a serum cap placed over the vacuum adapter. The atmosphere contained between the serum cap and vacuum tap was evacuated to $10^{-3}$ torr pressure with a syringe needle attached to the vacuum line prior to any gas-phase sampling.

The pyrolysis results for the (μ-alkylidene)dicobalt complexes (3.5), (3.6), (3.8), (3.9), (3.11) and (3.12) are listed in Table 7.1. Generally, decomposition of each sample to give a black coloured solution occurred within the first hour of pyrolysis. In each case the resultant dark green solid was unidentified. No cyclopropane formation was observed from these pyrolyses.

It was determined that ketene (CH₂O), prepared by pyrolysis of diketene, exhibits the same g.c. retention time as carbon dioxide.
Table 7.1: Pyrolysis Results for Some (μ-alkylidene)dicobalt Complexes

<table>
<thead>
<tr>
<th>[Co₂(CO)₄(μ-R)(μ-R')(μ-dppm)]</th>
<th>Amount (mg)</th>
<th>g.c. Analyzed Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3.5); R=CH₂, R'=CO</td>
<td>15</td>
<td>CH₂CO</td>
</tr>
<tr>
<td>(3.6); R=R'=CH₂</td>
<td>15</td>
<td>CH₂CO, C₂H₄</td>
</tr>
<tr>
<td>(3.8); R=R'=CHMe</td>
<td>15</td>
<td>C₂H₄</td>
</tr>
<tr>
<td>(3.9); R=CHO₂Et, R'=CO</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>(3.11); R=CH₂, R'=CHMe</td>
<td>10(oil)</td>
<td>CH₂CO, C₂H₄, C₃H₆</td>
</tr>
<tr>
<td>(3.12); R=CH₂, R'=CHO₂Et</td>
<td>15</td>
<td>CH₂CO</td>
</tr>
</tbody>
</table>
Methylketene (CH₂CHO) and carboethoxyketene (EtO₂CCHCO) were identified by subsequent ¹H NMR experiments in which their respective esters were trapped in the presence of CD₃OD and characterized in high yield (sections 7.4.4, 7.4.7 and 7.4.13).

Under identical conditions, both the complexes [Co₂(CO)₄(μ-CH₂)(μ-CHO₂Et)(μ-dppm)] (3.9) and [Co₂(CO)₄(μ-CH₂)(μ-CHO₂Et)(μ-dppm)] (3.12) were separately pyrolyzed in benzene-d₆ (15 mg in 1 g C₆D₆).

Subsequent ¹H NMR spectra of the filtered solutions did not reveal any trace of the high boiling organic products diethyl fumarate or diethyl maleate derived from an intermolecular coupling of two μ-CHO₂Et units, nor was any ethyl acrylate (CH₂=CHO₂Et) detected on pyrolysis of (3.12).

7.4.2 Studies of ethylene evolution

Equimolar amounts (20 mg, 3.12x10⁻⁵ mol) of [Co₂(CO)₄(μ-CH₂)₂(μ-dppm)] (3.6), [Co₂(CO)₄(μ-CD₂)₂(μ-dppm)] (4.4) and a 1:1 mixture of (3.6) and (4.4) were each placed in separate reaction vessels (~5 mL) fitted with a stopcock. To each vessel decalin (3.0 mL) was added and each solution was degassed at 77 K. Each sample was then pyrolyzed for 8 h at 80-85°C. After pyrolysis was complete, each vessel was attached to the gas inlet system of the mass spectrometer, the solution cooled to 77 K and the gas phase admitted to the spectrometer. The resulting mass spectral data in Table 4.1 determined the ratio of C₂H₄:C₂H₂D₂:C₂D₄ from pyrolysis of the 1:1 mixture of (3.6) and (4.4) as ca. 9.5:8.5:1.0.

This same result was obtained from the same experiment, except that the solvent decalin was omitted.
Table 7.2: Pyrolysis Results for Some (μ-Alkyldiene)dicobalt Complexes in the Presence of Hydrogen (1 atm)

\[
\begin{array}{ccc}
\text{[Co}_2\text{(CO)}_4(\mu-\text{R})(\mu-\text{R'})(\mu-\text{dppm})]} & \text{Amount (mg)} & \text{g.c. Analyzed Products} \\
\hline
(3.5); \text{R=CH}_2, \text{R'}=\text{CO} & 10 & \text{CH}_2\text{CO, CH}_4 \\
(3.6); \text{R=R'}=\text{CH}_2 & 12 & \text{CH}_2\text{CO, C}_2\text{H}_4[0.4\%], \text{C}_2\text{H}_6[5.5\%] \\
(3.8); \text{R=R'}=\text{CHMe} & 10 & \text{C}_2\text{H}_4[9\%], \text{C}_2\text{H}_6[36\%] \\
(3.11); \text{R=CH}_2, \text{R'}=\text{CHMe} & 8(\text{oil}) & \text{CH}_2\text{CO, C}_2\text{H}_4[10\%], \text{C}_2\text{H}_6[53\%], \text{C}_3\text{H}_8[20\%], \text{C}_3\text{H}_6[4\%] \\
\end{array}
\]
7.4.3 Pyrolysis Reactions of (μ-alkylidene)dicobalt Complexes Under Hydrogen

In a similar manner to that described in section 7.4.1, each (μ-alkylidene)dicobalt complex (3.5), (3.6), (3.8) and (3.11) was degassed in decalin (3.0 mL) in separate reaction vessels. Prior to sealing each evacuated vessel, hydrogen (1 atm) was charged into each vessel. The subsequent pyrolysis results in the presence of hydrogen are listed in Table 7.2. Concentrations of each gaseous product were estimated from comparison with g.c. peak areas from known authentic gas concentrations diluted in the same reaction vessels.

7.4.4 Carbon Monoxide Addition to (μ-alkylidene)dicobalt Complexes

Separate 5 mm NMR tubes fitted with a vacuum adapter were charged with a (μ-alkylidene)dicobalt complex (15-20 mg), an equimolar volume of CH₂Cl₂ (reference) and CD₂OD (50 μL) in CDCl₃ (1.5 mL). Each solution was then degassed prior to carbon monoxide introduction. Each system was charged with a measured amount of carbon monoxide, allowed to equilibrate for 20 min, and the tube was then flame sealed. A complete reaction at room temperature was monitored by ³¹P(¹H) NMR spectroscopy.

An insoluble green precipitate formed during the reaction interval (ca. 7-14 days). When a reaction was completed, a g.c. analysis was conducted. The volatile organic products were transferred under vacuum into another 5 mm NMR tube, leaving the remaining organometallic products in the initial NMR tube. Identification of the volatile organic products was determined via ¹H NMR spectroscopy and verified from spectroscopic comparison with authentic samples. A
column chromatograph on Florisil (100-200 mesh) with CH₂Cl₂ elution produced an orange coloured species in each case from the soluble organometallic residue identified as [Co₂(CO)₄(μ-CH₃)(μ-dppm)] (3.4); 8(^31P) 58.5; 8(CH₂P₂) 3.06 [t, J(PH) 10 Hz]. Both the yield and identification of reaction products from carbon monoxide addition to each (μ-alkylidene)dicobalt complex are listed in Table 4.2.

7.4.5 [Co₂(CO)₄(μ-SO₂)(μ-CH₂)(μ-dppm)] (4.19) and [Co₂(CO)₄(μ-SO₂)₂(μ-dppm)] (4.20)

Sulfur dioxide was very slowly bubbled through a CH₂Cl₂ (20 mL) solution of [Co₂(CO)₄(μ-CH₂)₂(μ-dppm)] (3.6) (35 mg, 5.45 x 10⁻⁵ mol) over 5 min. There was no significant colour change from the initial yellow after 1 h. The mixture was suction filtered to remove an orange precipitate (4.20), readily soluble in methanol only, identified as [Co₂(CO)₄(μ-SO₂)₂(μ-dppm)]: Yield 4.0 mg, 10%. decomp. 150-153°C.


IR (Table 4.3). NMR (CDCl₃) 8(^31P) 34.9; 8(CH₂P₂) 4.01 [t, J(PH) 14 Hz], 8(P-C₆H₅) 7.1-7.8, m.

A column chromatograph on Florisil (100-200 mesh) produced a yellow-orange product (4.19) after methanol elution and solvent removal. The product was recrystallized from CH₂Cl₂/pentane. Yield: 25.5 mg, 68%. Decomp. 158-160°C. Anal. Calc. for C₂₀H₅₂Co₂O₇P₂S₂: C, 52.04; H, 3.47. Found: C, 52.36; H, 3.41.

IR (Table 4.3). NMR (CDCl₃) 8(^31P) 60.2; 8(CH₂P₂) 5.18, 4.28 [t, J(PH) 20 Hz, J(H³Hβ) 4 Hz]; 8(CH2HβP₂) 3.41 [m, J(PH) 10 Hz, J(H³Hβ) 15 Hz], 8(CH₂HβP₂) 2.93 [m, J(PH) 10 Hz, J(H³Hβ) 15 Hz].
7.4.6 Pyrolysis of \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dpmm})]\) (4.19)

Complex (4.19), \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dpmm})]\) (15 mg, \(2.16\times10^{-5}\) mol), was dissolved in a solution containing CDCl \(_3\) (2 mL), CD\(_3\)OD (40 µL) and a reference CH\(_2\)Cl \(_2\) (\(2.16\times10^{-5}\) mol, \(\sim1.85\) µL). This mixture was degassed in a vial fitted with a vacuum tap and then sealed (\(10^{-3}\) torr). The reaction vessel's contents were heated at 60±3°C for 3 days. A g.c. analysis after this time revealed only traces of ketene.

A \(^1\text{H}\) NMR of the filtered solution revealed only DCH\(_2\)COOCD\(_3\) (65%) was present in solution with no identifiable organometallic species.

DCH\(_2\)COOCD\(_3\); \(8(\text{DCH}_2)\) 2.06, s.

When the identical reaction was repeated in the presence of a catalytic amount of Et\(_3\)N (3.0 µL), only DCH\(_2\)COOCD\(_3\) (60%) was again identified by \(^1\text{H}\) NMR spectroscopy to exist in solution.

7.4.7 Sulfur Dioxide Addition to (µ-alkylidene)dicobalt Complexes

The observation of insoluble product matter from the reactions described in section 7.4.4 prompted the design of a self-contained system to facilitate the vacuum distillation transfer of the volatile organic products on reaction completion. A 5 mm NMR tube was attached at a 90° angle to a 6" glass tube (5 mm), which in turn was connected at 90° to the reaction flask bulb at least 5" above the reacting solution meniscus. Above the point of attachment of the 6" tube to the neck of the reaction flask was fitted a vacuum adapter.

Each reaction bulb in the seven separate glassware systems was charged with a different (µ-alkylidene)dicobalt complex (15-25 mg), an equimolar volume of CH\(_2\)Cl \(_2\) and CD\(_3\)OD (50 µL) in CDCl \(_3\) (15 mL). Each solution was degassed, charged with sulfur dioxide (100 torr) and
flame-sealed above the point of attachment of the connecting glass tube. Generally, within 40 h, the solution colour changed to a dark maroon. The volatile organic products were then vacuum distilled into the 5 mm NMR tube to leave the solid matter in the reaction flask. The 5 mm NMR tube was then flame sealed and thereby maintained the initial reaction bulb under vacuum. Subsequent g.c. analyses for each reaction bulb revealed only ketene with the exception of the \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})]\) reaction residual, which also revealed only a trace of \(\text{C}_2\text{H}_4\). The \(^1\text{H}\) and \(^{31}\text{P}[^1\text{H}]\) NMR spectra of the soluble (CDCl\(_3\)) organometallic products from each reaction bulb showed \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)_2(\mu-\text{dppm})]\) (4.20) [CDCl\(_3\): \(\delta(^{31}\text{P}[^1\text{H}])\) 32.9; \(\delta(\text{CH}_2\text{P}_2)\) 4.01 [t, \(J(\text{PH})\) 14 Hz], \(\delta(\text{P-C}_6\text{H}_5)\) 7.1-7.8, m] was the only product formed in each case. Table 4.4 summarizes the identity and yields of the volatile organic products and complex (4.20), determined by \(^1\text{H}\) NMR spectroscopy of their respective solutions with respect to an internal CH\(_2\text{Cl}_2\) (equimolar volume) reference.

7.4.8 Diazomethane Addition to \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dppm})]\) (4.19)

A 1.1% solution of ethereal diazomethane was repetitively administered to (4.19) (25 mg, 3.60\times10^{-5} \text{ mol}) in small volumes (3 mL) every 30 min for 4 h at room temperature as described in section 7.3.3. A brown solution with high polymethylene yield was evident after this time interval. A \(^{31}\text{P}[^1\text{H}]\) NMR analysis of the filtered reaction mixture revealed two peaks at 6 60.2 and 8 40.8, indicative of (4.19) and \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})]\) (3.6). Complex (3.6) was detected in comparatively small yield.
7.4.9 Ethyl Diazooacetate Addition to \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dppm})]\)

\[(4.19)\]

\([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dppm})]\) (4.19) (15 mg, 2.16x10^{-5} \text{ mol}) was
degassed in \(\text{CH}_2\text{Cl}_2\) (5 mL) with a 3:1 molar excess of ethyl diazooacetate
(\(\sim 6.8 \mu\text{L}\)) in a vacuum vessel equipped with a stopcock adapter. The
vessel remained sealed for 6 days at room temperature. A g.c. analysis
revealed ketene only. A \(^{31}\text{P}[^{1}\text{H}]\) NMR spectrum revealed the products
were (4.20) [8(\(^{31}\text{P}[^{1}\text{H}]) 32.9] and [\(\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CHCO}_2\text{Et})(\mu-\text{dppm})]\)
(4.25) \([8(\(^{31}\text{P}[^{1}\text{H}]) 54.6]\). \(^1\text{H}\) NMR spectral data of (4.25) are discussed
in section 4.6.4.

7.4.10 Carbon Monoxide Addition to \([\text{Co}_2(\text{CO})_4(\mu-\text{SO}_2)(\mu-\text{CH}_2)(\mu-\text{dppm})]\)

\[(4.19)\]

As in section 7.4.4, complex (4.19) (15 mg, 2.16x10^{-5} \text{ mol}) was
prepared in the appropriate solvent mixture with CO (80.6 torr). After
7 days at room temperature, the reaction was stopped when a \(^{31}\text{P}[^{1}\text{H}]\) NMR
spectrum revealed no trace of (4.19) \([8(\(^{31}\text{P}[^{1}\text{H}]) 60.2]\) in solution,
only peaks at \(8(\(^{31}\text{P}[^{1}\text{H}]) 58.5\)' and \(8(\(^{31}\text{P}[^{1}\text{H}]) 50.2\), identified as
\([\text{Co}_2(\text{CO})_6(\mu-\text{dppm})]\) (3.4) and \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{SO}_2)(\mu-\text{dppm})]\) (4.26).
Vacuum distillation of the volatile organic products allowed a \(^1\text{H}\) NMR
spectrum (CDCl\(_3\)) of the remaining reaction mixture to detect (3.4)
\([8(\text{CH}_2\text{P}_2) 3.06 \text{ [t, } \text{ } 2\text{J(PP)} 10 \text{ Hz}]\) and (4.26) \([8(\text{CH}_2\text{P}_2) 3.25 \text{ [t, } \text{ } 2\text{J(PP)}
10 \text{ Hz}]\) in 35% and 25% yield respectively against an internal \(\text{CH}_2\text{Cl}_2\)
reference. A g.c. analysis of the reaction mixture revealed only a
trace of ketene. A subsequent \(^1\text{H}\) NMR of the volatile organic products
detected D\(\text{CH}_2\text{COOCD}_3\) \([8 2.06, s]\) in 65% yield.
7.4.11 Ethylene Addition to \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})(\mu-\text{CH}_2)(\mu-\text{dppm})]\) (3.5)

Complex (3.5) (15 mg, 2.28x10^{-5} \text{ mol}) was dissolved in CDCl_3 (1 mL) with a reference amount of CH_2Cl_2 (2.28x10^{-5} \text{ mol, } \sim 1.5 \text{ \mu L}) and placed in a 5 mm NMR tube equipped with a vacuum adapter. The yellow solution was degassed, C_2H_4 (50 torr) was added, and the tube flame sealed. A complete reaction occurred slowly at room temperature over 30 days to yield a red solution. NMR spectra identified product as \([\text{Co}_2(\text{CO})_4(\mu-\text{dppm})]\) (3.4): Yield 40\%; NMR (CDCl_3), 6(^{31}\text{P}(^{1}\text{H})) 58.5, 6(CH_2F_2) 3.06 [t, \text{ J(PH)} 10 \text{ Hz}]. A g.c. analysis identified ketene and propylene (25\%) only. The same reaction with C_2F_4 resulted in no reaction while monitoring the reaction via ^{31}\text{P}(^{1}\text{H}) NMR spectroscopy over 30 days; only insoluble, green decomposition products.

7.4.12 Ethylene Addition to \([\text{Co}_2(\text{CO})_4(\mu-\text{CH}_2)_2(\mu-\text{dppm})]\) (3.6)

The analogous reaction of complex (3.6) (15 mg, 2.34x10^{-5} \text{ mol}) with C_2H_4 (50 torr) over 10 days, as described in the previous section 7.4.11, resulted in the formation of (3.4) [50\%], propylene [30\%] and some ketene. No butenes or cyclopropane were observed from a g.c. analysis of the reaction mixture. Similarly, as in section 7.4.11, only insoluble green decomposition products along with unreacted (3.6) were observed after reaction of (3.6) with C_2F_4 (50 torr) at room temperature over the same 10 day period.
7.4.13 Reaction of Hexafluoro-2-butyne (HFB) with (μ-alkylidene)dicobalt Complexes

Each (μ-alkylidene)dicobalt complex (15-20 mg) listed in Table 4.4 was reacted with HFB (50-100 torr) as outlined in section 7.4.4. The sealed 5 mm NMR tubes were monitored via $^{31}$P($^1$H) NMR spectroscopy. Only ketene traces were observed in the g.c. spectrum for each reaction, with the exception of the bis(μ-methylene)dicobalt complex (3.6) which also revealed C$_2$H$_4$ (~3%). Each sealed reaction produced [Co$_2$(CO)$_4$(μ-HFB)(μ-dppm)] (4.50) as the only organometallic product: 8($^{31}$P($^1$H)) 36.6; 8(CH$_2$P$_2$) 3.45 [t, $^2$J(PH) 10 Hz]. The identity and yields of both (4.50) and the respective organic products are contained in Table 4.5.

7.4.14 Reaction of Diphenylacetylene with [Co$_2$(CO)$_4$(μ-CO)(μ-CH$_2$)$_2$(μ-dppm)] (3.5) and [Co$_2$(CO)$_4$(μ-CH$_2$)$_2$(μ-dppm)] (3.6)

In a similar manner as described in the preceding section, complex (3.5) (15 mg, 2.28x10$^{-5}$ mol) and (3.6) (15 mg, 2.34x10$^{-5}$ mol) were reacted in a sealed 5 mm NMR tube with an equimolar amount of C$_2$Ph$_2$. A g.c. analysis revealed only a trace of C$_2$H$_4$ [ca. 2%] from the (3.6) reaction. Each reaction produced [Co$_2$(CO)$_4$(μ-C$_2$Ph$_2$)(μ-dppm)] (4.51) as the lone organometallic product: 8($^{31}$P($^1$H)) 34.9; 8(CH$_2$P$_2$) 3.30 [t, $^2$J(PH) 10 Hz]. Both C$_2$Ph$_2$ addition to (3.5) and (3.6) induced methylacetate-d$_4$ (H$_2$COOOOCO$_3$) formation in 95% and 90% yield respectively. All yields are listed in Table 4.5.
7.4.15 Diazomethane Addition to \( [\text{Co}_2(\text{CO})_4(\mu-\text{RCCR})(\mu-\text{dppm})] (\text{R}=\text{Ph}, \text{CF}_3) \)

Excess ethereal diazomethane was added to a \( \text{CH}_2\text{Cl}_2 \) solution of complex (4.50) or complex (4.51) as outlined in section 7.3.3. Both complexes (4.50) and (4.51) were prepared by the literature methods. Subsequent work-up after 24 h revealed no reaction as determined by IR and \(^{31}\text{P}[^1\text{H}] \) NMR spectroscopy. Each alkyne-bridged complex was recovered in ca. 95% yield.
7.5 Experimental Details for Chapter Five

The preparation of each polynuclear cobalt complex discussed in this section required only dried solvents from the appropriate distillation under an N₂ atmosphere. Each preparative reaction was also conducted under an N₂ atmosphere or, when feasible, in a dry box.

7.5.1 [Co₂(CO)₆(μ-<CO)₂(μ-dmpm)] (5.10)

To a stirred solution of [Co₂(CO)₆] (350 g, 1.03x10⁻⁳ mol) in benzene (25 mL) was added dmpm (190 μL, 1.03x10⁻³ mol) in 50 μL additions over 5 min. Gas evolution (presumably of CO) was observed from the red solution with each addition of dmpm. After 1 h, the solvent was concentrated under vacuum (ca. 15 mL) and the added under N₂ to a Florisil (100-200 mesh) column for column chromatography. Elution with benzene produced a red solution which yielded a black solid on solvent removal under vacuum.

[Co₂(CO)₆(μ-<CO)₂(μ-dmpm)] (5.10) (295 mg, 68.2%); IR ν(CO) (cm⁻¹, cyclohexane) 2045(m), 2010(s), 1990(s), 1840(m), 1780(m); NMR ((CD₃)₂CO) δ(³¹P(¹H)) 39.0; δ(CH₂P₂) 2.01 [t, ²J(Ph) 10 Hz] and δ(CH₃) 1.66 [t, ²J(Ph) 4 Hz].

7.5.2 [Co₂(CO)₆(μ-<CH₂)₂(μ-dmpm)] (5.11)

A method identical to the one described in section 7.3.3 was used. The organometallic substrate employed in this case was [Co₂(CO)₆(μ-<CH₂)₂(μ-dmpm)] (5.10) (200 mg, 2.37x10⁻³ mol). After 10 h stirring at room temperature, the insoluble polymethylene was filtered under N₂ with Schlenk-ware. The filtered green solution was then taken to dryness under vacuum, redissolved under N₂ in CH₂Cl₂ (10 mL) and
then column chromatographed under N₂ on Florisil (100-200 mesh). Elution with CH₂Cl₂ produced a green band which produced only a green oil (ca. 25 mg) on solvent removal under vacuum. Both the product [Co₂(CO)₄(μ-CH₂)₂(μ-dmpm)] (5.11) and the precursor complex (5.10) were detected by ¹H NMR spectroscopy.

[Co₂(CO)₄(μ-CH₂)₂(μ-dmpm)] (5.11): ¹H NMR ((CD₃)₂CO, -35°C) δ(μ-CH₂)₂ 4.86, 4.05, 3.54 [t, ²J(PH) 22 Hz], 3.40; δ(CH₂HβP₂) 1.74 [m, ²J(PH) 10 Hz, J(HβHβ) 14 Hz]; δ(CH₃) 1.15, 1.35 [s, br].

[Co₂(CO)₄(μ-CO)₂(μ-dmpm)] (5.10): ¹H NMR ((CD₃)₂CO, -35°C) δ(CH₂P₂) 2.01 [t, ²J(PH) 10 Hz]; δ(PCH₃) 1.66 [t, ²J(PH) 4 Hz].

7.5.3 Reaction of [Co₂(CO)₄(μ-CO)₂(μ-dmpm)] (5.10) with Diazoethane

The exact procedure described in the preceding section 7.5.2 was followed but with excess diazoethane as opposed to diazomethane. Only the product (5.10) [δ(¹³²P(¹H)) 39.0] was spectroscopically detected in low yield in solution.

7.5.4 [Co₂(CO)₄(μ-CO)(μ-CHCO₂Et)(μ-dmpm)] (5.12)

Complex (5.10), [Co₂(CO)₄(μ-CO)₂(μ-dmpm)] (95 mg, 2.25x10⁻⁴ mol), was reacted with a five fold excess of N₂CHCO₂Et (118 μL, 1.12x10⁻¹ mol) in CH₂Cl₂ (20 mL) according to the procedure described in section 7.3.8. Only a red oil (63 mg, 58%) was obtained on solvent removal after a column chromatograph subsequently characterized as

[Co₂(CO)₄(μ-CO)(μ-CHCO₂Et)(μ-dmpm)] (5.12): IR ν(CO)(cm⁻¹, CH₂Cl₂) 1990(m), 1960(s), 1940(m), 1790(m); NMR ((CD₃)₂CO) δ(¹³²P(¹H)) 33.7; δ(μ-CHR) 3.90 [t, ²J(PH) 21 Hz]; (CO₂CH₂CH₃): δ(CH₂) 3.49 [q, J(HH) 8
Hz], 8(\text{CH}_3) [t, J(\text{HH}) 8 Hz]; 8(\text{CH}_3\text{H}^\beta\text{P}_2) 2.10 [m, 2J(\text{PH}) 12 Hz, 2J(\text{H}^\alpha\text{H}^\beta) 14 Hz], 8(\text{CH}_3) 1.15, 1.35 [s, br].

7.5.5 [\text{Co}_3(\text{CO})_7(\text{\mu}_3-\text{COO}_2\text{Et})(\text{\mu-dmpm})] (5.13):

Complex (5.12), [\text{Co}_2(\text{CO})_4(\text{\mu}-\text{CO})(\text{\mu-CHCO}_2\text{Et})(\text{\mu-dmpm})] (50 mg oil) in CH$_2$Cl$_2$ (20 mL) was mixed under N$_2$ with excess ethereal diazomethane and allowed to react for 4 h at room temperature. The resultant purple solution was taken to dryness under vacuum, redissolved in a minimum amount of CH$_2$Cl$_2$ (5 mL) and then column chromatographed under N$_2$ on Florisil (100-200 mesh). A purple oil (ca. 15 mg) was obtained on solvent removal of the CH$_2$Cl$_2$ eluted band.

[\text{Co}_3(\text{CO})_7(\text{\mu}_3-\text{COO}_2\text{Et})(\text{\mu-dmpm})] (5.13): IR ν(CO)(cm$^{-1}$, CHCl$_3)$ 2050(s), 2010(s), 1995(sh), 1980(sh), 1650(m); NMR (CD$_2$Cl$_2$) 8(31P$^1$H)$^1$ 11.9;

(CO$_2$CH$_2$CH$_3$): 8(CH$_2$) 4.28 [q, J(\text{HH}) 8 Hz], 8(CH$_3$) 1.34 [t, J(\text{HH}) 8 Hz];

8(\text{CH}_3\text{H}^\beta\text{P}_2) 2.26 [m, 2J(\text{PH}) 14 Hz, 2J(\text{H}^\alpha\text{H}^\beta) 14 Hz], 8(\text{CH}_3\text{H}^\alpha\text{H}^\beta) 2.99 [m, 2J(\text{PH}) 14 Hz, 2J(\text{H}^\alpha\text{H}^\beta) 14 Hz]; 8(\text{PCH}_3) 1.52 [t, 2J(\text{PH}) 12 Hz]. MS: parent ion (m/e 594), Table 5.3.

[\text{Co}_3(\text{CO})_7(\text{\mu}_3-\text{COO}_2\text{Et})(\text{\mu-dmpm})] (5.13) was also prepared from reaction of [\text{Co}_3(\text{CO})_6\text{COO}_2\text{Et}] (ca. 60 mg, 1.167x10$^{-4}$ mol) with dmpm (17.6 μL, 1.167x10$^{-4}$ mol) in THF (15 mL) under N$_2$ at room temperature over 8 h. [\text{Co}_3(\text{CO})_6(\text{\mu}_3-\text{COO}_2\text{Et})] was prepared by analogy to the literature procedure$^{15}$ for [\text{Co}_3(\text{CO})_6\text{COO}_2\text{Me}] substituting Cl$_3$COO$_2$Et in place of Cl$_3$COO$_2$Me.
7.6 Experimental Details for Chapter Six

7.6.1 Reduction of \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-L)] (L=\text{dmpm}(5.10), \text{dppm}(3.4))\)

In a typical reaction, the sodium salt of either \([\text{Co}_2(\text{CO})_6(\mu-L)]^2^-\)
\((L=\text{dmpm}, \text{dppm})\) species was prepared by stirring the respective,

\([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-L)] (L=\text{dmpm}(5.10), \text{dppm}(3.4))\) complex (250 mg) in
dried THF (50 mL) with either Na/Hg (2 equiv.) or powdered NaOH (50
to a 10 fold excess) in a dry box under nitrogen. The reduction was monitored
by IR spectroscopy and was generally complete after 24 h. Each
reduction progressed with a darkening of the initial solution colour.
The reduced product was filtered in solution, generally through
Schlenk-ware to remove insoluble matter; specifically Hg or excess
NaOH. NaI was subsequently noted to be slightly soluble in THF.

The potassium salt of either \([\text{Co}_2(\text{CO})_6(\mu-L)]^2^-\) \((L=\text{dmpm}, \text{dppm})\) was
prepared similarly using powdered KOH (50 fold excess).

The preferred method for these reduction reactions was the Na/Hg
route, since this pathway provided a greater yield of the reduced
species in each case.

\([\text{Co}_2(\text{CO})_6(\mu-\text{dmpm})]^2^-\): IR \text{v(CO)}(\text{cm}^{-1}, \text{THF}) 1830 (s, br)
\([\text{Co}_2(\text{CO})_6(\mu-dppm)]^2^-\): IR \text{v(CO)}(\text{cm}^{-1}, \text{THF}) 1910 (s, br)

7.6.2 Reaction of \([\text{Co}_2(\text{CO})_6(\mu-dmpm)]^2^-\) with I(\text{CH}_2)_n\text{I}(n=1,3)

Either CH\textsubscript{2}I\textsubscript{2} or I(\text{CH}_2)_3I, generally in a five fold excess assuming
100% reduction of \([\text{Co}_2(\text{CO})_4(\mu-\text{CO})_2(\mu-dmpm)] (5.10), \text{was added to the}
crude, filtered THF solution of \([\text{Co}_2(\text{CO})_6(\mu-dmpm)]^2^-\). The solution was
left to stir in the glove box for 6 h at room temperature. The absence
of the strong IR peak (1830 cm\textsuperscript{-1}) for the reduced species signified a
complete reaction. Solvent removal under vacuum produced a black oil
and evidence of white NaI byproduct. Dissolution in dried CH₂Cl₂ (5 mL) and a subsequent column chromatograph on Florisil (100-200 mesh) removed some NaI and produced two reaction products. Complex (5.10), [Co₂(CO)₄(μ-NO)₂(μ-dppm)] was separated with CH₂Cl₂ elution and identified via IR and ³¹P(¹H) NMR analyses. Elution with MeOH yielded an air-sensitive red oil on solvent removal in much lower yield assigned as [Co₂I₄(μ-dppm)₂] (6.2). Prior to NMR analyses, a dichloromethane solution of (6.2) was washed with three separate 5 mL additions of distilled H₂O to remove MeOH soluble NaI residues. The red dichloromethane solution was then dried with MgSO₄. Both the sodium and potassium salts of [Co₂(CO)₆(μ-dppm)]²⁻ gave these same reaction products.

[Co₂I₄(μ-dppm)₂] (6.2): ¹H NMR (CD₂Cl₂): δ(CH₂P₂) 4.34; δ(PCH₃) 2.14.

MS: parent ion (m/e 898), Table 6.1. HRMS calc. for C₁₀H₁₆Co₂I₄P₄: 897.5984. Found: 897.6020.

7.6.3 Reaction of [Co₂(CO)₆(μ-dppm)]²⁻ with I(CH₂)ₙI(n=1,3-5), RI(R=Me,Et)

These reactions were performed as described in the preceding section 7.6.2. A column chromatograph on Florisil (100-200 mesh) gave [Co₂(CO)₄(μ-NO)₂(μ-dppm)] (3.4) with CH₂Cl₂ elution. The red band, obtained with MeOH elution, was determined to contain two products, complexes (6.3) and (6.4). A suitable solvent mixture with the appropriate elution composition was not discovered, however complex (6.3) was identified when repetitive attempts isolated (6.3) as the lone MeOH eluted product from CH₂I₂ addition.

trans-[Co₂I₂(CO)₃(μ-CO)₂(μ-dppm)] (6.3): IR ν(CO)(cm⁻¹, CH₂Cl₂)
1970(s), 1820(w); NMR (CD$_2$Cl$_2$) $\delta$(H) 4.28 (qu.
J(\HH) 4 Hz); $\delta$(P-C$_6$H$_5$) 7.1-7.8, m; Anal. Calc. for C$_5$H$_4$Co$_2$L$_2$O$_4$P$_4$: C, 51.76; H, 3.51; I, 20.29. Found: C, 52.20; H, 3.68; I, 21.20.
Complex (6.4) (unidentified): NMR (CD$_2$Cl$_2$) $\delta$(H) 3.5; $\delta$(CH$_2$P)$_2$
4.48 (t, J(\PH) 13 Hz).
References


