# SYNTHESES AND INVESTIGATIONS
# OF
# BI- AND TRIMETALLIC ORGANOTRANSITION METAL CLUSTERS

by

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# BI- AND TRIMETALLIC ORGANOTRANSITION METAL CLUSTERS

Pour Brenda, épouse, amie,

affectueusement.

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# ABSTRACT

The reaction of dicobalt octacarbonyl with a series of 1,1,1-trichloro-2,2-bis(aryl)ethanes yields the corresponding $Co_3(CO)_9[\mu^3-CCHRR']$ tetrahedral clusters, where R= R′ = 4-methoxyphenyl or R = 4-chlorophenyl, R′ = 2-chlorophenyl. The nine-fold degeneracy of the cobalt carbonyl ligands in these clusters is split on the NMR time-scale at low temperature. In order to investigate the fluxional processes, the three axial carbonyl ligands were replaced by the tripodal moiety $HC(Ph_2P)_3$. The molecular structure of $(HC(Ph_2P)_3)Co_3(CO)_6[\mu^3-CCH_3]$ was determined by using X-ray crystallography. These data, in conjunction with the variable-temperature NMR results revealed the existence of several independent fluxional processes.

A series of enantiomerically pure dicobalt μ-alkyne clusters which possess diastereotopic cobalt vertices were synthesized by the treatment of $[Co_2(CO)_6][HC{\equiv}C-CH_2OH]$ with menthol or borneol, or by the reaction of $Co_2(CO)_8$ with 2-*endo*-propynyl-borneol; the latter cluster was characterized X-ray crystallographically. Carbonyl substitution by phosphines occurs with some degree of diastereoselectivity. Moreover, diastereoselective replacement of a metal vertex by isolobal groups $(C_5H_4R)M(CO)_2$, where R = H or $CH_3$ and M =

Mo or W, has been observed by using NMR spectrosopy.

The reaction of $[(C_5H_5)Mo(CO)_2]_2$ with 2-*endo*-propynyl-borneol yields the crystallographically characterized tetrahedral cluster $(R^*C{\equiv}CMe)Mo_2(CO)_4(C_5H_5)_2$, where R* is the 2-norbornenyl group. Protonation of this cluster and the above-mentioned hexacarbonyldicobalt species leads to metal stabilized cations which maintain their terpenoid skeletons and are stable towards carbocationic rearrangement. High field NMR studies on the mixed metal cationic clusters $[M\text{-}Co(CO)_3(HC{\equiv}C\text{-}CR_2)]^+$, where M = $(C_5H_5)Mo(CO)_2$, $(C_5H_4Me)W(CO)_2$ or $(C_5H_4Me)Mo(CO)_2$, reveal that the capping vinylidene moiety leans preferentially towards one vertex. NMR data, together with EHMO calculations, on the related trimetallic cluster cation $[(C_5H_5)Mo(CO)_2Co_2(CO)_6CCR_2]^+$ demonstrate that the positive charge is better tolerated by the $(C_5H_5)Mo(CO)_2$ fragment than at the $Co(CO)_3$ vertex.

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# CHAPTER ONE

# INTRODUCTION

## *1.1 Background*

By definition, organometallic chemistry is concerned with the study of complexes which possess metal-carbon bonds.[1] The presence of substantial and direct bonds between two or more metals is the required characteristic of a transition metal cluster.[2] Therefore, it logically follows that the syntheses and investigations of organotransition metal clusters would be concerned with compounds which contain both metal-carbon and metal-metal bonds.

This introduction will attempt to serve many masters. Since a great deal of the work that will be discussed involves the rational syntheses of bi- and trimetallic organotransition metal clusters, it is perhaps useful first to examine several of the fundamental concepts employed by cluster chemists to predict the probable outcome of their reactions. Moreover, many of the now familiar and established reactions which form the basis of this work and make use of these ideas will be discussed. Throughout this work, Nuclear Magnetic Resonance spectroscopy was the principal method used to investigate the structures and fluxional behaviour of the synthesized clusters; thus, the latter portion of this introduction will present ideas and literature examples which illustrate the importance of this spectroscopic technique to the cluster chemist.

When examining a class of compounds, it is helpful for researchers to have simple rules or concepts which will allow them to accurately predict which of the molecular formulations represent realistic, stable compounds. The Effective Atomic Number (EAN) Rule, sometimes referred to as the 18-Electron Rule, is a very useful method for predicting the stability and structures of small organometallic complexes.[3] This concept can be easily viewed as a corollary of the "Octet Rule" used in organic chemistry and, simply put, states that metals in stable diamagnetic molecules will possess 18 electron configurations.

The rationale behind the EAN Rule can be best understood if one considers the simple example of a mononuclear octahedral metal complex, $ML_6$.[3] First of all, one must recall that for any given d-block transition metal there are a total of nine valence atomic orbitals; five d orbitals, three p orbitals and one s orbital. When placed in an octahedral environment, the five d orbitals split into three orbitals of $t_{2g}$ symmetry and two of $e_g$ symmetry; the three p orbitals have $t_{1u}$ symmetry and the one s orbital has $a_{1g}$ symmetry. In turn, the six σ-bonded ligands contribute six atomic orbitals of their own; three of $t_{1u}$, two of $e_g$ and one of $a_{1g}$ symmetry. Since only atomic orbitals of the same symmetry are allowed to interact, the ligand and metal orbitals of the correct symmetry combine in the manner shown in Figure 1 to form the corresponding bonding and non-bonding molecular orbitals.[3] In addition, metal atomic orbitals which do not have the correct symmetry to interact with any of the ligand orbitals (the three $t_{2g}$ orbitals) remain as non-bonding molecular orbitals.

As is evident from Figure 1, 18 electrons completely fill the bonding and non-bonding molecular orbitals; it is the maximum number of valence electrons that can be accommodated without using the anti-bonding molecular orbitals.[3] In fact it turns out that, regardless of the molecular symmetry, the bonding and non-bonding molecular orbitals will always have the same total capacity of 18 electrons because the nine valence orbitals on the metal must each give rise to either a bonding or a non-bonding molecular orbital. When these nine molecular orbitals are filled completely, the metal attains the stable eighteen electron closed-shell configuration analogous to that of the Group 18 noble gas in its row, i.e, krypton, xenon or radon, and the metal is said to have the effective atomic number of that gas.[1]

For a cluster to be stable, the individual constituent metal atoms are normally expected to have an 18 electron closed shell configuration. However, now the total number of valence electrons required by the molecule to achieve

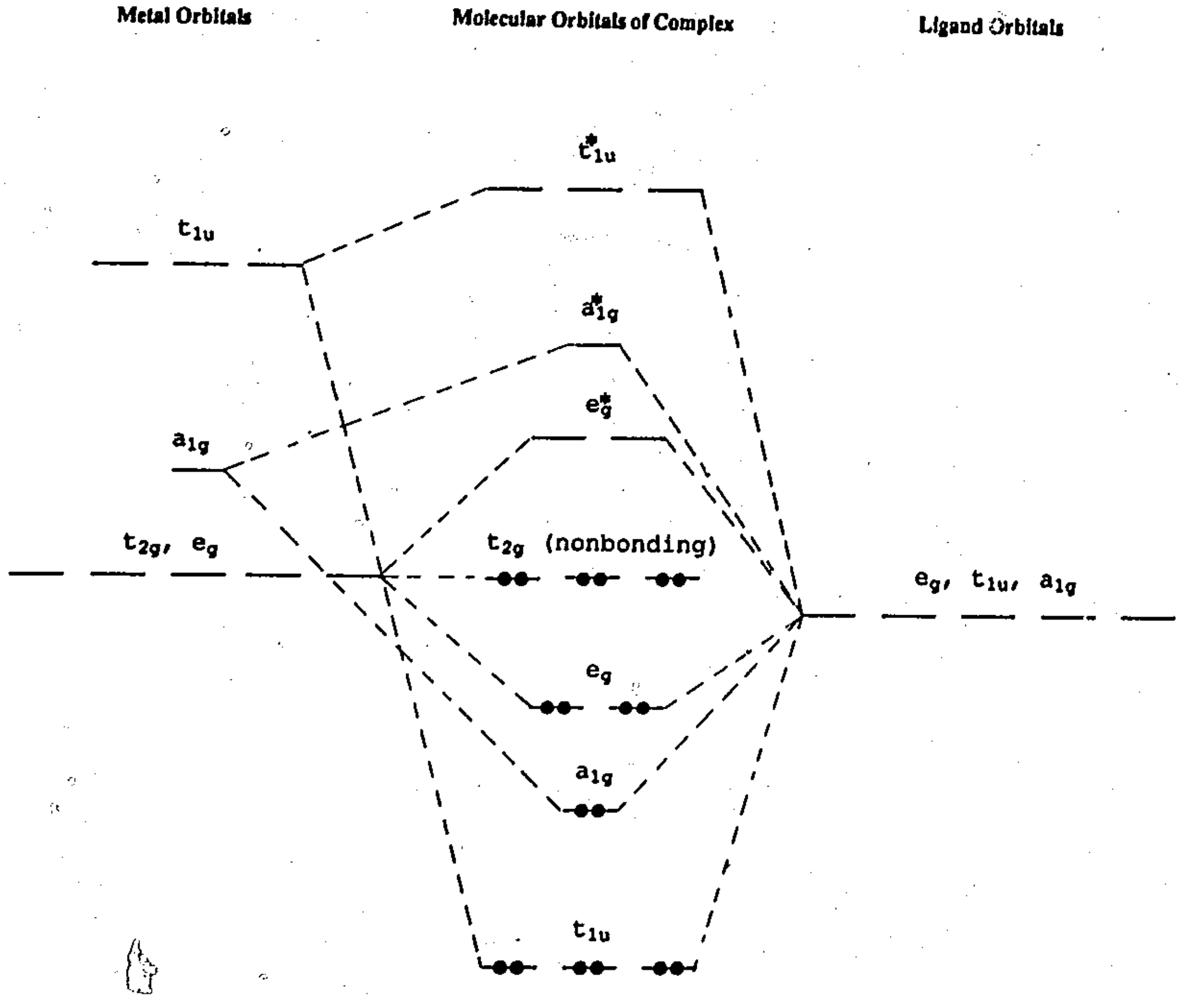


**Figure 1:** Orbital interaction diagram for an $ML_6$ complex.

stability, or the EAN electron count, no longer is eighteen; it varies depending on the number of metals present. In general, the expected EAN electron count for a cluster of nuclearity M and having B metal-metal bonds is given by[1]

$$\text{EAN count} = 18M - 2B$$

If the total number of valence electrons in the molecule and the calculated EAN count are the same, then the organometallic complex is predicted to be stable.

There are two different models, the covalent[4] and the ionic,[3] that one may employ to calculate the total number of valence electrons in an organometallic molecule. In both cases, the total number of valence electrons is arrived at by considering the electron contributions from the metals and the ligands with the two approaches differing in the manner in which they assign the origin of the electrons. Since the total number of valence electrons in an organometallic complex is independent of the technique used to count them, both methods will necessarily lead to the same result. The covalent model will be used in this work because of the simplicity of its approach.

In the covalent model, both the metal atoms and the ligands are assumed to be neutral. Thus, the number of electrons contributed by the metal will be equal to the number of d electrons formally consistent with its zero oxidation state, i.e., the number of d electrons equals its group number.[4] Ligands commonly encountered in organo-transition metal chemistry can donate anywhere from zero to eight electrons and the electron counts for some frequently used ligands are shown in Table 1.[4]

Table 1: Covalent Model Ligand Electron Counts.

| Ligand | Number of electrons donated |
|---|---|
| $BH_3$, O(oxide) | 0 |
| Halides, Alkyl and Aryl groups, H, $R_3Sn$, SCN, $NO_2$, $NO_3$ | 1 |
| CO, $NR_3$, $C_2H_2$, $PR_3$, $AsR_3$, RCN, RNC, $R_2O$, $R_2S$ | 2 |
| $\eta^3$-$C_3H_5$ (allyl), NO, $RN_2$ | 3 |
| $\eta^4$-$C_4H_4$ (cyclobutadiene), $\eta^4$-$C_4H_6$ (butadiene) | 4 |
| $\eta^5$-$C_5H_5$ (cyclopentadienyl), $\eta^5$-$C_9H_7$ (indenyl) | 5 |
| $\eta^6$-$C_6H_6$ (benzene), $\eta^6$-$C_7H_8$ (cycloheptatriene) | 6 |
| $\eta^7$-$C_7H_7$ (cycloheptratrienyl) | 7 |
| $\eta^8$-$C_8H_8$ (cyclooctatetrene) | 8 |

To arrive at the number of valence electrons in a molecule, the total number of electrons donated by all of the ligands is added to the number of electrons in the neutral metal atom.[4] The following two examples illustrate this method and also lead to the expected EAN electron count. Because they are the same value, one would correctly conclude that they would be stable molecules.

| $Cp_2Co^+$ | |
|---|---|
| Co(0) | 9e⁻ |
| 2 x $C_5H_5$ | 10e⁻ |
| +ve charge | <u>-1e⁻</u> |
| | 18e⁻ |
| EAN count | 18e⁻ |

| $Mn_2(CO)_{10}$ | |
|---|---|
| 2 x Mn(0) | 14e⁻ |
| 10 x CO | <u>20e⁻</u> |
| | 34e⁻ |
| EAN count | 34e⁻ |

Stable metal clusters tend to have the maximum number of metal-metal bonds possible because the individual fragments that make up the clusters are electron deficient.[1] In this way, the available electrons are allowed to be spread out over the entire cluster so that the system is delocalized. By counting the total number of valence electrons and also by knowing the number of metal atoms present, the number of metal-metal bonds that are present in a polymetallic complex can be predicted.[3] The assumption is made that the cluster obeys the EAN Rule (each metal in the cluster will have an 18e′ configuration) and that a metal-metal bond is a shared pair of electrons which makes a contribution of 1e′ to the 18e′ configuration of both metals.[3] The number of formal metal-metal bonds, B, is calculated as

$$B = (18M - N) \div 2$$

This equation is of course just a simple variation of the EAN equation given previously, where M is the number of metals and N is the total valence electron count.[3] This time, however, we have assumed the structure obeys the EAN rule, i.e., N = EAN electron count, and are trying to deduce the number of bonds whereas before the reverse was true. An example of the bond-determining approach is given below.

$Os_3(CO)_{12}$
$M = 3$,
$N = (3 \times 8) + (12 \times 2) = 48$
Predict $B = (54 - 48) \div 2 = 3$
Structure that will allow three metal-metal bonds is triangular
Structure observed[5] is triangular with three metal-metal bonds

Once the nuclearity of the clusters has reached more than 5 or 6 metals, using the EAN Rule to predict which molecules and structures are stable is no longer adequate. At this point, larger molecules are known to exist which do not obey the EAN Rule because the systems are too complex to be adequately described in terms of localized bonds. Fortunately, there is a method of counting electrons for these non-EAN clusters that does allow the stabilities and geometries of the higher nuclearity clusters to be accurately predicted. It is known as the Polyhedral Skeletal Electron Pair Theory or more commonly Wade's Rules.[6,7]

Wade's Rules were originally developed for use with borane ($B_nH_n^{2-}$) and carborane clusters. When applied to one of these clusters, the rules allow the shape of the cluster to be predicted solely on the basis of its skeletal electron count. The main features, or requirements, of Wade's rules are summarized into seven basic statements as follows.[7]

1. The structures of boranes and carboranes are based on triangular-faced polyhedra (see Figure 2).
2. All, all but one, or all but two of the vertices of the appropriate polyhedron are occupied by the skeletal boron or carbon atoms in *closo* (closed), *nido* (nest-like) and *arachno* (cobweb-like) compounds, respectively.

3. Each skeletal boron or carbon atom has a singly-bonded ligand (i.e., a hydrogen atom) terminally attached to it, by a bond radiating outward (exo) away from the centre of the polyhedron; one pair of electrons is allocated to this bond.
4. The remaining valence shell electrons ($b$ pairs) are regarded as skeletal electron bond pairs.
5. Each skeletal boron or carbon is considered to provide three AO's (atomic orbitals) for skeletal bonding.
6. The polyhedra possess symmetries such that ($n$+1) skeletal bonding MO's (molecular orbitals) are generated from these AO's, where $n$ = the number of polyhedron vertices [$n = (b-1)$]
7. Compounds with $a$ skeletal atoms and $b$ skeletal electron bond pairs adopt *closo* structures if $b = (a+1)$, *nido* structures if $b = (a+2)$, and *arachno* structures if $b = (a+3)$.

This structure prediction method is not limited solely to clusters that have boron or carbon as their skeletal atoms. Wade[7] and Mingos[8] have shown that it is possible to extend it to other main group, transition metal and mixed metal clusters by employing some simple skeletal electron counting procedures.

The main requirement[7] for these "borane analogue" clusters (in which the individual cluster atoms attain an inert gas configuration) is that each skeletal atom provides three AO's for cluster bonding. Any remaining valence shell orbital(s) on that atom are to be used for ligand bonding. Three valence shell atomic orbitals are available for a main group element E, such as carbon, provided it uses its one remaining AO either to bond a ligand or to accommodate a lone pair of electrons. The number of electrons that the atom E or the group EL supplies for skeletal bonding will be (v + x - 2) where v = # of electrons in the valence shell of the cluster atom E (its group number) and x = the number of

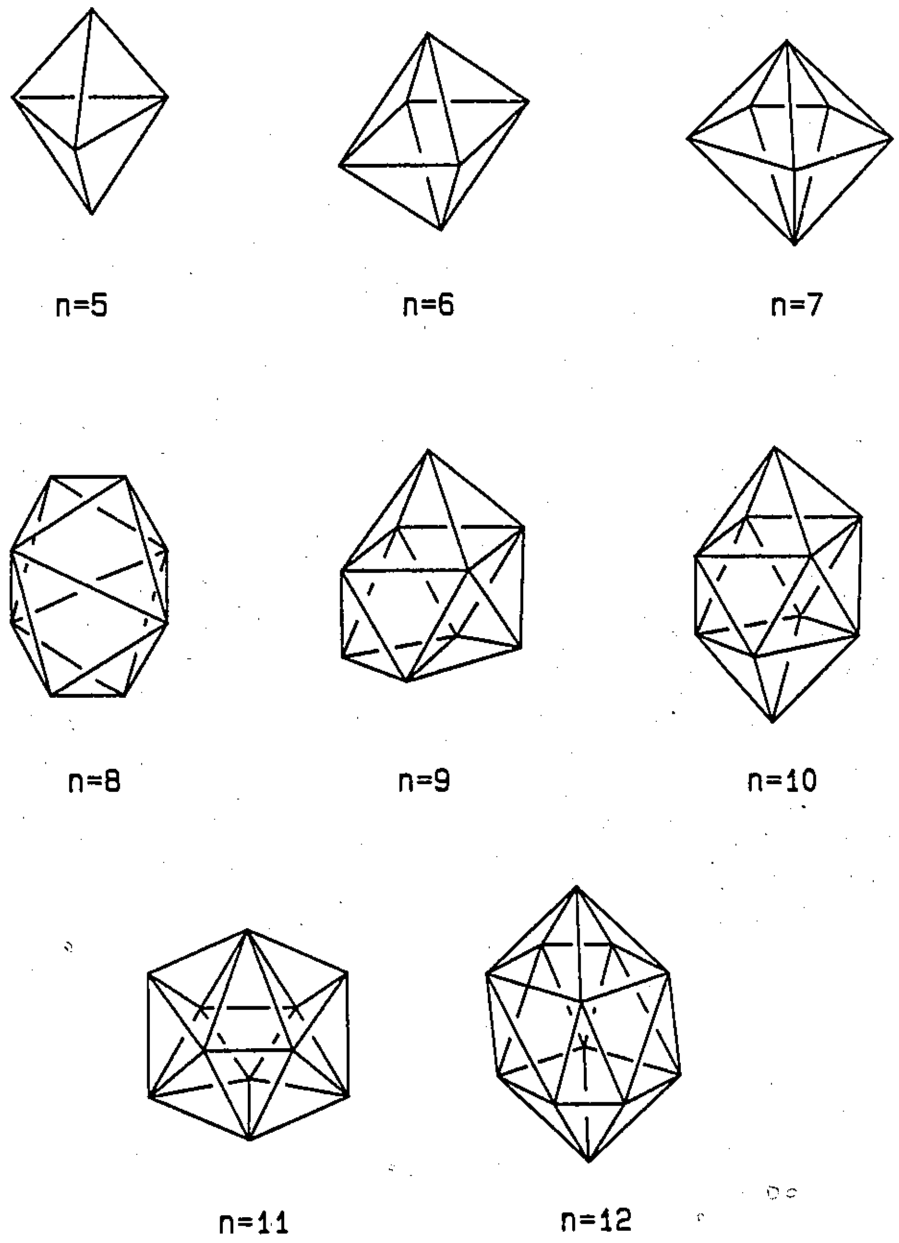


**Figure 2:** Geometries of *closo* polyhedra having 5 to 12 vertices

electrons supplied by the ligand L.[7] By virtue of the five additional orbitals in its valence shell, a transition metal M can necessarily accommodate more ligands than a main group element and it will supply (v + x - 12) electrons for cluster bonding.[7] This time x is taken to be the total number of electrons supplied by all of the ligands on the metal M.

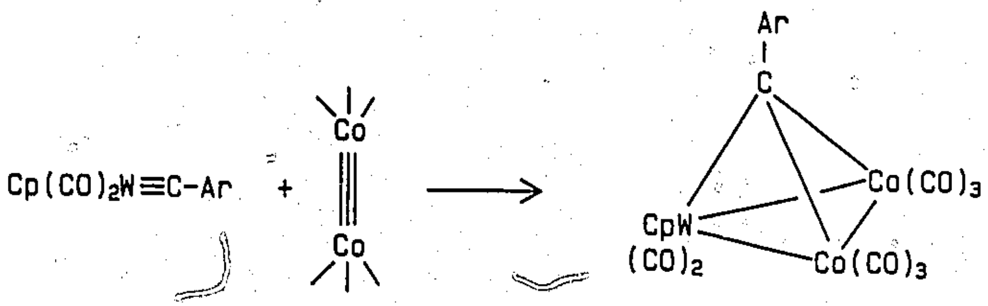
Essentially, the number of skeletal electron bond pairs (*b*) for any cluster can be obtained[6,7] by adding the number of skeletal atom valence shell and ligand electrons, subtracting two for each main group and twelve for each transition metal skeletal atom in the cluster, and then dividing by two. In the higher nuclearity clusters where the predictions of the EAN rule and Wade's rules are different, it is normal for the Wade's Rule structure to be the one actually observed.

For example, consider the known pseudo-octahedral cobalt-alkyne complex $Co_4(CO)_{10}C_2Et_2$.[9] The total number of valence electrons in the cluster is calculated to be (36+20+8+2)=66. The EAN count for this cluster, assuming there 12 Co-Co or Co-C bonds, is (4x18+2x8)-(2x12)=64 skeletal electrons (note that the octet rule is applied to main group atoms (if they are present) in the EAN calculation). Thus, by the EAN rule, the complex would be predicted to have one extra pair of electrons in order for it to have a stable octahedral geometry. On the other hand, Wade's approach would arrive at a cluster containing [66-(4x12)-(2x2)]÷2=7 skeletal electron bond pairs. Since the number of bond pairs is one greater than the number of skeletal atoms, Wade accurately predicts that the cluster would be found in its *closo* pseudo-octahedral form.

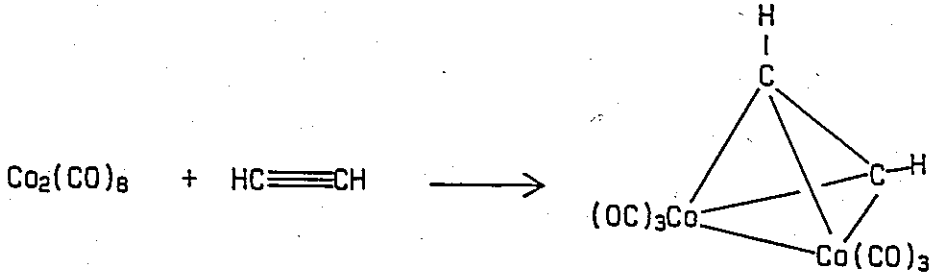
### *1.2 Synthetic Routes To Alkynyl And Carbynyl Clusters*

The syntheses of organometallic clusters have progressed a long way from the early days in which many were formed by serendipitous methods. There are now a large number of well-known and established methods for synthesizing a wide variety of clusters, including the class of organo-transition metal clusters which contain either alkynyl or carbynyl moieties.[10,11]

One of the routes to this type of cluster involves the addition of a metal-metal bond to either a metal-carbon multiple bond or a carbon-carbon multiple bond. Stone has used this reaction with a considerable deal of success in his work on trimetallic mixed metal alkylidyne clusters.[12]

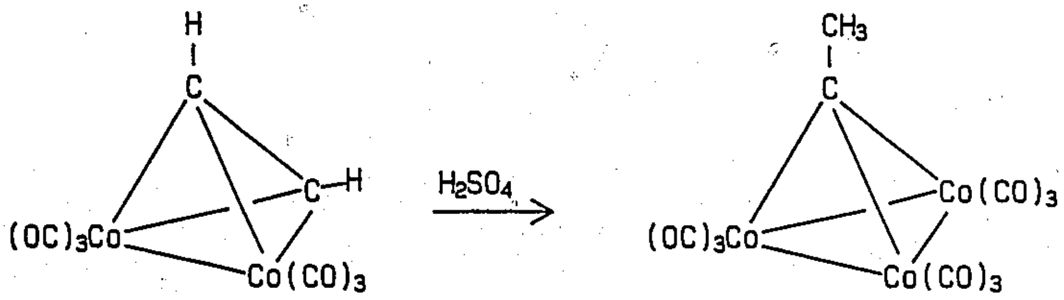


This synthetic approach is of particular relevance to this work because it is the best general method for generating tetrahedral dicobalt μ-alkyne clusters. Other routes to these species do exist,[13] but they lack the simplicity of this technique. By simply adding an alkyne, such as acetylene, to $Co_2(CO)_8$ in a suitable solvent it is possible to form the bimetallic cluster **1** quite readily.[14]



1

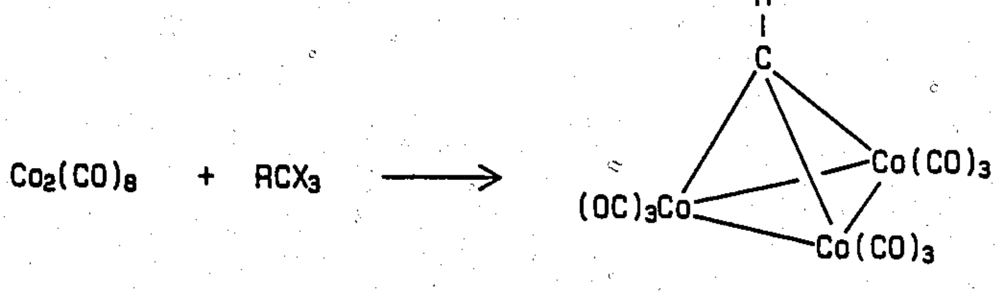
These dicobalt μ-alkyne clusters are themselves very useful starting materials for making other clusters. In fact, one of them was used to generate the first tricobalt alkylidyne cluster. It was discovered that the protonation of (μ-acetylene)hexacarbonyldicobalt, **1**, resulted in the formation of the tricobalt cluster bearing a methyl group as its apical substituent,[15] viz., **2**.



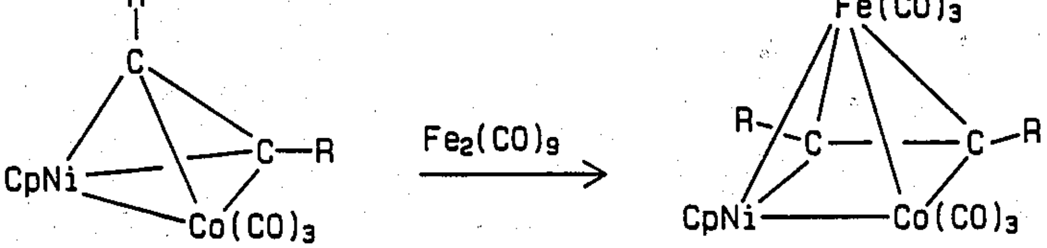
1 2

It was later established that this was actually a general route to tricobalt nonacarbonyl clusters provided the alkyne ligand in the dicobalt cluster had at least one terminally bonded hydrogen. Unfortunately, there is a drawback in that the tricobalt cluster generated will always have a $CH_2$ group in the α-position and this severely limits the type and number of clusters that can be made by using this method.

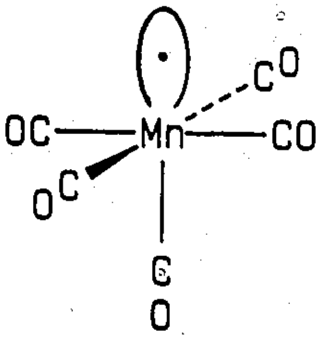
A more useful and general approach for synthesizing these organo-tricobalt clusters involves the reaction of an organic fragment containing an α,α,α-trihalo group with $Co_2(CO)_8$. By using this technique, clusters containing a wide variety of apical substitutents can be formed.[16,17] In addition to halogen, alkyl and aryl groups, it is possible to introduce substituents which have reactive functional groups present, e.g., esters. It has also been shown that, in some instances, organic reagents containing dihalomethyl groups will react with dicobalt octacarbonyl to give an alkylidyne cluster.

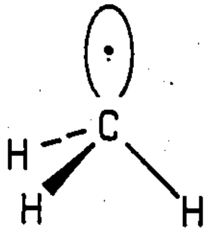


The bi- and trimetallic clusters exemplified above all adopt tetrahedral geometries; this can be very easily rationalized by using either the EAN or Wade's rules. However, by using the latter approach, a "40 electron" bimetallic μ-alkyne cluster can be thought of as having 6 skeletal electron bond pairs for its four vertices. Thus, it would be predicted that it would have a *nido* structure based on the five vertex trigonal bipyramid polyhedron, which is of course the tetrahedron. Because these *nido* clusters formally have a empty vertex, and thus are considered to be co-ordinatively unsaturated, it should be possible to introduce a metal fragment that acts as a net donor of zero cluster skeletal electrons into the cluster to generate a *closo* trigonal bipyramid cluster with five vertices and 6 skeletal electron bond pairs. Likewise, the addition of a metal fragment which "donates" one pair of skeletal bonding electrons should result in a *nido* octahedral cluster with seven bond pairs and five skeletal atoms. This was recognized by Jaouen and co-workers who successfully synthesized a series of square-based pyramidal trimetallic clusters from appropriate bimetallic μ-alkyne clusters and metal fragments.[18]



Another theoretical idea which has been applied successfully to the synthesis of clusters is the concept of isolobality.[19] This idea was initially advanced by Roald Hoffmann for use in comparing molecular fragments with one another and with organic moieties. Hoffmann defines two fragments as being isolobal if "the number, symmetry properties, approximate energy and shape of the frontier orbitals and number of electrons in them are similar."[3] An example of an isolobal relationship is found when the frontier orbitals of $CH_3^{\cdot}$ and $^{\cdot}Mn(CO)_5$ are examined.[3] They are isolobal because each of them has a single frontier orbital of $a_1$ symmetry containing a single electron.



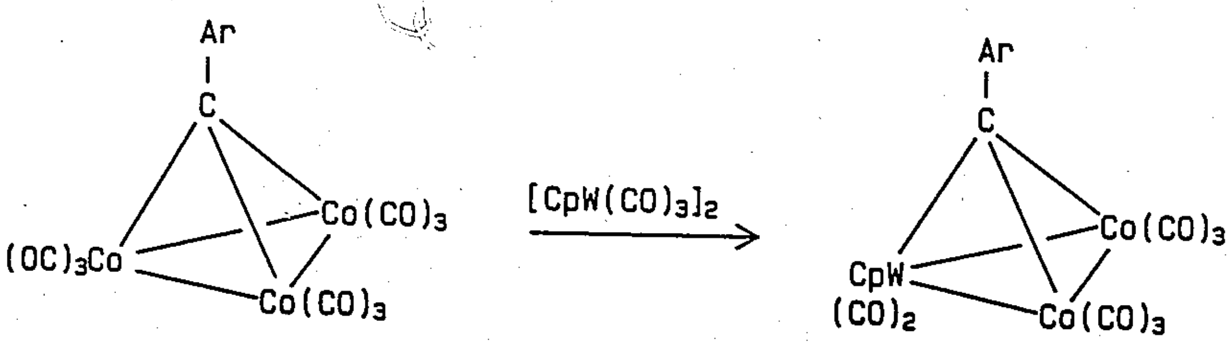


Additionally, it is clear that by adding an electron to both species the $[Mn(CO)_5]^-$ and $CH_3^-$ that are formed will also be isolobal. By definition, species which are isoelectronic are isolobal, therefore, $[Mn(CO)_5]^-$ is isolobal with $Fe(CO)_5$ which in turn must be isolobal with $CH_3^-$. In a similar fashion, the methylidyne group CH is isolobal to the metal fragment $Co(CO)_3$; both have three frontier orbitals containing three electrons available for bonding.[3] The analogous structural behaviour expected for these two latter fragments can be observed by comparing the tetrahedral geometries adopted by (μ-alkyne)hexacarbonyldicobalt and (μ-carbyne)-tricobaltnonacarbonyl (alkylidyne) clusters. The isolobal relationships that exist between some organic and inorganic fragments are shown in Table 2.[3] (Note that adding or subtracting a proton from the hydrocarbon fragments results in a new hydrocarbon fragment which is isolobal with the original one.)[3]

Table 2: Isolobal Relationships Among Organic and Metal Fragments.

| | | | | | |
|---|---|---|---|---|---|
| Neutral hydrocarbon fragment | $CH_4$ | $CH_3$ | $CH_2$ | CH | C |
| Charged hydrocarbon fragment (± $H^+$) | $CH_3^-$ | $CH_2^-$ | $CH^-$<br>$CH_3^+$ | $CH_2^+$ | $CH^+$ |
| Common transition metal fragment (1st series) | $Cr(CO)_6$<br>$Fe(CO)_5$<br>$Ni(CO)_4$ | $Mn(CO)_5$<br>$CpFe(CO)_2$<br>$Co(CO)_4$ | $Cr(CO)_5$<br>$Fe(CO)_4$<br>CpCo(CO)<br>$Ni(CO)_3$<br>CpCu | $CpCr(CO)_2$<br>$Mn(CO)_4$<br>CpFe(CO)<br>$Co(CO)_3$<br>CpNi | $Cr(CO)_4$<br>CpMn(CO)<br>$Fe(CO)_3$<br>CpCo |

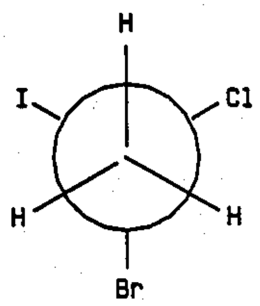
Based on these isolobal relationships, a number of groups[20-22] have carried out the syntheses of a wide variety of clusters. They correctly reasoned that the substitution of one metal vertex in an existing cluster by a different isolobal metal fragment should give a new cluster in good yield. An example of this approach is shown below in which a heterometallic cluster is generated from a homometallic compound.



Once these and other synthetic routes to this class of clusters became established, researchers began to move away from simply generating new clusters for their own sake and started to investigate the clusters themselves. Of particular interest to our group has been the use of Nuclear Magnetic Resonance (NMR) Spectroscopy as a tool to determine not only the structures, but also the mechanisms of rearrangement of metal clusters containing carbynyl or alkynyl moieties.

### *1.3 NMR Spectroscopy as a Probe for Structure and Mechanism*

Since a great deal of the work that will be discussed involves molecules lacking an improper axis of symmetry, viz., chiral clusters, it is perhaps worthwhile to remind ourselves about the phenomenon of diastereotopic nuclei. As is well known, all magnetically active nuclei in a molecule of $C_1$ symmetry are in different environments and should thus resonate at different frequencies. However, if there exists a particular molecular rotation or rearrangement pathway which interconverts two or more nuclei then this magnetic non-equivalence will be lost at some appropriate temperature dependent upon the activation energy barrier which must be overcome. As a trivial example we note that the methyl protons in the chiral ethane **3** are, in principle, magnetically different. However, it is readily apparent that simple rotation about the carbon-carbon bond axis brings all three methyl protons successively into identical positions. If one were to examine the $^1$H NMR spectrum of this molecule a single resonance would be observed for all three protons. In contrast, by substituting one of the hydrogens by another atom or group, as in **4**, the two remaining protons would be rendered permanently different regardless of the rate of rotation about the carbon-carbon axis. The $^1$H NMR spectrum of this molecule would consist of two signals, one for each of the so-called "diastereotopic nuclei". In this particular molecule, the diastereotopic hydrogens can only be equilibrated by inverting the chirality at the other carbon centre to give **5**, as shown.



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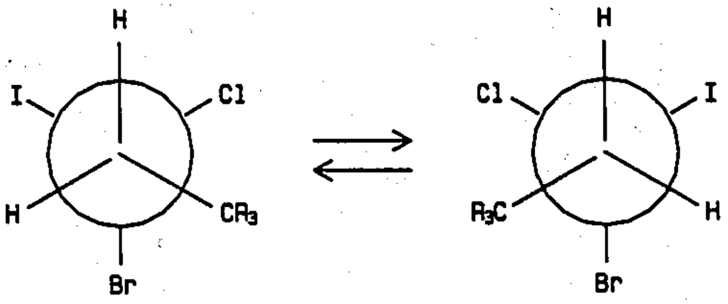
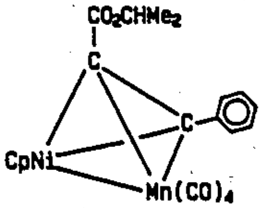


4

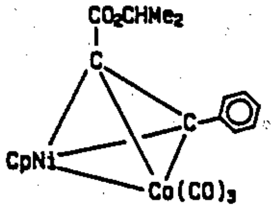
5

### *1.3.1 Alkyne-dimetallic tetrahedral clusters*

Over the last decade numerous clusters have been prepared, the chirality of which depended not merely on the use of mixed metal systems, such as **6** and **7**, but also by incorporating ligands which lowered molecular symmetry. Nevertheless, it became apparent to McGlinchey and his co-workers that several classes of clusters which would have appeared to be chiral were in fact undergoing intramolecular rearrangements which brought about loss of stereochemical integrity on the NMR time-scale.[23]

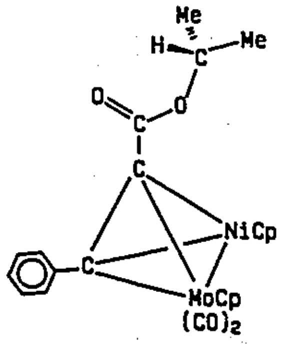


**6**

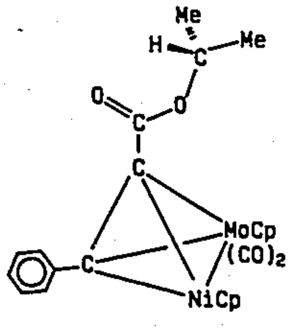


**7**

To investigate this, it was necessary for the authors to build an NMR active probe into the systems in order to ascertain the configurational stability of the molecules. In practice, a convenient probe is the isopropyl group which provides two potentially diastereotopic methyl resonances (in either $^{1}H$ or $^{13}C$ NMR spectroscopy) and we see this moiety was used in the bimetallic μ-alkyne tetrahedral clusters **8a** and **8b**.

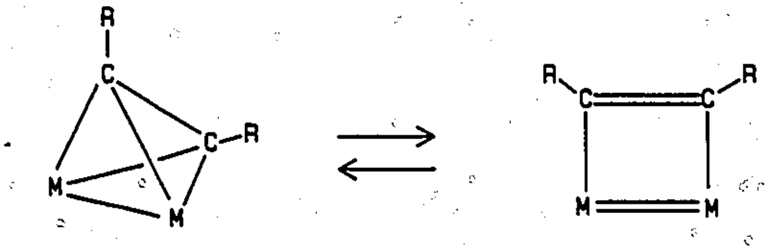


8a



8b

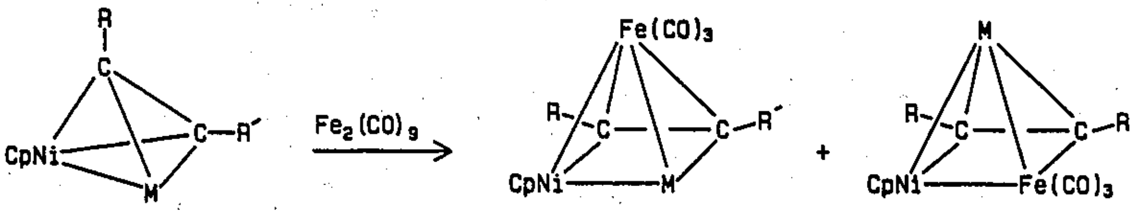
These clusters fulfill the criteria for chirality in that they are made up of four chemically different fragments arranged in a tetrahedral geometry. In principle, it should have been possible to resolve the two enantiomers but in practice they resisted all attempts by the authors. Subsequently, it was shown that although the two isopropyl methyls were indeed non-equivalent at room temperature, the NMR peaks coalesced at elevated temperatures which suggested that the molecule could racemize with a barrier that exceeded 20 kcal/mol.[24] One possible intramolecular mechanism for the racemization involves the following tetrahedral ⇌ square planar interconversion.[25]



This particular system illustrates some of the potential problems which may arise in investigations such as these. First of all, one must be certain that the coalescence phenomenon observed is not merely attributable to a temperature-dependent change in chemical shift. This was accomplished by recording the spectrum at temperatures below that required to see the limiting spectrum and then extrapolating any observed temperature dependence to higher temperatures. Secondly, when the proton spectrum of **8** was initially measured on a low field instrument only a single methyl environment was observed at any temperature which could have led them to suppose that the racemization was occurring rapidly on the NMR time-scale. In fact, it turned out that the chemical shift difference between the diastereotopic methyls was rather small in this system and it only became apparent on a high field (400 MHz) instrument. One drawback that was encountered in using the high field instrument to separate the methyl resonances was the consequence that the sample had to be heated to close to its decomposition point to bring about peak coalescence. This raised the possibility that alkyne dissociation, and not the postulated mechanism, was actually responsible for the racemization. Fortunately, in this particular case no exchange with added free alkyne was observed under the reaction conditions but clearly it is necessary to take such precautions to test for other plausible mechanisms.

### *1.3.2 Alkyne-trimetallic square pyramidal clusters*

As alluded to earlier, treatment of tetrahedral clusters of the form (RC≡CR)(CpNi)M, where M = Co(CO)$_3$, CpMo(CO)$_2$ or CpNi, with Fe$_2$(CO)$_9$ leads to cluster expansion, as exemplified below.[18] When the alkyne is unsymmetrical, as in Ph-C≡C-CO$_2$CHMe$_2$, the cluster that is formed is chiral even if the two original metal vertices were identical. The chiral nature of the system was readily detectable by use of the diastereotopic methyl groups on the isopropyl functionality.



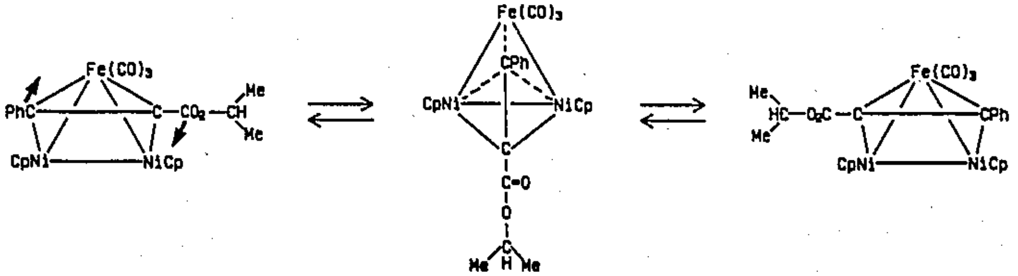
7 M = Co(CO)$_3$
8 M = CpMo(CO)$_2$
9 M = CpNi

10 M = Co(CO)$_3$
12 M = CpNi

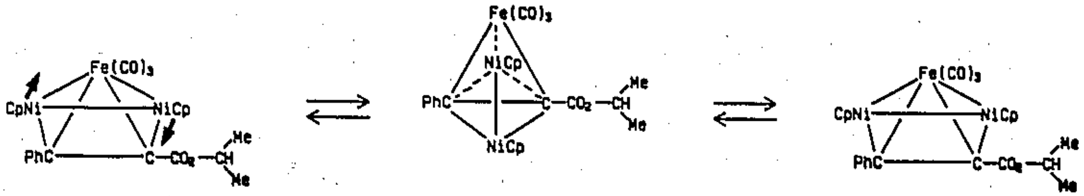
11 M = CpMo(CO)$_2$

One concern which is commonly raised regarding such sytems should be clarified at this time. It is true that the system being dealt with is a 50:50 mixture of enantiomers, that is a racemic system in which each enantiomer gives rise to the same spectrum (assuming that one is using an achiral solvent). However, the NMR experiment detects the chirality of each molecule individually; this situation is quite different from chiroptical measurements which detect, for example, the rotation of a plane polarized light beam by the entire sample. Since both enantiomers are present in equivalent amounts there would not be a rotation measurable by using a polarimeter. However, each individual chiral molecule, 100% of the sample in this case, will exhibit different resonances for diastereotopic pairs of nuclei unless there is a process which interconverts the enantiomers readily on the NMR time-scale.[26]

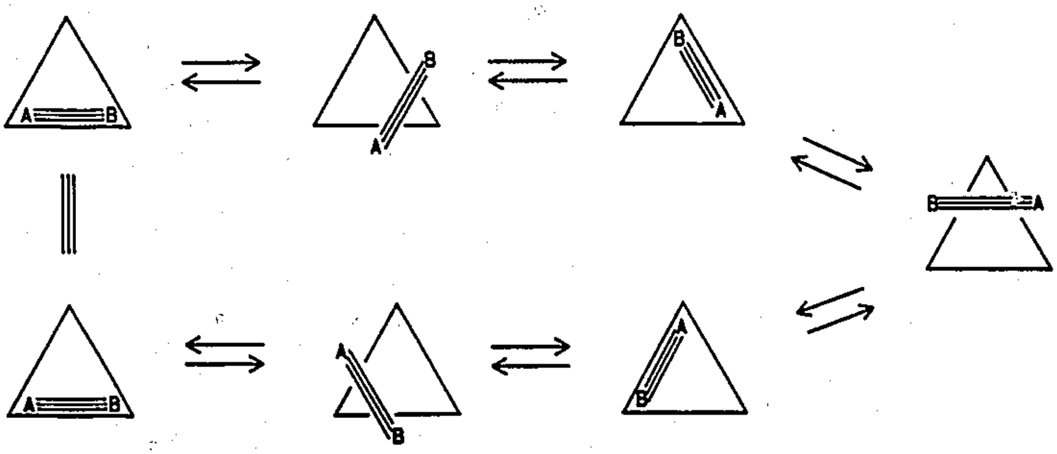
In the $Ni_2Fe$ complex, **12**, the room temperature $^1H$ NMR spectrum revealed a single cyclopentadienyl peak and a simple doublet for the isopropyl methyls.[27] In contrast, at low temperature, Mlekuz observed two equally intense cyclopentadienyl resonances and a pair of methyl peaks (each split by the unique isopropyl hydrogen to give a doublet). Clearly, there must have been a racemization process occurring which brought about interconversion not only of the diastereotopic methyl groups but also of the CpNi environments. For a triosmium cluster $HOs_3(C_6H_4)(PMe_2)(CO)_9$ which exhibited similar behaviour,[28] it was suggested there might be a rotation of the benzyne moiety relative to the metal triangle. When this idea was applied to the $Ni_2Fe$ cluster it was possible to visualize a process, shown in Scheme 1,[27] whereby the acetylene ligand rotated so as to generate an intermediate possessing a molecular mirror plane which would equilibrate not only the methyls but also the cyclopentadienyl rings.



**Scheme 1:** Racemization via rotation of the alkyne R-C≡C-R.



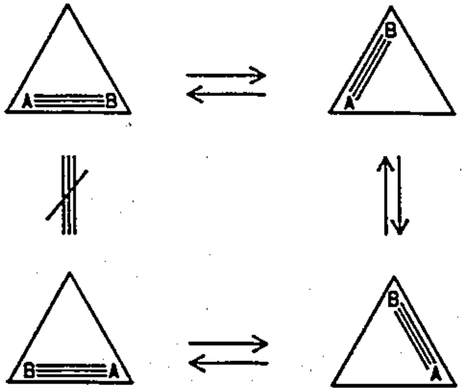
**Scheme 2:** Rotation of the pseudo-alkyne CpNi≡NiCp.



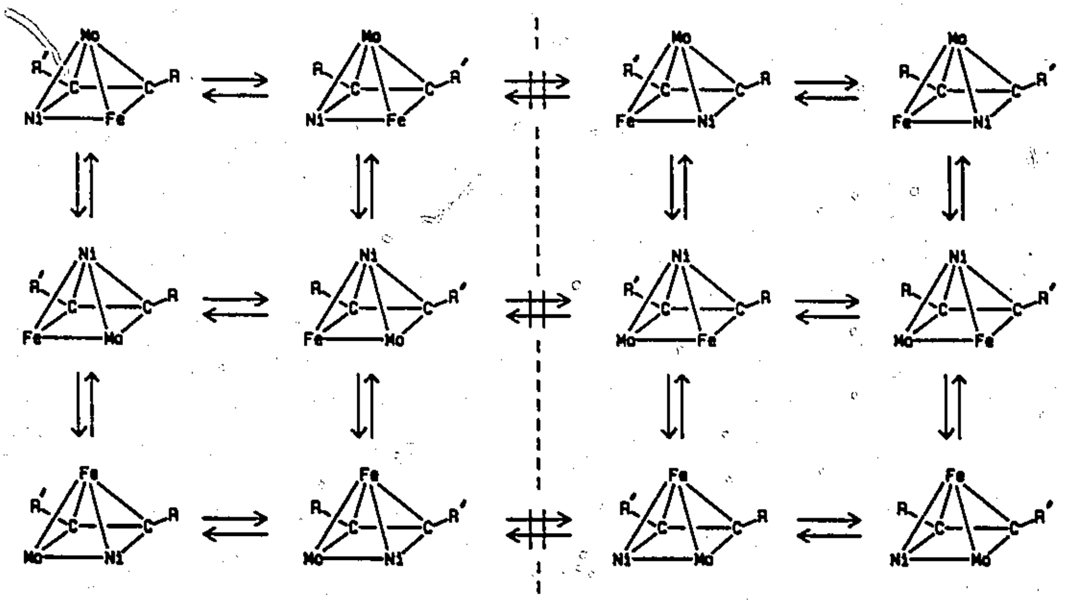
**Scheme 3:** Migration of an alkyne about the molecular periphery does not racemize the cluster.

It was also necessary to consider the possible existence of another process, that was the independent rotation of the CpNi-NiCp unit relative to the $FeC_2$ triangular face, as illustrated in Scheme 2.[27] The CpNi moiety is isolobal with a CH unit[19] thus making the $Cp_2Ni_2$ fragment a pseudo-alkyne. If such a process were to occur then it would be possible to interconvert the nickel vertices without racemizing the cluster; if this were the case, the isopropyl methyls would retain their diastereotopic nature. However, the activation energy barriers to methyl interconversion and cyclopentadienyl exchange were found to be the same within experimental error, ≈ 15 kcal/mol. Hence, only the single process shown in Scheme 1 needed to be invoked and the evidence thus favoured a process involving formal alkyne rotation relative to the trimetallic plane.[27] It was pointed out that such a rotation could not be a simple circumambulation of the alkyne around the periphery of the triangle (Scheme 3)[27] since the net result of such a rearrangement was the regeneration of the same enantiomer; instead, as had been suggested by Schilling and Hoffmann,[29] the alkyne would have to execute a more intricate series of manoeuvres (Scheme 4)[27] rather in the manner of a molecular windshield wiper.

The above mechanistic arguments[27] all assumed that the rearrangement pathway was entirely intramolecular, but an intermolecular process whereby the alkyne became detached



**Scheme 4:** "Windshield wiper" motion of an unsymmetrical alkyne leading to racemization of the cluster.

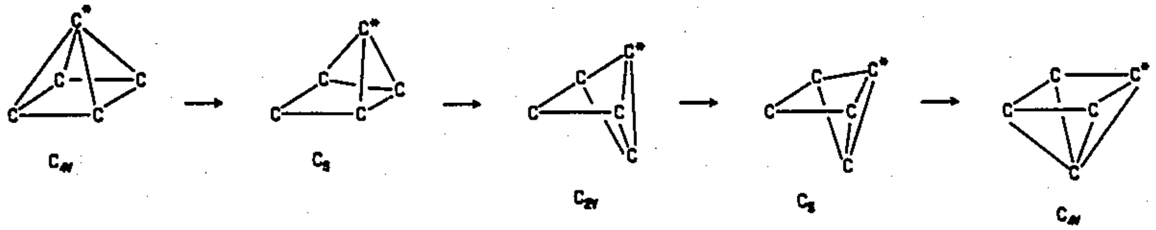


**Scheme 5:** Alkyne rotation on one face of a cluster showing interconversion of diastereomers but not of enantiomers.

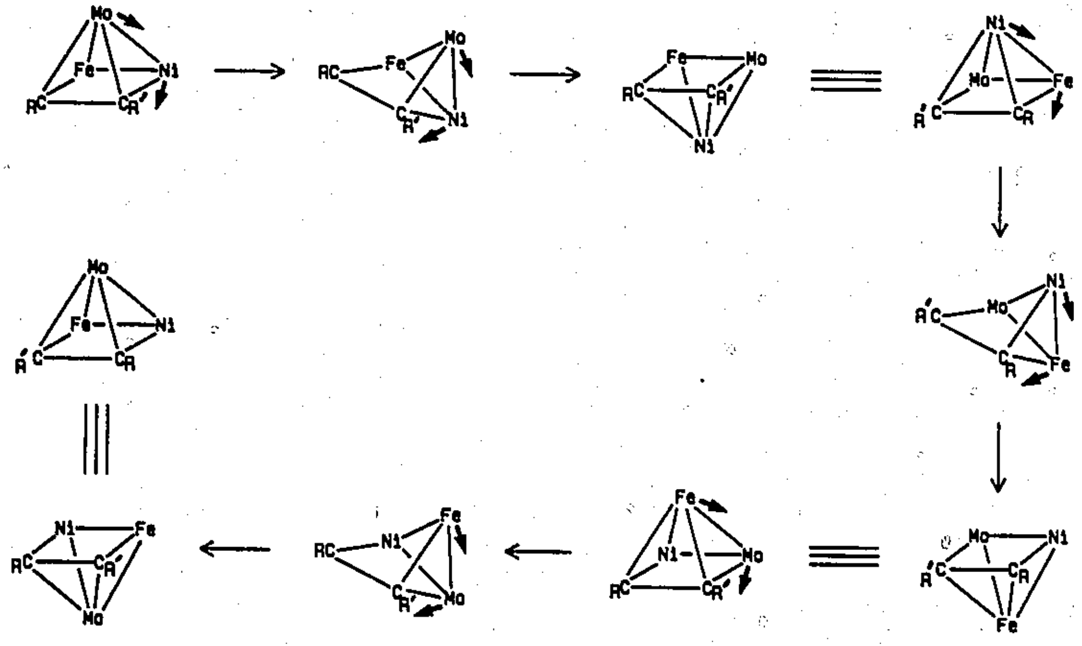
from the metal triangle could also be easily imagined. In order to verify the intramolecular nature of the process, clusters containing three different organometallic vertices were constructed and examined by the authors.[27] In such molecules, alkyne rotation would interconvert diastereomers rather than enantiomers, as shown in Scheme 5.[27] Thus, at the low temperature limit, each diastereomer should generate a pair of diastereotopic methyl doublets, but at high temperature one should observe only one pair of doublets attributable to a single isopropyl group still in a chiral environment.

In contrast, if the rearrangement were to proceed via an intermolecular decomposition pathway, then the alkyne would become free; such a process would not only equilibrate the CpNi vertices in **12** but also the isopropyl methyls in the liberated alkyne would become equivalent and hence exhibit a simple methyl doublet. The low temperature spectrum of **11** showed two pairs of methyl doublets (indicating the existence of two diastereomers) while at high temperature these peaks coalesced to give a single pair of methyl doublets (proving the chirality of the system was retained). These observations provided convincing evidence of the intramolecular nature of the rearrangement pathway. Furthermore, since the barrier to the interconversion of the trimetallic diastereomers of **11** was very similar to that for the racemization of the enantiomers **12**, it was concluded that the same rearrangement mechanism was operative in both. These experiments demonstrate the importance of incorporating multiple and independent probes for rearrangement processes to see whether they yield mechanistic results which are in agreement or which are mutually exclusive. Fortunately for the investigators, in the systems discussed above, the $^1$H and $^{13}$C NMR data on both the isopropyl and (cyclopentadienyl)nickel moieties reinforced one another.

A very insightful comment was made regarding the bonding in the five-vertex square-pyramidal clusters.[27] Originally classified as $\sigma$, $\pi$-acetylene complexes, these molecules are now more profitably viewed as *nido* octahedral clusters analogous to $B_5H_9$, according to Wade's rules. When the isolobal analogy of Hoffmann was followed to its logical conclusion, it was possible to relate the square-pyramidal $M_3C_2$ clusters to the carbocationic cluster $C_5H_5^+$, the molecular dynamics of which had been the subject of a theoretical calculation at the extended Hückel level.[30] These calculations revealed that in the interconversion of the various $C_{4v}$ isomers, the intermediacy of a $D_{3h}$ *closo* trigonal bipyramidal structure is strongly disfavoured. Instead, the lowest energy pathway (Scheme 6) involved the sequence $C_{4v}$-$C_s$-$C_{2v}$-$C_s$-$C_{4v}$, and Scheme 7 shows how such a rearrangement pathway could be applied to the $M_3C_2$ system.[27] The overall transformation is identical to that resulting from the



Scheme 6: Scrambling Mechanism for $[C_5H_5]^+$.



Scheme 7: Rearrangement mechanism for the $M_3C_2$ cluster analogous to that for the $[C_5H_5]^+$ system.

"windshield wiper" mechanism described above; that is, there is interconversion of diastereomers in **11** but not of enantiomers. In addition, the mechanistic proposals put forward by the authors are in complete accord with NMR data obtained for other mixed-metal square-pyramidal clusters.[31, 32]

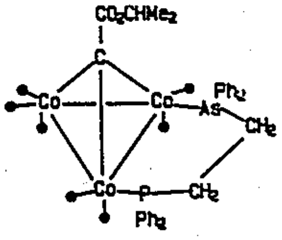
### *1.3.3 Tetrahedral Clusters Containing Arphos*

Although tetrahedral clusters can be rendered chiral by incorporating four chemically different vertices into the molecule, another method is to use an unsymmetrical bidentate ligand to destroy any molecular mirror planes. To achieve this purpose, Sutin et al. selected the ligand $Ph_2P-CH_2-CH_2-AsPh_2$ (arphos), which readily displaces two carbonyls from adjacent metal centres and thus generates a chiral cluster, for their study.[33]

From the X-ray crystal structure of $(arphos)Co_3(CO)_7CCO_2CHMe_2$, **13**, it was revealed that the arphos ligand occupied an equatorial position. However, the $^1H$ and $^{13}C$ NMR spectra of the isopropyl group measured at ambient temperature showed just a single methyl environment implying that the cluster was undergoing racemization on the NMR time-scale. Indeed, at -50°C, the diastereotopic character of the methyl protons was clearly evident and the barrier was evaluated as $\approx 13$ kcal $mol^{-1}$.

Because the racemization process was so much more facile than that described previously for tetrahedral clusters such as **8**, a mechanism that involved the interconversion of the metal vertices themselves was ruled out. The most likely process was proposed to be the migration of the diphenylarsinido terminus of the arphos ligand from one cobalt vertex to another, as depicted in Scheme 8.[33] In accordance with such a proposal, all four protons of the $-CH_2-CH_2-$ chain were distinguishable at low temperature. They were differentiated not only by their proximity to either arsenic or phosphorus but also by their *exo or endo* orientation with respect to the cluster. Upon raising the temperature, however, the *exo* and *endo* positions were interconverted and the protons were now differentiated solely by the identity of their neighbour, viz., P or As. This view was reinforced by the observation that in the corresponding diphos complex $(Ph_2PCH_2CH_2PPh_2)Co_3(CO)_7CCO_2CHMe_2$, **14**, they were able to observe only two methylene resonances (attributable to *exo* and *endo* protons) at all temperatures; hence the cobalt-phosphorus linkages apparently remained intact.

More recently, both of these ligands were incorporated into an existing chiral tricobalt cluster, $Co_3(CO)_9C-CO_2$-menthyl. The bidentate bridged clusters were examined by using $^{31}P$ NMR spectroscopy and the results obtained were found to support the original migration proposal.[34] Two resonances were observed in the $^{31}P$ NMR spectrum of the $(diphos)Co_3(CO)_7CCO_2$menthyl cluster at all temperatures,



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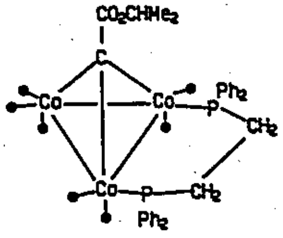

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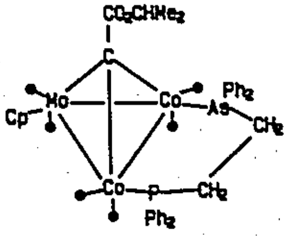

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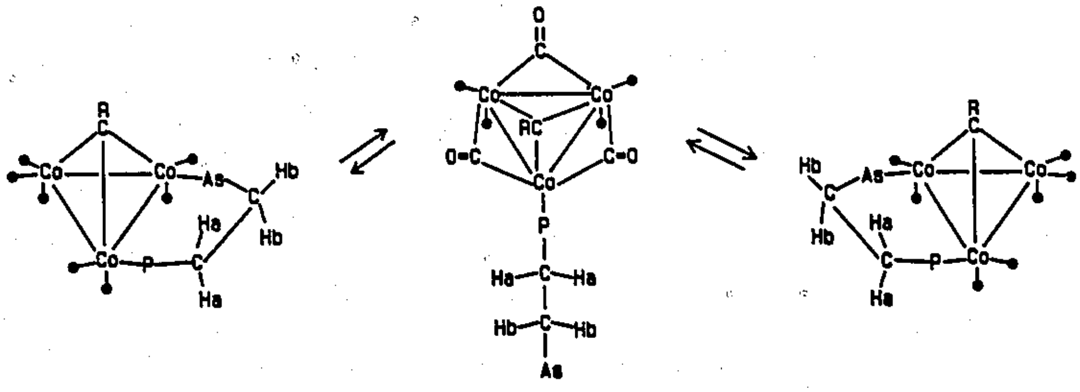
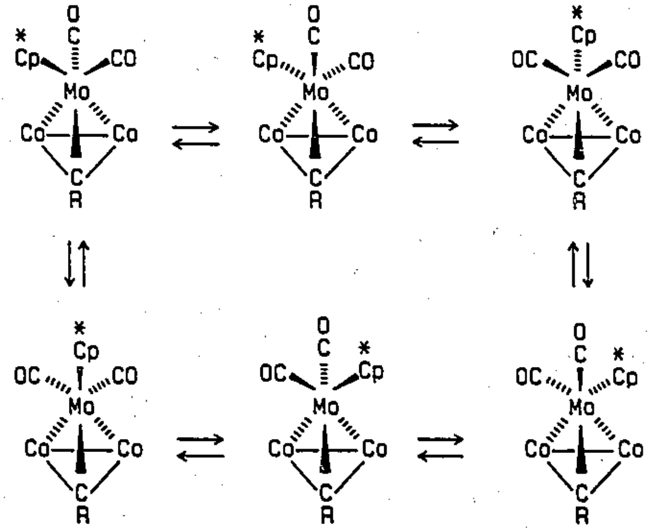


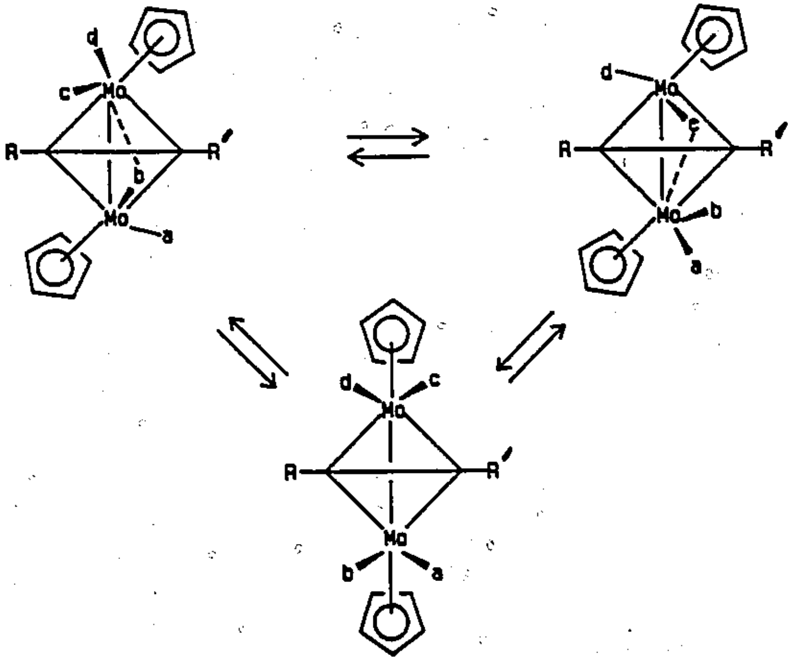
**Scheme 8:** Interconversion of the enantiomers of 13 via arsenic migration.

indicating that no chemical exchange occurred. On the other hand, the rapid interconversion of the two (arphos)$Co_3(CO)_7$-$CCO_2$menthyl diastereomers via migration of the diphenylarsenido terminus from one cobalt to another was clearly evident. In the $^{31}P$ NMR spectra, the two diastereotopic resonances were observed to coalesce into a single peak with a similar activation energy barrier of ≈ 13.1 kcal/mole. It was noted[34] that for migration of arsenic from one cobalt to another to occur there must be concomitant carbonyl migration; however, since exchange of carbonyl ligands between metal centres is usually much faster than cluster racemization the rate determining step was proposed to be the cobalt-arsenic bond-breaking process.

Arphos complexes in which one of the $Co(CO)_3$ vertices has been replaced by a $(C_5Me_5)Mo(CO)_2$ unit, such as **15**, have been found to retain their stereochemical integrity.[33] This was very clearly shown by the diastereotopic nature of the isopropyl methyls of **15** in the $^1H$ NMR even at high temperature. Furthermore, there was a serendipitous bonus in that the isopropyl methyls were further split at low temperature demonstrating the presence of other diastereomers. It has since been shown that these isomers arise because of restricted rotation of the $(C_5Me_5)Mo(CO)_2$ vertex relative to the dicobalt--carbynyl-carbon triangle, as shown in Scheme 9.[35] This idea of restricted rotation will be discussed in more detail later.



Scheme 9: Rotation of a Cp*Mo(CO)$_2$ vertex relative to a Co$_2$C triangular face. Other ligands have been omitted for simplicity.



Scheme 10: Semi-bridging carbonyl exchange process.

### 1.3.4 $^{13}$CO NMR Spectra As Structural Probes

The availability of high field instrumentation, in conjunction with $^{13}$CO isotopic enrichment, allows the use of carbonyl resonances not only to study rearrangement processes but also to elucidate molecular structures. Of course, metal carbonyl spectra have long been measurable[36] but, because of the enormous dispersion provided by high field instruments, it is now feasible to follow the process of ligand migrations occurring with very low activation energy barriers.

### 1.3.5 Dimetalla-tetrahedranes

The reactions of alkynes with metal-metal triple-bonded species provide a good route to dimetalla-tetrahedranes. By using this approach, a series of clusters of the general type $[(C_5Me_xH_{5-x})M(CO)_2]_2[RC{\equiv}CR']$, where M = Mo or W, and x = 0, 1 or 5, were prepared and their variable-temperature NMR spectra recorded.[37,38] Crystallographic data on $[CpMo(CO)_2]_2[RC{\equiv}CR']$, where R = R′ = Ph revealed the presence of a single semi-bridging carbonyl ligand.[37] In accordance with this structure, the low temperature $^{13}$C NMR spectra for this cluster and the analogous R = H, R′ = Ph cluster consisted of three terminal and one semi-bridging carbonyl environments. As would be expected for molecules of $C_1$ symmetry, their two cyclopentadienyl moieties were also magnetically non-equivalent in the low temperature spectra. Upon raising the temperature, the semi-bridging carbonyl was observed to exchange with a terminal carbonyl and the CpMo(CO)$_2$ moiety underwent partial rotation, as depicted in Scheme 10.

This fluxional process had the effect of generating a system of time-averaged $C_{2v}$ symmetry for the symmetrical alkyne and it exhibited only the expected single carbonyl environment and single cyclopentadienyl environment. For the unsymmetrical alkyne this exchange process created a system of time-averaged $C_s$ symmetry and two carbonyl environments (b=d, a=c) and a single cyclopentadienyl environment were observed. The latter result supported the absence of inter-metallic carbonyl ligand scrambling in the proposed mechanism.

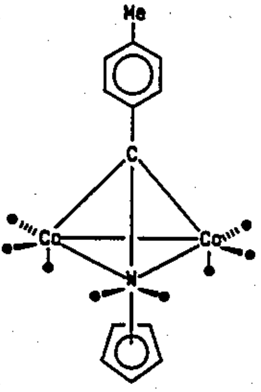
When the analogous variable-temperature $^{13}$C NMR studies were carried out for the series of methyl-substituted (cyclopentadienyl)molybdenum molecules discussed above, it was found that all of the clusters demonstrated this same type of fluxional behaviour.[38] The barrier to carbonyl exchange was calculated to be *ca.* 8 kcal/mol but this was found to increase in proportion to the steric bulk of the substituted cyclopentadienyl group.

However, when the same studies were carried out on the analogous tungsten compounds containing both symmetrical and unsymmetrical alkynes only a single carbonyl resonance and a single cyclopentadienyl environment were observed even when using a 400 MHz instrument at -100°C.[38] Infra-red data on these clusters had indicated the presence of semi-bridging carbonyls on these clusters but the researchers were unable to freeze out the exchange. (Whether or not it is possible to observe a "frozen out" structure is often dependent on the time-scale of the spectroscopic technique used. IR spectroscopy has a time-scale of $10^{-13}$ sec, much shorter than the lifetimes of molecular configurations, thus it will allow the determination of instantaneous structures. NMR spectroscopy, on the other hand, has a time-scale ($10^{-1}$ to $10^{-9}$ sec) which is comparable to those for molecular structures; therefore, individual configurations may not be observed in all cases.[39]) It was assumed that the tungsten carbonyl chemical shift differences would be comparable to those on molybdenum; therefore, it was not clear why the barrier to exchange in the tungsten clusters was considerably lower than in the molybdenum complexes. The tungsten clusters also appeared to undergo the additional carbonyl ligand scrambling process not seen for the molybdenum clusters. Interestingly, it has been demonstrated that carbonyl fluxionality in these tungsten molecules can be stopped on the NMR time-scale when the cyclopentadienyl rings bear extremely bulky phenyl substituents, although once again the reason is not obvious.[40]

### *1.3.6 Trimetallic tetrahedranes*

There now exist many examples of mixed metal tetrahedral clusters containing three organometallic vertices and a capping carbynyl fragment. The two most widely used routes to these clusters involve either interaction of a metal-metal triple bonded unit with a metal carbyne complex or the isolobal substitution of one organometallic vertex for another in a readily available precursor, as shown before.[12,20]

The first two X-ray crystal structures of such clusters, **16** and **17**, were almost identical and showed the cyclopentadienyl ring was positioned below the trimetallic plane and distal with respect to the capping aryl-carbynyl unit. The $^{13}C$ NMR spectrum of these molecules at -50°C showed a single averaged peak for all of the CO ligands indicating that rapid interchange of the cobalt and tungsten bound carbonyls was occurring. Nevertheless, both Stone[41] and Vahrenkamp[42] noted that there were too many IR bands in the carbonyl stretching region to be assigned to a single isomer and it was proposed that the $CpM(CO)_2$ vertex might be able to adopt more than one rotameric conformation. Subsequent X-ray structural determinations[43,44] of related molecules revealed that the cyclopentadienyl ring could indeed adopt other orientations in the solid state, as in **18** and **19**.



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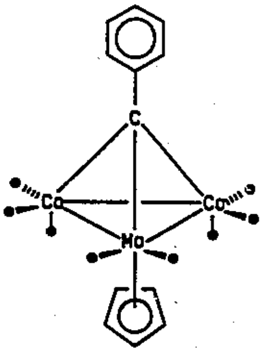

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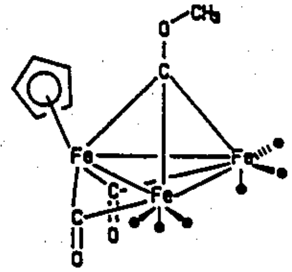

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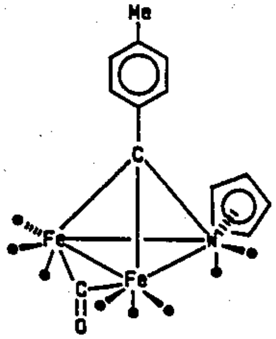

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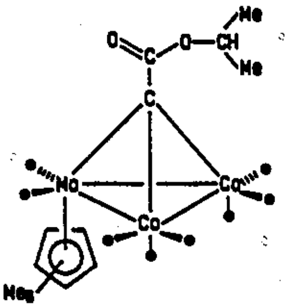

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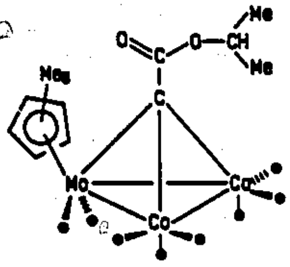


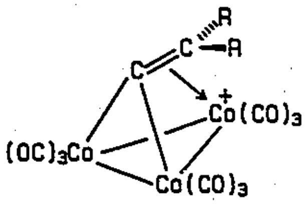
20b

Recently, the first evidence that this facile rotation could be stopped on the NMR time-scale came when the $^{13}$C NMR spectrum of $(C_5Me_5)Mo(CO)_2Co_2(CO)_6CCO_2CHMe_2$ was recorded at -100°C on a 400 MHz instrument.[33] At that temperature, it was possible to observe not only two carbonyl resonances at ≈ 200 and 230 ppm in the ratio 6:2 as anticipated for CO's bound to cobalt and molybdenum respectively, but also another less intense set of peaks (also in a 6:2 ratio) attributable to a different rotamer. In addition, the pentamethylcyclopentadienyl resonance split into two peaks whose intensities corresponded to those of their carbonyl partners in the two rotamers. In each of the rotamers, the isopropyl groups showed no evidence of diastereotopic behaviour which suggested that both isomers were achiral. Thus, it was proposed that the two rotamers differed only in the orientation of the five-membered ring; in one isomer (**20a**) the pentamethylcyclopentadienyl ring lay below the plane of the metals, and vice versa for the other (**20b**). At that time there was no way of identifying which isomer was the major rotamer and which was the minor.

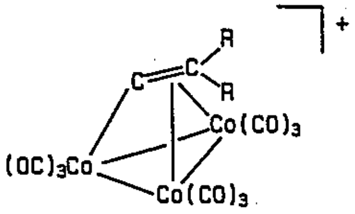
This pattern of behaviour has since been extended to the complete set of clusters $[(C_5Me_xH_{5-x})M(CO)_2Co_2(CO)_6C\text{-}CO_2CHMe_2]$, where M = Mo or W, and x = 0, 1 or 5.[35] Interestingly, for the clusters bearing $C_5H_5$ or $C_5H_4Me$ rings, the predominant rotamer in solution was the opposite isomer to that observed for the clusters with $C_5Me_5$ rings. It was hypothesized[35] that due to a combination of steric and electronic effects the major isomer in clusters possessing the $C_5Me_5$ rings (and thus the minor isomer in the other clusters) had the ring situated above the plane of the metal, as in **20b**. By having the pentamethylcyclopentadienyl ring (a better electron donating group than either of the other two ring systems) oriented in this fashion, the molybdenum (or tungsten) carbonyls were placed in a better position to form bridging carbonyls and thus reduce the additional electron density at that metal. In fact, when the crystal structure of the $C_5Me_5$ molybdenum cluster was solved it was found to demonstrate exactly this behaviour.[35]

### *1.3.7 Structures of Cluster Stabilized Cations*

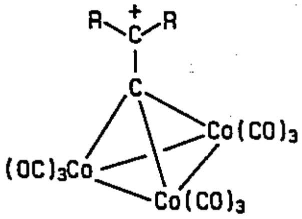
The ability of both vinylidene and ketenylidene tricobalt-carbyne clusters to stabilize a positive charge at a position α to their tetrahedral cores has been well established by Seyferth.[16] With typical insight he proposed that this stabilization could be attributed to a delocalization of the charge onto the carbonyl ligands via a direct interaction with a metal centre. However, despite numerous attempts to obtain good crystallographic data, the structures of both cations remained a matter of conjecture.



21a



21b

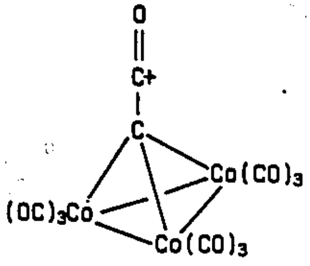


21c

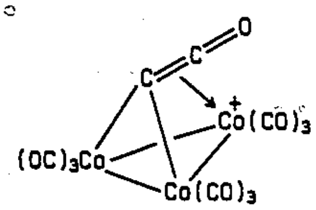
Extended Hückel Molecular Orbital calculations[45] by Schilling and Hoffmann on the trimetallic vinylidene system $[Co_3(CO)_9C\text{-}CH_2]^+$ predicted that the capping group is preferentially sited over a metal vertex as in **21a**; it was also reported that the structure **21b**, in which the plane of the methylene group bisects a cobalt-cobalt vector, could provide a pathway by which the capping group could migrate around the basal triangle. Both of these bent forms were envisaged as being more stable than the linear isomer **21c**. Still, the geometry of this cation was not verified experimentally for several years.

By incorporating an isopropyl group into the tricobalt vinylidene cluster $[Co_3(CO)_9CCH(CHMe_2)]^+$ to serve as an NMR probe, Mislow[46] was able to demonstrate in an elegant and ingenious variable-temperature $^{13}C$ NMR study that the cation behaved in the manner expected from the Schilling-Hoffmann model.[45] Despite the methyls of the isopropyl being enantiotopic (and thus appearing as a single peak) at higher temperatures, two resonances were observed for the isopropyl methyls at -65°C. The existence of two diastereotopic methyl groups could only be rationalized if the cluster was chiral; this requirement can be fulfilled only by having the C=CR$_2$ moiety lean towards a cobalt vertex, as in **21a**. The coalescence of the methyl signals observed at higher temperatures (with a barrier of 10.5 kcal/mol) was presumed to reflect the enantiomerization of the cluster via the intermediate **21b** formed by correlated rotations about the $Co_3(CO)_9$--C and C--CHCHMe$_2$ axes.

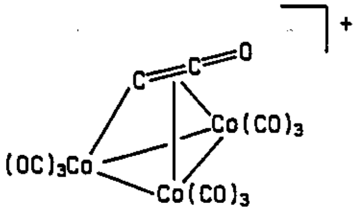
With the ketenylidene complex $[Co_3(CO)_9C=C=O]^+$, the incorporation of an NMR probe to determine the structure was not a feasible option. However, it was realized that the proposed stuctures, either linear **22a**, bent towards one vertex **22b**, or leaning between two vertices **22c**, had different point groups which would impose different splittings in degeneracy in the metals and their associated carbonyls.



**22a**



**22b**

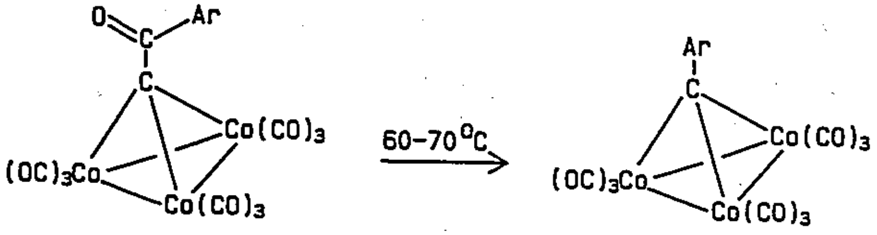


**22c**

The $^{13}$CO NMR of the cluster[47] showed a 6:3 splitting at low temperature which was consistent with two different scenarios. The first involved the cluster maintaining the linear ($C_{3v}$) geometry of **22a**, with a slowed exchange of axial and equatorial ligands on the NMR time-scale, while the second ($C_s$) invoked tilting of the ketenylidene moiety (as in either **22b** or **22c**) so as to render two $Co(CO)_3$ vertices different from the third. At that time it was thought to be highly unlikely that one could stop rapid tripodal rotation of the $Co(CO)_3$ moieties because all available evidence pointed to it being a very low energy barrier process. Since axial-equatorial interchange was assumed to continue in the bent structures, it was proposed that the cluster adopted a bent geometry in which the ketenylidene moiety leaned either towards a single vertex or towards the middle of a cobalt-cobalt vector. Although Extended Hückel Molecular Orbital calculations were carried out and showed that either of these bent structures were favoured over the linear isomer,[47] it was not possible to comment on which of the $C_s$ conformations was the predominant isomer in solution (either **22b** or **22c**), as had been done for the vinylidene cation, $[Co_3(CO)_9CCHCHMe_2]^+$.

### *1.3.8 The Mechanism of Decarbonylation of Ar-CO-CCo$_3$(CO)$_9$ to Ar-CCo$_3$(CO)$_9$*

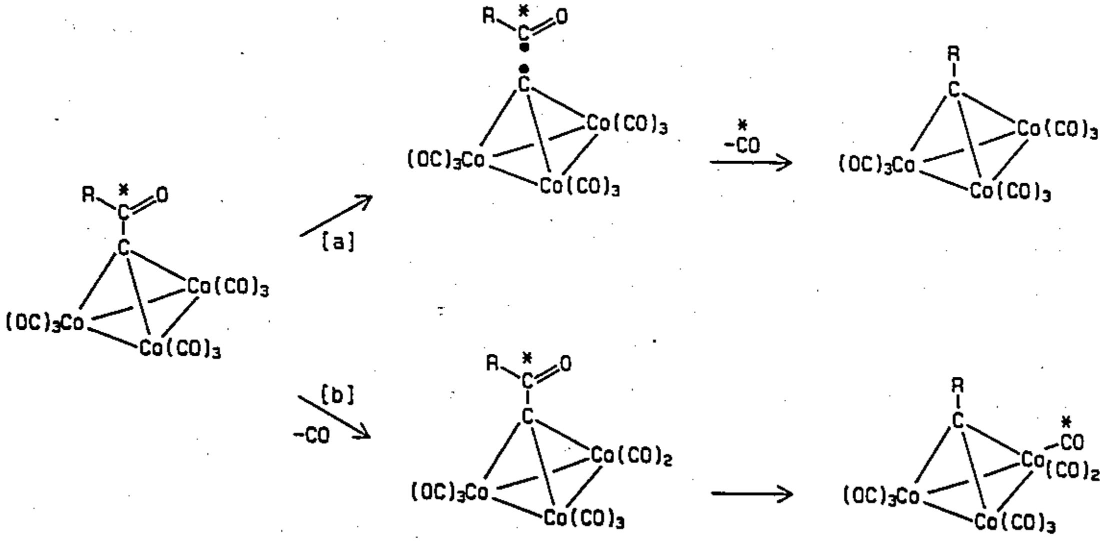
In the course of his pioneering work on the $RCCo_3(CO)_9$ cluster system, Seyferth reported that the aryl ketones **23** readily underwent decarbonylation to yield the aryl clusters **24**.[48] However the identity of the CO which had been eliminated was unknown and two mechanistically



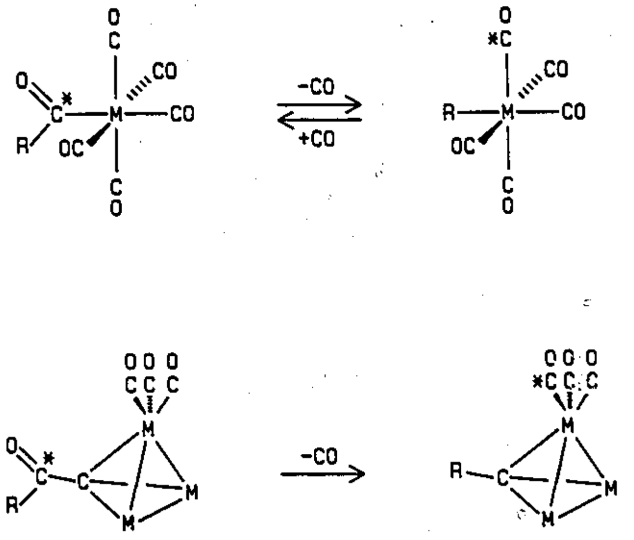
23 24

reasonable proposals were advanced. The first required the homolytic cleavage of the carbynyl-carbon--ketonic-carbon bond with the eventual loss of the originally ketonic carbonyl; the second involved initial loss of a cobalt carbonyl ligand with the subsequent migration of the ketonic carbonyl into the vacant site at the coordinatively unsaturated metal vertex. As is apparent in Scheme 11, these two mechanistic possibilities can be distinguished by labelling the ketonic carbon and then locating the label in either the eliminated carbon monoxide or as a CO now bonded to cobalt.[49]

When a $^{13}C$ NMR study was subsequently carried out by Gates and his colleagues to elucidate the origin of the extruded CO, it turned out to be experimentally easier to enrich only the cobalt carbonyls with $^{13}CO$ rather than to exclusively label the ketonic carbon with $^{13}C$. Thus, if pathway (a) had been operative, the $^{13}C$ enrichment factor for the metal carbonyls relative to the naturally abundant $^{13}C$ nuclei in the aryl capping group would have remained unchanged; in contrast, if the CO being lost had been a



**Scheme 11:** Proposed pathways for loss of CO from aroyl tricobalt clusters.



**Scheme 12:** Decarbonylation mechanisms for a monometallic system and for a trimetallic tetrahedral cluster.

cobalt carbonyl, as in pathway (b), then the vacant metal site generated would end up being filled by the naturally abundant CO from the ketonic position.

The experimental result was unequivocal, the relative integrated intensity of the cobalt carbonyl $^{13}C$ resonance in the decarbonylated product decreased by ≈12% with respect to the remaining carbon nuclei in the cluster. This was in complete accord with the second pathway, i.e., the CO which was eliminated was originally bonded to cobalt. Therefore, only eight of the original nine enriched cobalt carbonyl ligands remained after decarbonylation and so the intensity of the metal carbonyl $^{13}CO$ resonance at 200 ppm was correspondingly diminished.[49]

The significance of this finding was the realization that the mechanism of decarbonylation (and presumably of carbonylation) of metal clusters paralleled that established for monometallic complexes,[50] as shown in the generalized reactions in Scheme 12.

### *1.4 Statement of Problem*

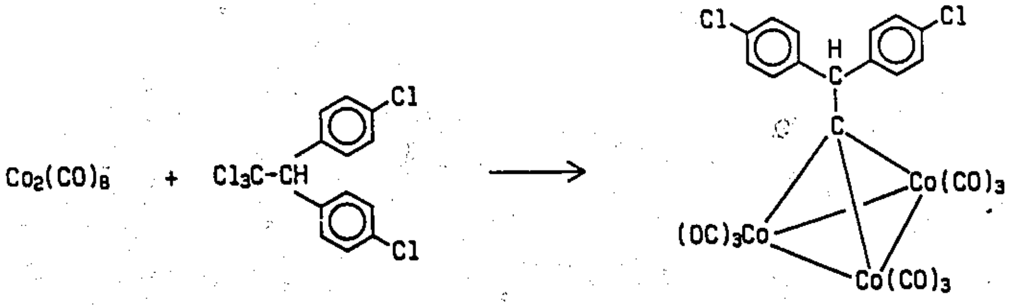
It is apparent from the examples presented here (as well as others in the literature) that NMR spectroscopy has become an exceedingly powerful technique for the determination of mechanisms of reaction and for the unravelling of molecular rearrangement which have the appropriate activation energy barriers. Therefore, it is proposed that a number of discrete projects, involving both syntheses and NMR investigations, be undertaken on small organometallic clusters containing alkynyl and carbynyl moieties to help facilitate a better understanding of this intriguing class of compounds.

# CHAPTER TWO

# FLUXIONALITY IN ORGANO-TRICOBALT CLUSTERS: THE MECHANISM OF CARBONYL EXCHANGE

## *2.1 Background*

The ability of the carbynyl-tricobalt nonacarbonyl group to stabilize a positive charge in the α-position, as in the cluster $Co_3(CO)_9(\mu^3\text{-}C{=}CR_2)^+$, has been attributed to its ability to delocalize the charge onto the carbonyl ligands via the cobalts.[16,45,46,47] At one time, one of the themes being studied in our laboratory involved a comparison of the relative charge-stabilizing abilities of a $C_6H_5$ unit and a $(OC)_9Co_3(\mu^3\text{-}C)$ moiety; for this reason it was deemed necessary to find a route to a molecule in which a phenyl ring and a carbynyl-nonacarbonyltricobalt unit were both attached to the same electron-rich or electron-deficient centre. To this end, Gates et al.[51] proposed that molecules be constructed which had one or more phenyl groups bonded to a methynyl group which in turn would be situated in a position α to the nonacarbonyltricobalt fragment. In this way, it would have been possible to remove the α hydrogen either as a hydride, or as a proton, to prepare the cluster stabilized cation or anion, respectively. For each case, their plan was to determine the barrier to phenyl rotation by using variable-temperature NMR measurements. By comparing these rotational barriers to the one for the neutral cluster, it was hoped that one could detect any increased rotational resistance about the bond between the ipso carbon of the phenyl ring and the α-carbon in the charged species. (This would have been attributable to the formation of a partial "double bond" between the two centres so that the charge could be delocalized into the phenyl ring.) However, it was first necessary to find a general route to clusters containing such arylmethyl- or diarylmethyl-capping functionalities. The direct reaction of dicobalt octacarbonyl with an organic precursor containing a trihalomethyl moiety is the preferred route to nonacarbonyl tricobalt clusters and one such readily available organic compound which filled the requirements perfectly was the commercial pesticide 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane, more commonly known as DDT.



25

After the usual purification procedures, a mixture of black and white crystalline products was obtained from the reaction of DDT with $Co_2(CO)_8$ but despite repeated attempts the compounds could not be easily separated. In order to isolate the two materials, Gates et al. resorted to picking out the individual crystals with the aid of a microscope. The black product (formed as the minor product) was characterized by a variety of methods, including solving its X-ray crystal structure (shown in Figure 3), and found to be the desired cluster, $Co_3(CO)_9(\mu^3\text{-}CCH(p\text{-}C_6H_4Cl)_2)$, **25**. The white species was later identified as 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD) by comparing its $^1H$ and $^{13}C$ NMR spectra to those obtained from an authentic sample of the compound.

Since Gates wished to gain some insight into the molecular dynamics of the neutral cobalt cluster, **25**, its variable-temperature $^{13}C$ NMR spectra were recorded. It had been thought that there might be restricted rotation of the phenyl rings such that the ortho and meta carbons of the aryl rings would not be magnetically equivalent at low temperature (this is precisely what happens for diarylmethyl anions or their $Cr(CO)_3$ complexes[52,53]). Experimentally, any potential splittings in the $^{13}C$ NMR were obscured by the solvent signal overlapping with the important resonances. Concomitantly, however, it was observed that the cobalt carbonyls split into a 6:3 pattern at -120°C.[51]

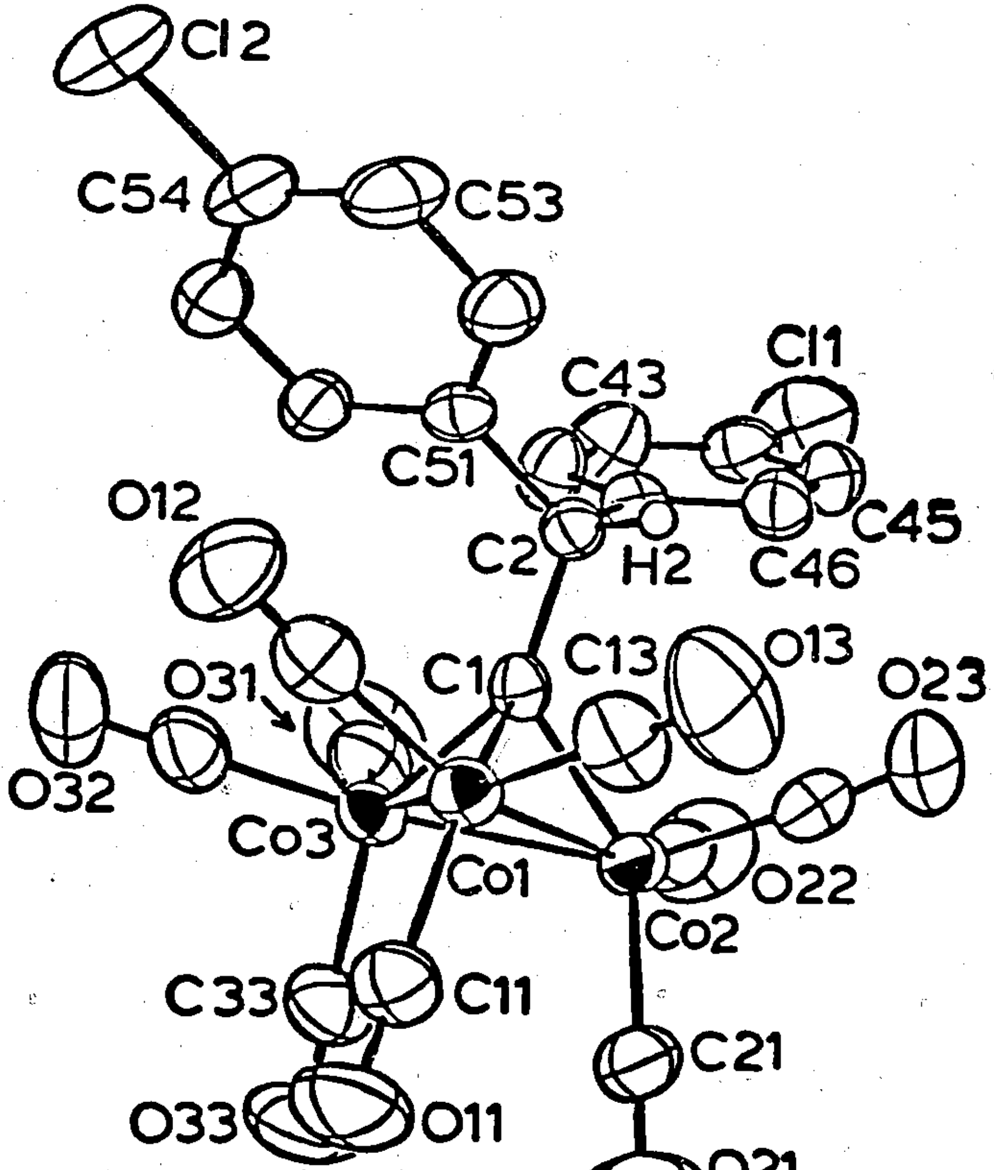
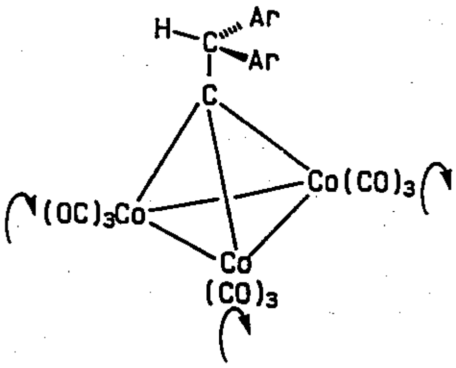
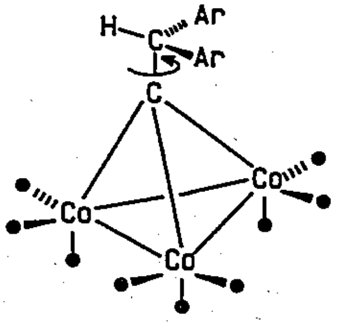


**Figure 3:** X-ray crystal structure of $Co_3(CO)_9(\mu^3\text{-}CCH(p\text{-}C_6H_4Cl)_2)$, 25.



**26a**



**26b**

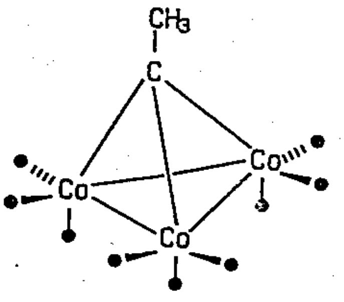
At that time, several plausible interpretations were advanced that could have accounted for the unexpected result. First of all, there could have been slowed rotation of the capping carbynyl unit about the alkylidyne carbon -- α-carbon bond on the NMR time-scale with inter-cobalt carbonyl exchange stopped, as illustrated in **26a**. This would have given a molecule with $C_s$ symmetry (similar to that observed in the X-ray crystal structure of this cluster) and thus, a splitting of the three-fold degeneracy of the $Co(CO)_3$ vertices would have resulted. As a second possibility, shown in **26b**, it was proposed that local rotation of the $Co(CO)_3$ vertices could be slowed on the NMR time-scale to give a two distinct types of carbonyls (three axial and six equatorial); this molecule would have pseudo-$C_{3v}$ symmetry provided the capping group continued to spin. (Of course this would be true with or without inter-cobalt carbonyl exchange). In the first case, it was necessary to stop inter-cobalt carbonyl exchange, something which had been established for related clusters,[54] whereas the second postulate required cessation of axial-equatorial carbonyl interchange, an unprecedented phenomenon for $Co(CO)_3$ vertices in nonacarbonyl clusters.[55-57]

Our own involvement with the problem started at that time. The intent was to investigate this unusual carbonyl behaviour by incorporating other independent NMR probes which might cast some light on these earlier observations.

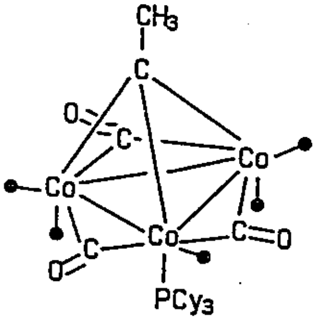
## *2.2 Results and Discussion*

The series of investigations presented here were undertaken with two goals in mind. The first was to try to distinguish between the possibilities suggested by Gates et al. for their observation of a 6:3 carbonyl splitting in a nonacarbonyltricobalt cluster at low temperature, while the second was the more general one of trying to develop a better understanding of the mechanisms of carbonyl exchange in organo-tricobalt clusters.

A multitude of X-ray crystallographic structural determinations[17] have shown that clusters of the type $RCCo_3(CO)_9$ or $RCCo_3(CO)_{9-x}L_x$ adopt one of two isomeric forms. All of the carbonyl groups can be terminal, as in **27a**, so that there are six equatorial and three axial ligands,[58] or the molecule can have three bridging, three axial and three radial ligands as in **27b**.[59]



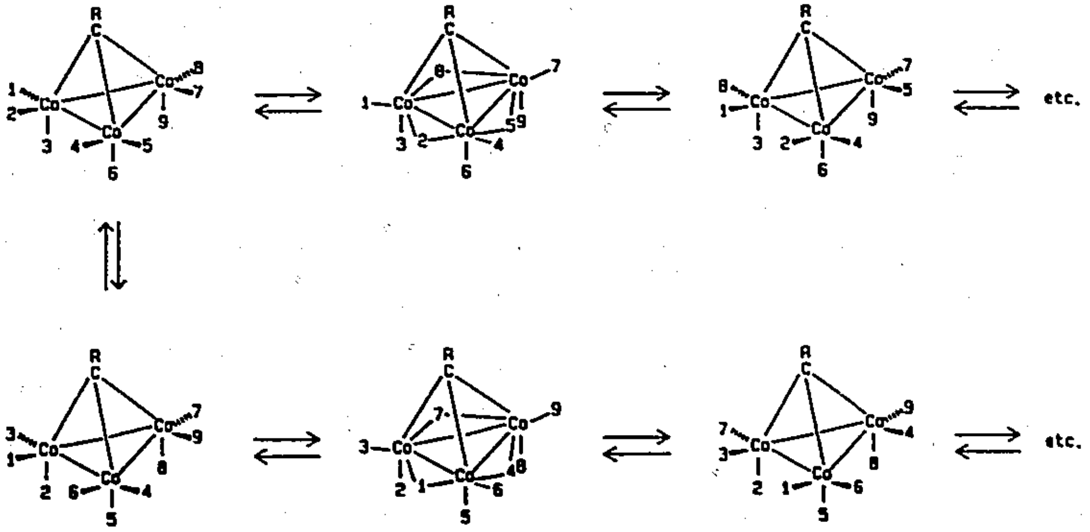
27a



27b

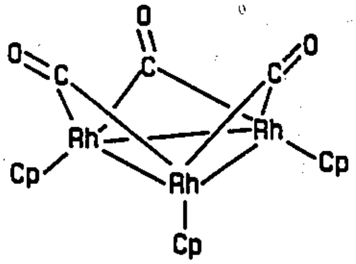
It is generally assumed that inter-metal exchange of the six equatorial carbonyl environments can be accomplished via the Muetterties "merry-go-round", with the triply-bridging species serving as an intermediate in the process. On the other hand, axial-equatorial interchange of the carbonyls merely requires a local rotation in an "all terminal" species.[60] Scheme 13 shows how a combination of these two mechanisms will allow all of the carbonyls access to each of the nine possible sites.

Until Gates' work, only a single $^{13}CO$ resonance had been observed for all known neutral $Co_3(CO)_9CR$ clusters indicating that rapid axial-equatorial interchange of the carbonyls (and presumably inter-cobalt exchange) was occurring on the NMR time-scale, even at low temperatures. The existence of inter-cobalt exchange can not be proven because the detection of $^{59}Co$-$^{13}C$ coupling is restricted to those geometries (*Oh* or *Td*) in which quadrupolar line-broadening does not obscure the splitting.[61] In contrast, in $[Cp_3Rh_3\mu$-$(CO)_3]$, **28**, the carbonyl resonance appears as a triplet at

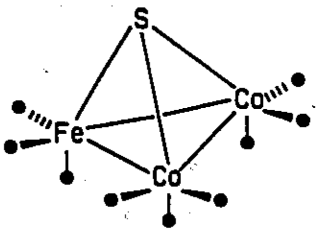


**Scheme 13:** Mechanisms for complete interconversion of carbonyl ligands in $Co_3(CO)_9CR$ clusters.

low temperature which can be attributed to the coupling of the carbonyls to two equivalent $^{103}$Rh nuclei. Upon warming, the $^{13}$CO resonance becomes a quartet since rapid inter-rhodium exchange of the carbonyls allows each carbonyl carbon to interact equally with all three rhodium atoms.[62] The slowing of inter-metal exchange of the carbonyls on the NMR time-scale is also readily observable in **29** which, upon cooling, show a 6:3 peak pattern for the $Co(CO)_3$ and $Fe(CO)_3$ groups. This eventually splits out to give a 6:2:1 pattern because it is possible to freeze out local rotation or axial-equatorial interchange in the iron tricarbonyl fragment but local rotation of the $Co(CO)_3$ vertices has not been stopped.[56] (However, in molecules bearing three bridging carbonyls, e.g., **27b**, all the different carbonyl environments are detectable.[57])

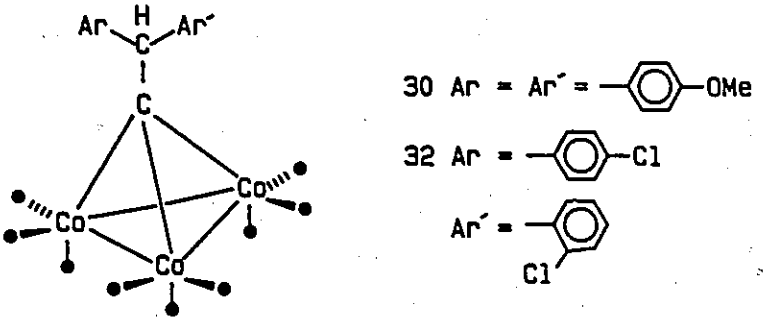


**28**



**29**

In order to resolve the ambiguity as to the origin of the 6:3 splitting of the carbonyl resonances, it was decided initially to examine the likelihood of rotation of the capping moiety becoming slow on the NMR time-scale. To accomplish this, it was planned to incorporate an NMR-active probe into a nonacarbonyl tricobalt cluster that displayed the unusual splitting pattern. Although it may have been possible to use the DDT-derived cluster **25** during our investigations, the fact that it could not be cleanly isolated in large quantities did not make it a desirable starting material.



The tricobalt cluster **30** formed from the reaction of $Co_2(CO)_8$ and 1,1,1-trichloro-2,2-bis(4-methoxyphenyl), also known as Methoxychlor, proved to be a much more well-behaved cluster than the one studied by Gates. This cluster could be generated in higher yields and was easy to isolate by using flash chromatography. In this case, the phenyl ring resonances are widely split and, by -80°C, the ortho and meta carbons are split in the $^{13}C$ NMR spectra, indicating that aryl rotation has slowed on the NMR time-scale. Furthermore, the carbonyls in this cluster also exhibited the aforementioned 6:3 splitting pattern at low temperature, as can be seen in Figure 4. These variable-temperature $^{13}CO$

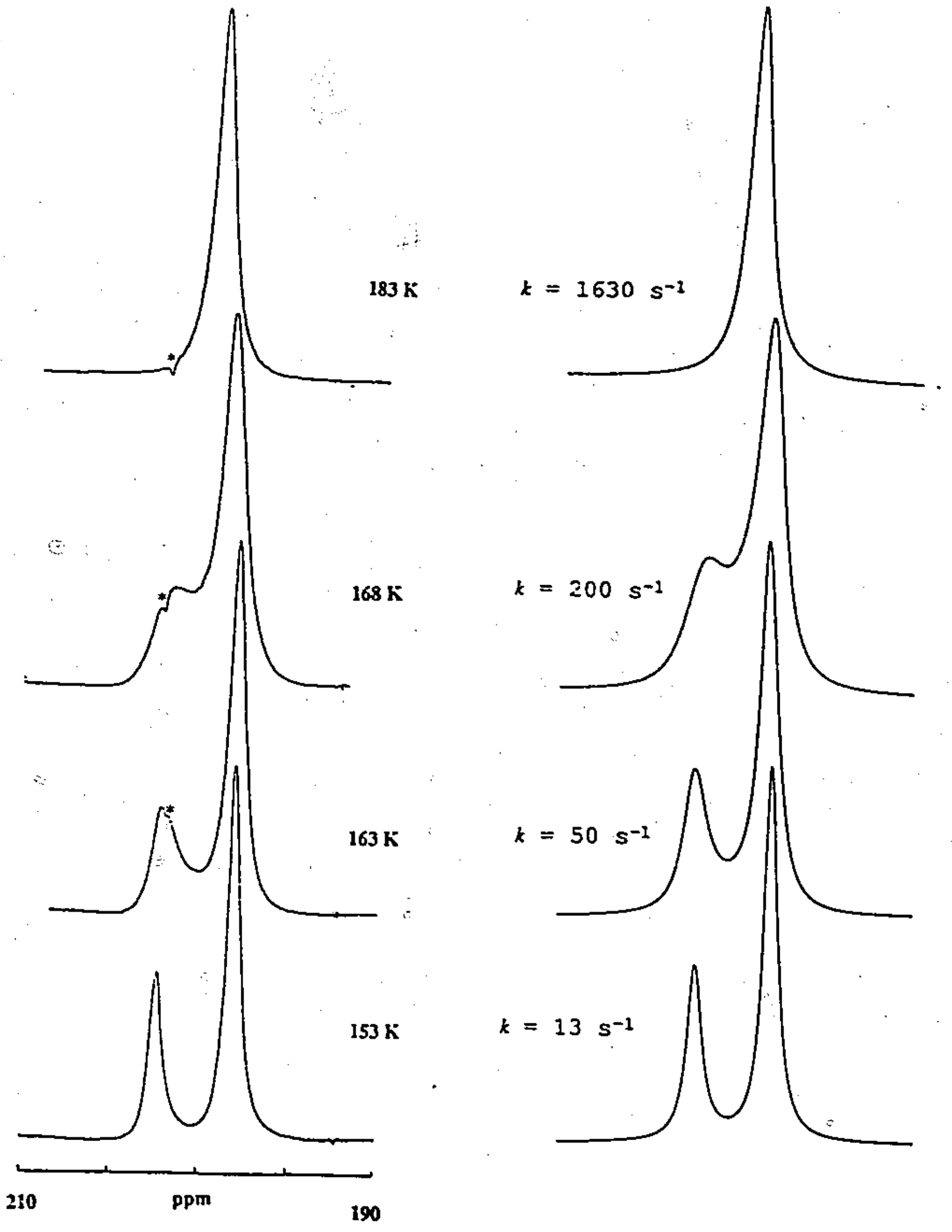
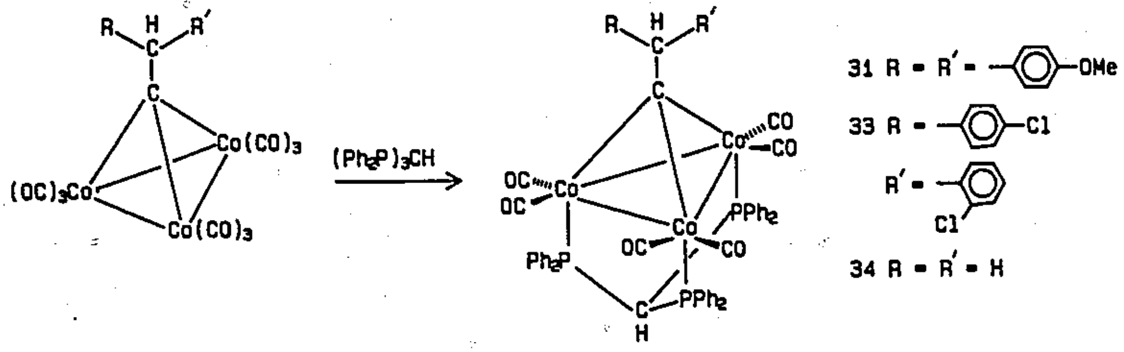


**Figure 4:** Experimental and simulated 62.5 MHz variable-temperature $^{13}CO$ NMR spectra of 30. Location of folded carbynyl resonance indicated by an asterisk.

spectra were simulated by using the DNMR3 program[63] and the activation energy barrier ($E_a$) to the exchange process was calculated as ≈ 9.2 kcal/mole by use of the Arrhenius equation for site exchange.[64] Since **30** is essentially the same molecule as the DDT-derived compound, except for the replacement of the Cl atoms in the para positions of the phenyl rings by methoxy groups, the previously outlined proposals for the carbonyl splitting in **25** could also be used to rationalize the behaviour of the carbonyls of **30**.

If it could be shown, by an attached NMR probe, that rotation of the capping moiety had stopped it would follow that the 6:3 carbonyl splitting came about as a direct result of this behaviour. Continued rotation would necessarily mean the second explanation held, namely cessation of local rotation. To this end, it was decided to replace the three axial carbonyls in **30** by the tripodal ligand, $(Ph_2P)_3CH$, and record the variable-temperature $^{31}P$ NMR spectra of the product, **31**.



However, the synthesis of **31** was not as straightforward as had been expected;[65] indeed it presented us with a Catch-22 situation. The thermal conditions required for all three phosphorus atoms of the tripod to attach themselves to the cluster were very close to those which brought about decomposition of both the desired product **31** and the starting material **30**. Fortunately, it was eventually possible to generate sufficient quantities of the tripodal complex to carry out the NMR studies. At room temperature, the $^{31}P$ NMR spectrum of **31** consists of a singlet at ≈ 45 ppm. Stopping rotation of the capping group in **31** would generate a molecule of $C_s$ symmetry and so should split the $^{31}P$ resonance into a 1:2 peak pattern. In contrast, if the capping group continued to spin freely, the molecule would retain its pseudo three-fold symmetry and so the $^{31}P$ peak should remain a sharp singlet. The continued observation of a singlet in the $^{31}P$ NMR spectra at low temperatures appears to demonstrate that the carbynyl capping substituent is still spinning rapidly on the NMR time-scale. Assuming that the same situation prevails in the tricobalt nonacarbonyl clusters **25** and **30**, that is, rotation of the capping moiety continues unhindered, the explanation for the 6:3 splitting of the carbonyls necessarily invokes the cessation of axial-equatorial interchange of the carbonyls.

The above approach is not without its disadvantages, one of which is that the results obtained were from a modified hexacarbonyl cluster and they may not accurately reflect the true behaviour of the nonacarbonyl clusters. By treating the trihalo-containing compound o,p-DDT (1-(2-chlorophenyl)-1-(4-chlorophenyl)-2,2,2-trichloroethane) with dicobalt octacarbonyl, it is possible to generate the nonacarbonyl tricobalt cluster **32**. It is very closely related to the other two clusters, **25** and **30**, but has the added feature of possessing three different substituents in its diarylmethyl capping group; it is a chiral molecule.

When the variable-temperature $^{13}C$ NMR spectra were obtained for this cluster (**32**), the single carbonyl resonance detected at room temperature was seen to split into the now familiar 6:3 pattern upon cooling to low temperature. The presence of the chiral capping moiety would further reduce the effective symmetry of the molecule to $C_1$ if it had stopped rotating and thus caused all three $Co(CO)_3$ vertices to be magnetically different. The explanation which best accounts for the observed 6:3 result involves stopping axial-equatorial carbonyl interchange but continuing the rotation of the capping carbynyl group. In addition, for all six equatorial ligands to be equivalent it would appear that inter-cobalt exchange continues at low temperature in this molecule or else a 3:3 splitting pattern should be observed for them. The attractive feature of this investigative approach was that it was possible to observe and explain the carbonyl splitting without having to resort to using a model system with electronically different substituents, as in the Methoxychlor-derived cluster **30**.

Once again, we succeeded in synthesizing enough of the hexacarbonyl-tripodal derivative **33** of the nonacarbonyl cluster **32** to examine its fluxional behaviour by NMR spectroscopy. The observation of a singlet in the low temperature $^{31}$P NMR spectrum of **33** also serves to confirm the initial conclusion; the capping groups continue to rotate in these clusters.

In an attempt to determine how the capping group was able to slow axial-equatorial interchange of the $Co(CO)_3$ vertices, i.e., possibly via a steric interaction between the terminal carbonyl ligands and the bulky capping group, the crystallographically derived atomic co-ordinates of the DDT-derived cluster **25** were manipulated by using the molecular modelling program CHEM-X.[66] The diaryl-methyl carbynyl fragment was rotated so as to position a phenyl ring between two carbonyl ligands either (a) on the same cobalt or (b) on adjacent cobalts. These situations are depicted in Figure 5 and show that even when the carbonyl ligands are positioned at the most energetically reasonable of orientations, the *ortho*-hydrogens of the chlorophenyl rings can get uncomfortably close to the metal carbonyls. In the more extreme positions that are encountered in the axial-equatorial carbonyl interchange, there was a definite interaction between the carbonyls and the rings which would

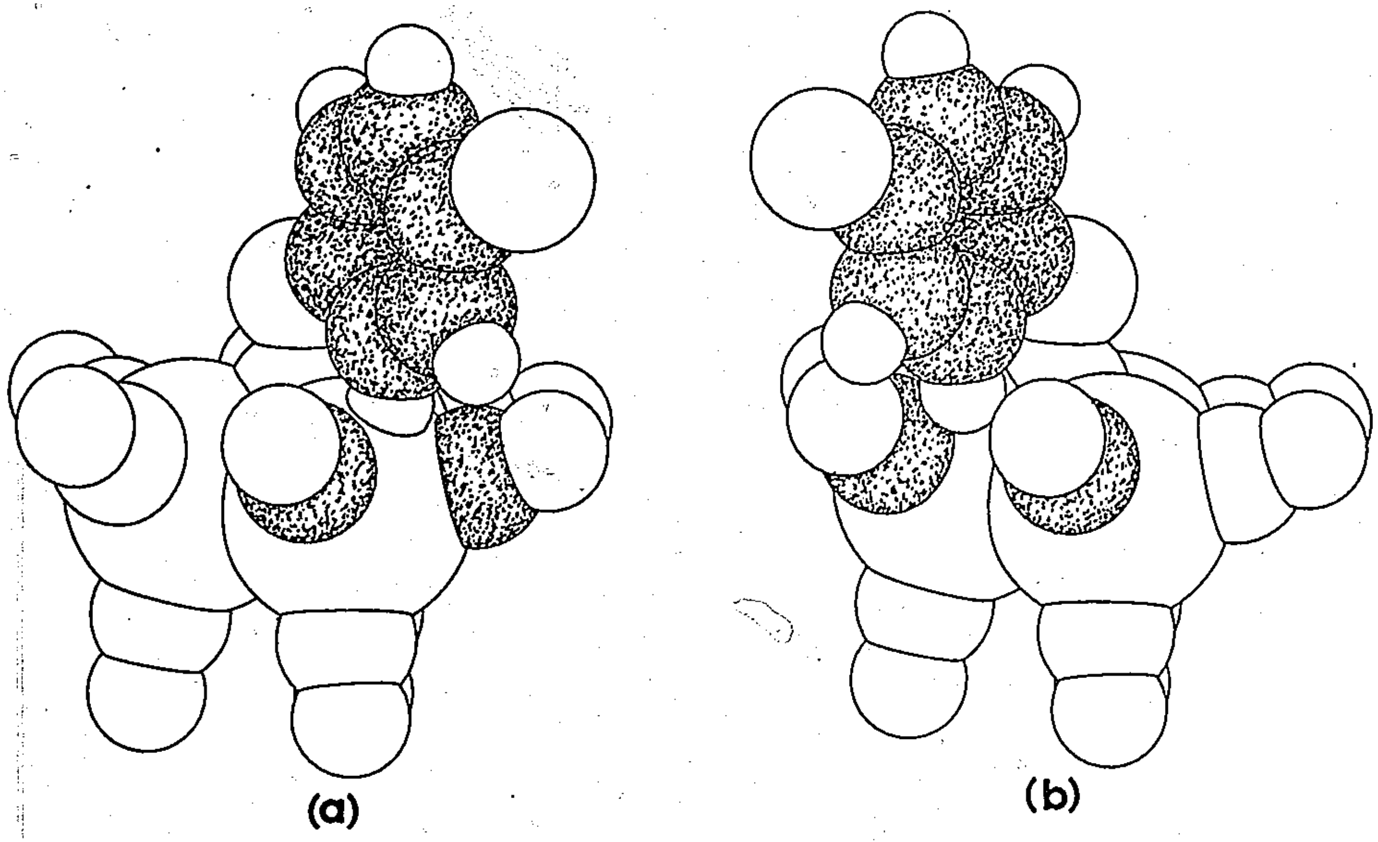


**Figure 5:** CHEM-X plots of selected conformations (see text) of $Co_3(CO)_9(\mu^3\text{-}CCH(p\text{-}C_6H_4Cl)_2)$, 25. For clarity only one chlorophenyl ring is depicted.

suggest that there could be a significant barrier to the local rotation of a $Co(CO)_3$ moiety in these types of clusters. This same effect may be responsible for the slowed rotation of the aryl rings in **30**, as detected by $^{13}C$ NMR spectroscopy.

Interestingly, at -120°C the $^{13}CO$ resonances of the tripodal clusters, **31** and **33**, were observed to split from single resonances (at room temperature) into two equally intense peaks at ≈ 206.6 ppm and 204.7 and ≈ 206.6 and 204.6 ppm, respectively. Unlike the analogous $Co_4(CO)_9$(tripod)[67a] and ($\pi$-toluene)$Co_4(CO)_6[(PPh_2)_3CH]$[67b] clusters in which the carbonyls attached to the phosphorus-bonded cobalts were shown by X-ray crystallography to be three terminal and three bridging ligands, the $^{13}CO$ chemical shifts in **31** and **33** are quite clearly attributable to terminally bound carbonyl ligands. It became apparent to us that in the tripodal clusters **31** and **33** the molecular symmetry was not $C_{3v}$ but rather $C_3$. We hypothesized that this phenomenon arose because at low temperature the six phenyls of the tripod froze out in a propellor conformation and thus reduced the symmetry of the molecule. (This conformational preference for the rings is also exhibited in $Co_4(CO)_9((PPh_2)_3CH)$.[67a]) In conjunction with continued rotation of the capping group and no inter-cobalt carbonyl exchange, this lowered symmetry explains the 1:1 $^{13}CO$ spectrum obtained. However, a second explanation for the appearance of the two equally intense carbonyl environments was suggested to us and had to be given due consideration. In this proposal, the capping group continues to spin and the carbonyls continue to undergo inter-cobalt exchange but the phenyl rings of the tripod freeze out in both clockwise and counter-clockwise directions, to generate two visibly diastereotopic carbonyl environments.

To resolve this ambiguity, we synthesized the tricobalt-hexacarbonyl-tripod cluster **34** which has a methyl group as its apical substituent. The variable-temperature $^{13}C$ NMR study which was carried out on **34** also showed the two equally intense carbonyl resonances at low temperature. The splitting can only be rationalized by our first explanation, i.e., inter-cobalt exchange is not occurring and the phenyl rings freeze out in the propellor arrangement. If, as had been suggested, inter-cobalt exchange continues and the rotation of the phenyl rings stops in both clockwise and counterclockwise directions, the molecules formed would both have $C_3$ symmetry and the carbonyls in the two products would be enantiomeric. In that case, only a single carbonyl resonance would have been detected because enantiomers can not be differentiated by NMR spectroscopy in an achiral solvent.

In order to provide concrete evidence for our proposed "propellor-like" conformation of the phenyl rings in the tripodal clusters, it was decided to obtain the X-ray crystal structure of one of the compounds. Red/purple crystals of **34** suitable for X-ray diffraction studies were grown from the mixed solvent system $CH_2Cl_2$/pentane. The X-ray crystal structure and labelling scheme of molecule **34** is shown in Figure 6 while the crystallographic data for this molecule are collected in Tables 3 through 5. As anticipated from the I.R. and NMR spectroscopic results, all of the carbonyl ligands in **34** are terminally bound. The phenyl rings in **34** adopt the hypothesized "propellor-type" orientation (seen previously for $Co_4(CO)_9((PPh_2)_3CH)$) and this is illustrated in Figure 7. The cobalt-cobalt bond distances (average 2.484 Å) and the cobalt to capping carbon lengths (average 1.907 Å) in **34** are comparable to those found in other $Co_3C$ tetrahedra reported elsewhere.[51] The crucial point which this structure illustrates is that the phenyl rings in **34** are twisted approximately 30° from a perpendicular alignment. Thus the $C_{3v}$ symmetry is broken to $C_3$ and this accounts for the 3:3 splitting of the degeneracy of the $^{13}CO$ ligands in the low temperature NMR spectrum.

Despite the fact that the available crystals of **31** were not of very high quality, a partial X-ray crystallographic data set was obtained for **31**. Although it was not possible to solve the structure completely, the co-ordinates of the phenyl ring carbons in the tripodal ligand could be determined. As can be seen in Figure 8, the rings in this cluster also adopt a propellor-like orientation.

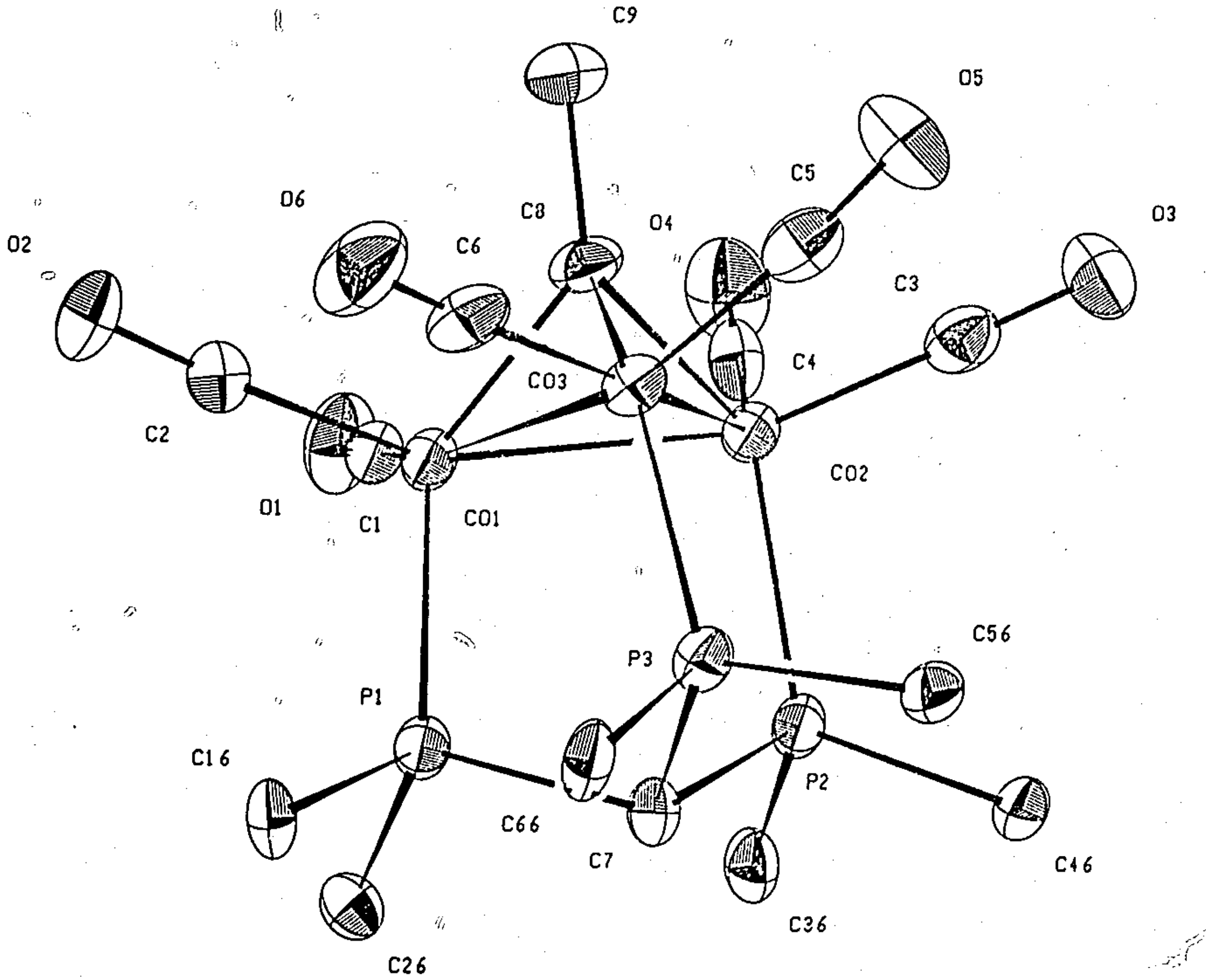


**Figure 6:** X-ray crystal structure of $(HC(Ph_2P)_3)Co_3(CO)_6CCH_3$, 34. For clarity, only the ipso carbons of the tripod phenyl rings are shown.

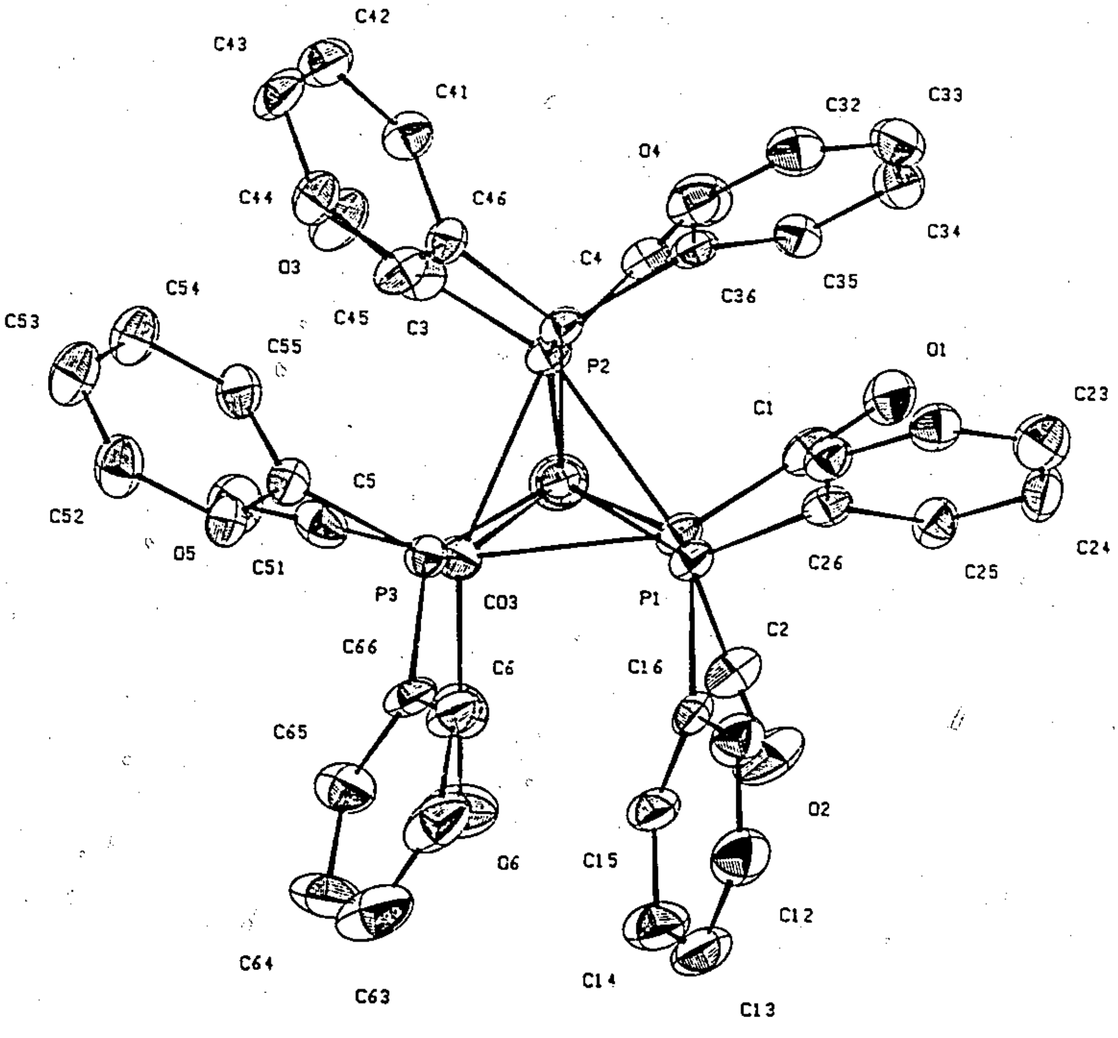


**Figure 7:** View of 34 showing the "propellor-type" orientation of the phenyl rings on the tripodal ligand.

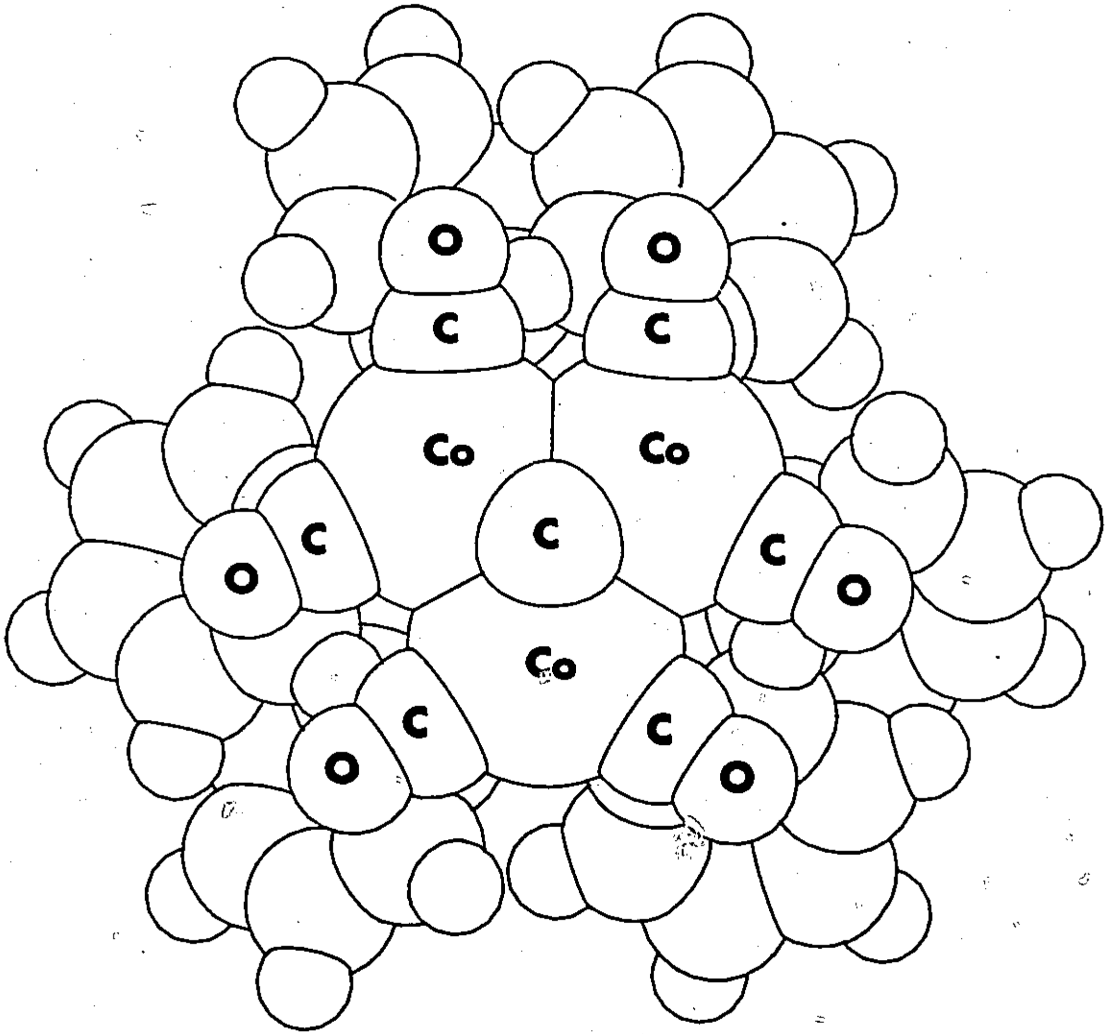
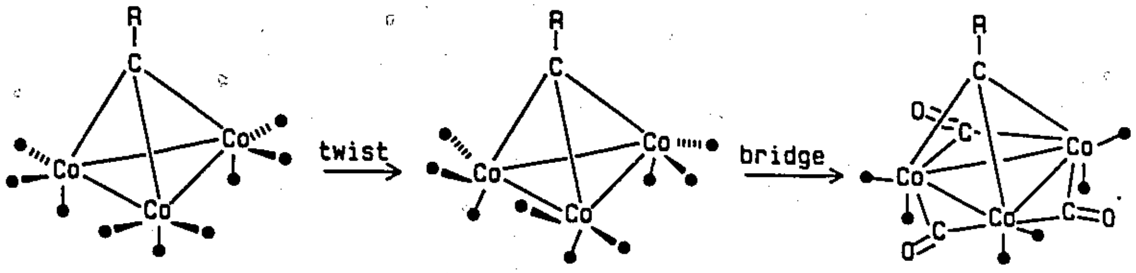


**Figure 8:** CHEM-X plot showing the "propellor-type" orientation of the phenyl rings in the tripod ligand of 31.

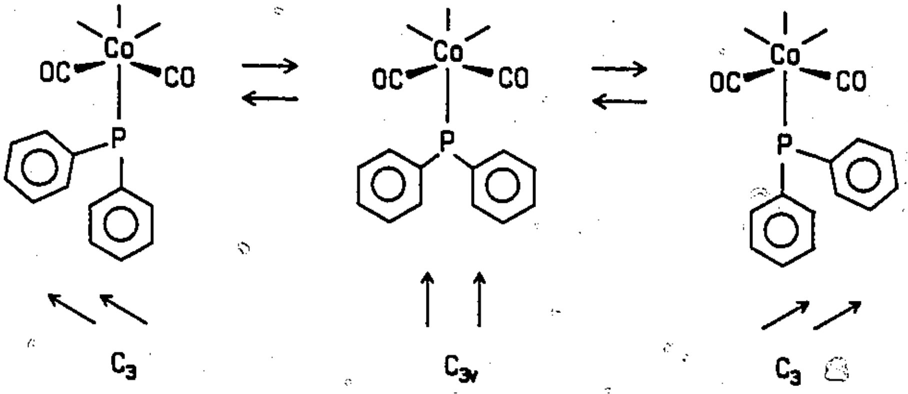
At the beginning of this project, we had several preconceived notions regarding organo-tricobalt clusters. In particular, we believed that the two carbonyl exchange mechanisms operative were not entirely independent of each other but were related such that the requirement for inter-metal carbonyl exchange was the ability of the cobalt vertex to undergo a form of axial-equatorial carbonyl interchange. For the "merry-go-round" inter-cobalt carbonyl exchange to occur it was proposed that initially the cobalt carbonyl vertices had to twist slightly so that they brought themselves into a favourable position for the formation of the intermediate bridging carbonyl species, as illustrated.



Therefore, the observation of the low temperature $^{13}$CO 6:3 splitting for **32** and the subsequent observation of a single carbonyl resonance for its tripodal derivative **33** in its room temperature $^{13}$C NMR spectrum was very intriguing to us. In the former, **32**, it appears that inter-cobalt exchange is continuing after axial-equatorial interchange had ceased while in the latter, 33, the observation of a single peak for this chiral cluster means that inter-cobalt exchange was occurring in spite of the presence of the "rigid" tripod which would preclude any axial-equatorial interchange. (Had inter-metal exchange been slow on the NMR time-scale for 33 there should have been two carbonyl signals. The presence of a chiral capping group creates two chemically different and non-interconvertible carbonyl sites on each $Co(CO)_2P$ moiety.) Since these results directly contradicted our original proposal, they prompted us to investigate further the ability of the trimetallic clusters to undergo inter-cobalt carbonyl exchange in situations where axial-equatorial interchange was definitely not possible.

The tripod containing cluster, 34, had originally been made to elucidate the behaviour of the phosphorus-bonded phenyl rings by variable-temperature $^{13}C$ NMR spectroscopy. However, since it could formed in good yield, we decided to resynthesize this cluster (after first enriching the carbonyls of its nonacarbonyl parent with $^{13}CO$) and take another look at its $^{13}C$ NMR spectrum. We had hoped to be able to observe a splitting pattern in the carbonyl region of the room temperature $^{13}C$ NMR spectrum that we could attribute to $^{31}P-^{13}C$ coupling between the carbonyls and the phosphorus of the tripod. If inter-cobalt carbonyl exchange were occurring one would expect to see a quartet in the carbonyl region because of the coupling of each carbonyl carbon to three equivalent $^{31}P$ nuclei. A doublet arising from the coupling of each carbonyl carbon to a single $^{31}P$ nucleus would be anticipated if the carbonyls remained fixed to individual cobalts. Despite repeated attempts, this experiment failed to provide any conclusive evidence for either scenario; a single carbonyl peak with no visible carbon-phosphorus coupling was always observed at room temperature even when the sample was dissolved in a viscous solvent (something which had been done to observe $^{13}C$-$^{31}P$ couplings in other cobalt clusters[68]).

However, because this cluster no longer possessed phenyl rings in the capping group, we were now able to identify the carbon resonances attributable to the phosphorus-bound phenyl rings. (In the other tripod clusters it was not possible to unequivocally assign resonances as belonging to the ligand or to the capping group.) From the variable-temperature $^{13}C$ NMR spectra obtained for **34**, the "freezing out" of complete rotation of the phenyl rings could be observed and we calculated this barrier ($\Delta G^{\ddagger}$) to be ≈ 10 kcal/mole by using the Gutowsky-Holm approximation for two site exchange.[69] Meanwhile, the carbonyl resonance of **34** was seen to split into two equally intense peaks as the temperature was lowered and the barrier for this phenomenon was calculated to be ≈ 8 kcal/mole. We initially thought that it would be possible to use these different barriers to draw some conclusions regarding the carbonyl fluxionality. Unfortunately, upon re-examining the fluxional behaviour of the cluster on the 500MHz spectrometer (initial work was done on the 250MHz), further splitting of the ring carbons was subsequently observed and it also had a barrier of ≈ 8 kcal/mole barrier. The splitting can be attributed to local ring motion (shown below for a single cobalt centre), and not complete rotation of the rings, which allows the phenyl rings to twist from one propellor form to the other. Because the transition-state structure in such a process is a cluster which has $C_{3v}$ symmetry, the mirror planes in the molecule equilibrate the two rings attached to the same phosphorus; in addition, this would equilibrate the two carbonyl ligands attached to any given cobalt.



If the carbonyl splitting process had possessed a lower activation energy barrier than either of the other two, as it had initially appeared, it would have indicated that inter-cobalt exchange was occurring even after phenyl rotation had ceased. In turn, this would have provided more evidence for the existence of inter-cobalt exchange without the necessity of local rotation of the cobalt vertex. However, since the carbonyl barrier and the second phenyl ring fluxional process are very similar, it is not possible to decide which process stops first and thus one can not draw any unequivocal conclusions regarding the occurrence of inter-cobalt carbonyl exchange in **34**.

It was already known that axial-equatorial carbonyl interchange proceeds in the absence of inter-cobalt carbonyl exchange. From the NMR results for the o,p-DDT derived cluster, **32**, and for its tripod substituted analogue, **33**, it appears that the reverse is also true. In other words, the two mechanisms used to explain carbonyl exchange in these clusters are just that - two independent mechanisms.

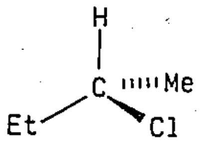
Overall, the information obtained in the preceding study regarding the fluxional behaviour of organo-tricobalt clusters can be summarized as follows: (1) local axial-equatorial carbonyl interchange can be stopped on the NMR time-scale, with a calculated barrier of $\approx$ 9.2 kcal/mole, (2) rotation of the apical capping group continues in these DDT-type clusters, (3) inter-cobalt carbonyl exchange does occur and (4) inter-cobalt carbonyl exchange is independent of the ability to undergo any form of local axial-equatorial carbonyl interchange.

# CHAPTER THREE

# DIASTEREOSELECTIVE LIGAND AND VERTEX SUBSTITUTION REACTIONS IN BIMETALLIC BRIDGED ALKYNE CLUSTERS

## *3.1 Introduction*

It is possible to synthesize chiral organo-transition metal clusters containing either a carbynyl or alkynyl moiety via any one of a number of routes.[10] For many individuals, the term chirality is associated with an organic molecule that contains a carbon atom bonded to four different groups, as in **35**. These molecules are easily visualized as being tetrahedra that have four unique corners. In fact, some of the earliest synthetic approaches to the chiral clusters of interest to us involved making tetrahedral compounds such as **36** which had four different vertices,[70] not unlike the simplest chiral organic species. Similarly, one may arrive at a cluster that has four non-identical vertices by substituting an unsymmetrical ligand, such as arphos, into an existing prochiral cluster. Unlike the original nonacarbonyl cluster from which it was derived, the three cobalt vertices in **13** are differentiated by their having either three carbonyls, two carbonyls and a phosphorus, or two carbonyls and an arsenic, directly bonded to



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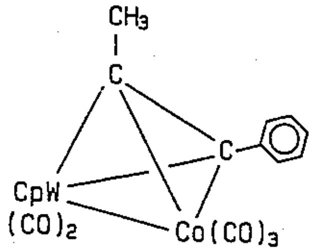

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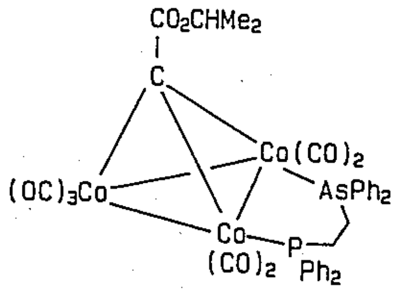

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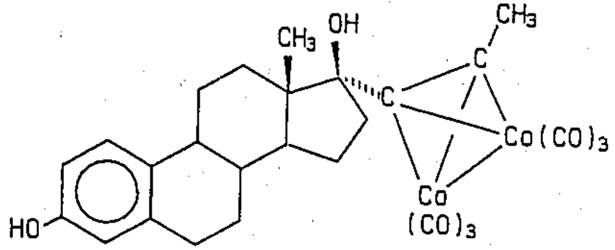

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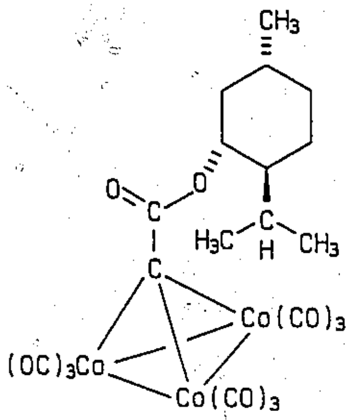

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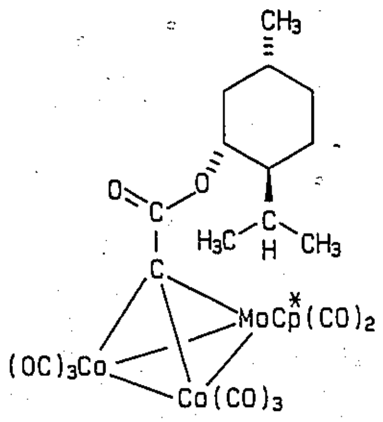
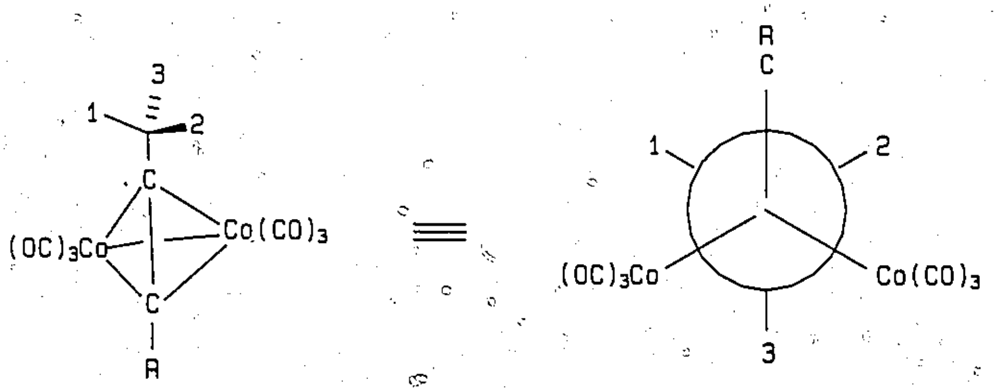


39

them.[24] For a tetrahedral cluster to be chiral, however, it is not always necessary that the stoichiometric makeup of its four vertices be different. As a number groups have demonstrated, it is possible to have a chiral tetrahedral cluster with either two $Co(CO)_3$, **37**, or three $Co(CO)_3$, **38**, vertices present by incorporating a chiral natural product into the alkynyl[71,72] or carbynyl[34,73] substituent, respectively. In these cases, the chiral centre is not present in the tetrahedral core of the cluster, rather it is located on one of the substituents.

While the three cobalt vertices in the carbynyl cluster **38** can be equilibrated by a simple rotation about the alkylidyne -- α-carbon bond (recall this was the case for the simple ethane described before), this is not true for the cobalt carbonyl vertices in the bimetallic cluster **37**. As can be seen from the Newman projection of this cluster, (with 1, 2, 3 representing the chiral substituent)



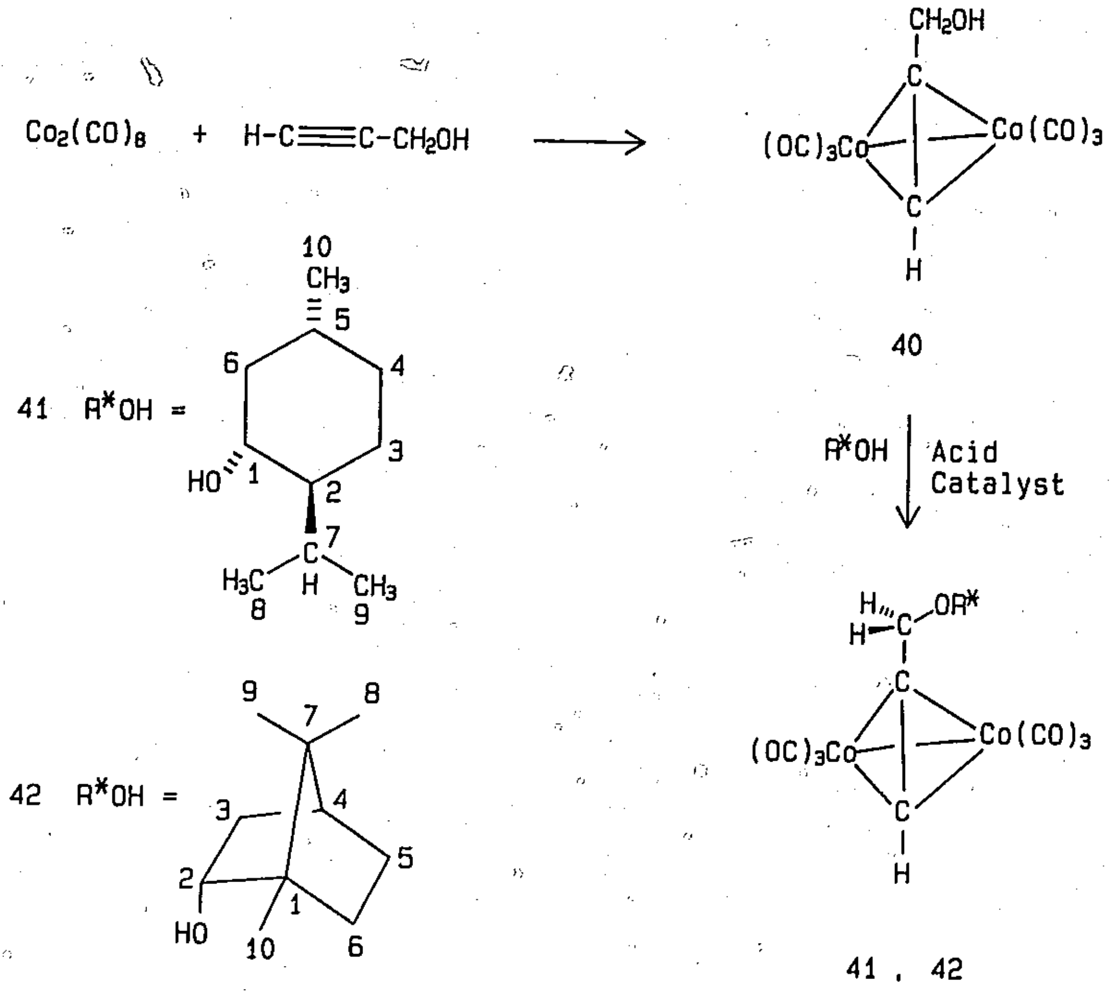
the situation is very similar to that of the previously discussed substituted chiral ethane. Now, however, it is the tricarbonyl cobalt vertices which are diastereotopic instead of the protons and theoretically there would be two resonances in the $^{59}$Co NMR spectrum of such a cluster (one for each unique cobalt). In order to generate diastereotopic Co(CO)$_3$ vertices in the tricobalt cluster **38**, it is necessary to substitute one of the cobalt carbonyl moieties by an isolobal metal fragment to give a molecule like **39**.[34] Actually, it was the existence of chemically distinct cobalt tricarbonyl vertices in clusters such as these that provided the stimulus for this series of investigations.

One of the assumptions that has been made regarding the possible use of organometallic clusters as catalysts in organic syntheses[74] is that a process which is cluster-catalyzed should be capable of inducing optical activity in the product when the cluster itself is chiral. It logically follows, therefore, that if the cluster was enantiomerically pure then the product formed during the reaction would be of only a single enantiomeric form. With an enantiomerically pure homo-bimetallic cluster such as **37**, there are two potentially catalytic metal sites present which are differentiated by their spatial orientation with respect to the chiral substituent. As a result, each of the sites could possibly give rise to a different product. Moreover, by tailoring the chiral group in the cluster it might be possible to carry out reactions with 100% selectivity for one vertex to give only a single enantiomerically pure product. Indeed, it was recently observed in our laboratory that the chiral substituents in some trimetallic tetrahedral systems can help to influence the course of ligand substitution reactions.

By using $^{31}P$ NMR spectroscopy,[34] Clark and her colleagues demonstrated that reactions of bulky phosphines with clusters of the type $R^*CCo_2(CO)_6Mo(CO)_2(C_5Me_5)$, **39**, where $R^*$ is derived from a natural product such as a terpenoid, occurred to a different degree or exhibited chiral discrimination at the diastereotopic cobalt vertices. Since these hetero-trimetallic carbynyl clusters are isolobal with dicobalt alkyne clusters (a $CpMo(CO)_2$ moiety is isolobal with a CH fragment), it was proposed that vertex selectivity by an incoming phosphine might also be observed in enantiomerically pure homo-bimetallic clusters which possessed diastereotopic cobalt vertices. Furthermore, the intrinsic diastereotopic nature of the cobalt vertices in these homo-bimetallic clusters also raised the possibility that the chiral substituents could be used to control the site of substitution of one metal fragment by an isolobal moiety; theoretically, one could therefore generate an enantiomerically pure chiral hetero-bimetallic cluster without resorting to time-consuming diastereomer separations. To this end, we have prepared several different enantiomerically pure dicobalt μ-alkyne clusters by incorporating natural products into the complexes and performed both individual ligand and complete vertex substitution reactions on them.

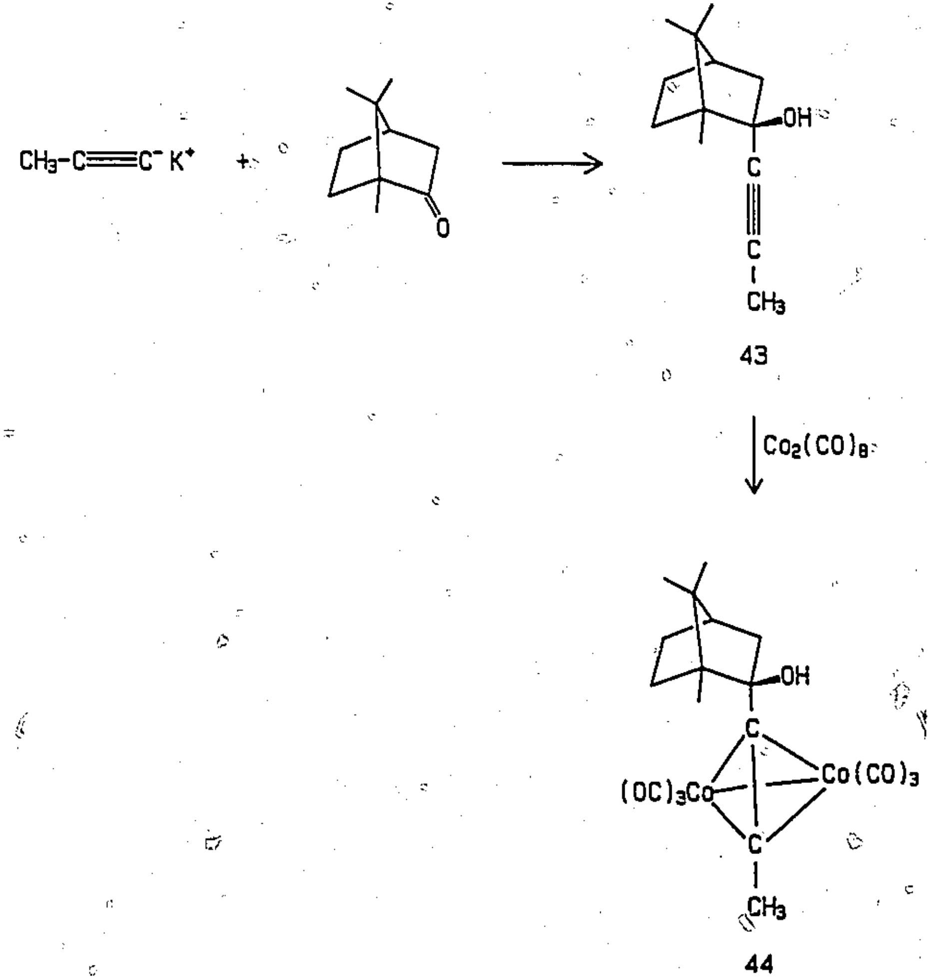
During the course of this project, three different enantiomerically pure chiral dicobalt μ-alkyne clusters were used as starting materials. Two of these dicobalt species were synthesized by following the same general route as was used by Schreiber[72] and involve the incorporation of a natural product into an existing bimetallic cluster. As shown in Scheme 14, the reaction of $Co_2(CO)_8$ with propargyl alcohol in THF at room temperature generates, in good yield, the μ-alkyne species **40** bearing a hydroxymethyl substituent. After recrystallizing this achiral cluster from hexane, subsequent treatment with a $CH_2Cl_2$ solution of either (1*R*,2*S*,5*R*)-(-)-menthol or [(1*S*)-*endo*]-(-)-borneol in the presence of an acid catalyst (i.e., $HBF_4$-$Et_2O$) over activated 4Å molecular sieve gives the enantiomerically pure chiral ether clusters **41** and **42**, respectively. This reaction presumably involves the initial generation of the cluster stabilized cation by protonating the α-hydroxy group of **40** and then losing water from that species. In turn, electrophilic attack by the cluster cation at the hydroxyl oxygen of the chiral alcohol, followed by proton elimination, gives the neutral ether derivatives.

The second approach taken to generate a chiral cluster involved the reaction of dicobalt octacarbonyl with an alkyne derivative of a natural product. In this



**Scheme 14:** **Synthetic route to the chiral ether clusters 41 and 42.**

instance, it was decided to position the chiral entity closer to the cobalt vertices when forming the resultant bimetallic μ-alkyne compound. This was accomplished by first allowing the propynyl anion, formed from the reaction of KOH and propyne, to react with (1*R*)-(+)-camphor. As illustrated, the presence of the bulky dimethyl bridge causes the alkyne anion to approach the ketonic carbon only from the lower face of the molecule thus generating 2-*endo*-propynylborneol, **43**, exclusively.[75] Subsequent reaction with $Co_2(CO)_8$ led to the desired molecule **44**.



These clusters, along with all of the others reported herein, were fully characterized by using a variety of techniques including $^{13}C$, $^{1}H$ and $^{31}P$ NMR as well as I.R. spectroscopy, mass spectrometry and elemental analyses. Conventional one-dimensional $^{13}C$ NMR experiments, such as the "spin sort" and the "gated decoupled" experiments which allow the identity of carbon atoms to be determined by the phase of the signal and the multiplicity of the signal, respectively, were used. Furthermore, some two-dimensional NMR spectroscopic techniques were employed to help in the assigning of the spectra.

For the starting cluster 44, these included the $^{1}H$-$^{1}H$ COSY and the $^{1}H$-$^{13}C$ shift-correlated NMR experiments[76] and the spectra obtained from both experiments are shown in Figures 9 and 10, respectively. The two-dimensional spectrum from the first experiment is presented as a contour plot in which the conventional one dimensional $^{1}H$ spectrum lies along the diagonal and the off-diagonal contours correlate those protons which are connected via scalar coupling. Thus, it is relatively straightforward to assign the proton resonances in a molecule by determining where scalar coupling is present. These assignments can be confirmed by using the second NMR technique, the $^{1}H$-$^{13}C$ shift-correlated experiment, whose spectrum consists of a one-dimensional $^{1}H$ spectrum projected along the vertical axis while the one-dimensional $^{13}C$ spectrum is aligned along the horizontal

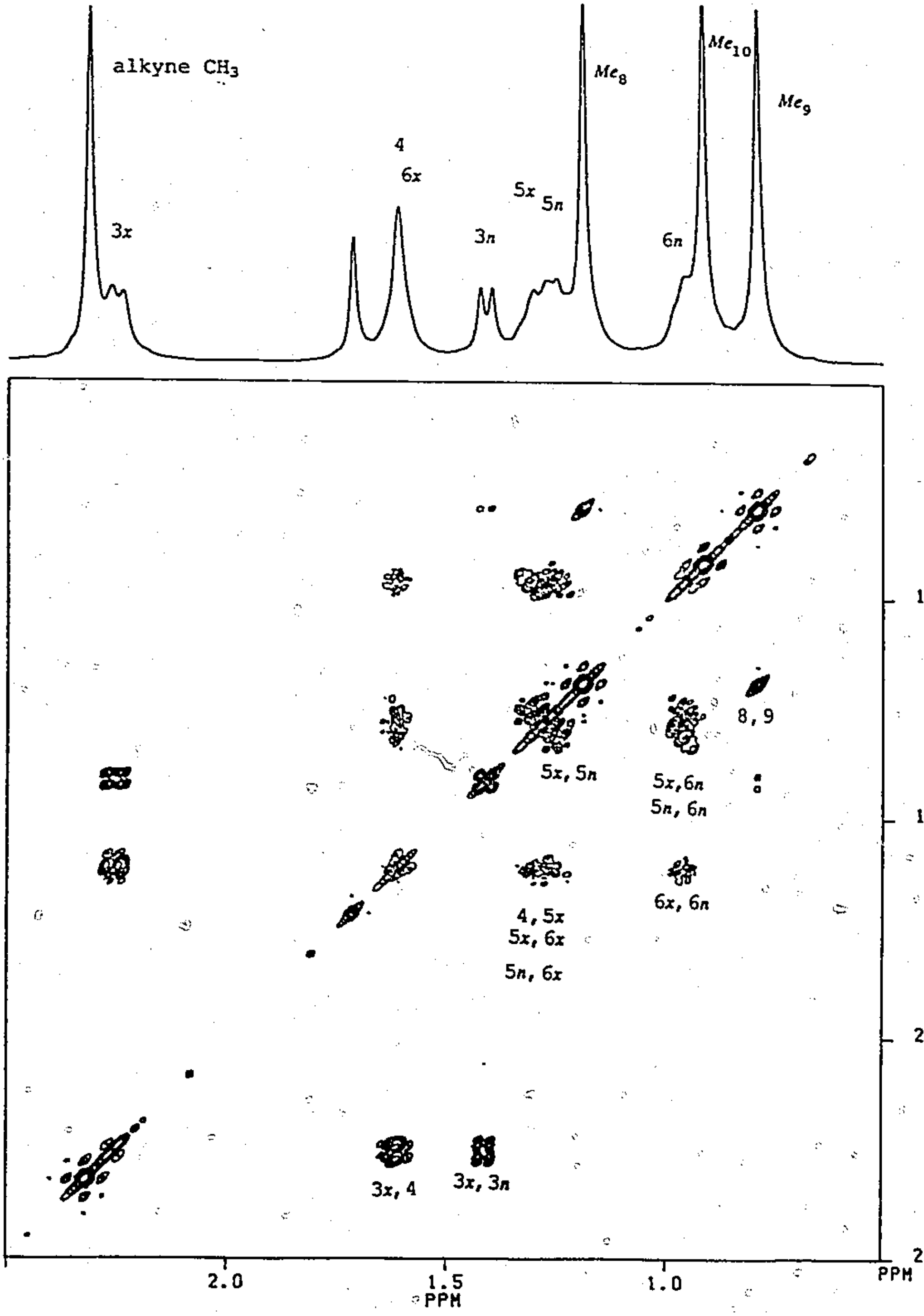


Figure 9: 500 MHz $^1$H-$^1$H COSY NMR spectrum of 44 in $C_6D_6$.

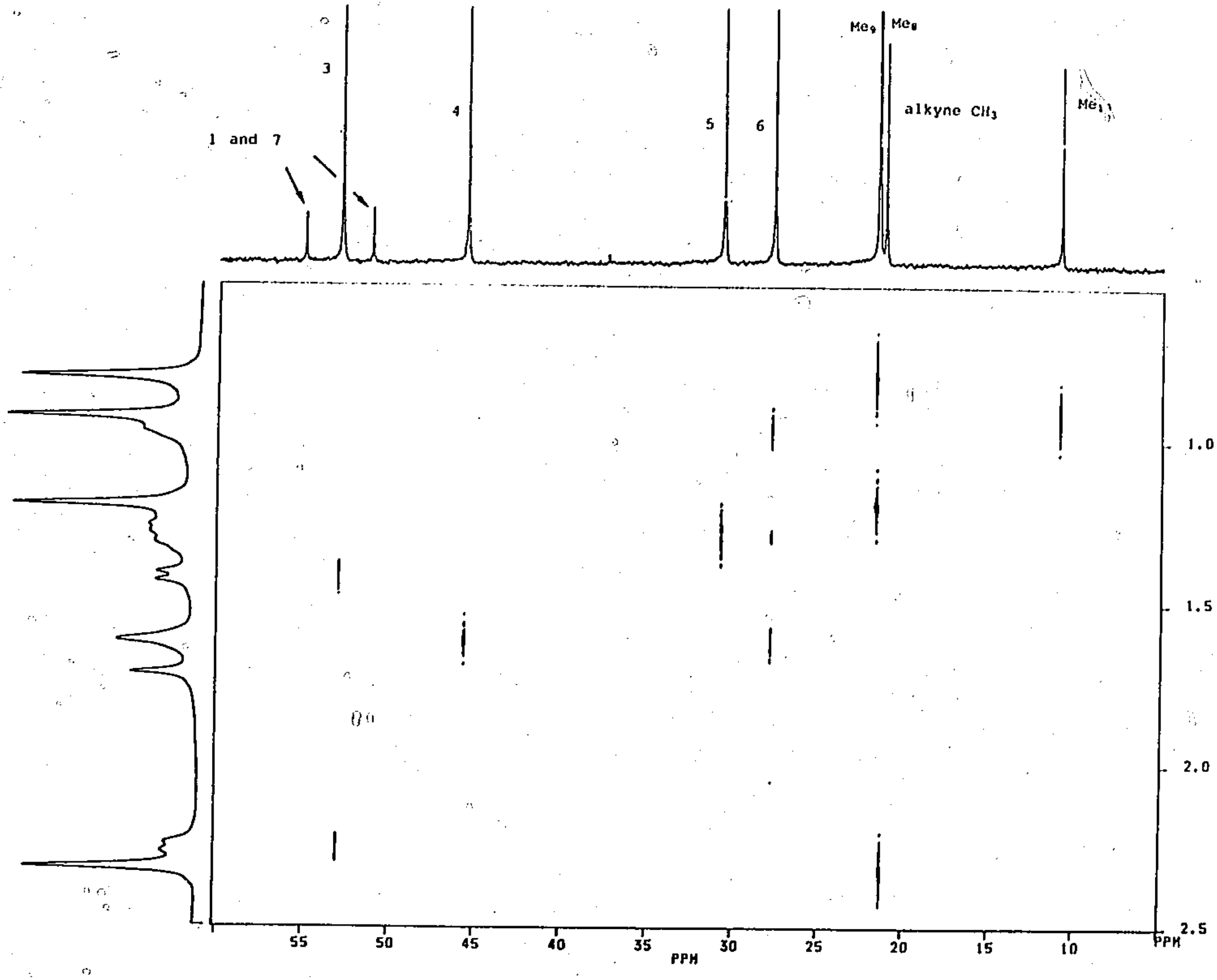


Figure 10: $^1H$-$^{13}C$ Shift-correlated NMR spectrum of 44 in $C_6D_6$.

axis. The determination of which protons are bonded to a particular carbon can be made by examining the contour map.

Furthermore, in an attempt to gain an understanding of the steric factors involved in these substitution reactions, the structure of the chiral dicobalt cluster **44** was determined X-ray crystallographically by Dr. C.S. Frampton.

### *3.3 X-ray Crystal Structure of* **44**

Reddish-black prismatic crystals of **44** were grown from dichloromethane/hexane. Figure 11 shows a view of the molecule showing the atom numbering scheme, while a stereo-view of the unit cell contents down *b* appears as Figure 12. The crystallographic data for molecule **44** are collected in Tables 6 through 8 and reveal that the alkyne-dicobalt moiety adopts the characteristic pseudo-tetrahedral core typical of such clusters. As shown in Figure 11, the $Co_2C_2$ cluster is indeed attached to the borneol at the 2-*endo*-position thus confirming that the attack by the propynyl anion at the ketonic carbon in the camphor had occurred on the less hindered face. The bonding within the cluster fragment is rather reminiscent of that previously reported[77] for (t-Bu-C≡C-Bu-t)$Co_2(CO)_6$, **45**, in which the alkyne substituents are sterically demanding. Thus, for **44** and **45**, the Co-Co distances are 2.467(1) Å and 2.463 (1) Å, respectively. The average Co-CO and CoC-O distances (1.811 and 1.129 Å for **44**; 1.805 and 1.133 for **45**) are also similar. The cobalt--alkyne-carbon bonds average to 1.985 Å and 1.996 Å for **44** and **45**, respectively, but the alkyne carbon-carbon bonds are rather short at 1.327 Å for **44** and 1.335 Å for **45**. These values may be compared to those for clusters bearing less bulky substituents in which alkyne carbon-carbon distances normally range from 1.35 Å to 1.38 Å.[78-81] In alkyne-dimetal cluster complexes the R-C≡C-R moiety is no longer linear and in **44** the substituents are bent back by approximately 35°. Furthermore, in **44** the bulk of the substituents leads to a twisting of the C(12)-C(13) bond relative to the C(11)-C(2) vector; this dihedral angle is 11.7°. Figure 13 depicts a view along the C(2)-C(11) bond and shows the "staggered-ethane type" conformation adopted by this fragment. The dihedral angle C(1)-C(2)-C(11)-C(12) would be 60° for perfect staggering and is 80.4° in **44**. An interesting point is the orientation of the α-hydroxy substituent which is directed between the two cobalts. Only two other systems of this type appear to have been characterized crystallographically.[82,83] In both cases the hydroxy group is oriented in a similar fashion to **44** and it might be speculated that there is an interaction between the hydroxy moiety and the cobalt atoms.

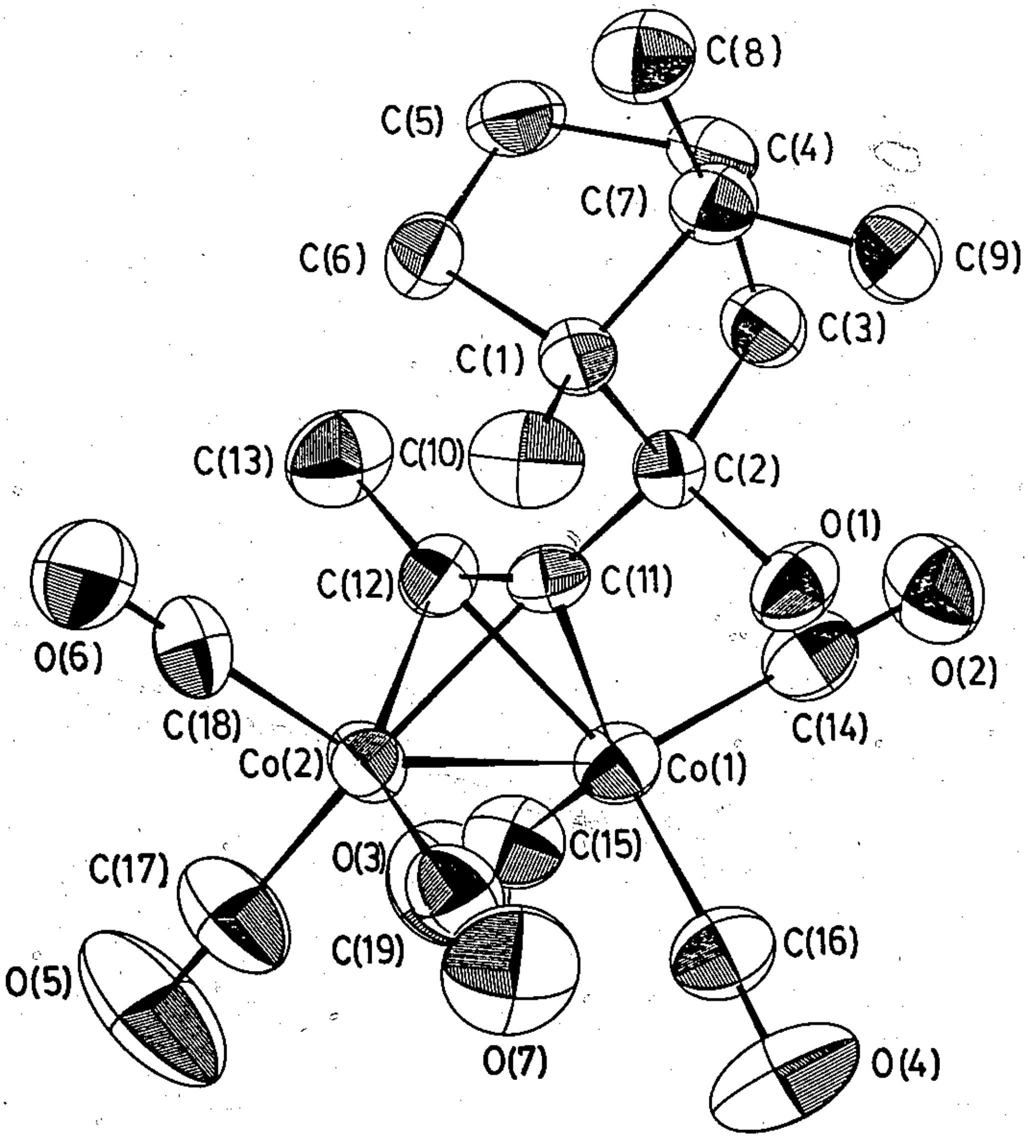


Figure 11: View of 44 showing the atom numbering scheme.

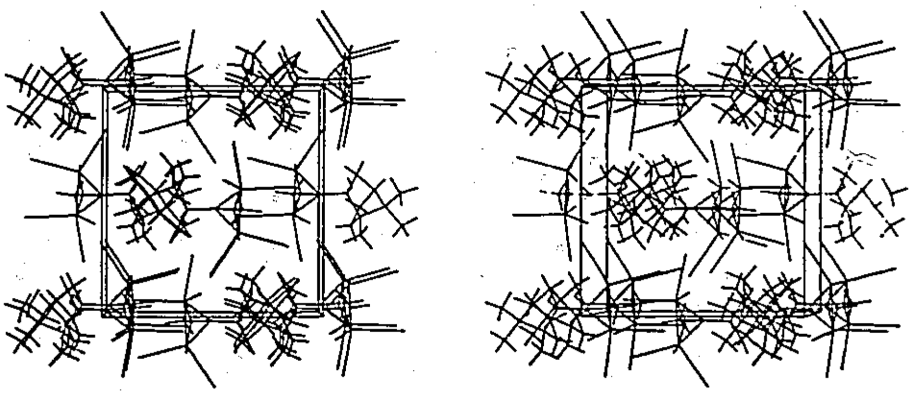


Figure 12: Stereoview of the unit cell contents of 44, the view is down the *b* axis.

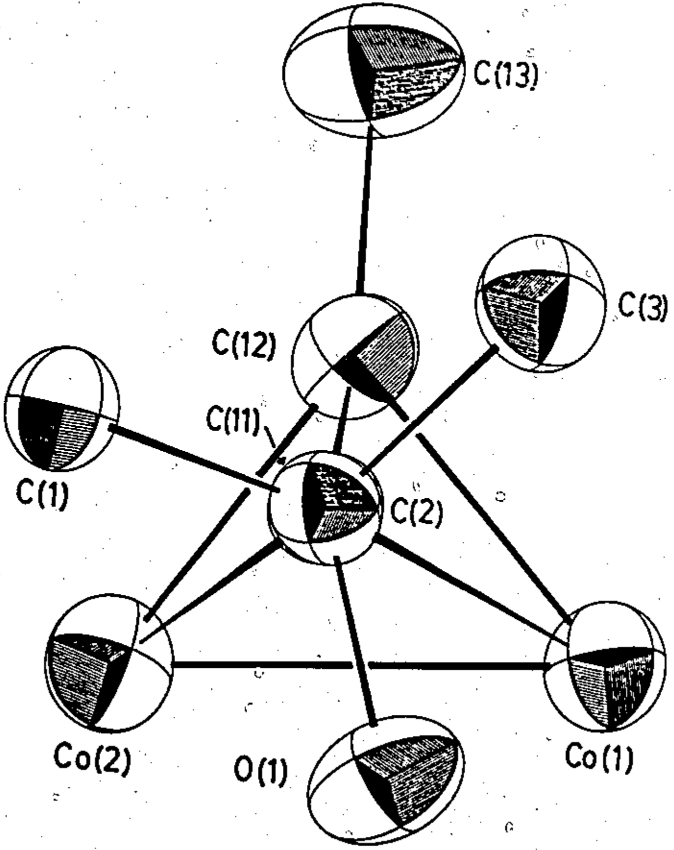
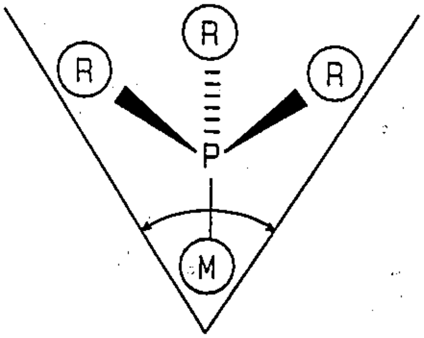


Figure 13: View along the C(2)---C(11) bond in 44 showing the approximately staggered orientation of this "ethane-type" fragment.

### *3.4 Substitutions with Phosphines*

As an extension of the previous work done in our laboratory on reactions of phosphines with carbyne-capped trimetallic tetrahedral clusters, each of the bimetallic clusters, viz., **41**, **42** and **44**, was subjected to ligand substitution reactions involving a variety of phosphines. It is possible to replace a carbonyl ligand in a cobalt cluster with a phosphine by using any one of a number of techniques, including both thermal and catalytic routes. The method employed in this work for the generation of the mono-phosphine-substituted clusters was modelled on that of Robinson et al.[84] in which a THF solution of the cluster and the phosphine was stirred at room temperature along with benzophenone ketyl (BPK) under an atmosphere of nitrogen. This synthetic technique is advantageous in that it allows one to generate the mono-substituted cluster in good yields under mild conditions. The latter point is very significant when one wishes to carry out the substitution reactions under kinetic control.

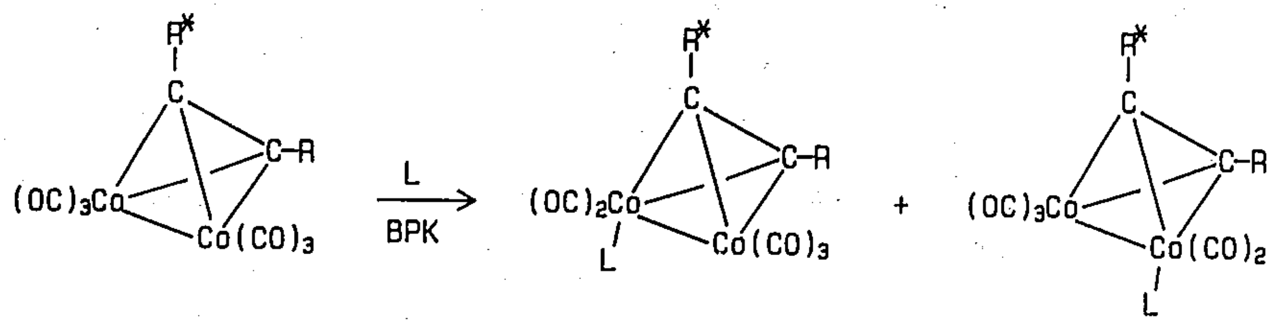
The cobalt carbonyl vertices in clusters **41** and **42** are diastereotopic and hence should not be equally susceptible to the substitution of a carbonyl group by a phosphine ligand. In the trimetallic clusters described previously, the extent of phosphine attack at the two cobalt vertices was monitored via $^{31}$P NMR spectroscopy.[34] If one carbonyl of each tricarbonyl-cobalt vertex was replaced by a phosphine to give both possible pentacarbonyl-monophosphine clusters, a pair of diastereomers would be generated and phosphorus nuclei attached to different cobalt sites would be expected to give rise to different $^{31}P$ NMR resonances. By using two different phosphine ligands, triphenyl phosphine and tricyclohexyl phosphine, in conjunction with the starting clusters it was hoped that a simple reactivity pattern could be established from the $^{31}P$ NMR results on the mono-phosphine-substituted clusters. Because tricyclohexyl phosphine is of comparable basicity to triphenyl phosphine, any difference in the degree of selectivity exhibited by the phosphines for one of the cobalt carbonyl vertices in a specific cluster could be correlated to the differences in the steric bulk of the incoming phosphines. (The cone angle, a barometer for the bulkiness of the ligand, illustrated below is 170° for tricyclohexyl phosphine while in triphenyl phosphine it is 145°.[85]) On the other hand, by



comparing the degree of selectivity observed in the clusters by a particular phosphine it might be possible to comment on which of the chiral substituents was the one better able to bring about diastereoselective substitutions. Accordingly, $PPh_3$ and $PCy_3$ were allowed to react with the ether clusters **41** and **42** to give the complexes **46** through **49**, as in Scheme 15.

The two pairs of mono-phosphine-substituted dicobalt clusters were synthesized, characterized and examined for diastereoselectivity by using $^{31}P$ NMR. However, in each of the four cases, the $^{31}P$ spectrum consisted of a single line. This observation could be interpreted in two way: either (i) the substitutions were completely selective (i.e., 100% diastereoselectivity) for one cobalt vertex over the other in all cases, or (ii) it was not possible in these molecules to resolve the different resonances for the two diastereotopic substitution sites because the chemical shift differences were small. Although accepting the first explanation would have fulfilled the goal of the experiments, the more conservative position was adopted and it was decided to try to establish the existence of two overlapping resonances.

The first attempt made to determine if there was a more than one type of phosphorus present in the mono-phosphine-substituted clusters, i.e., if a mixture of diastereomers existed in solution, involved using the DANTE NMR pulse sequence[86] to perform a "hole burning experiment" on the phosphine substituted cluster **49**. Theoretically, from this NMR experiment if there were two distinct



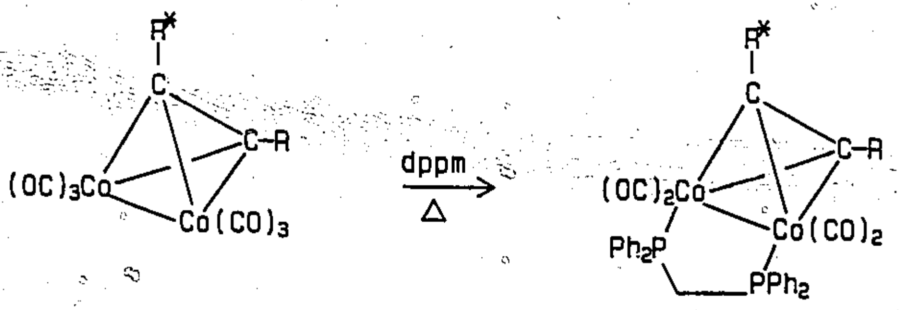
41 $R = H$, $R^* = -CH_2-O-$menthyl
42 $R = H$, $R^* = -CH_2-O-$bornyl
44 $R = CH_3$, $R^* =$ borneol

46 $R = H$, $R^* = -CH_2-O-$menthyl, $L = PPh_3$
47 $R = H$, $R^* = -CH_2-O-$menthyl, $L = PCy_3$
48 $R = H$, $R^* = -CH_2-O-$bornyl, $L = PPh_3$
49 $R = H$, $R^* = -CH_2-O-$bornyl, $L = PCy_3$
53 $R = CH_3$, $R^* =$ borneol, $L = PPh_3$

**Scheme 15:** **Synthetic route to phosphine-substituted diastereomers.**

phosphorus nuclei present the peak associated with one of the groups should have collapsed during the irradiation while the other phosphorus peak remained unchanged. On the other hand, if only one type of phosphorus environment existed the irradiation should have collapsed that peak to give a null spectrum. In our case, however, the results of the experiment proved inconclusive. Although the single $^{31}P$ resonance was observed to collapse upon irradiation, it could not be certain if the conditions of the "hole burning" experiment, which require the chemical shifts of the nuclei to be sufficiently different to allow selective irradiation of a single signal, had been met. It soon became apparent that another approach would have to be taken.

To this end, the molecules **50** and **51**, each of which contain the bridging diphenylphosphinomethane ligand, were prepared from the two starting hexacarbonyl clusters by stirring them under reflux in hexane with dppm. (It is necessary to use a thermal route to bring about the formation of the bridging ligand in dicobalt clusters because the catalytic approach is known to yield a chelated cluster.[84]) In both cases, mass spectral analysis confirmed the successful replacement of two carbonyl groups by dppm while the $^{13}C$ NMR spectroscopic results demonstrated that the dppm was bridging the two cobalts rather that forming a chelate at a single cobalt centre. (The carbonyl region of the dppm bridged clusters appeared as two peaks in the ratio 1:1. If chelation had occurred, two peaks in a 3:1 pattern would have been expected.) Since there can be no doubt that two unique phophorus environments were present in **50** and **51**, it follows that two different resonances should have been observed in the $^{31}P$ NMR of **50** and **51**, provided the chemical shifts of the nuclei were well separated and did not overlap. The $^{31}P$ NMR spectra obtained for both **50** and **51** were single lines clearly indicating that the phosphorus nuclei in these clusters did not possess distinct chemical shifts and in fact were overlapping, even at high magnetic field. The same explanation, i.e., overlapping $^{31}P$ resonances, can therefore be invoked for the mono-phosphine-substituted clusters **46** through **49**.



41 R = H, R* = $-CH_2-O-$menthyl
42 R = H, R* = $-CH_2-O-$bornyl
44 R = $CH_3$, R* = borneol

50 R = H, R* = $-CH_2-O-$menthyl
51 R = H, R* = $-CH_2-O-$bornyl
52 R = $CH_3$, R* = borneol

Nevertheless, this does not answer the question of whether any diastereoselectivity was occurring during the ligand substitution reactions. Although it was not possible to observe two resonances in the $^{31}P$ NMR spectra, pairs of corresponding carbons in the two diastereomers were detectable in the $^{13}C$ NMR spectra and it was apparent that some degree of selectivity by the incoming phosphine had taken place. By comparing the intensities of the corresponding carbons, it was possible to draw conclusions regarding the extent of selective ligand substitution. When triphenylphosphine is used as the attacking ligand on either of the starting clusters there does not appear to be any selectivity and the two possible diastereomers are formed in equivalent amounts; the ratio of the diastereotopic pairs of carbons is 1:1. In contrast, use of tricyclohexyl phosphine as the incoming ligand towards either **41** or **42** reveals (see Figure 14) that one diastereomer is being preferentially formed over the other isomer in a ratio of approximately 3:2, in both cases. Since the latter ligand possesses a larger cone angle than does triphenylphosphine the small discrimination in selectivity is presumably governed largely by steric factors. It would also appear that both of the chiral substituents were equally effective in their influence on the selectivity shown by the incoming ligand because of their similiar diastereomer ratios.

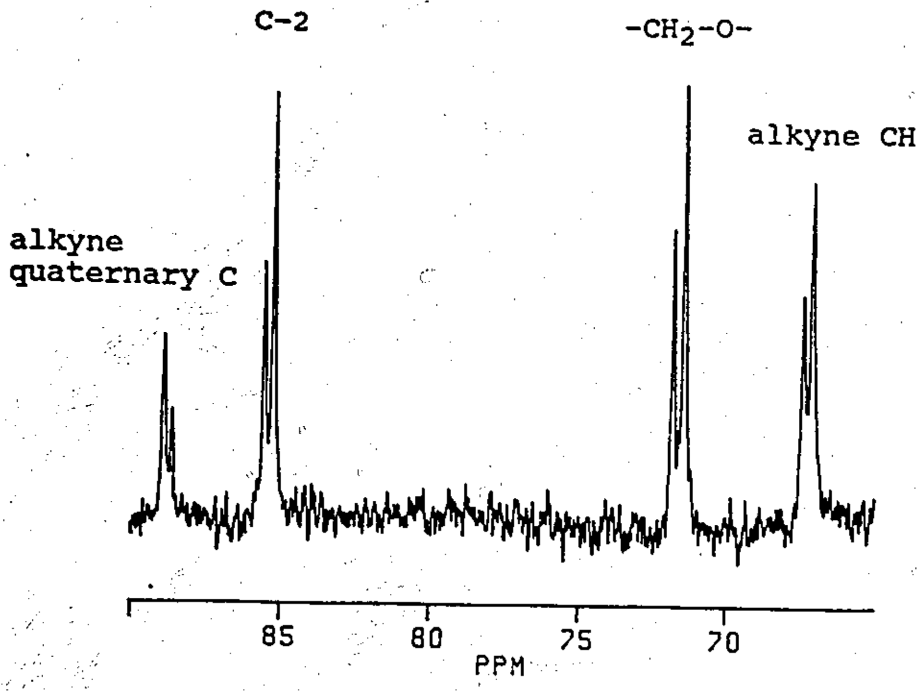


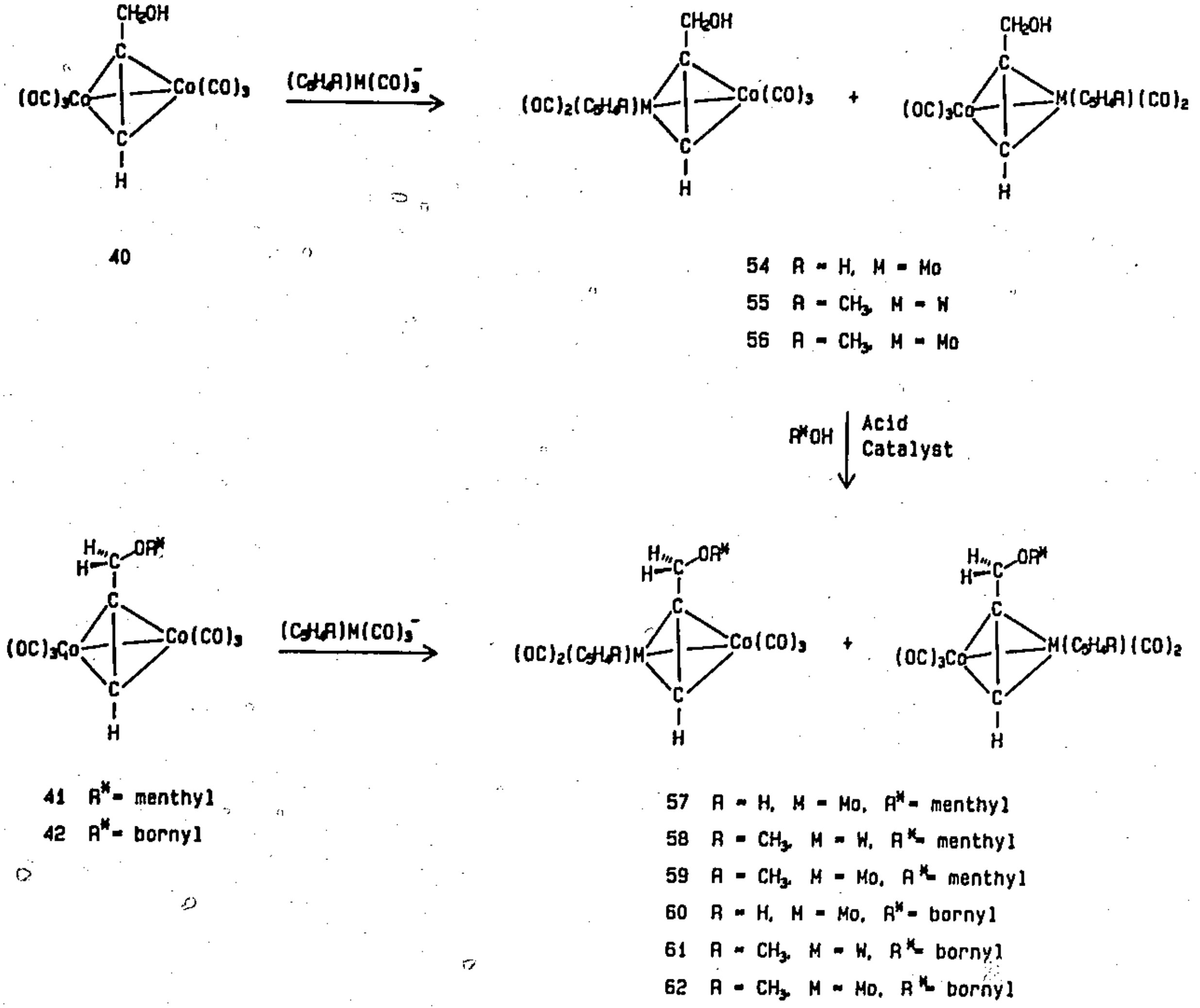
**Figure 14:** Section of the 62.5 MHz $^{13}C$ NMR spectrum of 49 showing the presence of major and minor diastereomers derived from the reaction of tricyclohexylphosphine with 42.

In the cluster **44**, which is derived from 2-*endo*-propynylborneol, the chiral substituent is situated substantially closer to the cobalt vertices than is the case for the ether clusters **41** and **42** discussed above. It might be anticipated that for **44** even greater discrimination between the two vertices would be observed. Indeed, the corresponding dppm derivative, **52**, which was synthesized by the thermal reaction of dppm with the hexacarbonyl cluster **44**, exhibited two well separated $^{31}$P NMR resonances. However, treatment of **44** with $Ph_3P$ under catalytic conditions yielded only a 1:1 mixture of the diastereomeric mono-phosphine-substituted clusters **53**. This was an unexpected and puzzling result until molecular modelling (CHEM-X) studies were carried out on the cluster **44** using its crystallographically determined co-ordinates. They revealed that incorporation of a bulky triphenylphosphine ligand into an equatorial position *trans* to the cobalt-cobalt vector leads to major steric problems. Consequently, it was concluded that the phosphine had to be replacing a pseudo-axial ligand in **44**, rather than a pseudo-equatorial ligand. Thus, the diastereoselectivity was much less influenced by the chiral substituent than would otherwise have been the case. Attempts to carry out the analogous substituion reaction with tricyclohexylphosphine were unsuccessful so at this point it was decided to focus on complete vertex substitution.

## 3.5 Hetero-bimetallic Clusters

Hetero-bimetallic μ-alkyne transition metal clusters have been the subject of numerous investigations over the past few years.[24,70,87-90] These compounds are normally generated either through the interaction of an alkyne with a heterobimetallic complex or by the isolobal substitution of a different organometallic vertex into an appropriate alkyne--homo-bimetallic cluster. The presence of the bulky chiral substituent in the enantiomerically pure dicobalt clusters suggested that it might be feasible to generate mixed metal bimetallic clusters with some degree of control over the ratio of the diastereomeric products. Through the use of high field $^{13}C$ NMR, it is possible to estimate the degree of chiral discrimination that occurs in the substitution of a (cyclopentadienyl)dicarbonylmolybdenum or -tungsten fragment for a $Co(CO)_3$ moiety. This is accomplished by comparing the intensities of the peaks assigned to corresponding pairs of carbons in the two diastereomers (as before). However, in order to ensure that the $^{13}C$ NMR results obtained would not prejudiced as a consequence of different relaxation times for the corresponding carbons in the resultant diastereotopic mixed metal clusters (as well as confirming that the corresponding pairs of carbons were actually visible for comparison), two different routes to the chiral mixed metal ether clusters were derived.

As shown in Scheme 16, the diastereomers are necessarily formed in a 50:50 ratio by the first route. Once again the propargyl alcohol-derived dicobalt μ-alkyne species **40** was used as the primary starting material. In order to prepare the mixed metal cluster derivative, it is necessary to substitute an isolobal metal fragment for one of the $Co(CO)_3$ vertices; in our work these included $(C_5H_5)Mo(CO)_2$, $(C_5H_4CH_3)Mo(CO)_2$ and $(C_5H_4CH_3)W(CO)_2$. To achieve this substitution, the cyclopentadienyl metal tricarbonyl anion was first prepared by reducing a THF solution of the corresponding metal dimer with finely divided sodium metal under an atmosphere of dry nitrogen gas. After filtering under nitrogen to remove excess sodium, a sample of the hydroxymethyl cluster **40** dissolved in THF was added to the solution and the combination was stirred under reflux to give an equimolar mixture of the hetero-bimetallic enantiomers, **54**, **55** or **56**. A racemic mixture is obtained because at the time of the isolobal substitution there is no way for the incoming metal fragment to differentiate between the two cobalt carbonyl moieties. These racemic complexes were then treated with either (1*R*,2*S*,5*R*)-(-)-menthol or [(1*S*)-*endo*]-(-)-borneol and an acid catalyst over activated 4Å molecular sieve to give 50:50 diastereomeric mixtures of the hetero-bimetallic species possessing a chiral natural product substituent, **57** through **62**. Now a simple reversal of these steps results in



40

54 R = H, M = Mo
55 R = CH$_3$, M = W
56 R = CH$_3$, M = Mo

41 R* = menthyl
42 R* = bornyl

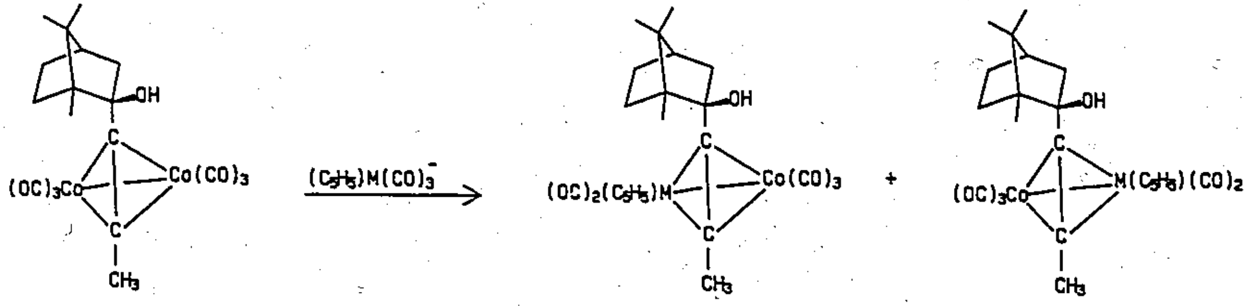
57 R = H, M = Mo, R* = menthyl
58 R = CH$_3$, M = W, R* = menthyl
59 R = CH$_3$, M = Mo, R* = menthyl
60 R = H, M = Mo, R* = bornyl
61 R = CH$_3$, M = W, R* = bornyl
62 R = CH$_3$, M = Mo, R* = bornyl

**Scheme 16:** Synthetic routes to metal-substituted diastereomers.

conditions in which there is the potential for selective vertex replacement. Reaction of the (cyclopentadienyl)-$M(CO)_3^-$ anions with the already enantiomerically pure chiral clusters **41** and **42** produces diastereomeric mixtures of clusters **57** through **62** which are not necessarily in a 50:50 ratio.

By following this procedure, the $^{13}C$ NMR spectra of the 50:50 mixtures obtained via the first synthetic procedure could be used as standards against which to normalize the spectra obtained for the substitution products derived from the latter route. A careful scrutiny of the normalized $^{13}C$ spectra revealed a small degree of diastereoselectivity during the course of the vertex substitution reactions on **41** and **42** such that the hetero-bimetallic diastereomers were present in a ratio of approximately 55:45 in all cases.

In an attempt to improve upon the chiral discrimination observed with the ether clusters **41** and **42**, a similar set of isolobal replacement reactions was carried out with the 2-*endo*-propynylborneol cluster **44** in which the chiral fragment is situated much closer to the $Co(CO)_3$ vertices. Gratifyingly, the $^{13}C$ NMR spectra of the reaction products revealed that isolobal replacement of a tricarbonylcobalt vertex by $(C_5H_5)Mo(CO)_2$ yielded a 65:35 mixture of the diastereomeric hetero-bimetallic clusters, **63**. Furthermore, the analogous reaction with $(C_5H_5)W(CO)_3^-$ gave a 75:25 diastereomeric mixture **64** of the tungsten containing species. This diastereoselectivity is quite evident in Figure 15 which depicts the resonances associated with the carbonyl and cyclopentadienyl carbons derived from the tungsten reaction.



44

63 M = Mo
64 M = W

Efforts to obtain crystals of the hetero-bimetallic clusters suitable for X-ray diffraction studies were unsuccessful so, at this point, an attempt was made to determine the solution structures of the two diastereomers of **63** and **64** in order to identify which isomer was being formed preferentially. By synthesizing the dimolybdenum and ditungsten complexes of 2-*endo*-propynylborneol, viz., **65** and **66**, it was anticipated that NMR studies (in particular, nOe measurements) would allow the orientations of the cyclopentadienyl rings with respect to the bridgehead methyl of the borneol to be determined. A comparison of the NMR shifts of the diastereomeric hetero-bimetallic mixture and of the homo-bimetallic cluster would then allow conclusions to be drawn regarding which vertex in the dicobalt-μ-alkyne

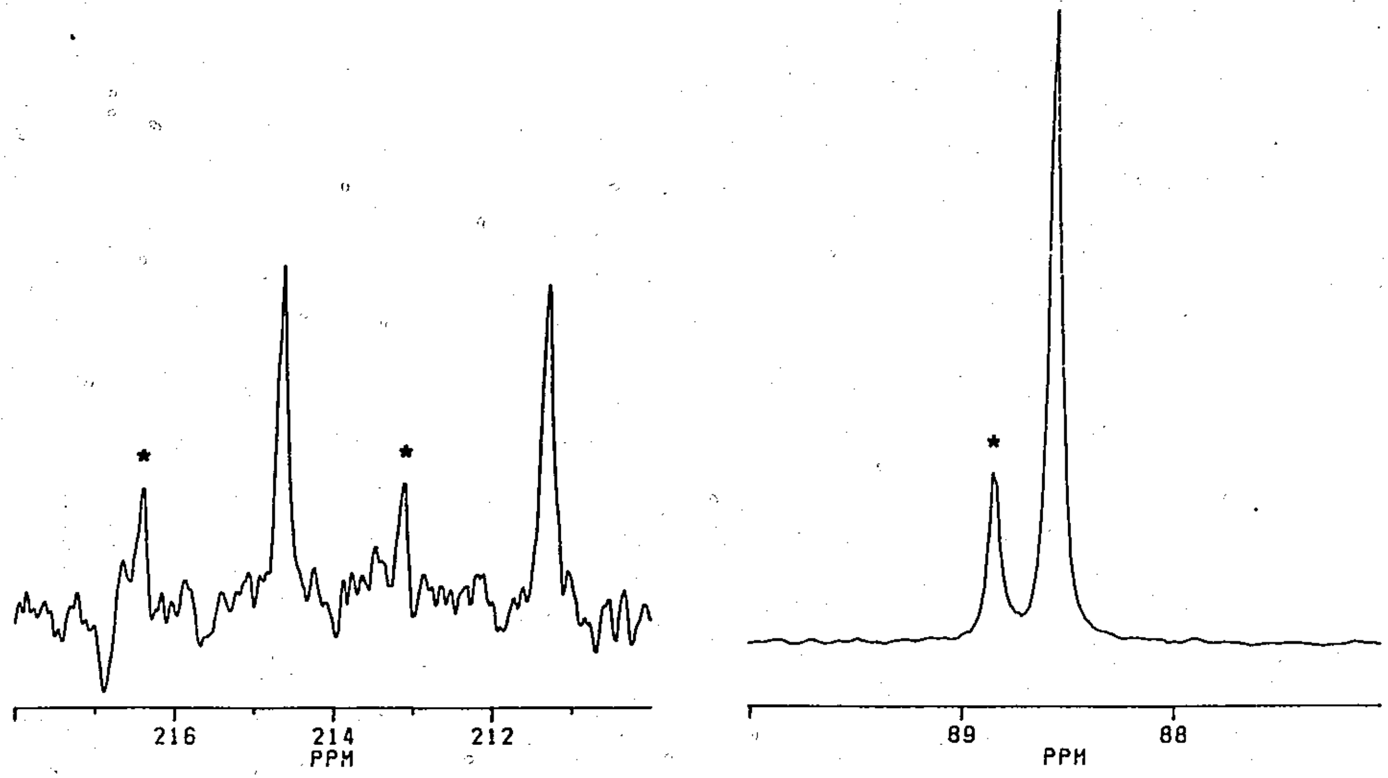
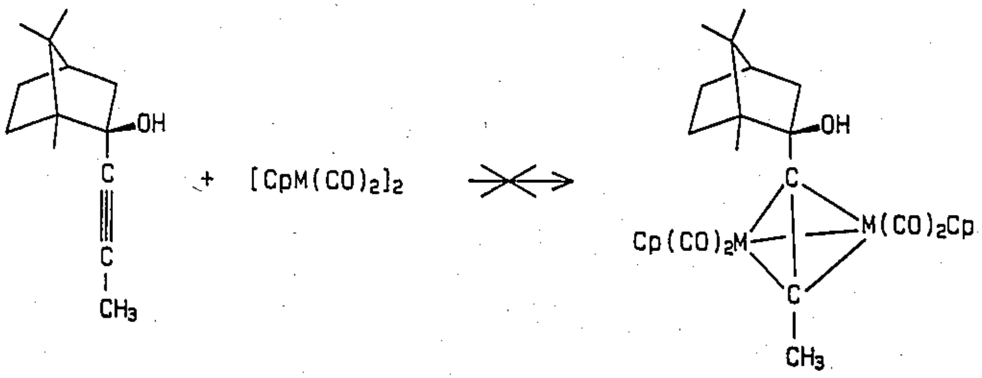


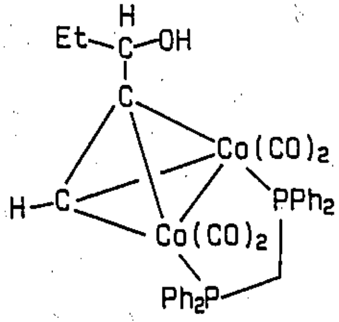
**Figure 15:** Section of the 62.5 MHz $^{13}C$ NMR spectrum of 64 showing the cyclopentadienyl and tungsten carbonyl resonances for the major and minor (*) diastereomers.

starting cluster was the preferred site for substitution. Unfortunately, the proposed NMR experiment was circumvented by the inability to synthesize either of the clusters, **65** and **66**.

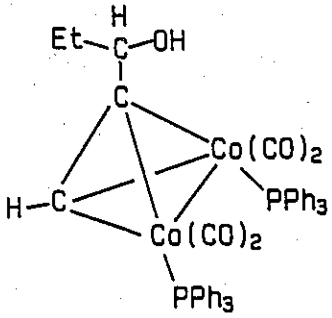


**65** M = Mo
**66** M = W

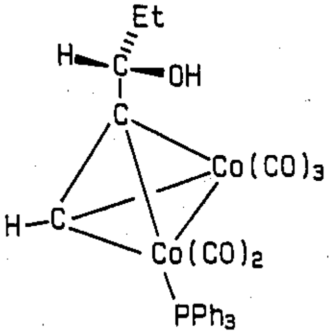
As the final synthetic aspects of this work were being completed, a paper appeared in the literature which described reactions of triphenylphosphine with racemic mixtures of $(H\text{-}C{\equiv}C\text{-}CH(R)OH)Co_2(CO)_6$ clusters.[83] In these systems, the chiral nature of the α-carbon rendered the $Co(CO)_3$ vertices diastereotopic and selective substitution of triphenylphosphine for CO at one cobalt vertex was observed. Furthermore, it was established crystallographically that the carbonyl ligand which had been preferentially replaced was an equatorial ligand *trans* to the cobalt-cobalt bond and situated proximal to the less sterically demanding hydrogen atom. In light of these interesting observations, it was decided to extend our study to include racemic propargyl alcohol complexes of the type described by Nicholas. The compound $(HC{\equiv}C\text{-}CH(Et)OH)Co_2(CO)_6$, **67**, was selected as being a representative cluster which had not been previously examined. Treatment of **67** with $Ph_2PCH_2PPh_2$ yielded the complex **68** which exhibited only a single $^{31}P$ signal despite the diastereotopic character of the phosphorus nuclei. The $^{13}CO$ peaks appeared as two broad resonances at 207.9 and 203.9 ppm. As anticipated from the work of Nicholas, the reaction of **67** with triphenylphosphine gave major (67%) and minor (33%) diastereomers, **69a** and **69b**, respectively, which were separable by column chromatography; the disubstituted cluster **70** was also obtained.



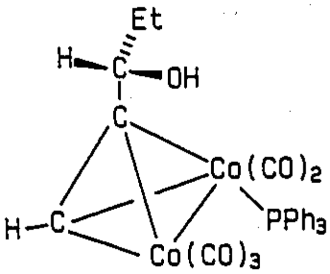
68



70



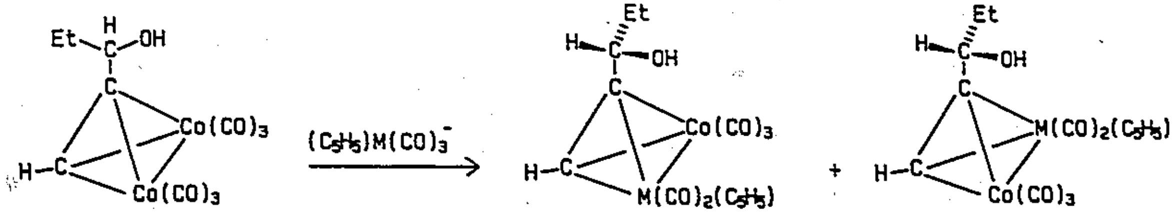
69a



69b

The rationale for the noticeably better diastereoselectivity observed for the attack of $Ph_3P$ on **67** (and the related clusters described by Nicholas) than that found with the borneol cluster **44** is really quite simple. In the former cluster(s), there exists the possibility of substituting at the pseudo-equatorial positions which are differentiated to a greater degree by being either proximal or distal to a hydrogen atom on the α-carbon, as Nicholas' crystal structure demonstrated. On the other hand, the inability to substitute anywhere but at a pseudo-axial position in **44** means that the chiral substituent does not play a significant role in the diastereoselectivity.

Treatment of the dicobalt cluster **67** with the (cyclopentadienyl)tricarbonyl molybdenum anion led to a 70:30 diastereomeric mixture, **71**; the diastereomer ratio was readily determined from the relative intensities of the signals in the $^{13}C$ NMR spectrum. Although these molybdenum clusters were not readily separable chromatographically, the analogous tungsten complexes, **72**, were synthesized in a 60:40 ratio and the major isomer (the first to elute from the column) was cleanly isolable. It must be reiterated, however, that the phosphine-substituted or metal-substituted clusters obtained by attack on such systems as **41**, **42** and **44** are diastereomers and are optically active whereas the products **69a** and **69b** (which were obtained via the Nicholas procedure) and also the mixed metal clusters **71** and **72** are still racemic mixtures since the starting cluster **67** is a racemate. (For simplicity only a single enantiomer of each cluster is shown.)



67

71 M = Mo

72 M = W

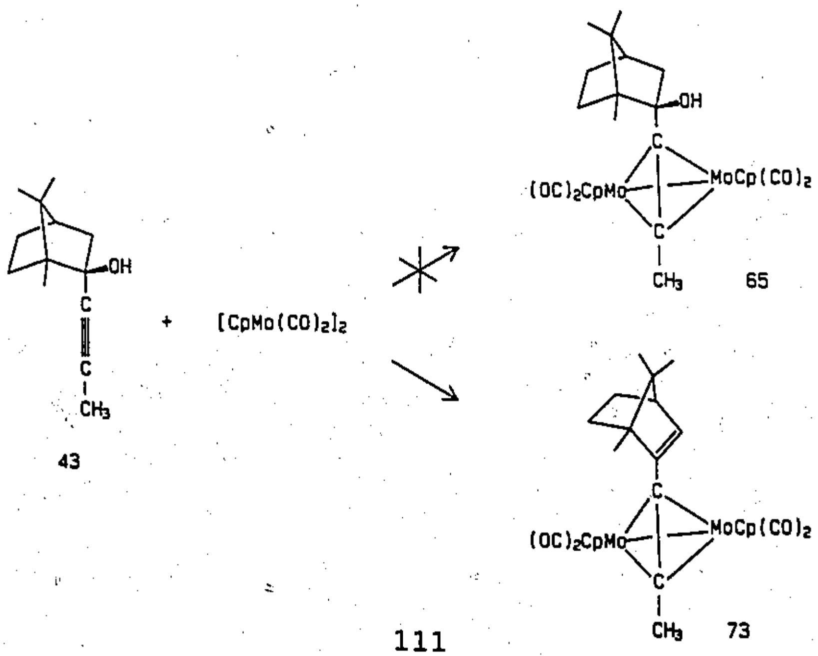
To conclude, in chiral hexacarbonyl-dicobalt μ-alkyne clusters, the sites of carbonyl ligand substitutions or of tricarbonyl vertex substitutions by a variety of isolobal organometallic fragments can be influenced by the nature and proximity of the alkyne substituents. The observed preferential formation of one diastereomer over another suggests that careful control of vertex substitution reactions may provide a simple and direct route to enantiomerically pure heterobimetallic chiral clusters without the need for tedious separations.

# CHAPTER FOUR

## MIXED METAL CATIONIC CLUSTERS

### *4.1 Background*

During the investigation of diastereoselective ligand and vertex substitution reactions on the enantiomerically pure (μ-alkyne) dicobalt cluster, **44**, it was proposed that the analogous dimolybdenum cluster, **65**, which also contained the natural product "borneol" as a substituent be synthesized and examined by NMR spectroscopy. In an attempt to obtain this complex, a product was isolated which the $^{13}$C NMR and mass spectroscopic data indicated to be the alkene cluster **73** and not the sought after species **65**.



The formation of the dimolybdenum complex **73** was interesting in its own right and when suitable purple-black prismatic crystals were obtained an X-ray diffraction study was undertaken. Figure 16 shows a view of the molecule **73** and reveals that the original borneol moiety has indeed been dehydrated across the C(2)-C(3) bond, as indicated from the spectroscopic data. Unlike the dicobalt complex **44**, in which the tetrahedral nature of the C(2) centre brings about some degree of steric crowding at one of the $Co(CO)_3$ vertices (and thus accounts for the diastereoselective vertex substitutions observed), the two dicarbonyl(cyclopentadienyl)molybdenum fragments are relatively unencumbered by the chiral organic group. The $sp^2$ character of C(2) in **73** leaves the cluster core splayed away from the terpene and the basic $Mo_2C_2$ framework adopts the tetrahedral geometry so typical of these molecules.[37,91,92] The Mo-Mo bond length of 2.972(1) Å is in the normal range for these systems. The crystallographic data including all the important bond lengths and angles are collected in Tables 9 through 11.

A characteristic feature of many of these ($\mu^2$-alkyne)$Mo_2(CO)_4Cp_2$ clusters is the asymmetric nature of the tetrahedral unit. As was first pointed out by Cotton,[37] the two cyclopentadienyl rings are oriented so as to generate a system with almost $C_2$ symmetry; moreover the chiral nature of the tetrahedron is accentuated by the presence of a semi-bridging carbonyl ligand. This asymmetry is also apparent

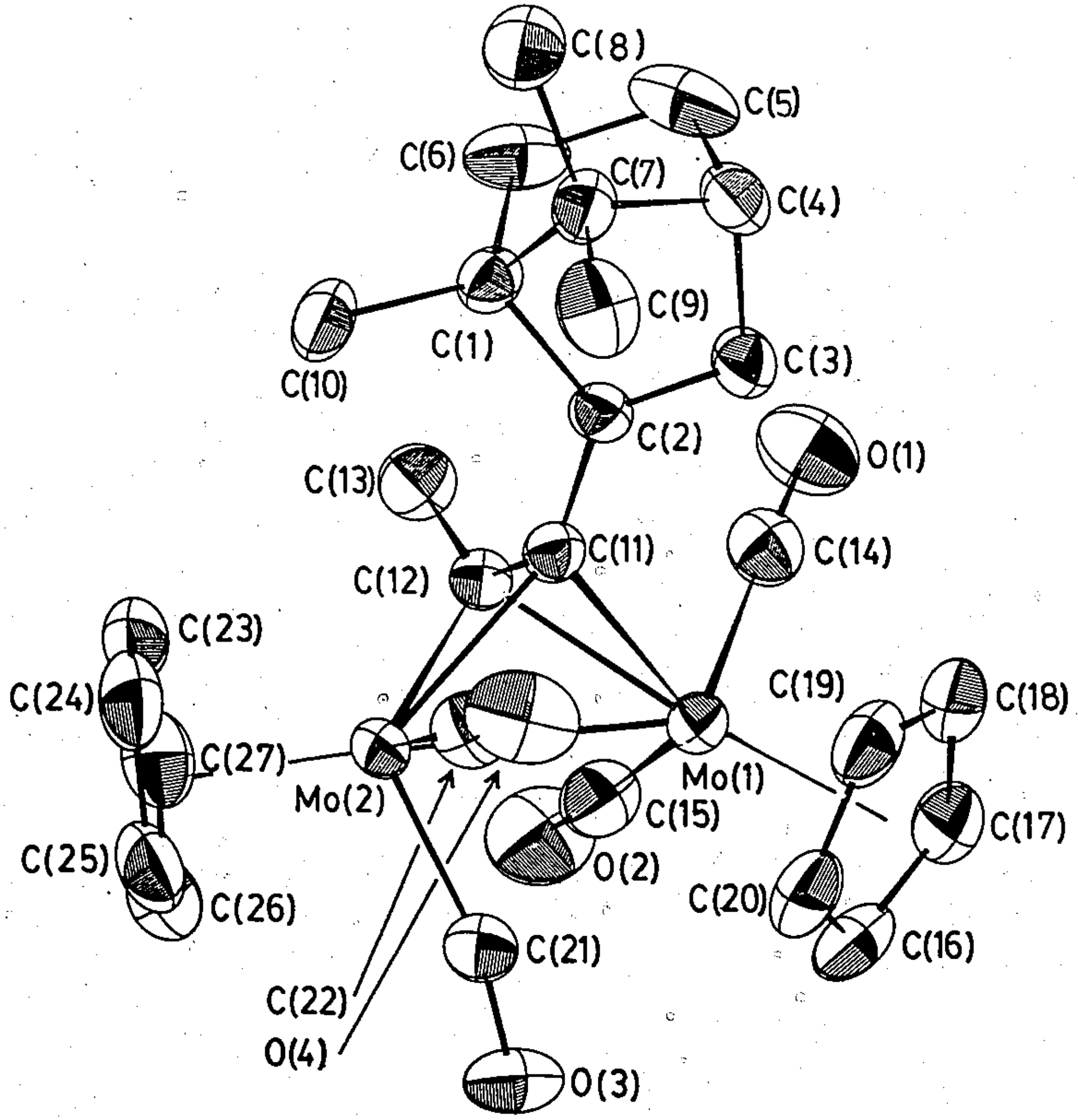
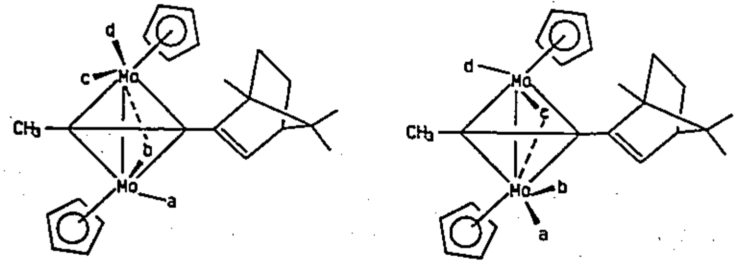


**Figure 16:** View of (1,7,7-trimethyl-$\mu^2$-2-propynylnorbornene)bis(cyclopentadienyl)tetracarbonyldimolybdenum, 73.

in cluster **73**; the cyclopentadienyl rings are twisted so as to make a Cp(centroid)-Mo-Mo-Cp(centroid) dihedral angle of 143°. As expected, one of the carbonyls occupies a semi-bridging position; the Mo(2)-C(21)-O(3) angle is 167° whereas the corresponding angles for the terminal Mo-CO ligands are ≈ 178°. As discussed earlier, Cotton and others were able to demonstrate[37,38] that two fluxional processes are detectable in these systems by NMR spectroscopy: the first involves an exchange of terminal and semi-bridging carbonyls while the second process equilibrates the environments of the cyclopentadienyl units. In the present molecule, the chiral nature of the terpene group renders all four molybdenum carbonyls non-equivalent even at room temperature and so, at low temperature when these fluxional processes are slow on the NMR time-scale, one can detect diastereomers in the $^{13}C$ NMR produced by having semi-bridging carbonyls in different positions. Figure 17 shows the limiting spectra obtained for this system as well as two possible diastereomeric forms. However, a full discussion of the variable-temperature NMR spectra of **73** will not be undertaken at the present time.

The unexpected appearance of the "alkene" cluster **73** led us to ponder its mechanism of formation. The molecular modelling program CHEM-X[66] was used to examine a model of the anticipated cluster **65**, constructed from the crystallographically determined co-ordinates of **44** and **73**, and found



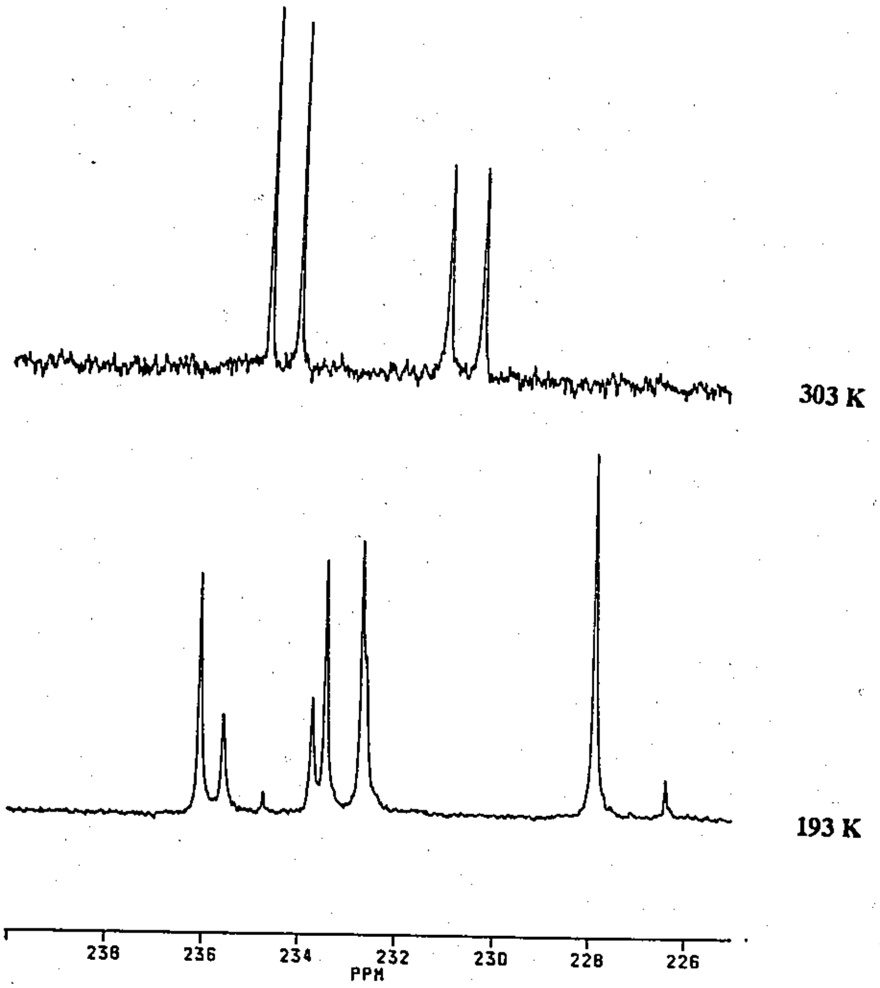
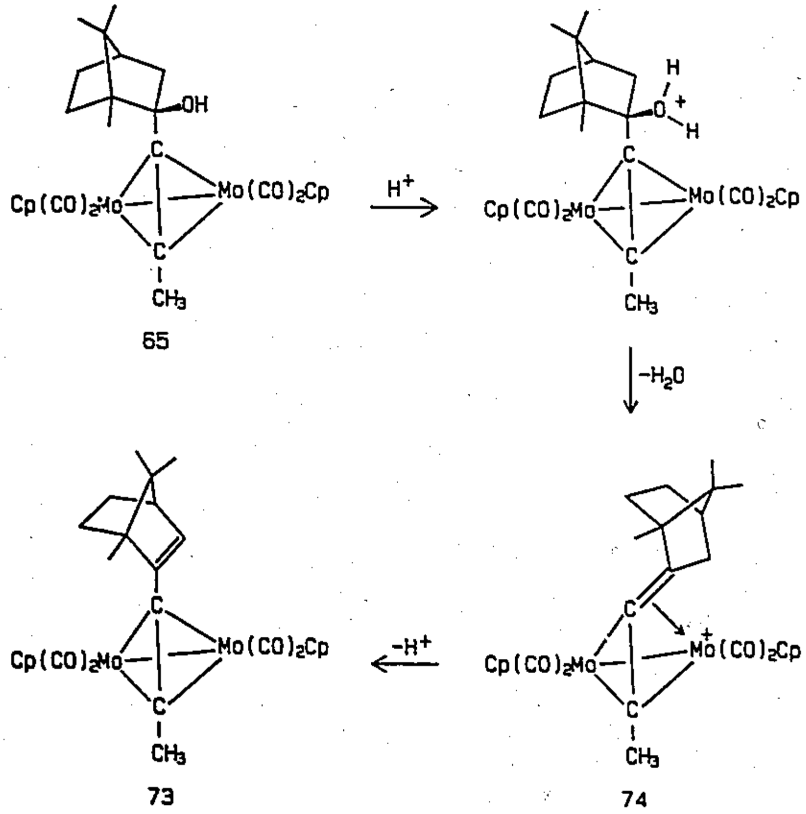
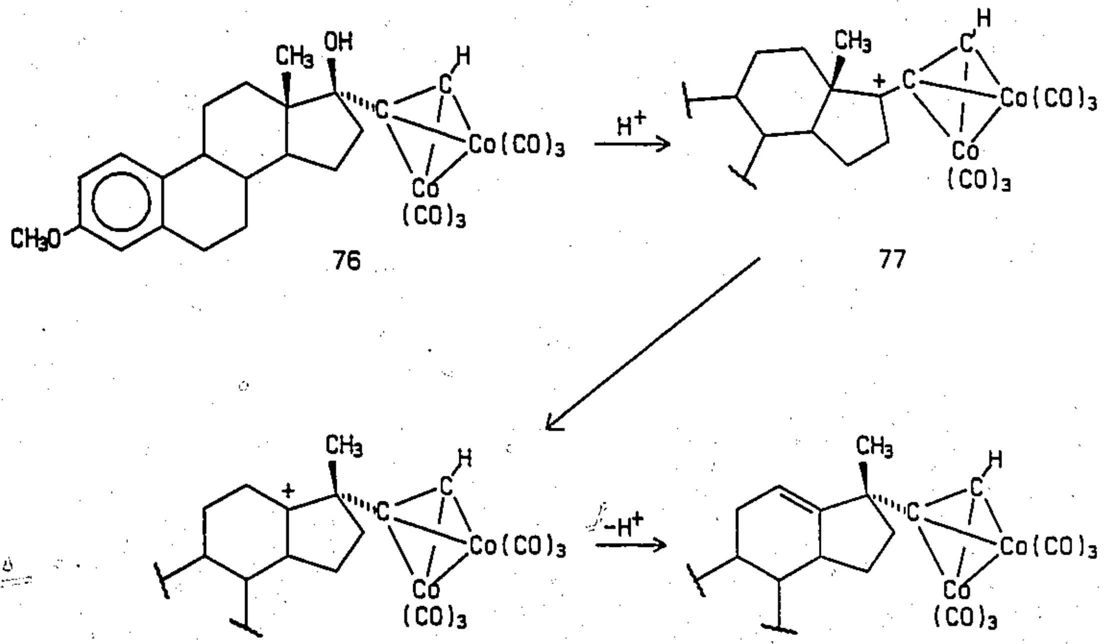


Figure 17: Variable-temperature 125 MHz $^{13}$CO NMR spectra of 73.

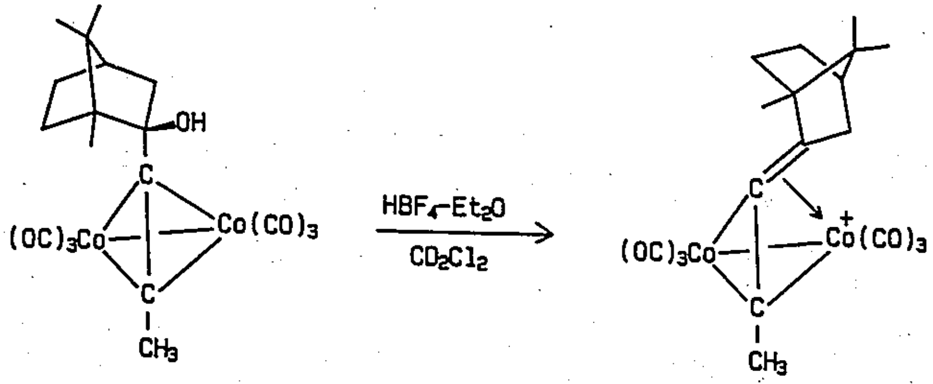

OH
Cp(CO)$_2$Mo
Mo(CO)$_2$Cp
CH$_3$
65
H$^+$
-H$_2$O
-H$^+$
73
74


CH$_3$O
CH$_3$
OH
H
Co(CO)$_3$
Co
(CO)$_3$
76
H$^+$
77
-H$^+$

that its formation was not sterically forbidden . Thus, a plausible route to **73** involves the initial formation of **65**, protonation of its hydroxyl function, loss of water to yield the cation **74**, and finally deprotonation to give the alkene **73**. The presumed intermediacy of the metal cluster-stabilized cation raises two key questions (i) can one isolate the cations **74** and **75** by protonation of **73** and **44**, respectively (ii) are the cations stable or do they undergo rearrangement as is common for terpenoid systems?[93] In connection with the latter point, it was learned that the low temperature protonation of the steroidal complex **76** yields the cation **77** which undergoes methyl group migration at ambient temperature.[94]

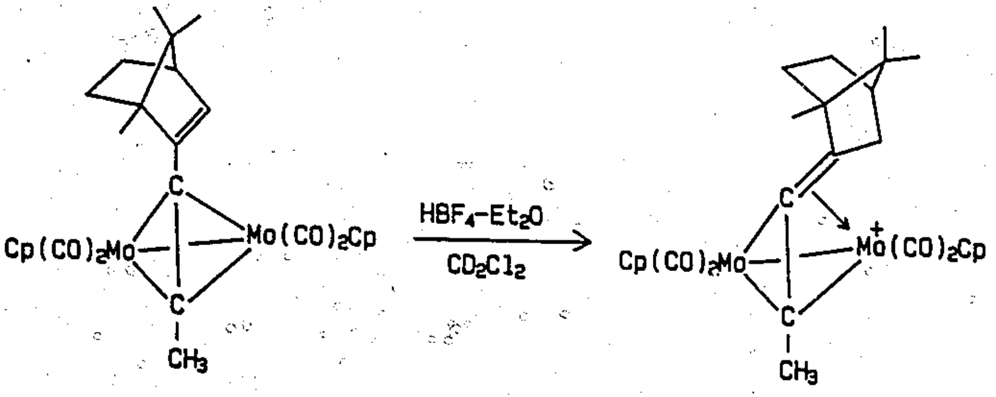
### *4.2 Protonation Studies*

Upon protonation of a $CD_2Cl_2$ solution of either **44** or **73** in an NMR tube with $HBF_4$-$Et_2O$ at approximately -40°C, an immediate colour change to a deeper red was observed. In each case, the $^1H$ and $^{13}C$ NMR spectra of the cations at -40°C were readily interpretable in terms of a single unrearranged species. The resonances were once again assigned with the aid of conventional two-dimensional NMR techniques and the spectra obtained from the 500 MHz $^1H$-$^1H$ COSY and $^1H$-$^{13}C$ shift-correlated experiments on the dicobalt cation **75** are given in Figures 18 and 19, respectively.


OH
(OC)$_3$Co
Co(CO)$_3$
C
CH$_3$
HBF$_4$-Et$_2$O
CD$_2$Cl$_2$
$\overset{+}{\text{Co}}$(CO)$_3$

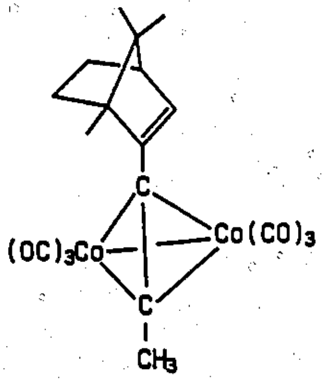
44

75


Cp(CO)$_2$Mo
Mo(CO)$_2$Cp
C
CH$_3$
HBF$_4$-Et$_2$O
CD$_2$Cl$_2$
$\overset{+}{\text{Mo}}$(CO)$_2$Cp

73

74


(OC)$_3$Co
Co(CO)$_3$
C
CH$_3$

78

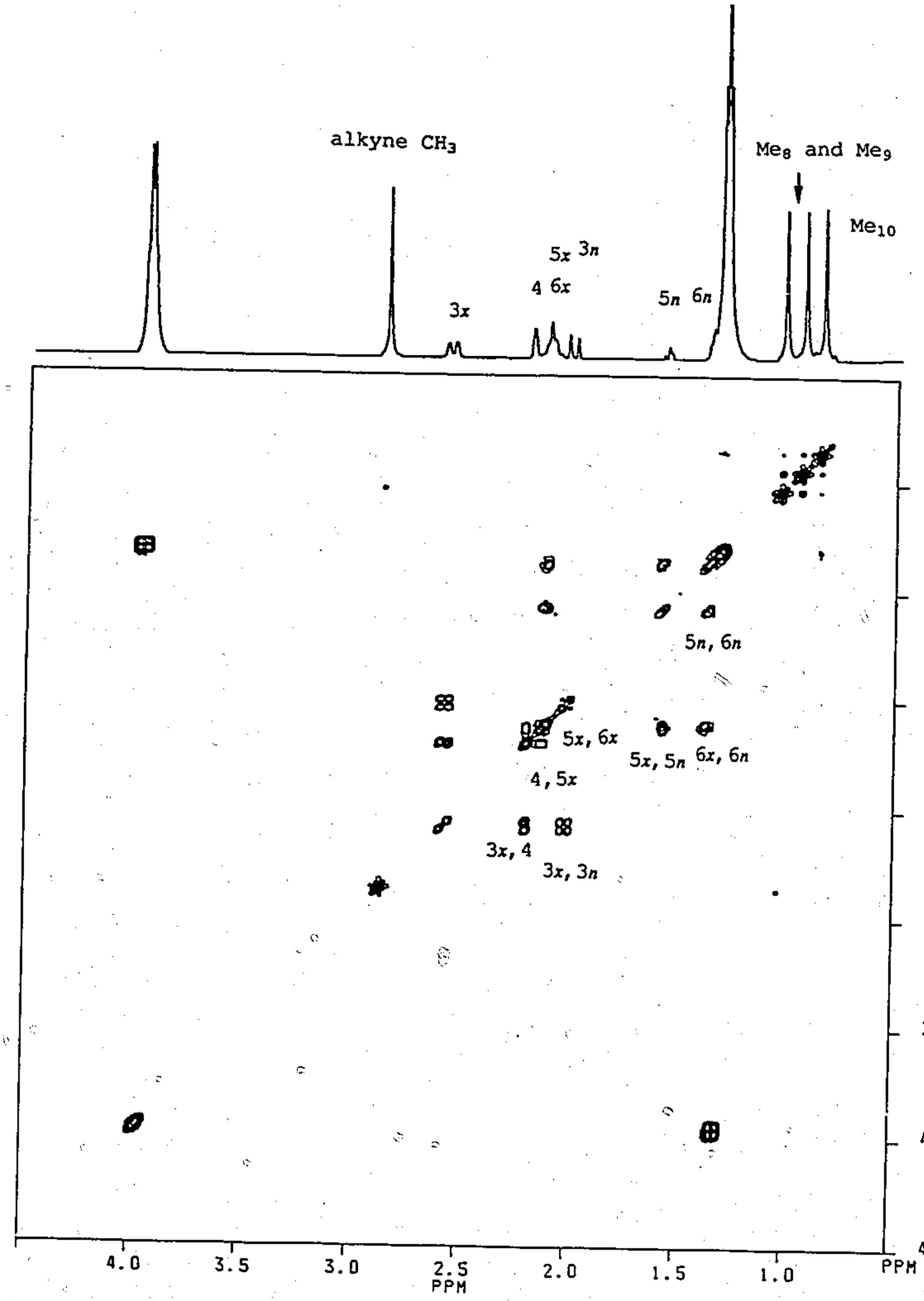


**Figure 18:** 500 MHz $^1$H-$^1$H COSY NMR spectrum of 75 in $CD_2Cl_2$ at -40° C.

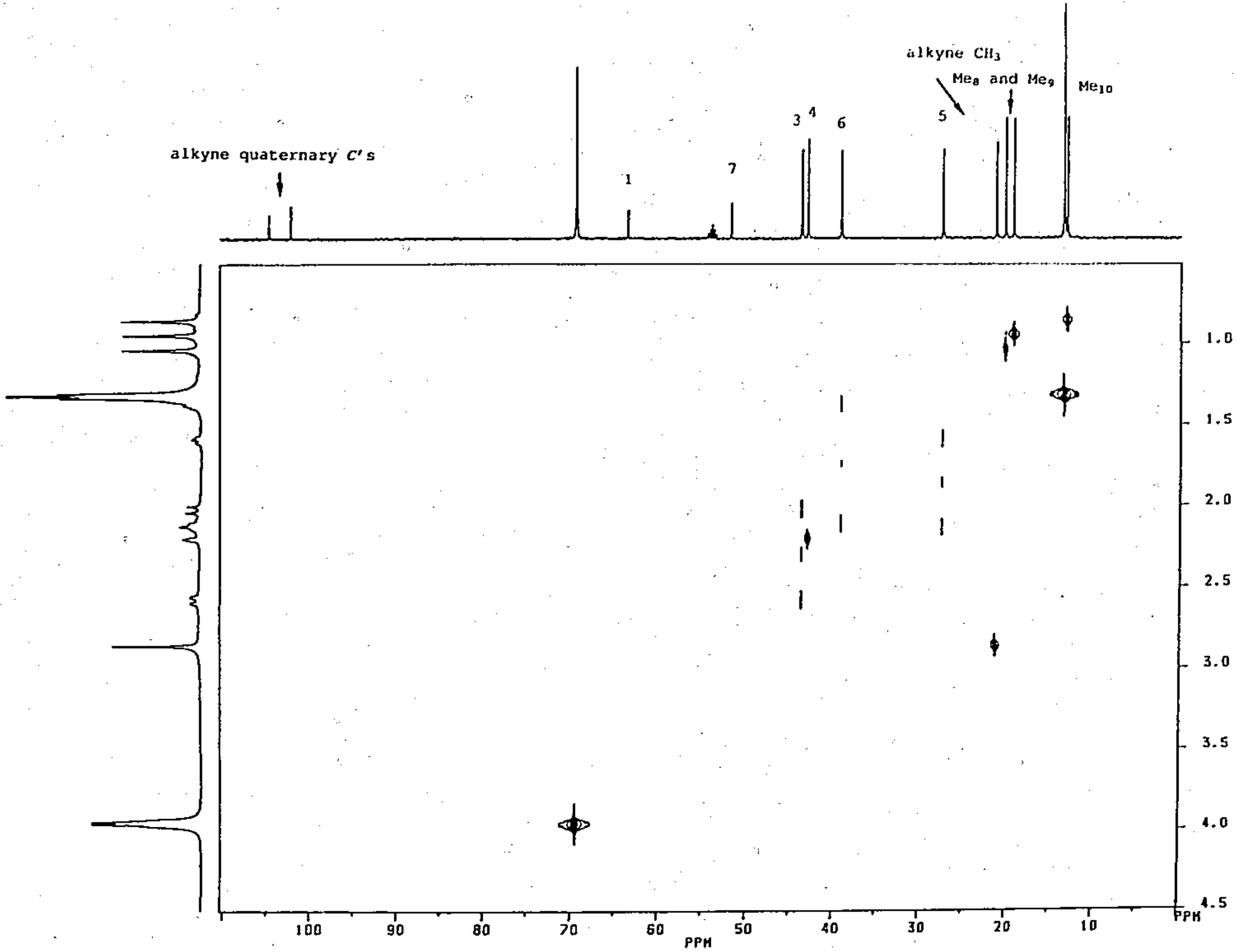
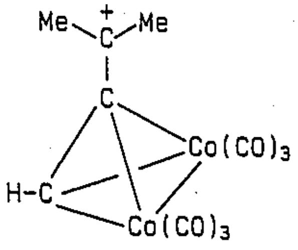


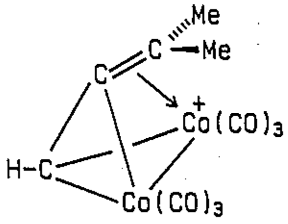
Figure 19: $^1H$-$^{13}C$ Shift-correlated NMR spectrum of 75 in $CD_2Cl_2$ at -40 °C.

Upon raising the temperature to +20°C no noticeable spectral changes were observable; apparently the presence of either a dicobalt or dimolybdenum tetrahedral cluster in a position $\alpha$ to the cationic site successfully stabilizes the terpene moiety against skeletal rearrangement. Furthermore, when a cooled sample of the dicobalt cation **75** was quenched with $H_2O$ and allowed to warm gradually to room temperature the product was shown by $^{13}C$ NMR spectroscopy to be not the original alcohol **44** but rather the dicobalt alkene cluster **78** analogous to **73**. These observations support the proposal that the cation **74** acts as an intermediate in the dehydration of the hydroxylated cluster **65**. A similar picture can also account for an observation made by Seyferth who described the generation of $Co_3(CO)_9CCMe_2OMe$ from $[Co_3(CO)_9\text{-}CCMe_2]^+PF_6^-$ and MeOH. It was found that the product obtained was critically dependent on the work-up procedure. Sublimation of the crude product mixture gave the desired product, while column chromatography on silicic acid yielded the alcohol derivative $Co_3(CO)_9CCMe_2OH$.[95] It would appear that, under acidic conditions, the ether cluster gave rise to the metal-stabilized cation which subsequently reacted with traces of water to give the alcohol.

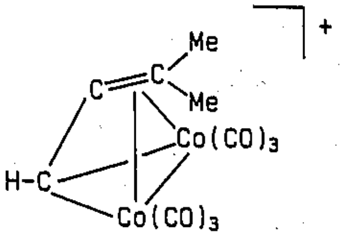
NMR observations on dimetalla-tetrahedrane cluster cations have been previously reported by a number of groups. Nicholas[96] has shown that the methyl groups in $[Co_2(CO)_6\text{-}(HC{\equiv}C\text{-}CMe_2)]^+$ **79** are non-equivalent at low temperature; this behaviour supports the idea that the positive charge is not sited merely on an upright $\alpha$-carbon, **79a**, but rather is delocalized onto the cluster. This could come about as a result of a direct bonding interaction between the CMe$_2$ fragment and either one vertex, **79b**, or both of the cobalt vertices, **79c**.



79a



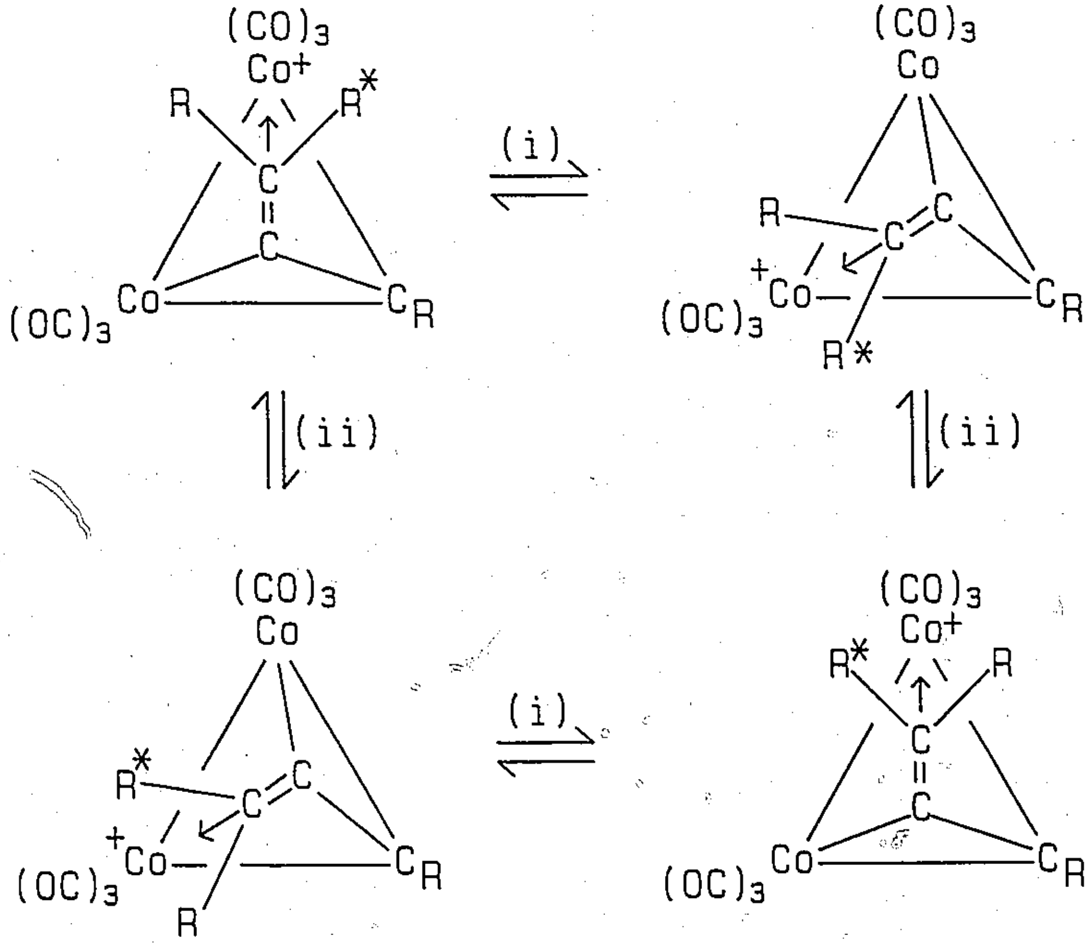
79b



79c

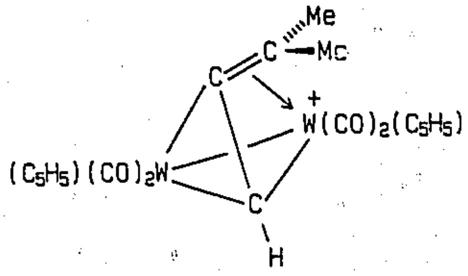
This work has since been elegantly extended by Schreiber[72] who, in an approach that mirrored the one used by Mislow for the tricobalt cation **21** discussed previously,[46] demonstrated that the vinylidene moiety in $[Co_2(CO)_6(R-C\equiv C-CR(CHMe_2)]^+$, **80**, had to be leaning towards one vertex (rather than being stabilized between two vertices) in order to bring about the observed diastereotopicity of the isopropyl methyl groups in this cation. In addition, Schreiber was able to detect the appearance of diastereomers by NMR because the triangular base towards which the vinylidene ligand was bending no longer possessed the pseudo $C_{3v}$ symmetry found in **21**. This ultimately allowed the establishment of the existence of two distinct fluxional processes in the cation **80** which led to an equilibration of all possible isopropyl methyl group environments, as depicted in Scheme 17: (i) a low energy (≈ 10 kcal/mole) antarafacial migration of an alkylidene moiety from one $Co(CO)_3$ to the other, entirely analogous to the known behaviour of $[Co_3(CO)_9C\text{-}CH(CHMe_2)]^+$ reported by Mislow; (ii) a higher energy process (≈ 13 kcal/mole) which equilibrates *syn* and *anti* isomers. The presumed existence of an upright carbocationic intermediate for the latter exchange is in accord with the observation that the energy barrier for the second fluxional process is lower for 3° than for 2° cations. It might be reasonably assumed that the more stable carbocation, viz., the 3° system, has less need for anchimeric assistance from a metal than does the 2° carbocation. Although not observed experimentally, Schreiber proposed that the barrier to the first exchange process would increase as the stability of the carbocation decreased from 3° to 2° to 1°, also as a result of the intermediate having to endure increased localization of positive charge on the $\alpha$-carbon.

Furthermore, following earlier NMR reports by Russian workers[97], Curtis[98], Green[99] and more recently Jaouen[94] have obtained X-ray crystallographic evidence which confirms the idea of the carbocationic vinylidene centre interacting with a single metal vertex in $[M_2(CO)_4Cp_2](R\text{-}C{\equiv}C\text{-}CR_2)^+$ clusters, where M = Mo or W. Once again, these molecules exhibit fluxional behaviour on the NMR time-scale

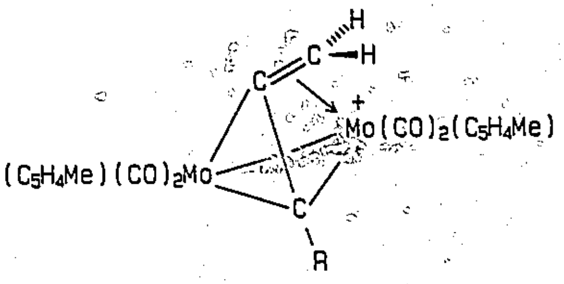


**Scheme 17:** The fluxional processess occurring in $[Co_2(CO)_6(HC{\equiv}C\text{-}CRR^*)]^+$ systems:
(i) antarafacial migration resulting in racemization of the complex;
(ii) interconversion of diastereomers, presumably via an upright cationic centre as in 79a.

and Green demonstrated that the C=CMe$_2$ fragment in **81** can migrate from tungsten to tungsten (presumably via both of the above mentioned processes) with an activation energy barrier of approximately 10 kcal/mole.[99] Interestingly, in the [(C$_5$H$_4$Me)$_2$Mo$_2$(CO)$_4$(R-C≡C-CH$_2$)]$^+$ system, **82**, studied by Curtis[98] the activation energy for migration of the C=CH$_2$ moiety from molybdenum to molybdenum via (i) (which was detected as an equilibration of the methylcyclopentadienyl rings) is noticeably higher (≈ 17 kcal/mole) than for the corresponding C=CMe$_2$ exchange between tungsten sites. Moreover, the higher energy process (ii) which exchanges the two methylene proton signals and is thought to require an upright carbocation is not observed for this primary (-CH$_2$$^+$) species. Both of these results are in agreement with Schreiber's proposal outlined above.[72]



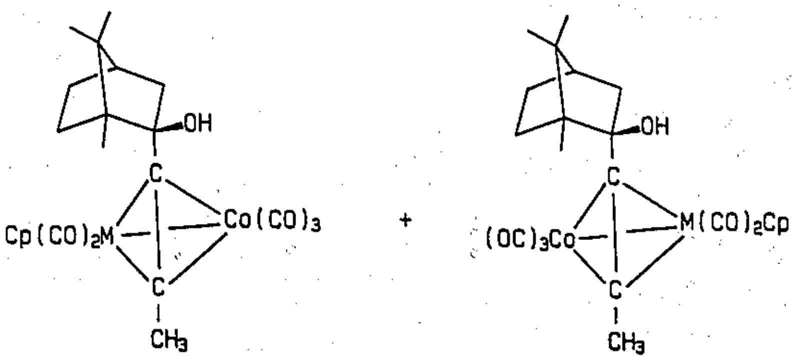
81



82

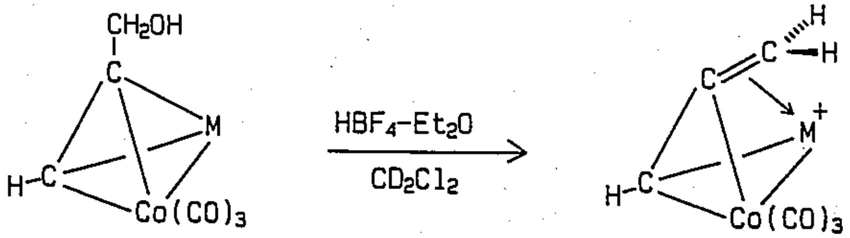
These published results on homo-bimetallic species, together with our own observations on the behaviour of the dimolybdenum and dicobalt cluster cations **74** and **75** led us to consider which organometallic fragment, namely Co(CO)$_3$ or (C$_5$H$_5$)M(CO)$_2$, where M = Mo or W, was better able to stabilize a positive charge in the α position.

Although the work in the previous chapter had established the synthetic routes to the hetero-bimetallic analogues, **63** and **64**, of the dicobalt borneol cluster **44** in which both a Co(CO)$_3$ and a $(C_5H_5)M(CO)_2$ vertex were present, the complexity of the spectra associated with these systems would undoubtedly have proven overwhelming if we had tried to carry out a competitive protonation study on them. Instead we chose to examine the simpler propargyl alcohol derivatives of hetero-bimetallic clusters which had also been synthesized during our diastereoselectivity study.



63 M = Mo
64 M = W

Reacting (propargyl alcohol)-$Co_2(CO)_6$ (**40**) with $(C_5H_5)Mo(CO)_3^-$ or with $(C_5H_4Me)W(CO)_3^-$ yields the chiral hetero-bimetallic clusters $[Co(CO)_3M](\mu^2\text{-}HC{\equiv}C\text{-}CH_2OH)$, where M = $(C_5H_5)Mo(CO)_2$ **54**, or M = $(C_5H_4Me)W(CO)_2$ **55**. Treatment of a $CD_2Cl_2$ solution of the alcohols **54** or **55** in an NMR tube with $HBF_4\text{-}Et_2O$ generates the cations $[Co(CO)_3M](\mu^2\text{-}HC{\equiv}C\text{-}CH_2)]^+$ **83** and **84**, respectively.



54 M = $(C_5H_5)Mo(CO)_2$ 83 M = $(C_5H_5)Mo(CO)_2$

55 M = $(C_5H_4Me)W(CO)_2$ 84 M = $(C_5H_4Me)W(CO)_2$

First of all, the simplest system will be examined to see what information can be extracted from its NMR behaviour. The cation $[(C_5H_5)Mo(CO)_2Co(CO)_3(HC{\equiv}C\text{-}CH_2)]^+$, **83**, yields a room temperature $^1H$ NMR spectrum consisting of four resonances in the ratio 5:1:1:1. The same pattern is observed over the entire range of temperatures from +30°C down to -90°C. Clearly then the methylene hydrogens are magnetically non-equivalent in this cation and do not interconvert on the NMR time-scale. This means the $CH_2^+$ groups is not a vertically oriented freely spinning carbynyl substituent. (Had this been the case, the methylene protons would resonate at the same frequency.) Instead, the vinylidene unit must be leaning or bent over towards the Co-Mo-C triangular base to generate a cluster of $C_1$ symmetry. In accord with this view, the $^{13}C$ NMR spectrum of **83** exhibits a single cyclopentadienyl signal, two separate molybdenum carbonyl resonances, a single tricarbonylcobalt peak and also three signals attributable to $C$, $CH$ and $CH_2$ environments. Analogously, in the slightly more complex $[(C_5H_4Me)W(CO)_2Co(CO)_3$-

$(HC{\equiv}C{-}CH_2)]^+$, **84**, similar peak patterns are observed over the range of temperatures from -80°C up to ambient temperature except that, instead of the single cyclopentadienyl resonance, the methylcyclopentadienyl ring gives rise to a *$CH_3$* and four different *CH* signals in both the $^1H$ and $^{13}C$ NMR spectra. By using a combination of $^1H$-$^{13}C$ heteronuclear double-resonance and $^1H$-$^1H$ COSY experiments it was possible to identify the origin of the peaks.

The reaction of $(C_5H_5)W(CO)_3^-$ with $Co_2(CO)_6[H{-}C{\equiv}C{-}CH(OH)Et]$ **67** yields $(C_5H_5)W(CO)_2Co(CO)_3[H{-}C{\equiv}C{-}CH(OH)Et]$, **72**, which exists in two diastereomeric forms (60:40). The isomers are separable and the major diastereomer was protonated at -40°C to minimize the possibility of proton elimination from the cation to give the corresponding alkene $(C_5H_5)W(CO)_2Co(CO)_3[H{-}C{\equiv}C{-}CH{=}CHMe]$. As shown in Figure 20, the $^{13}C$ NMR spectra of the resulting product, $[C_5H_5)W(CO)_2Co(CO)_3(HC{\equiv}C{-}CHEt)]^+$, **85**, revealed that the protonation of a single diastereomer of **72** yielded two cations in the ratio of approximately 2:1. These cations were not interconvertible on the NMR time-scale.

It has already been pointed out that antarafacial migration (i) of vinylidene fragments from Co to Co or from W to W have barriers of ≈ 10 kcal/mole. In all of the Mo-Co or W-Co cationic species described herein there is no evidence for a fluxional process which stops at low temperature. It is difficult to envisage an exchange process

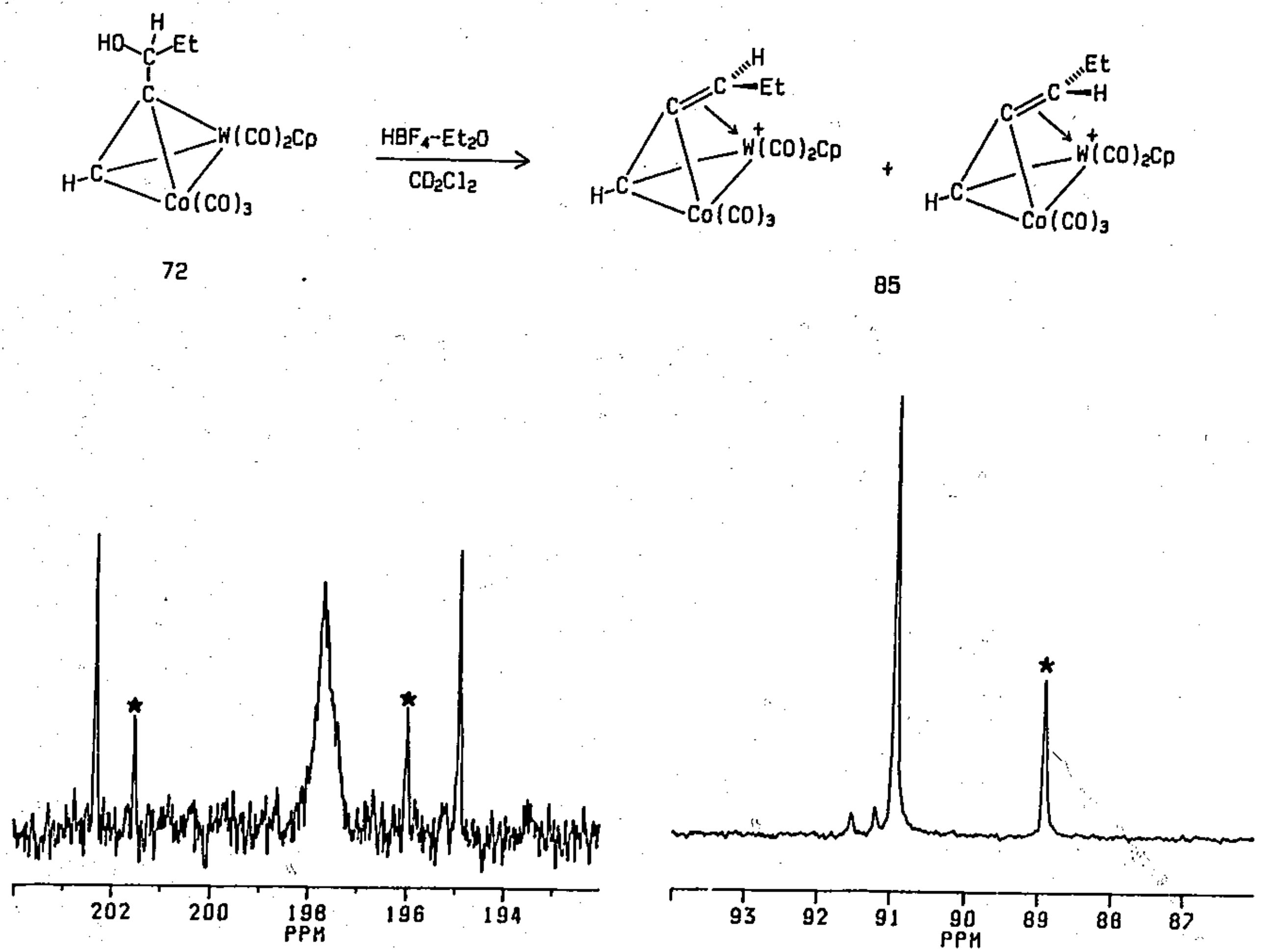
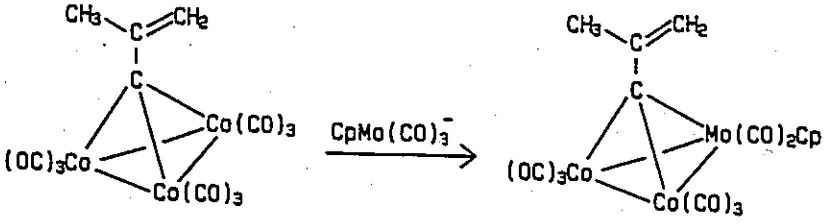


**Figure 20:** Section of the 125 MHz $^{13}C$ NMR spectrum of the diastereomers of $[(C_5H_5)W(CO)_2Co(CO)_3(HC{\equiv}C\text{-}CHEt)]^+$, 85, showing two cyclopentadienyl resonances, two pairs of tungsten carbonyl peaks and a broad $Co(CO)_3$ absorption. The peaks for the minor diastereomer are each marked with an asterisk.

between the two metal sites with a barrier too low to be detected even when using an 11.7 Tesla instrument (500 MHz for $^{1}H$; 125 MHz for $^{13}C$). In particular, if migration between cobalt and molybdenum (tungsten) were occurring, one would expect to freeze out two chemically distinct $C_5H_5$ environments in the $^{13}C$ NMR spectrum at low temperature; typically, in $[(C_5H_5)Mo(CO)_2Co(CO)_3(HC{\equiv}C{-}CH_2)]^+$, **83**, a single sharp cyclopentadienyl resonance is observed at all temperatures.

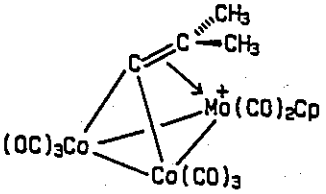
The most straightforward explanation for these observations is that the C=CR'R" moiety lies above and is directly bonded to only one of the metal vertices -- probably the CpM(CO)$_2$ vertex. Thus the NMR spectra of $[(C_5H_5)Mo(CO)_2Co(CO)_3(HC{\equiv}C{-}CH_2)]^+$, **83**, and $[(C_5H_4Me)Wo(CO)_2{-}Co(CO)_3(HC{\equiv}C{-}CH_2)]^+$, **84**, reveal in each case a single species in which one of the methylene hydrogens is *syn* to the alkyne CH group while the other is *anti*. Similarly, in $[C_5H_5)W(CO)_2Co(CO)_3(HC{\equiv}C{-}CHEt)]^+$, **85**, the diastereomers differ in that the ethyl substituents can be either *syn* or *anti* to the alkyne CH unit. In particular, the large chemical shift difference between the $^{13}C$ resonances of the -*C*H$_2$Me substituents in the *syn* and *anti* isomers should be noted; certainly, these methylene carbon nuclei could be in very different environments relative to the anisotropic shielding cones associated with the cyclopentadienyl groups.[100] The ready isolation and crystallographic characterization of Mo- and W-stabilized cations suggests that the vinylidene moiety is localized on the Group VI vertex rather than on the $Co(CO)_3$ unit. To assess the viability of this hypothesis, the trimetallic cation $[(C_5H_5)Mo(CO)_2Co_2(CO)_6C\text{-}CMe_2]^+$, **88**, in which an isolobal replacement of CH by $Co(CO)_3$ has been realized, was synthesized and examined by $^{13}C$ NMR. The procedure described by Seyferth[95] was used to prepare the alkene cluster $[Co_3(CO)_9CC(Me)=CH_2]$, **86**. Vertex replacement of a $Co(CO)_3$ fragment by the isolobal $(C_5H_5)Mo(CO)_2$ group yielded **87** and subsequent protonation of the capping $-C(Me)=CH_2$ moiety led to the desired isopropyl cation, **88**.

It is relevant to mention that, although the present work describes cationic clusters with capping vinylidene groups, there are crystallographically characterized neutral clusters which have the same overall electron count. In $[(C_5H_5)_2W_2(CO)_4Fe(CO)_3C=CH_2]$, **89**, and in $[Co_2(CO)_6Ru(CO)_3\text{-}C=CH{\it t}Bu]$, **90**, the vinylidene ligand leans towards the $Fe(CO)_3$ or $Ru(CO)_3$ vertex, respectively.[101,102] One can thus formally assign an eighteen electron configuration to all three metal atoms in each cluster. Had the vinylidene moiety leaned towards a $(C_5H_5)W(CO)_2$ in **89** or a $Co(CO)_3$ vertex in **90** it would have been necessary to write formally zwitterionic structures, as in **91**. In such cases the system frequently tries to address the electron imbalance via a semi-bridging carbonyl interaction, as in **92**.[27] In the

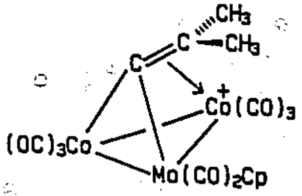


86

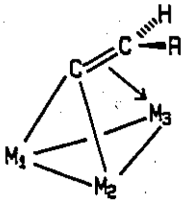
87



88a



88b

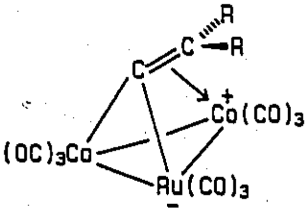


89 $M_1 = M_2 = CpW(CO)_2$

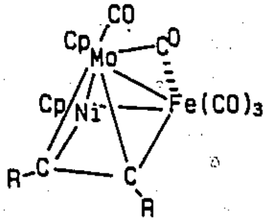
$M_3 = Fe(CO)_3$; R = H

90 $M_1 = M_2 = Co(CO)_3$

$M_3 = Ru(CO)_3$; R = tBu



91



92

cation **88**, there is no obvious *a priori* reason for preferentially localizing the charge on a $(C_5H_5)Mo(CO)_2$ rather than a $Co(CO)_3$ vertex and so, in principle, **88a** and **88b** are both viable isomers.

Now if the reasonable assumption is made that any vinylidene migration process would be slow on the NMR time-scale at low temperature, it should be possible to differentiate between **88a** and **88b** (or a mixture of both) simply on the basis of molecular symmetry. In **88a**, the cluster has $C_s$ symmetry and the two methyls would remain degenerate; in **88b** the chiral nature of the cluster would render these nuclei magnetically non-equivalent. The experimental result is rather clearcut: the methyl groups maintain their sharp $^{13}C$ singlet character over the temperature range 0° to -90°C. One must thus conclude that the vinylidene group remains firmly attached to the molybdenum vertex.

It is noteworthy that in $[Co_3(CO)_9C\text{-}CMe_2]^+$, which is well established to adopt a bent structure, the $^{13}C$ NMR spectra of the carbonyl ligands exhibit a 6:3 pattern at low temperature. This observation is in accord with the $^{13}CO$ data on $[Co_3(CO)_9C\text{-}C{=}O]^+$ (discussed previously) which also yields a 6:3 pattern at 163 K.

In light of these observations, an orbital explanation was sought for the marked preference of the vinylidene group to lean towards the molybdenum rather than remain upright or bend towards (or between) the $Co(CO)_3$ vertices. To complement the experimental data on cluster cations, molecular orbital calculations at the extended Hückel level were carried out. As was first shown[45] by Schilling and Hoffmann, $[Co_3(CO)_9C{=}CH_2]^+$ can be constructed from a tricobalt nonacarbonyl fragment, represented formally as $[Co_3(CO)_9]^{3+}$, and a vinylidene moiety , $[C{=}CH_2]^{2-}$. The former presents a set of three orbitals ($2a_1$ + $2e$) well oriented for interaction with a capping unit. Below them lies another set of three frontier orbitals ($1a_1$ + $1e$). There is a strong stabilizing interaction of the vinylidene lone pair with the vacant $2a_1$ frontier orbital of the metal system. However, the relatively low energy of the $\pi^*$ orbital of the vinylidene produces a rather low-lying LUMO. Overall this yields a small HOMO-LUMO gap which leaves open the possibility of geometric deformation to stabilize the system. When the vinylidene cap bends towards a cobalt atom, there is a very favourable interaction between the symmetrical component of the $2e$ set of the metal triangle and the $\pi$ orbital of the $C{=}CH_2$ unit. The latter orbital is well-localized on the methylene carbon and creates direct bonding between this carbon and a cobalt atom (see Figure 21a); as a result, the HOMO-LUMO gap increases markedly on bending the C=$CH_2$ vertex towards a $Co(CO)_3$ vertex.

In an earlier study on trimetallic clusters, McGlinchey[103] described how the doubly degenerate frontier orbitals of the $M_3$ moiety split when one of the $Co(CO)_3$ units is replaced by an isolobal fragment; this is observed for the $[(C_5H_5)Mo(CO)_2Co_2(CO)_6]^{3+}$ fragment in Figure 22. The 4*s* orbital in this $M_3$ unit is still capable of accepting the vinylidene lone pair in either the upright or bent mode and a strong stabilizing interaction is observed. An important new factor which differentiates the $[(C_5H_5)Mo(CO)_2Co_2(CO)_6]^{3+}$ fragment from the $[Co_3(CO)_9]^{3+}$ triangle discussed previously is the very localized nature of the 3*s* orbital on Mo (40% vs 4% for the Co atoms). The filled π orbital of the C=$CH_2$ unit (too low in energy to be displayed in this figure) interacts with the empty 3*s* orbital of the metal fragment; the energy of the former decreases slightly while the energy of the latter increases. The relatively low energy of the vinylidene $\pi^*$ orbital remains important because, as before, its interaction with the 3*s* metal fragment orbital produces a rather low-lying LUMO. Once again, this yields a small HOMO-LUMO gap and raises the possibility of a geometric deformation to stabilize the cation.

Figure 23 shows the effect of tilting the C=$CH_2$ capping group towards either a $Co(CO)_3$ or a $(C_5H_5)Mo(CO)_2$

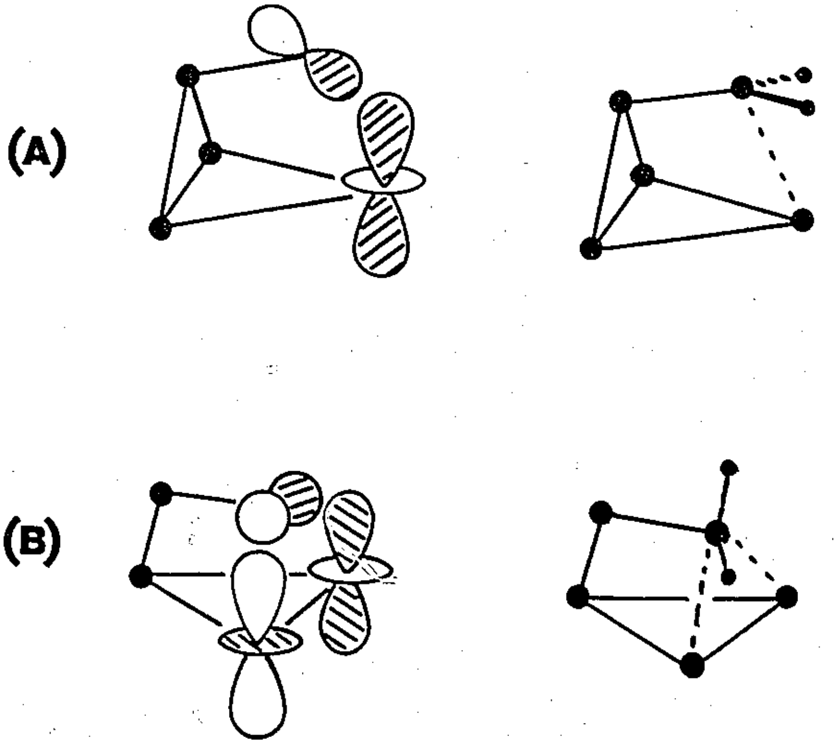


**Figure 21:** The interaction of the methylene p orbital with cobalt dz$^2$ orbital(s) in $[Co_3(CO)_9C\text{-}CH_2]^+$ (A) when the vinylidene fragment is bonded to a single $Co(CO)_3$ centre and the molecular mirror plane bisects the $CH_2$ unit and (B) when the $CH_2$ moiety is migrating from one cobalt vertex to another.

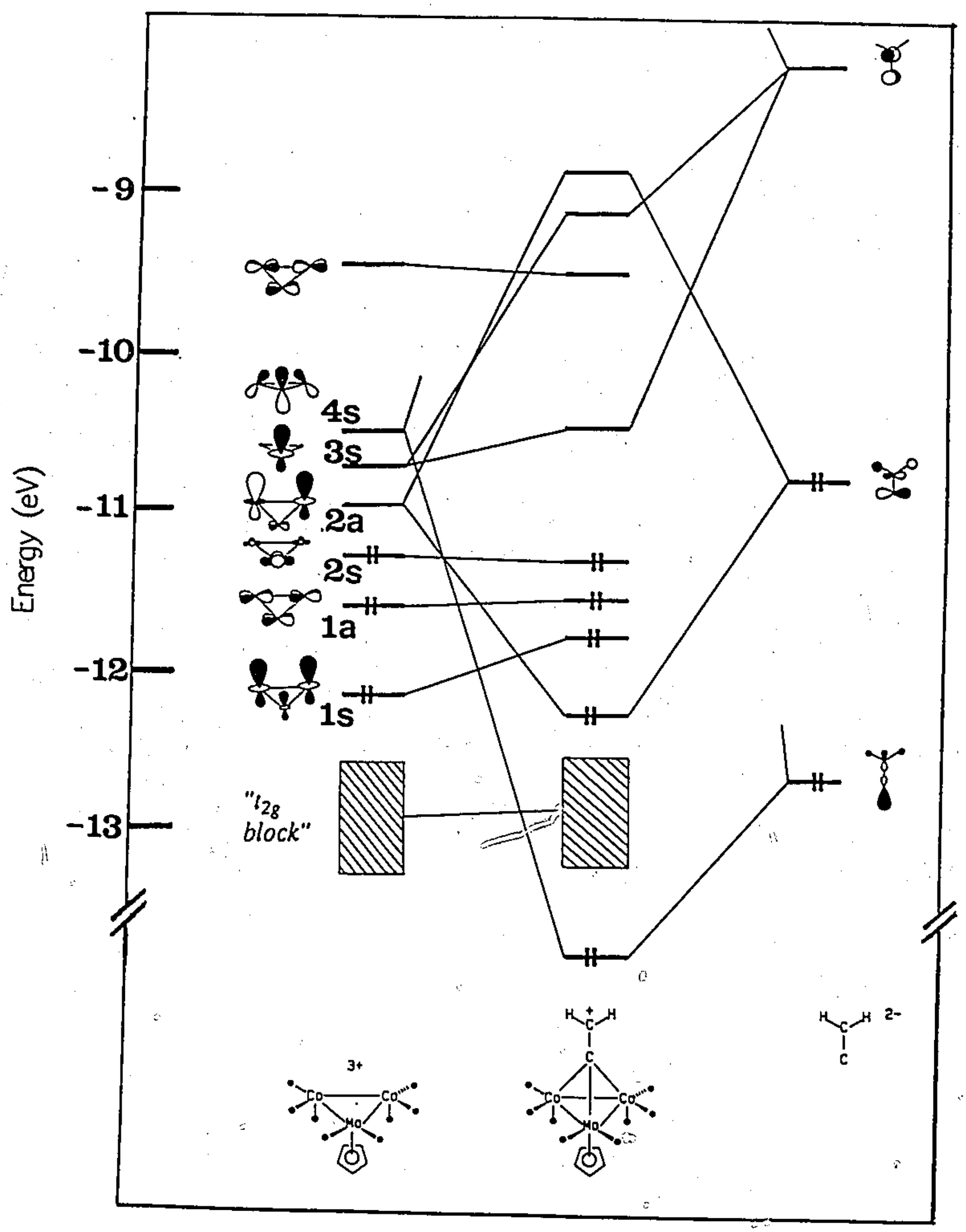


**Figure 22:** Orbital interaction diagram showing the formation of $[(C_5H_5)Mo(CO)_2$-$Co_2(CO)_6C$-$CH_2]^+$ from $[(C_5H_5)Mo(CO)_2Co_2(CO)_6]^{3+}$ and $[CH_2C{=}C]^{2-}$ fragments.

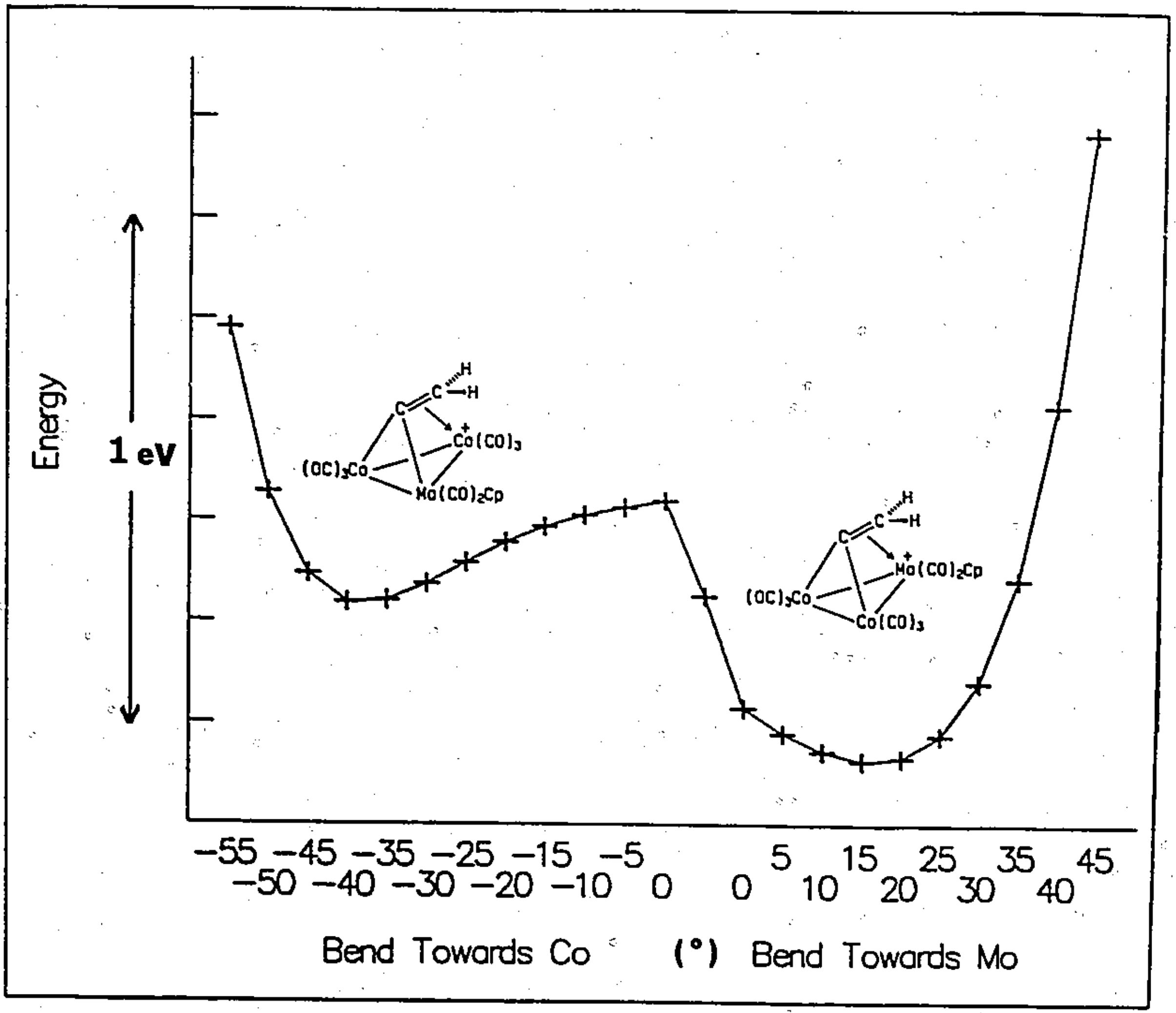


**Figure 23:** Energy level diagram showing the effect of the tilt angle (in degrees) of the capping vinylidene unit from the axis perpendicular to the plane of the metals in the cationic clusters 88a and 88b.

vertex. The most favourable interaction occurs between the 3*s* metal orbital and the π orbital of the $C=CH_2$ unit to create a direct bond between the methylene carbon and the molybdenum. The preference for bonding to the molybdenum rather than to a cobalt is augmented if the entire $(C_5H_5)$-$Mo(CO)_2$ fragment is allowed to swivel 10° downwards away from the approaching vinylidene group. This has the effect of minimizing unfavourable steric interactions with the molybdenum carbonyls and concomitantly increases the HOMO-LUMO gap. Schilling and Hoffmann[45] noted that antarafacial migration of the $C=CH_2$ cap in $[Co_3(CO)_9C=CH_2]^+$ is facilitated by an interaction between the antisymmetric component of the tricobalt 2*e* set with the π orbital of the vinylidene group, as shown in Figure 21b. In contrast it can be seen from Figure 22 that in the $[(C_5H_5)Mo(CO)_2Co_2(CO)_6C=CH_2]^+$ system no such stabilization is available in terms of a suitable out-of-phase combination of Mo and Co $d_{z^2}$ orbitals. Thus any migration of the $C=CH_2$ group between these two metals must inevitably surmount a rather large barrier.

To conclude, therefore, the vinylidene capping unit is particularly well stabilized by direct interaction with the molybdenum atom while migration to a cobalt centre is severely disfavoured. These EHMO results are in excellent accord with the experimental data and together they provide a consistent picture of these fascinating cationic clusters.

# CHAPTER FIVE

## EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.[104] Removal (evaporation) of solvents was accomplished under reduced pressure by using either a rotovap or a vacuum line. $^{13}C$ NMR spectra were recorded using Bruker AM 500, WM 250 and AC 200 spectrometers. $^{1}H$ NMR spectra were recorded using Bruker AM 500 and AC 200 and Varian EM390 spectrometers. $^{31}P$ NMR spectra were recorded using a Bruker WM 250 spectrometer. $^{13}C$ and $^{1}H$ chemical shifts reported were referenced to tetramethylsilane while $^{31}P$ chemical shifts were referenced to 85% $H_3PO_4$. [When diastereomers are present in other than a 50:50 ratio, the resonances attributed to the minor isomer are marked with an asterisk. *Exo* hydrogens (H*x*) are situated proximal to the dimethyl bridge; analogously, *endo* hydrogens (H*n*) occupy positions away from the bridging group.] Infrared spectra were recorded on a Perkin-Elmer 283 instrument using KBr solution cells. Mass spectra were obtained with a double-focusing VG ZAB-E mass spectrometer under positive ion fast atom bombardment (FAB+) and negative ion fast atom bombardment (FAB-) conditions. 3-Nitrobenzyl alcohol was used as the matrix and xenon was the bombarding species (8 keV). Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario.

$Co_3(CO)_9(\mu^3\text{-}CCH(p\text{-}C_6H_4\text{-}OCH_3)_2)$, **30**. A THF solution (100 $cm^3$) of $Co_2(CO)_8$ (10.88 g, 31.8 mmole) and Methoxychlor (6.11 g, 17.7 mmole) was stirred at reflux under an atmosphere of $N_2$ for 4 hours. The solution was allowed to cool to room temperature and filtered (under $N_2$ pressure) to remove any cobalt salts. The solvent was removed under reduced pressure and the residue was dissolved in hexane. After any insoluble material was filtered off, the hexane solution was evaporated and purification of the resultant solid by flash chromatography on silica gel (eluent, ether/hexane, 10/90) yielded the product **30** ($R_f$ 0.30) as purple crystals (1.32 g, 2.0 mmole, 11.2%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.65 (d, 2H); 6.92(d, 2H); 5.95(s, 1H); 3.76(s, 6H). $^{13}C$ NMR ($CDCl_3$) (room temperature): $\delta$ 311.1(alkylidyne *C*); 199.7 (carbonyls); 158.9(MeO-*C*); 138.9(*C*-1, ipso carbons); 129.7 (*C*-2, *C*-6); 114.1 (*C*-3, *C*-5); 76.8(Ar-*C*H-Ar); 55.3(O-$CH_3$). $^{13}C$ NMR ($CD_2Cl_2/CFCl_3$) (-120°C): $\delta$ 202.3(3, axial carbonyls); 198.0(6, equatorial carbonyls); 157.5(MeO-*C*); 137.8(*C*-1, ipso carbons); 129.3, 128.8(*C*-2, *C*-6); 113.1, 112.7(*C*-3, *C*-5). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2100(m), 2050(vs), 2030(s), 2010(sh) $cm^{-1}$. Mass spectrum (FAB+): *m/z* (%) 668

(3) $C_{25}H_{15}O_{11}Co_3$ $(M)^+$; 640 (12) $(M-CO)^+$; 584 (100) $(M-3CO)^+$; 556 (50) $(M-4CO)^+$; 528 (28) $(M-5CO)^+$; 500 (48) $(M-6CO)^+$; 472 (25) $(M-7CO)^+$; 44 (22) $(M-8CO)^+$; 416 (18) $(M-9CO)^+$. Analysis: Found: C, 44.69; H, 2.22. $C_{25}H_{15}O_{11}Co_3$ calcd.: C, 44.94; H, 2.26%.

$(HC(Ph_2P)_3)Co_3(CO)_6(\mu^3\text{-}CCH(p\text{-}C_6H_4\text{-}OCH_3)_2)$, **31.** A solution of $Co_3(CO)_9(\mu^3\text{-}CCH(p\text{-}C_6H_4\text{-}OCH_3)_2)$, **30**, (0.486 g, 0.73 mmole) and $(PPh_2)_3CH$ (0.417 g, 0.73 mmole) in toluene (100 $cm^3$) was stirred at 70°C under an atmosphere of $N_2$ for 14 hours. After removing the solvent, flash chromatographic purification of the residue (initial eluent, ether/hexane, 30/70; final eluent, ether/hexane, 50/50) yielded a red-brown solid. The impurities were removed by dissolving this solid in a minimum amount of $CCl_4$ and filtering the slurry through glass wool. The red solid collected on the glass wool (0.035 g, 0.030 mmole, 4.1%) was the desired product **31.** $^{31}P$ NMR ($CH_2Cl_2$): $\delta$ (Room temperature) 45.5; (-100°C) 45.1. $^{13}C$ NMR (Carbonyl Region) ($CH_2Cl_2/CFCl_3$): $\delta$ (-65°C) 206.0(6 carbonyls); (-110°C) 206.6(3 carbonyls) and 204.7(3 carbonyls). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2010(m), 1990(vs) and 1960(sh) $cm^{-1}$. Mass spectrum (FAB+): *m/z* (%) 1152 (10) $C_{59}H_{46}O_8P_3Co_3$ $(M)^+$; 1124 (8) $(M-CO)^+$; 1097 (22) $(M+H-2CO)^+$; 1068 (12) $(M-3CO)^+$; 1041 (32) $(M+H-4CO)^+$; 1013 (44) $(M+H-5CO)^+$; 1012 (68) $(M-5CO)^+$; 984 (100) $(M-6CO)^+$. Analysis: Found: C, 61.70; H, 4.09; P, 8.23. $C_{59}H_{46}O_8P_3Co_3$ calcd.: C, 61.48; H, 4.02; P, 8.06%.

$Co_3(CO)_9(\mu^3\text{-}CCH(o\text{-}C_6H_4\text{-}Cl)(p\text{-}C_6H_4\text{-}Cl))$, **32**. A THF ($35\ cm^3$) solution of $Co_2(CO)_8$ (1.74 g, 5.09 mmole) and o,p-DDT (1.00 g, 2.84 mmole) was stirred at reflux under an atmosphere of $N_2$ for 3 hours. The solution was allowed to cool to room temperature and filtered (under $N_2$ pressure) to remove any insoluble species. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (eluent, ether/petroleum ether, 15/85). The first band, an oily purple material, was recrystallized from hexane to give the product **32** as purple crystals (0.815 g, 1.20 mmole, 48.4%). $^1H$ NMR (*d*-6 acetone): 7.75(m, 8H, phenyl *H'*s) and 6.82(s, 1H, Ar-C*H*-Ar). $^{13}C$ NMR ($CH_2Cl_2$) (room temperature): δ 199.6(carbonyls); 143.9, 142.5, 133.4, 130.2, 130.0, 129.8, 129.0, 128.7, 127.1(phenyl carbons); 70.7(Ar-*C*H-Ar). $^{13}C$ NMR (Carbonyl Region) ($CH_2Cl_2$/Freon) (-120°C): δ 202.6(3, axial carbonyls) and 198.3(6, equatorial carbonyls). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2100(m), 2050(vs), 2040(vs), 2020(s) $cm^{-1}$. Mass Spectrum (FAB+): *m/z* (%) 648 (14) $C_{22}H_9O_8Cl_2Co_3$ $(M-CO)^+$; 620 (20) $(M-2CO)^+$; 592 (16) $(M-3CO)^+$; 564 (100) $(M-4CO)^+$; 536 (44) $(M-5CO)^+$; 508 (8) $(M-6CO)^+$; 480 (9) $(M-7CO)^+$; 452 (24) $(M-8CO)^+$; 424 (55) $(M-9CO)^+$; 389 (8) $(M-9CO-Cl)^+$. Analysis: Found: C, 40.63; H, 1.54%. $C_{23}H_9O_9Cl_2Co_3$ calcd.: C, 40.80; H, 1.34%.

$(HC(Ph_2P)_3)Co_3(CO)_6(\mu^3\text{-}CCH(o\text{-}C_6H_4\text{-}Cl)(p\text{-}C_6H_4\text{-}Cl)$, **33**. A toluene solution (50 $cm^3$) of $Co_3(CO)_9(\mu^3\text{-}CCH(o\text{-}C_6H_4\text{-}Cl)(p\text{-}C_6H_4\text{-}Cl)$, **32**, (0.60 g, 0.89 mmole) and $(Ph_2P)_3CH$ (0.506g, 0.90 mmole) was stirred under an atmosphere of $N_2$ at 70°C for 24 hours and then at 85°C for a further 48 hours. After cooling to room temperature and evaporating the toluene, the residue was filtered through silica gel (eluent, $CH_2Cl_2$) to give a crude product. Recrystallization from $CCl_4$, followed by flash chromatographic purification on silica gel (eluent, ether/petroleum ether, 40/60), yielded the product, **33** as a red solid (0.079 g, 0.068 mmole, 7.6%). $^{31}P$ NMR ($CH_2Cl_2$): $\delta$ (-30°C) 44.9; (-110°C) 45.0. $^{13}C$ NMR (Carbonyl Region) ($CH_2Cl_2/CFCl_3$): $\delta$ (room temperature) 205.8(6 carbonyls); (-120°C) 206.6 (3 carbonyls), 204.6(3 carbonyls). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2020(m), 2000(vs) and 1965(sh) $cm^{-1}$. Mass Spectrum (FAB+): *m/z* (%) 1160 (6) $C_{57}H_{40}O_6Cl_2P_3Co_3$ $(M)^+$; 1048 (8) $(M\text{-}4CO)^+$; 1020 (100) $(M\text{-}5CO)^+$; 992 (25) $(M\text{-}6CO)^+$. Analysis: Found: C, 58.66; H, 3.60; P, 7.71%. $C_{57}H_{40}O_6Cl_2P_3Co_3$ calcd.: C, 58.94; H, 3.47; P, 8.00%.

$(HC(Ph_2P)_3)Co_3(CO)_6(\mu^3\text{-}CCH_3)$, **34**. A toluene solution (60 $cm^3$) of $Co_3(CO)_9(\mu^3\text{-}CCH_3)$ (0.950 g, 2.08 mmole) and $(Ph_2P)_3CH$ (1.03 g, 1.81 mmole) was stirred under an atmosphere of $N_2$ at 70°C for 12 hours. After evaporating the solvent, the residue was purified by flash chromatography on silica gel (eluent, ether/petroleum ether, 40/60) to yield the product **34** as a red solid (0.216 g, 0.23 mmole, 12.7%). $^{31}P$ NMR ($CH_2Cl_2$) (Room Temperature): δ 46.2. $^{1}H$ NMR (*d*-6 acetone): δ 7.4(m, 12H), 6.8(m, 15H), 4.05(q, 1H) and 2.7(s, 3H). $^{13}C$ NMR (THF): δ (Room Temperature) 206.1 (6 carbonyls); 135.6 ($C_1$,ipso *C*); 134.1(ortho *C*); 129.0(para *C*); 127.3(meta *C*); 47.6($CH_3$); (-85°C) 206.6(6 carbonyls); 134.7, 133.2($C_1$ and ortho *C*); 129.1(para *C*); 127.5, 127.1 (meta *C*); (-110°C) 207.4(3 carbonyls), 205.7(3 carbonyls). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2020(s), 2000(vs) and 1960(sh) $cm^{-1}$. Mass Spectrum (FAB+): m/z *(%)* 941 (10) $C_{45}H_{35}O_6P_3Co_3$ $(M+H)^+$; 912 (5) $(M-CO)^+$; 884 (7) $(M-2CO)^+$; 856 (74) $(M-CO)^+$; 828 (54) $(M-4CO)^+$; 800 (35) $(M-5CO)^+$;772 (100) $(M-6CO)^+$. Analysis: Found: C, 57.66; H, 3.43; P, 9.51. $C_{45}H_{34}O_6P_3Co_3$ calcd.; C, 57.47; H, 3.64; P, 9.88%

$[(OC)_3Co-Co(CO)_3][HC{\equiv}C-CH_2OH]$, **40**. A THF solution (100 $cm^3$) of $Co_2(CO)_8$ (13.812 g, 40.39 mmole) and propargyl alcohol (2.4 $cm^3$, 41.23 mmole) was stirred for 1 hour at room temperature under an atmosphere of $N_2$. After the solvent was removed, the cluster **40** was obtained in approximately 83% yield by recrystallization from hexane.

$[(OC)_3Co-Co(CO)_3][HC{\equiv}C-CH_2-O\text{-menthyl}]$, **41**. A solution of $[Co_2(CO)_6][HC{\equiv}C-CH_2OH]$ **40** (0.568 g, 1.66 mmole), (1*R*,2*S*,5*R*)-(-)-menthol (0.478 g, 3.06 mmole) and $HBF_4$-$Et_2O$ (4 drops) in $CH_2Cl_2$ (30 $cm^3$) was stirred under $N_2$ in the presence of activated 4Å molecular sieve for 0.5 hours. The solution was filtered to separate off the molecular sieve. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, hexane) yielded **41** ($R_f$ 0.22) as a red-orange oil (0.606 g, 1.26 mmole, 75.9%). $^1$H NMR ($C_6D_6$): δ 5.50(s, 1H); 4.44(d, 1H); 4.14 (d, 1H); 3.01(m, 1H); 2.42(m, 1H); 1.92(d, 1H); 1.50(d, 1H); 1.30(m, 1H); 1.14(m, 1H); 0.96(d, 3H); 0.92(m, 1H); 0.84 (overlapping peaks, 8H) and 0.75(m, 1H). $^{13}$C NMR ($C_6D_6$): δ 199.9(carbonyls); 93.5(alkyne quaternary *C*); 79.2(*C*-1); 71.1(alkyne *C*H); 68.0(-$CH_2$-O-); 48.3(*C*-2); 40.2(*C*-6); 34.5 (*C*-4); 31.5(*C*-5); 25.6(*C*-7); 23.3(*C*-3); 22.2 (*C*-8); 20.9 (*C*-10) and 16.2(*C*-9). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2090(m), 2050 (s) and 2020(vs) $cm^{-1}$. Mass spectrum (FAB+): *m/z* (%) 480 (10) $C_{19}H_{22}O_7Co_2$ $(M)^+$; 452 (20) $(M-CO)^+$; 424 (38) $(M-2CO)^+$; 396 (100) $(M-3CO)^+$; 368 (90) $(M-4CO)^+$; 340 (16) $(M-5CO)^+$; 312 (12) $(M-6CO)^+$; 325 (52) (M-(-O-menthyl))$^+$; 297 (67) (M-(-O-menthyl)-CO)$^+$; 269 (33) (M-(-O-menthyl)-2CO)$^+$; 241 (25) (M-(-O-menthyl)-3CO)$^+$; 213 (12) (M-(-O-menthyl)-4CO)$^+$. Analysis: Found: C, 47.32; H, 4.65. $C_{19}H_{22}O_7Co_2$ calcd.: C, 47.52; H, 4.62%.

[$(OC)_3Co-Co(CO)_3$][HC≡C-$CH_2$-O-bornyl], **42**. A solution of [$Co_2(CO)_6$][HC≡C-$CH_2OH$] **40** (0.685 g, 2.00 mmole), [(1*S*)-endo]-(-)-borneol (0.591 g, 3.83 mmole) and $HBF_4$-$Et_2O$ (4 drops) in $CH_2Cl_2$ (35 $cm^3$) was stirred under an atmosphere $N_2$

in the presence of excess activated 4Å molecular sieve for 2 hours. After filtration to remove the molecular sieve and evaporation of the resultant solution, the crude material was purified by flash chromatography on silica gel (eluent, hexane) to give **42** ($R_f$ 0.30) as a red-orange oil (0.728 g, 1.52 mmole, 76.0%). $^1H$ NMR ($C_6D_6$): δ 5.50(s, 1H); 4.33(d, 1H); 4.22(d, 1H); 3.60(d, 1H); 2.33(br., 1H); 2.03(br., 1H); 1.74(br., 1H); 1.60(br., 1H); 1.34(m, 2H); 1.08(d, 1H); 0.98 (s, 3H); 0.83(s, 3H) and 0.82(s, 3H). $^{13}C$ NMR ($C_6D_6$): δ 200.2 (carbonyls); 93.6(alkyne quaternary *C*); 85.3(*C*-2); 71.0(alkyne *C*H); 69.8($-CH_2-O-$); 49.7(*C*-1 or *C*-7); 48.1(*C*-1 or *C*-7); 45.5(*C*-4); 36.3(*C*-3); 28.6(*C*-5); 26.9(*C*-6); 19.9 (*C*-9); 19.0(*C*-8); 14.1(*C*-10). I.R.($CH_2Cl_2$): $\nu_{CO}$ at 2085(m), 2045(s) and 2020(vs) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 450 (14) $C_{18}H_{20}O_6Co_2$ $(M-CO)^+$; 422 (15) $(M-2CO)^+$; 394 (100) $(M-3CO)^+$; 366 (95) $(M-4CO)^+$; 338 (36) $(M-5CO)^+$; 325 (33) $(M-(\text{-O-bornyl}))^+$; 310 (10) $(M-6CO)^+$; 297 (56) $(M-(\text{-O-bornyl})-CO)^+$; 269 (45) $(M-(\text{-O-bornyl})-2CO)^+$; 241 (48) $(M-(\text{-O-bornyl})-3CO)^+$; 213 (20) $(M-(\text{-O-bornyl})-4CO)^+$. (FAB-): *m/z* (%) 450 (100) $(M-CO)^-$; 421 (32) $(M-H-2CO)^-$; 394 (20) $(M-3CO)^-$; 338 (11) $(M-5CO)^-$. Analysis: Found: C, 47.50; H, 4.17. $C_{19}H_{20}O_7Co_2$ calcd.: C, 47.72; H, 4.22%.

$[(OC)_3Co-Co(CO)_3][CH_3-C\equiv C\text{-borneol}]$, **44**. A solution of $Co_2(CO)_8$ (1.694 g, 4.95 mmole) and *endo*-2-propynyl-borneol **43** (0.768 g, 4.00 mmole) in THF (40 $cm^3$) was stirred under a nitrogen atmosphere for 0.5 hours. After removal of the solvent, the crude mixture was purified by flash chromatography on silica gel (eluent, hexane) to give **44** ($R_f$ 0.18) as a red solid (1.290 g, 2.70 mmole, 67.5%). $^1$H NMR ($C_6D_6$): δ 2.32(3H, alkyne C*H*$_3$); 2.25(1H, *H*-3*x*); 1.71(1H,-O*H*); 1.62 (1H, *H*-4); 1.61(1H, *H*-6*x*); 1.41(1H, *H*-3*n*); 1.31(1H, *H*-5*x*); 1.23(1H, *H*-5*n*); 0.95(H, *H*-6*n*); 1.19(3H, C*H*$_3$-8); 0.91(3H, C*H*$_3$-10); 0.79(3H, C*H*$_3$-9). $^{13}$C NMR ($C_6D_6$): δ 200.5(carbonyls); 108.3, 94.2(alkyne quaternary *C'*s); 82.9(*C*-2); 55.1 (*C*-1 or *C*-7); 53.0(*C*-3); 51.2(*C*-1 or *C*-7); 45.7(*C*-4); 30.8(*C*-5); 27.8(*C*-6); 21.7(*C*-9); 21.6(*C*-8); 21.2(alkyne $CH_3$); 10.9(*C*-10). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2080(m), 2040(s) and 2020(s) cm$^{-1}$. Mass spectra: (FAB+): *m/z* (%) 461 (14) $C_{19}H_{19}O_6Co_2$ (M-OH)$^+$; 450 (45) (M-CO)$^+$; 433 (15) (M-OH-CO)$^+$; 422 (90) (M-2CO)$^+$; 405 (18) (M-OH-2CO)$^+$; 394 (100) (M-3CO)$^+$; 377 (14) (M-OH-3CO)$^+$; 366 (13) (M-4CO)$^+$; 338 (55) (M-5CO)$^+$; 310 (52) (M-6CO)$^+$; 293 (10) (M-OH-6CO)$^+$. (FAB-): *m/z* (%) 477 (16) (M-H)$^-$; 450 (100) (M-CO)$^-$; 422 (24) (M-2CO)$^-$; 393 (9) (M-H-3CO)$^-$; 366 (6) (M-4CO)$^-$. Analysis: Found: C, 47.73; H, 4.12. $C_{19}H_{20}O_7Co_2$ calcd.: C, 47.72; H, 4.22%.

Benzophenone Ketyl, (BPK). As described by Robinson and Simpson[84], a solution of benzophenone ketyl can be prepared by refluxing benzophenone in deoxygenated tetrahydrofuran with a slight molar excess of sodium. However, as suggested by the authors[84], for most of the reactions described herein the BPK solution was simply syringed from a still used to purify THF.

[$Ph_3P(OC)_2Co-Co(CO)_3$][HC≡C-$CH_2$-O-menthyl], **46**. A solution of [$(OC)_3Co-Co(CO)_3$][HC≡C-$CH_2$-O-menthyl] **41** (0.385 g, 0.80 mmole), triphenylphosphine (0.262 g, 1.00 mmole) and BPK (1.5 $cm^3$) in THF (35 $cm^3$) was stirred overnight under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95) which showed the formation of the product as reddish band ($R_f$ 0.32). After the solvent was removed, the crude material was purified by flash chromatography on silica gel (eluent, hexane) to give **46** as an orange-red solid (0.475 g, 0.66 mmole, 82.5%) containing an approximately 50:50 mixture of the diastereomers. $^{31}P$ NMR ($CD_2Cl_2$): $\delta$ 54.2 (single peak). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 205.9(2 carbonyls); 202.5(3 carbonyls); 135.4(d, ipso *C*'s of phenyl rings, $^1J(^{13}C-^{31}P)$=41.0Hz); 133.6(d, ortho *C*'s of phenyl rings, $^2J(^{13}C-^{31}P)$=10.5Hz); 130.7(para *C*'s of phenyl rings); 129.0(d, meta *C*'s of phenyl rings, $^3J(^{13}C-^{31}P)$= 9.5Hz); 90.5(alkyne quaternary *C*); 79.7(*C*-1); 72.0(alkyne *C*H); 68.9, 68.5(-$CH_2$-O-); 49.1, 48.9(*C*-2); 41.4, 41.1(*C*-6); 35.1(*C*-4); 32.1(*C*-5); 25.7(*C*-7); 23.8(*C*-3); 22.6(*C*-8); 21.4 (*C*-10); 16.5(*C*-9). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2050(m), 2000(s) and 1970(sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 630 (6) $C_{33}H_{37}O_3PCo_2$ $(M-3CO)^+$; 602 (12) $(M-4CO)^+$; 574 (100) $(M-5CO)^+$. (FAB-): *m/z* (%) 452 (100) $(M-PPh_3)^-$; 423 (30) (M-H-

PPh$_3$-CO)$^-$; 396 (12) (M-PPh$_3$-2CO)$^-$. Analysis: Found: C, 60.22; H, 5.41; P, 4.48. $C_{36}H_{37}O_6PCo_2$ calcd.: C, 60.52; H, 5.22; P, 4.33%.

[Cy$_3$P(OC)$_2$Co-Co(CO)$_3$][HC≡C-CH$_2$-O-menthyl], **47**. A solution of [(OC)$_3$Co-Co(CO)$_3$][HC≡C-CH$_2$-O-menthyl] **41** (0.358 g, 0.75 mmole), tricyclohexylphosphine (0.266 g, 0.95 mmole) and BPK (1.5 cm$^3$) was stirred in THF (35 cm$^3$) overnight under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, hexane) which showed the formation of the product as orange-red band ($R_f$ 0.20). The solvent was removed and the crude material purified by flash chromatography on silica gel (eluent, hexane) to give **47** as an orange-red solid (0.228 g, 0.31 mmole, 41.3%) containing an approximately 60:40 mixture of the diastereomers. $^{31}$P NMR ($C_6D_6$): δ 65.3 (single peak). $^{13}$C NMR ($C_6D_6$): δ 208.4, 207.2, 202.9(carbonyls, 1:1:3 ratio); 88.7(alkyne quaternary *C*); 79.8, *79.5 (*C*-1); 70.3, *69.9 (-*C*H$_2$-O-); 67.9, *68.5 (alkyne *C*H); 49.0(*C*-2); 41.3(*C*-6); 37.3(d, ipso *C*'s of cyclohexyl rings, $^1J(^{13}C-^{31}P)$=15.9Hz); 34.9(*C*-4); 31.9(*C*-5); 30.0(d, α *C*'s of cyclohexyl rings, $^2J(^{13}C-^{31}P)$=14.7Hz); 27.9(β *C*'s of cyclohexyl ring); 26.6(γ *C*'s of cyclohexyl rings); 25.8(*C*-7); 23.7(*C*-3); 22.6(*C*-8); 21.3(*C*-10); 16.6 (*C*-9). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2040(m), 1995(s) and 1950(sh) cm$^{-1}$. Mass spectra: (FAB+): *m/z* (%) 648 (100) $C_{33}H_{55}O_3PCo_2$ (M-3CO)$^+$; 538 (22) (Co$_2$(CO)$_5$PCy$_3$)$^+$. (FAB-): *m/z* (%) 537 (5)

$((Co_2(CO)_5PCy_3)\text{-}H)^-$; 452 (100) $(M\text{-}PCy_3)^-$; 423 (65) $(M\text{-}H\text{-}PCy_3\text{-}CO)^-$; 396 (23) $(M\text{-}PCy_3\text{-}2CO)^-$. Analysis: Found: C, 58.69; H, 7.72; P, 4.12. $C_{36}H_{55}O_6PCo_2$ calcd.: C, 59.02; H, 7.57; P, 4.23%.

$[Ph_3P(OC)_2Co\text{-}Co(CO)_3][HC{\equiv}C\text{-}CH_2\text{-}O\text{-}bornyl]$, **48**. A solution of $[(OC)_3Co\text{-}Co(CO)_3][HC{\equiv}C\text{-}CH_2\text{-}O\text{-}bornyl]$ **42** (0.499 g, 1.04 mmole), triphenylphosphine (0.273 g, 1.04 mmole) and BPK (1.5 $cm^3$) was stirred in THF (30 $cm^3$) under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, hexane) and the formation of the product as an orange-red band ($R_f$ 0.17) was detected. After stirring the mixture overnight, the solvent was removed and the residue purified by flash chromatography on silica gel (eluent, hexane) to yield **48** as an orange-red solid (0.409 g, 0.57 mmole, 54.8%) containing an approximately 50:50 mixture of the diastereomers. $^{31}P$ NMR ($CD_2Cl_2$): δ 54.4 (single peak). $^{13}C$ NMR ($CDCl_3$): δ 205.7, 205.5, 201.8(carbonyls, 1:1:3 ratio); 135.0(d, ipso *C*'s of phenyl rings, $^1J(^{13}C\text{-}^{31}P)$= 40.9Hz); 133.0(d, ortho *C*'s of phenyl rings, $^2J(^{13}C\text{-}^{31}P)$= 10.9Hz); 130.1(para *C*'s of phenyl rings); 128.2(d, meta *C*'s of phenyl rings, $^3J(^{13}C\text{-}^{31}P)$=9.5Hz); 90.3, 89.9(alkyne quaternary *C*); 84.9, 84.5(*C*-2); 70.8, 70.3($-CH_2-$); 69.8, 69.4(alkyne *C*H); 49.4(*C*-1 or *C*-7); 47.9, 47.4(*C*-1 or *C*-7); 45.2 (*C*-4); 36.2, 35.9(*C*-3); 28.2(*C*-5); 26.9(*C*-6); 19.8 (*C*-9); 18.9(*C*-8); 14.0(*C*-10). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2050 (m), 2000(s) and 1970(sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 656 (4) $C_{34}H_{35}O_4PCo_2$ $(M-2CO)^+$; 628 (13) $(M-3CO)^+$; 600 (24) $(M-4CO)^+$; 572 (100) $(M-5CO)^+$. (FAB−): 450 (100) $(M-PPh_3)^-$; 421 (29) $(M-H-PPh_3-CO)^-$; 394 (13) $(M-PPh_3-2CO)^-$. Analysis: Found: C, 60.98; H, 5.27; P, 4.13. $C_{36}H_{35}O_6PCo_2$ calcd.: C, 60.69; H, 4.95; P, 4.35%.

$[Cy_3P(OC)_2Co-Co(CO)_3][HC{\equiv}C-CH_2-O\text{-bornyl}]$, **49**. A solution of $[(OC)_3Co-Co(CO)_3][HC{\equiv}C-CH_2-O\text{-bornyl}]$ **42** (0.377 g, 0.79 mmole), tricyclohexylphosphine (0.331 g, 1.18 mmole) and BPK (1.5 $cm^3$) in THF (35 $cm^3$) was stirred under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, hexane) which showed the formation of the product as an orange-red band ($R_f$ 0.20). After further stirring of the mixture overnight, the solvent was removed and the residue purified by flash chromatography on silica gel (eluent, hexane) to yield **49** as an orange-red solid (0.287 g, 0.39 mmole, 49.4%) containing an approximately 60:40 mixture of the diastereomers. $^{31}P$ NMR ($C_6D_6$): δ 65.6 (single peak). $^{13}C$ NMR ($C_6D_6$): δ 208.3, 207.1, 203.0 (carbonyls, 1:1:3 ratio); 88.9, *88.6 (alkyne quaternary *C*); 85.2, *85.5(*C*-2); 71.4, *71.8($-CH_2-$); 67.1, *67.4(alkyne *C*H); 49.9(*C*-1 or *C*-7); 48.0(*C*-1 or *C*-7); 45.7(*C*-4); 37.2 (d, ipso *C*'s of cyclohexyl rings, $^1J(^{13}C-^{31}P)$=16.4Hz); 36.5, *36.7(*C*-3); 29.9(d, α *C*'s of cyclohexyl rings, $^2J(^{13}C-^{31}P)$= 17.0Hz); 28.7(*C*-5); 27.8(d, β *C*'s of cyclohexyl rings,

$^3J(^{13}C-^{31}P)$=9.3Hz); 27.1(*C*-6); 26.5(γ *C'*s of cyclohexyl rings): 19.9(*C*-9); 19.1(*C*-8); 14.3(*C*-10). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2045(m), 2000(s) and 1950(sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 730 (7) $C_{36}H_{53}O_6PCo_2$ $(M)^+$; 702 (25) $(M-CO)^+$: 675 (5) $(M+H-2CO)^+$; 646 (100) $(M-3CO)^+$; 577 (14) $(M-(-O-bornyl))^+$: 549 (11) $(M-(-O-bornyl)-CO)^+$; 493 (11) $(M-(-O-bornyl)-3CO)^+$. (FAB-): *m/z* (%) 450 (100) $(M-PCy_3)^-$; 421 (44) $(M-H-PCy_3-CO)^-$. Analysis: Found: C, 59.71; H, 7.43; P, 4.15. $C_{36}H_{53}O_6PCo_2$ calcd.: C, 59.18; H, 7.31; P, 4.24%.

[(dppm)((OC)$_2$Co-Co(CO)$_2$)][HC≡C-CH$_2$-O-menthyl], **50**. A solution of [(OC)$_3$Co-Co(CO)$_3$][HC≡C-CH$_2$-O-menthyl] **41** (0.408 g, 0.85 mmole) and dppm (0.461 g, 1.20 mmole) in hexane (30 $cm^3$) was stirred at reflux under an atmosphere of $N_2$ for 2.5 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 10/90) which showed the formation of the product as an orange-red band ($R_f$ 0.31). After cooling to room temperature and removal of the solvent, the residue was purified by flash chromatography on silica gel (eluent, ether/hexane, 3/97) to give **50** as an orange oily material (0.596 g, 0.74 mmole, 87.0%). $^{31}P$ NMR ($CD_2Cl_2$): δ 42.0 (single peak). $^{13}C$ NMR ($CD_2Cl_2$): δ 207.4, 204.6(carbonyls, 2:2 ratio); 137.5(d, ipso *C'*s of phenyl rings, $^1J(^{13}C-^{31}P)$= 20.4 Hz); 132.3(d, ortho *C'*s of phenyl rings, $^2J(^{13}C-^{31}P)$= 5.7Hz); 129.9(para *C'*s of phenyl rings); 128.7(d, meta *C'*s of phenyl rings, $^3J(^{13}C-^{31}P)$=4.1Hz); 98.6(alkyne quaternary

*C*); 79.8(*C*-1); 74.4(alkyne *C*H); 72.0(-*C*$H_2$-); 49.1(*C*-2); 41.6 (t, *C*$H_2$ of dppm, $^1J(^{13}C-^{31}P)$=20.8Hz); 41.3(*C*-6); 35.3(*C*-4); 32.2(*C*-5); 25.9(*C*-7); 23.9(*C*-3); 22.7(*C*-8); 21.4(*C*-10); 16.6(*C*-9). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2010(m), 1995(s), 1970(m), 1950(sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 780 (12) $C_{41}H_{44}O_4P_2Co_2$ $(M-CO)^+$; 724 (35) $(M-3CO)^+$; 696 (100) $(M-4CO)^+$; 625 (5) (M-(-O-menthyl)-CO)$^+$: 542 (20) (M+H-(-O-menthyl)-4CO)$^+$; 425 (62) (M+H-dppm)$^+$. (FAB-): 807 (100) $(M-H)^-$; 780 (97) $(M-CO)^-$; 752 (10) $(M-2CO)^-$; 586 (20) $(Co_2(CO)_3dppm)^-$. Analysis: Found: C, 61.34; H, 5.58; P, 7.58. $C_{42}H_{42}O_5P_2Co_2$ calcd.: C, 62.39; H, 5.48; P, 7.66%.

[(dppm)($(OC)_2$Co-Co$(CO)_2$)][HC≡C-$CH_2$-O-bornyl], **51**. A solution of [$(OC)_3$Co-Co$(CO)_3$][HC≡C-$CH_2$-O-bornyl] **42** (0.589 g, 1.23 mmole) and dppm (0.614 g, 1.60 mmole) in hexane (35 $cm^3$) was stirred at reflux under an atmosphere of $N_2$ for 6.0 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95) which showed the formation of the product as an orange-red band ($R_f$ 0.17). After cooling to room temperature and removing the solvent, the residue was purified by flash chromatography on silica gel (eluent, ether/hexane, 5/95) to give **51** as an orange-red solid (0.766 g, 0.95 mmole, 77.2%). $^{31}P$ NMR ($CDCl_3$): δ 42.3 (single peak). $^{13}C$ NMR ($CDCl_3$): δ 206.8, 203.8(carbonyls, 2:2 ratio); 137.0(d, ipso *C*'s of phenyl rings, $^1J(^{13}C-^{31}P)$=18.8 Hz); 131.8(ortho *C*'s of phenyl rings); 129.4(para *C*'s of phenyl rings); 128.2(meta *C*'s of phenyl rings); 97.9(alkyne quaternary *C*); 84.2(*C*-2); 73.5(alkyne *C*H); 72.6(-$CH_2$-); 49.4(*C*-1 or *C*-7); 47.9(*C*-1 or *C*-7); 45.2(*C*-4); 41.4(t, $CH_2$ of dppm, $^1J(^{13}C-^{31}P)$=20.3Hz); 36.2(*C*-3); 28.3(*C*-5); 26.7 (*C*-6); 19.9(*C*-9); 18.9(*C*-8); 14.1(*C*-10). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2010(m), 1995(s), 1975(m), 1950(sh) $cm^{-1}$. Mass spectra: (FAB+): 778 (15) $C_{41}H_{42}O_4P_2Co_2$ $(M-CO)^+$; 722 (40) $(M-3CO)^+$; 694 (100) $(M-4CO)^+$; 542 (100) $(M+H-(-O\text{-bornyl})-4CO)^+$; 502 (45) $(Co_2dppm)^+$; 443 (65) $(Co(dppm))^+$; 425 (59) $(Co_2dppm-C_6H_5)^+$; 348 (40) $(Co_2dppm-2C_6H_5)^+$. (FAB-): 805 (95) $(M-H)^-$; 778 (100) $(M-CO)^-$; 750 (18) $(M-2CO)^-$; 721 (7) $(M-H-3CO)^-$. Analysis: Found: C, 62.87; H, 5.42; P, 7.68. $C_{42}H_{42}O_5P_2Co_2$ calcd.: C, 62.54; H, 5.25; P, 7.68%.

[(dppm)((OC)$_2$Co-Co(CO)$_2$][$CH_3$-C≡C-borneol], **52**. A solution of [(OC)$_3$Co-Co(CO)$_3$][$CH_3$-C≡C-borneol] **44** (0.623 g, 1.30 mmole) and dppm (0.650 g, 1.69 mmole) in hexane (50 $cm^3$) was stirred at reflux under an atmosphere of $N_2$ for 1.5 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95) which showed the formation of the product as a red band ($R_f$ 0.15). After cooling the mixture to room temperature and removing the solvent, the residue was purified by flash chromatography on silica gel (eluent, ether/hexane, 5/95) to yield **52** as an orange-red solid (0.577 g, 0.72 mmole, 55.4%). $^{31}P$ NMR ($CDCl_3$): δ 42.1(d, $^2J(^{31}P-^{31}P)$= 125Hz); 40.9(d, $^2J(^{31}P-^{31}P)$=125Hz).

$^{13}$C NMR (carbonyls) ($CDCl_3$): δ 207.3, 206.7, 204.3, 203.7 (1:1:1:1 ratio). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2005(m), 1990(s), 1965(m), 1940(sh) cm$^{-1}$. Mass spectra: (FAB+): 789 (3) $C_{42}H_{41}O_4P_2Co_2$ $(M-OH)^+$; 778 (11) $(M-CO)^+$; 761 (5) $(M-OH-CO)^+$; 732 (3) $(M-H_2O-2CO)^+$; 722 (16) $(M-3CO)^+$; 704 (9) $(M-H_2O-3CO)^+$; 694 (11) $(M-4CO)^+$; 676 (100) $(M-H_2O-4CO)^+$; 502 (33) $(Co_2dppm)^+$; 425 (30) $(Co_2dppm-C_6H_5)^+$; 348 (27) $(Co_2dppm-2C_6H_5)^+$. (FAB-): 805 (100) $(M-H)^-$; 778 (74) $(M-CO)^-$; 586 (30) $(Co_2(CO)_3dppm)^-$; 393 (26) $(M-CO-dppm-H)^-$. Analysis: Found: C, 62.54; H, 6.17; P, 7.53. $C_{42}H_{42}O_5P_2Co_2$ calcd.: C, 62.54; H, 5.25; P, 7.68%.

$[Ph_3P(OC)_2Co-Co(CO)_3][CH_3-C{\equiv}C\text{-borneol}]$, **53**. A solution of $[(OC)_3Co-Co(CO)_3][CH_3-C{\equiv}C\text{-borneol}]$ **44** (0.453 g, 0.95 mmole), triphenylphosphine (0.248 g, 0.95 mmole) and BPK (1.5 cm$^3$) in THF (35 cm$^3$) was stirred overnight under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95) which showed the formation of the product as an red band ($R_f$ 0.27). The solvent was removed and the residue purified by flash chromatography on silica gel (eluent, ether/hexane, 1/99) to yield **53** as a red oily material (0.132 g, 0.19 mmole, 20.0%) containing an approximately 50:50 mixture of the diastereomers. $^{31}$P NMR ($CDCl_3$): δ 48.8, 44.2 (1:1 ratio). $^{13}$C NMR (carbonyls) ($CDCl_3$): 205.4, 201.5 (2:3 ratio). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2040(m), 2000(s), 1995(s), 1960(sh) cm$^{-1}$.

Mass spectra: (FAB+): *m/z* (%) 695 (2) $C_{36}H_{34}O_5PCo_2$ $(M-OH)^+$; 684 (2) $(M-CO)^+$; 667 (2) $(M-OH-CO)^+$; 656 (19) $(M-2CO)^+$; 639 (6) $(M-OH-2CO)^+$; 628 (2) $(M-3CO)^+$; 600 (100) $(M-4CO)^+$; 572 (78) $(M-5CO)^+$; 554 (13) $(M-H_2O-5CO)^+$. (FAB-): 711 (5) $(M-H)^-$; 450 (100) $(M-PPh_3)^-$; 422 (30) $(M-PPh_3-CO)^-$; 393 (11) $(M-PPh_3-2CO-H)^-$; 258 (44) $(Co_2(CO)_5)^-$. Analysis: Found: C, 58.03; H, 5.12; P, 4.64. $C_{36}H_{35}O_6PCo_2$ calcd.: C, 60.69; H, 4.95; P, 4.34%.

$(C_5H_4R)M(CO)_3^-Na^+$ (R = H, $CH_3$; M = Mo, W). To a solution of $[(C_5H_4R)M(CO)_3)]_2$ (1.0mmole) in THF (25 $cm^3$) was added an excess of finely divided Na metal. The mixture was stirred at room temperature under an atmosphere of $N_2$ until the solution lost the red colour associated with the presence of the dimer and took on the yellow colour of the anion. Filtration under $N_2$ to remove any solid present gave a clear solution of the anion which was then used in subsequent reactions.

$[(C_5H_5)Mo(CO)_2-Co(CO)_3][HC\equiv C-CH_2OH]$, **54**. A solution of $(C_5H_5)Mo(CO)_3^-Na^+$ (prepared as described above) and $[Co_2(CO)_6][HC\equiv C-CH_2OH]$ **40** (0.342 g, 1.0 mmole) in THF (25 $cm^3$) was stirred at reflux for 30 minutes under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 35/65) which showed the formation of the product as an orange band ($R_f$ 0.14).

Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 35/65) yielded the product **54** as an orange-red solid (0.326 g, 0.78 mmole, 78.4%). $^1$H NMR ($C_6D_6$): δ 5.58(s, 1H, alkyne CH), 5.35(s, 5H, Cp ring H's), 4.71(m, 2H, $-CH_2-$) and 1.46(br, 1H, -OH). $^{13}$C NMR ($CDCl_3$): δ 225.1(molybdenum carbonyls), 203.0(cobalt carbonyls), 90.4(Cp ring *C*H's), 74.5(alkyne *C*H) and 66.5($-CH_2-$) (Note: Despite running the sample in a variety of solvents the alkyne quaternary carbon was not found). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2050(m), 1990(s), 1950(br,sh) and 1890(br,sh) cm$^{-1}$. Mass spectrum (FAB+): *m/z* (%) 418 (27) $C_{13}H_9O_6MoCo$ $(M)^+$; 401 (16) $(M-OH)^+$; 390 (73) $(M-CO)^+$; 373 (35) $(M-OH-CO)^+$; 362 (100) $(M-2CO)^+$; 334 (40) $(M-3CO)^+$; 317 (13) $(M-OH-3CO)^+$; 306 (31) $(M-4CO)^+$; 278 (40) $(M-5CO)^+$. Analysis: Found: C, 37.85; H, 2.39. $C_{13}H_9O_6MoCo$ calcd.: C, 37.53; H, 2.18%.

$[(C_5H_4CH_3)W(CO)_2-Co(CO)_3][HC{\equiv}C-CH_2OH]$, **55**. A solution of $(C_5H_4CH_3)W(CO)_3^-Na^+$ and $[Co_2(CO)_6][HC{\equiv}C-CH_2OH]$ **40** (0.513 g, 1.50 mmole) in THF (35 cm$^3$) was stirred at reflux for 30 minutes under $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 50/50) which showed the formation of the product as an orange spot ($R_f$ 0.22). Removal of the solvent and purification of the residue by flash chromatography on silica gel (eluent, ether/hexane, 30/70) yielded the product **55** as a burnt-orange solid (0.451

g, 0.87 mmole, 58.0%). $^1$H NMR ($CDCl_3$): δ 5.35(s, 1H, alkyne *C**H*), 5.27(br, 4H, Cp ring *H'*s), 4.90(m, 2H, $-C\mathit{H}_2-$), 2.16(s, 3H, Cp ring $C\mathit{H}_3$) and 1.43(m, 1H, O*H*). $^{13}$C NMR ($CDCl_3$): δ 212.6, 212.3(tungsten carbonyls, 1:1 ratio); 202.0(cobalt carbonyls); 106.0(Cp ring quaternary *C*), 89.7, 88.4, 88.0, 87.7(Cp ring *C*H's); 84.6(alkyne quaternary *C*); 67.8(alkyne *C*H); 66.4($-\mathit{C}H_2-$); 14.0(Cp ring $\mathit{C}H_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2040(m), 2000(s), 1980(s), 1940(br,sh) and 1880(br,sh) cm$^{-1}$. Mass spectrum (FAB+): *m/z* (%) 518 (23) $C_{14}H_{11}O_6CoW$ $(M)^+$; 501 (18) $(M-OH)^+$; 490 (45) $(M-CO)^+$; 477 (28) $(M-OH-CO)^+$; 462 (100) $(M-2CO)^+$; 445 (13) $(M-OH-2CO)^+$; 434 (42) $(M-3CO)^+$; 417 (9) $(M-OH-3CO)^+$; 406 (33) $(M-4CO)^+$; 389 (12) $(M-OH-4CO)^+$; 378 (31) $(M-5CO)^+$; 361 (12) $(M-OH-5CO)^+$. Analysis: Found: C, 32.78; H, 2.24. $C_{14}H_{11}O_6WCo$ calcd.: C, 32.46; H, 2.14%.

$[(C_5H_4CH_3)Mo(CO)_2-Co(CO)_3][HC{\equiv}C-CH_2OH]$, **56**. A solution of $(C_5H_4CH_3)Mo(CO)_3^-Na^+$ and $[Co_2(CO)_6][HC{\equiv}C-CH_2OH]$ **40** (0.622 g, 1.82 mmole) in THF (30 cm$^3$) was stirred at reflux for 30 minutes under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 30/70) and the formation of the product as an orange band ($R_f$ 0.16) was observed. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 25/75) yielded the product **56** as a red oily solid (0.384 g, 0.89 mmole, 48.9%). $^{13}$C NMR ($C_6D_6$): 226.5, 226.4(molybdenum carbonyls, 1:1 ratio); 204.3

(cobalt carbonyls); 108.4(Cp ring quaternary *C*); 91.3, 90.3, 90.2, 89.8(Cp ring *C*H's); 75.6(alkyne *C*H); 66.1(-$CH_2$-); 13.7 (Cp ring $CH_3$) (Note: alkyne quaternary *C* not located). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2040(m), 1990(s), 1945(br,sh), 1890(br,sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 432 (12) $C_{14}H_{11}O_6CoMo$ $(M)^+$; 415 (16) $(M-OH)^+$; 404 (38) $(M-CO)^+$; 387 (48) $(M-OH-CO)^+$; 376 (100) $(M-2CO)^+$; 359 (40) $(M-OH-2CO)^+$; 348 (66) $(M-3CO)^+$; 331 (24) $(M-OH-3CO)^+$; 320 (40) $(M-4CO)^+$; 303 (25) $(M-OH-4CO)^+$; 292 (49) $(M-5CO)^+$; 275 (30) $(M-OH-5CO)^+$. (FAB-): 431 (78) $(M-H)^-$; 387 (45) $(M-OH-CO)^-$; 401 (100) $(M-CH_2OH)^-$; 359 (28) $(M-OH-2CO)^-$; 373 (60) $(M-CH_2OH-CO)^-$; 331 (34) $(M-OH-3CO)^-$. Analysis: Found: C, 38.47; H, 2.60. $C_{14}H_{11}O_6MoCo$ calcd.: C, 39.10; H, 2.58%.

$[(C_5H_5)Mo(CO)_2-Co(CO)_3][HC\equiv C-CH_2-O\text{-menthyl}]$, **57**. (Method 1) A solution of $[(C_5H_5)Mo(CO)_2-Co(CO)_3][HC\equiv C-CH_2OH]$ **54** (0.262 g, 0.63 mmole), (1*R*,2*S*,5*R*)-(-)-menthol (0.196 g, 1.26 mmole) and a small amount of pTsOH (50 mg) in $CH_2Cl_2$ (25 $cm^3$) was stirred under $N_2$ in the presence of excess activated 4Å molecular sieve for 18 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 15/85) which showed the formation of the product as a red band ($R_f$ 0.50). After the solution was filtered to remove the molecular sieve and the solvent was evaporated, flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 15/85) yielded **57** as a red-orange oil (0.240 g, 0.43 mmole, 63.0%) containing a 50:50 mixture of the diastereomers. (Method 2) A solution of $(C_5H_5)Mo(CO)_3^-Na^+$ and $[(OC)_3Co-Co(CO)_3][HC\equiv C-CH_2-O-menthyl]$ **41** (0.20 g, 0.42 mmole) in THF (25 $cm^3$) was stirred at reflux for 1.0 hours under an $N_2$ atmosphere. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded the product **57** as a red-orange oil (0.187 g, 0.34 mmole, 81.0%) containing an approximately 55:45 mixture of the diastereomers. $^{13}C$ NMR $(C_6D_6)$: δ 90.5(Cp ring *C*H's); 89.4(alkyne quaternary *C*); 79.2(*C*-1); 74.2, *74.7(alkyne *C*H); 71.9, *71.6(-*C*$H_2$-); 48.8(*C*-2); 40.7(*C*-6); 34.8(*C*-4); 31.8(*C*-5); 25.9(*C*-7); 23.6 (*C*-3); 22.6(*C*-8); 21.3(*C*-10) and 16.5(*C*-9). I.R. $(CH_2Cl_2)$: $\nu_{CO}$ at 2040(m), 1990(s), 1940(br,sh) and 1880(br,sh) $cm^{-1}$. Mass spectrum (FAB+): *m/z* (%) 500 (34) $C_{21}H_{27}O_4CoMo$ $(M-2CO)^+$; 472 (100) $(M-3CO)^+$; 444 (5) $(M-4CO)^+$; 416 (12) $(M-5CO)^+$; 401 (8) $(M-(-O-menthyl))^+$. Analysis: Found: C, 49.59; H, 4.68. $C_{23}H_{27}O_6CoMo$ calcd.: C, 49.83; H, 4.91%.

$[(C_5H_4CH_3)W(CO)_2-Co(CO)_3][HC\equiv C-CH_2-O-menthyl]$, **58**. (Method 1) A solution of $[(C_5H_4CH_3)W(CO)_2-Co(CO)_3][HC\equiv C-CH_2OH]$ **55** (0.473 g 0.91 mmole), (1*R*,2*S*,5*R*)-(-)-menthol (0.354 g, 2.27 mmole) and a small amount of $HBF_4-Et_2O$ (6 drops) in $CH_2Cl_2$ (30 $cm^3$) was stirred in the presence of activated 4Å molecular sieve under an atmosphere of $N_2$ for 18 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95) which showed the formation of the product as an orange-red band ($R_f$ 0.30). The solution was filtered to remove the molecular sieve and the solvent was evaporated. Flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 2/98) yielded **58** as an orange-red oil (0.112 g, 0.17 mmole, 18.7%) containing a 50:50 mixture of the diastereomers. (Method 2) A solution of $(C_5H_4CH_3)W(CO)_3^-Na^+$ and $[(OC)_3Co\text{-}Co(CO)_3]$-$[HC{\equiv}C\text{-}CH_2\text{-}O\text{-menthyl}]$ **41** (0.600 g, 1.25 mmole) in THF (30 $cm^3$) under an atmosphere of $N_2$ was stirred at reflux for 1.0 hours. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded the product **58** as an orange-red oil (0.473 g, 0.72 mmole, 57.6%) containing an approximately 55:45 mixture of the diastereomers. $^{13}C$ NMR ($C_6D_6$): $\delta$ 213.6, 213.4(tungsten carbonyls, 1:1 ratio); 202.9(cobalt carbonyls); 105.6(Cp ring quaternary *C*); 89.8, 89.3, 88.7, 88.2, 87.7, 87.4(Cp ring *CH*'s); 83.6(alkyne quaternary *C*); 79.2, *79.1(*C*-1); 72.0, *71.5(-$CH_2$-); 67.8(alkyne *C*H); 48.9, *48.7(*C*-2); 40.8(*C*-6); 34.8(*C*-4); 31.8(*C*-5); 25.8(*C*-7); 23.6(*C*-3); 22.6(*C*-8); 21.3(*C*-10); 16.5(*C*-9); 13.5(Cp ring $CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2035(m) 1995(s), 1980(s), 1940(br,sh), 1870(br,sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 600 (29) $C_{22}H_{29}O_4CoW$ $(M\text{-}2CO)^+$; 572 (100) $(M\text{-}3CO)^+$; 544 (9) $(M\text{-}4CO)^+$; 516 (20) $(M\text{-}5CO)^+$; 501 (4) $(M\text{-}(\text{-O-menthyl}))^+$; 473 (15) $(M\text{-}(\text{-O-menthyl})\text{-}CO)^+$; 445 (12) $(M\text{-}(\text{-O-menthyl})\text{-}2CO)^+$. (FAB-):

655 (8) $(M-H)^-$; 627 (100) $(M-H-CO)^-$; 600 (28) $(M-2CO)^-$. Analysis: Found: C, 44.01; H, 4.05. $C_{24}H_{29}O_6CoW$ calcd.: C, 43.92, H, 4.45%.

$[(C_5H_4CH_3)Mo(CO)_2-Co(CO)_3][HC\equiv C-CH_2-O\text{-menthyl}]$, **59**. (Method 1) A solution of $[(C_5H_4CH_3)Mo(CO)_2-Co(CO)_3][HC\equiv C-CH_2OH]$ **56** (0.262 g, 0.61 mmole), (1*R*,2*S*,5*R*)-(-)-menthol (0.302 g, 1.93 mmole) and $HBF_4-Et_2O$ (6 drops) in $CH_2Cl_2$ (35 $cm^3$) was stirred overnight under $N_2$ in the presence of an excess of activated 4Å molecular sieve. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95) which showed the formation of the product as a red band ($R_f$ 0.42). The solution was filtered to remove the molecular sieve. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 3/97) yielded **59** as a red oil (0.126 g, 0.22 mmole, 36.1%) containing a 50:50 mixture of the diastereomers. (Method 2) A solution of $(C_5H_4CH_3)Mo(CO)_3^-Na^+$ and $[(OC)_3Co-Co(CO)_3][HC\equiv C-CH_2-O\text{-menthyl}]$ **41** (0.417 g, 0.87 mmole) in THF (30 $cm^3$) was stirred at reflux for 1.0 hours under $N_2$. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, hexane) yielded the product **59** as a red oil (0.436 g, 0.77 mmole, 88.5%) containing an approximately 55:45 mixture of the diastereomers. $^{13}C$ NMR ($C_6D_6$): $\delta$ 226.9, 226.5(molybdenum carbonyls, 1:1 ratio); 204.3(cobalt carbonyls); 108.3(Cp ring quaternary *C*); 91.6, 91.3, 90.8, 90.5, 90.4, 89.9, 89.6(Cp ring *C*H's); 89.4(alkyne quaternary *C*); 79.2, *79.1(*C*-1); 75.4, *75.2(alkyne *C*H); 71.8, *71.3(-$CH_2$-); 48.8, *48.6(*C*-2); 40.7(*C*-6); 34.8(*C*-4); 31.8(*C*-5); 25.7(*C*-7); 23.5(*C*-3); 21.5 (*C*-8); 21.3(*C*-10); 16.5(*C*-9); 13.8(Cp ring $CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2040(m), 1990(s), 1940(br,sh), 1885(br,sh) $cm^{-1}$. Mass spectrum: (FAB+): *m/z* (%) 542 (10) $C_{23}H_{29}O_5CoMo$ $(M-CO)^+$; 514 (30) $(M-2CO)^+$; 486 (100) $(M-3CO)^+$; 458 (8) $(M-4CO)^+$; 430 (18) $(M-5CO)^+$. Analysis: Found: C, 50.62; H, 5.38. $C_{24}H_{29}O_6CoMo$ calcd.: C, 50.72, H, 5.14%.

[$(C_5H_5)Mo(CO)_2$-$Co(CO)_3$][HC≡C-$CH_2$-O-bornyl], **60**. (Method 1) A solution of [$(C_5H_5)Mo(CO)_2$-$Co(CO)_3$][HC≡C-$CH_2$OH] **54** (0.365 g, 0.88 mmole), [(1*S*)-endo]-(-)-borneol (0.403 g, 2.61 mmole) and pTsOH (50 mg) in $CH_2Cl_2$ (25 $cm^3$) was stirred under an atmosphere of $N_2$ in the presence of excess activated 4Å molecular sieve for 18 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95) which showed the formation of the product as a red spot ($R_f$ 0.41). The solution was filtered to remove the molecular sieve. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded **60** as a red oil (0.334 g, 0.61 mmole, 69.3%) containing a 50:50 mixture of the diastereomers. (Method 2) A solution of $(C_5H_5)Mo(CO)_3^-Na^+$ and [$(OC)_3Co$-$Co(CO)_3$][HC≡C-$CH_2$-O-bornyl] **42** (0.300 g, 0.63

mmole) in THF (25 $cm^3$) was stirred at reflux for 1.0 hours under $N_2$. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded the product **60** as a red oil (0.224 g, 0.41 mmole, 64.4%) containing an approximately 55:45 mixture of the diastereomers. $^{13}C$ NMR ($C_6D_6$): $\delta$ 225.9, 225.8, 225.7, 225.6 (molybdenum carbonyls, 1:1:1:1 ratio); 204.4 (cobalt carbonyls); 90.4 (Cp ring *CH*'s); 88.9 (alkyne quaternary *C*); 85.0, *85.1 (*C*-2); 74.5, *74.3 (alkyne *CH*); 73.5 (-*C*$H_2$-); 49.6 (*C*-1 or *C*-7); 48.0 (*C*-1 or *C*-7); 45.5 (*C*-4); 36.4, *36.3 (*C*-3); 28.6, *28.5 (*C*-5); 27.0 (*C*-6); 19.9 (*C*-9); 19.0 (*C*-8); 14.3, *14.1 (*C*-10). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2050 (m), 1985 (s), 1945 (br,sh) and 1885 (br,sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 554 (6) $C_{23}H_{25}O_6MoCo$ $(M)^+$; 498 (56) $(M-2CO)^+$; 470 (100) $(M-3CO)^+$; 442 (18) $(M-4CO)^+$; 414 (12) $(M-5CO)^+$; 401 (10) $(M-(-O\text{-bornyl}))^+$; 373 (22) $(M-(-O\text{-bornyl})-CO)^+$; 345 (20) $(M-(-O\text{-bornyl})-2CO)^+$. (FAB-): 553 (10) $(M-H)^-$; 525 (100) $(M-H-CO)^-$; 497 (35) $(M-H-2CO)^-$. Analysis: Found: C, 49.59; H, 4.73. $C_{23}H_{25}O_6CoMo$ calcd.: C, 50.02; H, 4.56%.

$[(C_5H_4CH_3)W(CO)_2\text{-}Co(CO)_3][HC{\equiv}C\text{-}CH_2\text{-}O\text{-bornyl}]$, **61**. (Method 1) A solution of $[(C_5H_4CH_3)W(CO)_2\text{-}Co(CO)_3][HC{\equiv}C\text{-}CH_2OH]$ **55** (0.451 g, 0.87 mmole), [(1*S*)-endo]-(-)-borneol (0.402 g, 2.61 mmole) and $HBF_4\text{-}Et_2O$ (4 drops) in $CH_2Cl_2$ (30 $cm^3$) was stirred under an atmosphere of $N_2$ in the presence of activated 4Å molecular sieve overnight. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 6/94) which showed the formation of the product as a red spot ($R_f$ 0.47). The solution was filtered to remove the molecular sieve and then the solvent was evaporated. Flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 1/99) yielded **61** as an orange-red oil (0.089 g, 0.14 mmole, 16.1%) containing a 50:50 mixture of the diastereomers. (Method 2) A solution of $(C_5H_4CH_3)W(CO)_3^-$ $Na^+$ and $[(OC)_3Co-Co(CO)_3][HC\equiv C-CH_2-O\text{-bornyl}]$ **42** (0.609 g, 1.27 mmole) in THF (35 $cm^3$) under $N_2$ was stirred at reflux for 1.0 hours. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, hexane) yielded the product **61** as an orange-red oil (0.552 g, 0.84 mmole, 66.9%) containing an approximately 55:45 mixture of the diastereomers. $^{13}C$ NMR ($C_6D_6$): δ 213.4, 212.9(tungsten carbonyls, 1:1 ratio); 203.0(cobalt carbonyls); 105.6(Cp ring quaternary *C*); 89.6, 88.4, 88.3, 87.8 (Cp ring *CH*'s); 85.1, *85.2(*C*-2); 83.1(alkyne quaternary *C*); 73.6($-CH_2-$); 68.1, *68.3(alkyne *CH*); 49.7(*C*-1 or *C*-7); 48.0 (*C*-1 or *C*-7); 45.6(*C*-4); 36.4, *36.5(*C*-3); 28.6(*C*-5); 27.1 (*C*-6); 19.9(*C*-9); 19.0(*C*-8); 14.3(*C*-10); 13.5(Cp ring $CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2040(m), 1995(s), 1980(s), 1940 (br, sh), 1880(br,sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 626 (8) $C_{23}H_{27}O_5CoW$ $(M-CO)^+$; 598 (40) $(M-2CO)^+$; 570 (100) $(M-3CO)^+$; 542 (20) $(M-4CO)^+$; 514 (24) $(M-5CO)^+$; 473 (19) $(M-(-O\text{-bornyl})-CO)^+$; 445 (15) $(M-(-O\text{-bornyl})-2CO)^+$. (FAB-): 653

(15) $(M-H)^-$; 625 (100) $(M-H-CO)^-$; 597 (51) $(M-H-2CO)^-$; 570 (27) $(M-3CO)^-$; 542 (15) $(M-4CO)^-$. Analysis: Found: C, 44.21; H, 4.38. $C_{24}H_{27}O_6CoW$ calcd.: C, 44.06; H, 4.16%.

$[(C_5H_4CH_3)Mo(CO)_2-Co(CO)_3][HC\equiv C-CH_2-O\text{-bornyl}]$, **62**. (Method 1) A solution of $[(C_5H_4CH_3)Mo(CO)_2-Co(CO)_3][HC\equiv C-CH_2OH]$ **56** (0.341 g, 0.79 mmole), [(1*S*)-endo]-(-)-borneol (0.359 g, 2.32 mmole) and a small amount of $HBF_4-Et_2O$ (2 drops) in $CH_2Cl_2$ (30 $cm^3$) was stirred under $N_2$ over an excess of activated 4Å molecular sieve for 1.0 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/ hexane, 3/97) which showed the formation of the product as a red band ($R_f$ 0.30). After filtering off the molecular sieve and removing the solvent, flash chromatographic purification of the residue on silica gel (eluent, ether/ hexane, 3/97) yielded **62** as a red oil (0.202 g, 0.36 mmole, 45.6%) containing a 50:50 mixture of the diastereomers. (Method 2) A solution of $(C_5H_4CH_3)Mo(CO)_3^-Na^+$ and $[(OC)_3Co-Co(CO)_3]-[HC\equiv C-CH_2-O\text{-bornyl}]$ **42** (0.532 g, 1.11 mmole) in THF (30 $cm^3$) was stirred at reflux for 1.0 hours under an atmosphere of $N_2$. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, hexane) yielded the product **62** as a red oil (0.342 g, 0.60 mmole, 54.1%) containing an approximately 55:45 mixture of the diastereomers. $^{13}C$ NMR ($C_6D_6$): δ 226.5, 226.4(molybdenum carbonyls, 1:1 ratio); 204.5(cobalt carbonyls); 108.2(Cp ring quaternary *C*); 91.3, 90.4, 89.8(Cp ring *CH'*s); 88.9 (alkyne quaternary *C*); 85.0, *85.2(*C*-2); 75.2(alkyne *C*H); 73.4, *73.3(-$CH_2$-O-); 49.7(*C*-1 or *C*-7); 48.0(*C*-1 or *C*-7); 45.5(*C*-4); 36.4(*C*-3); 28.6(*C*-5); 27.0(*C*-6); 19.9(*C*-9); 19.0(*C*-8); 14.3(*C*-10); 13.8(Cp ring $CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2040(m), 1985(s), 1940 (br,sh), 1890(br,sh) $cm^{-1}$. Mass spectrum: (FAB+): *m/z* (%) 540 (9) $C_{23}H_{27}O_5CoMo$ $(M-CO)^+$; 512 (56) $(M-2CO)^+$; 484 (100) $(M-3CO)^+$; 456 (18) $(M-4CO)^+$; 428 (14) $(M-5CO)^+$; 387 (19) $(M-(-O\text{-bornyl})-CO)^+$; 359 (12) $(M-(-O\text{-bornyl})-CO)^+$. Analysis: Found: C, 50.71; H, 5.05. $C_{24}H_{27}O_6CoMo$ calcd.: C, 50.90; H, 4.81%.

$[(C_5H_5)Mo(CO)_2-Co(CO)_3][CH_3-C{\equiv}C\text{-borneol}]$, **63**. A solution of $(C_5H_5)Mo(CO)_3^-Na^+$ and $[(OC)_3Co-Co(CO)_3][CH_3-C{\equiv}C\text{-borneol}]$ **44** (0.629 g, 1.32 mmole) in THF (55 $cm^3$) was stirred at reflux for 2.0 hours under $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95) which showed the formation of the product as a red band ($R_f$ 0.25). After cooling to room temperature, the reaction mixture was allowed to stir overnight. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 2/98) yielded the product **63** as a red solid (0.319 g, 0.58 mmole, 43.9%) containing an approximately 65:35 mixture of the diastereomers. $^{13}C$ NMR ($C_6D_6$): δ 227.1, *228.8(1 molybdenum carbonyl); 225.3, *226.9(1 molybdenum carbonyl); 204.5(cobalt carbonyls); 102.2, *102.6(quaternary *C*); 90.5, *90.7(Cp ring *C*H's); 85.2, *85.4(quaternary *C*); 55.3, *56.1(quaternary *C*); 53.5, *50.9(*C*-3); 51.5, *51.3(quaternary *C*); 49.9(quaternary *C*); 45.9, *45.4(*C*-4); 33.0, *27.4(*C*-5 or *C*-6); 30.4, *28.0 (*C*-5 or *C*-6); 22.5, 22.1, 21.6, 21.3(alkyne $CH_3$, *C*-8 and *C*-9); 12.0, *11.4(*C*-10). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2025(m), 1995 (s), 1980(br), 1935(br) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 526 (30) $C_{22}H_{25}O_5CoMo$ $(M-CO)^+$; 498 (100) $(M-2CO)^+$; 480 (44) $(M-H_2O-2CO)^+$; 470 (24) $(M-3CO)^+$; 452 (95) $(M-H_2O-3CO)^+$. (FAB-): 553 (19) $(M-H)^-$; 526 (12) $(M-CO)^-$; 373 (13) $(M-borneol-CO)^-$; 334 (18) $(CpMoCo(CO)_4)^-$; 306 (100) $(CpMoCo(CO)_3)^-$. Analysis: Found: C, 49.57; H, 4.41. $C_{23}H_{25}O_6CoMo$ calcd.: C, 50.02; H, 4.56%.

$[(C_5H_5)W(CO)_2-Co(CO)_3][CH_3-C\equiv C-borneol]$, **64**. A solution of $(C_5H_5)W(CO)_3^-Na^+$ and $[(OC)_3Co-Co(CO)_3][CH_3-C\equiv C-borneol]$ **44** (1.371 g, 2.86 mmole) in THF (65 $cm^3$) under $N_2$ was stirred at reflux for 3.0 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95) which showed the formation of the product as a red-orange band ($R_f$ 0.07). Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded the product **64** as a red-orange solid (0.280 g, 0.44 mmole, 15.4%) containing an approximately 75:25 mixture of the diastereomers. $^{13}C$ NMR ($C_6D_6$): δ 214.7, *216.4(1 tungsten carbonyl); 211.4, *213.2(1 tungsten carbonyl); 204(cobalt carbonyls); 95.7, *96.3 (quaternary _C_); 88.6, *88.9(Cp ring _C_H's); 84.9, *86.3 (quaternary _C_); 55.3, *55.9(quaternary _C_); 53.5, *50.7(_C_-3); 51.5, *51.2(quaternary _C_); 49.0(quaternary _C_); 46.0, *45.2 (_C_-4); 30.2, *33.0(_C_-5); 27.9, *27.4(_C_-6); 22.2, 22.1 21.6, 21.3(alkyne $CH_3$, _C_-8 and _C_-9); 12.2, *11.4(_C_-10). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2020(m), 1995(s), 1975(br), 1925(br) cm$^{-1}$. Mass spectra: (FAB+): _m/z_ (%) 640 (3) $C_{23}H_{25}O_6CoW$ (M)$^+$; 623 (3) (M-OH)$^+$; 612 (12) (M-CO)$^+$; 595 (5) (M-OH-CO)$^+$; 584 (95) (M-2CO)$^+$; 566 (30) (M-$H_2O$-2CO)$^+$; 556 (11) (M-3CO)$^+$; 538 (95) (M-$H_2O$-3CO)$^+$; 528 (38) (M-4CO)$^+$; 510 (100) (M-$H_2O$-4CO)$^+$; 500 (22) (M-5CO)$^+$; 482 (25) (M-$H_2O$-5CO)$^+$. (FAB-): 639 (88) (M-H)$^-$; 612 (78) (M-CO)$^-$; 583 (34) (M-H-2CO)$^-$; 459 (100) (M-borneol-CO)$^-$; 431 (26) (M-borneol-2CO)$^-$; 420 (83) (CpWCo(CO)$_4$)$^-$. Analysis: Found: C, 42.58; H, 4.31. $C_{23}H_{25}O_6CoW$ calcd.: C, 43.15; H, 3.94%.

[(OC)$_3$Co-Co(CO)$_3$][HC≡C-CH(OH)Et], **67**. A solution of $Co_2(CO)_8$ (3.964 g, 11.59 mmole) and 1-pentyn-3-ol (1.0 cm$^3$, 11.59 mmole) in THF (40 cm$^3$) was stirred under $N_2$ for 2 hours. After the solvent was removed and the residue extracted with hexane, the cluster **67** was obtained as a reddish oil (3.809 g, 10.29 mmole, 88.8%). $^1H$ NMR ($CDCl_3$): δ 6.06(s, 1H); 4.60(t, 1H); 1.80(overlapping multiplets, 3H); 1.14(t, 3H). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2090(m), 2050(s), 2030(s) cm$^{-1}$. Mass Spectra: (FAB+): _m/z_ (%) 370 (8)

$C_{11}H_8O_7Co_2$ $(M)^+$; 353 (20) $(M-OH)^+$; 342 (65) $(M-CO)^+$; 325 (38) $(M-OH-CO)^+$; 314 (97) $(M-2CO)^+$; 297 (21) $(M-OH-2CO)^+$; 286 (100) $(M-3CO)^+$; 269 (12) $(M-OH-3CO)^+$; 258 (38) $(M-4CO)^+$; 241 (23) $(M-OH-4CO)^+$; 230 (11) $(M-5CO)^+$; 213 (12) $(M-OH-5CO)^+$; 202 (14) $(M-6CO)^+$. (FAB-): 369 (35) $(M-H)^-$; 342 (100) $(M-CO)^-$; 314 (30) $(M-2CO)^-$; 286 (16) $(M-3CO)^-$; 258 (20) $(M-4CO)^-$; 230 (9) $(M-5CO)^-$.

$[(dppm)((OC)_2Co-Co(CO)_2)][HC{\equiv}C-CH(OH)Et]$, **68**. A solution of $[(OC)_3Co-Co(CO)_3][HC{\equiv}C-CH(OH)Et]$ **67** (0.570 g, 1.54 mmole) and dppm (0.576 g, 1.50 mmole) in hexane (50 cm$^3$) was stirred at reflux under an atmosphere of $N_2$ for 1.0 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 15/85) which showed the formation of the product as a blood red band ($R_f$ 0.11). After removing the solvent, the residue was purified by flash chromatography on silica gel (eluent, ether/ hexane, 15/85) to give **68** as a red solid (0.369 g, 0.53 mmole, 35.3%). $^{31}P$ NMR ($CH_2Cl_2$): δ 43.0(single peak). $^{13}C$ NMR ($CH_2Cl_2$): δ 207.9, 203.9(carbonyls, 2:2); 136.6(d, ipso *C*'s of phenyl rings, $^1J(^{13}C-^{31}P)$=19.9Hz); 132.0(d, ortho *C*'s of phenyl rings, $^2J(^{13}C-^{31}P)$=14.6Hz); 129.8(para *C*'s of phenyl rings); 128.4 (meta *C*'s of phenyl rings); 107.2(alkyne quaternary *C*); 75.6 (-*C*H-); 73.1(alkyne *C*H); 41.3(t, *C*$H_2$ of dppm, $^1J(^{13}C-^{31}P)$= 21.5Hz); 32.7($-CH_2-$); 10.7($-CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2010(m), 1995(s), 1970(m) cm$^{-1}$. Mass spectra: (FAB+): *m/z*

(%) 681 (2) $C_{34}H_{29}O_4P_2Co_2$ $(M-OH)^+$; 670 (14) $(M-CO)^+$; 642 (4) $(M-2CO)^+$; 614 (43) $(M-3CO)^+$; 586 (65) $(M-4CO)^+$; 568 (10) $(M-H_2O-4CO)^+$; 519 (35) $(M-H_2O-3CO-C_6H_5)^+$; 502 (28) $(Co_2dppm)^+$; 443 (100) $(M-OH-3CO-2C_6H_5)^+$; 425 (30) $(Co_2dppm-C_6H_5)^+$; 348 (26) $(Co_2dppm-2C_6H_5)^+$. (FAB-): 697 (95) $(M-H)^-$; 670 (100) $(M-CO)^-$; 641 (20) $(M-H-2CO)^-$; 586 (14) $(M-4CO)^-$.

Thermal reaction of $Ph_3P$ with $[(OC)_3Co-Co(CO)_3]-[HC{\equiv}C-CH(OH)Et]$. A $THF/Et_2O$ (40 $cm^3$/15 $cm^3$) solution of $[(OC)_3Co-Co(CO)_3][HC{\equiv}C-CH(OH)Et]$ **67** (0.617 g, 1.67 mmole) and triphenylphosphine (0.350 g, 1.34 mmole) was stirred at 50°C under an atmosphere of $N_2$ for 5 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/pentane, 20/80) which showed the formation of three products as reddish-orange bands ($R_f$'s: 0.28, 0.18, 0.10). After cooling to room temperature and allowing the mixture to stir overnight, the solvent was removed and the crude material purified by flash chromatography on silica gel (eluent, $Et_2O$/pentane, 20/80). The three bands were collected and subsequently identified as the major mono-substituted diastereomeric product **69a** (0.411 g, 0.68 mmole, 50.8%), the bis(triphenylphosphine) substituted cluster **70** (0.111 g, 0.13 mmole, 19.9%) and the minor mono-substituted diastereomeric product **69b** (0.201 g, 0.33 mmole, 24.6%).

Major Diastereomer **69a**: $^{31}P$ NMR ($CH_2Cl_2$): $\delta$ 54.1 (single peak). $^{13}C$ NMR ($CH_2Cl_2$): $\delta$ 205.9, 205.3, 201.8(carbonyls, 1:1:3); 134.3(d, ipso *C*'s of phenyl rings, $^{1}J(^{13}C-^{31}P)=$ 41.8Hz); 132.9(d, ortho *C*'s of phenyl rings, $^{2}J(^{13}C-^{31}P)=$ 11.1Hz); 130.4(para *C*'s of phenyl rings); 128.5(d, meta *C*'s of phenyl rings, $^{3}J(^{13}C-^{31}P)=9.8$Hz); 96.4(alkyne quaternary *C*); 72.6(-*C*H-); 71.7(alkyne *C*H); 33.3(-$CH_2$-); 10.3(-$CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2060(m), 2005(s), 1970(sh) cm$^{-1}$. Mass spectra: (FAB+): *m/z* (%) 604 (3) $C_{28}H_{23}O_6PCO_2$ $(M)^+$; 587 (4) $(M-OH)^+$; 576 (2) $(M-CO)^+$; 559 (4) $(M-OH-CO)^+$; 548 (18) $(M-2CO)^+$; 531 (4) $(M-OH-2CO)^+$; 520 (35) $(M-3CO)^+$; 503 (7) $(M-OH-3CO)^+$; 492 (55) $(M-4CO)^+$; 475 (6) $(M-OH-4CO)^+$; 464 (100) $(M-5CO)^+$; 447 (8) $(M-OH-5CO)^+$; 397 (60) $(M-H_2O-4CO-C_6H_5)^+$; 321 (50) $(M-OH-4CO-2C_6H_5)^+$. (FAB-): 603 (15) $(M-H)^-$; 342 (100) $(M-PPh_3)^-$; 314 (25) $(M-PPh_3-CO)^-$; 286 (12) $(M-PPh_3-2CO)^-$.

Disubstituted Cluster **70**: $^{31}P$ NMR ($CH_2Cl_2$): 51.6, 50.0 (2 signals in a 1:1 ratio). $^{13}C$ NMR (carbonyls) ($CH_2Cl_2$): $\delta$ 207.3(single resonance). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2020(m), 1990(w), 1970(s,br) cm$^{-1}$. Mass spectra: (FAB+): *m/z* (%) 810 (2) $C_{44}H_{38}O_4P_2Co_2$ $(M-CO)^+$; 782 (4) $(M-2CO)^+$; 726 (22) $(M-4CO)^+$; 642 (10) $(Co_2(PPh_3)_2)^+$; 565 (110) $(Co_2(PPh_3)_2-C_6H_5)^+$; 520 (8) $(M-PPh_3-2CO)^+$; 492 (10) $(M-PPh_3-3CO)^+$; 464 (100) $(M-PPh_3-4CO)^+$. (FAB-): 837 (15) $(M-H)^-$; 576 (90) $(M-PPh_3)^-$; 314 (100) $(M-2PPh_3)^-$.

Minor Diastereomer **69b**: $^{31}P$ NMR ($CH_2Cl_2$): $\delta$ 53.0 (single peak). $^{13}C$ NMR ($CH_2Cl_2$): $\delta$ 205.9, 205.2, 201.9(carbonyls, 1:1:3); 134.5(d, ipso *C*'s of phenyl rings, $^{1}J(^{13}C-^{31}P)=$

41.6Hz); 132.9(d, ortho *C*'s of phenyl rings, $^2J(^{13}C-^{31}P)=$ 11.1Hz); 130.4(para *C*'s of phenyl rings); 128.6(d, meta *C*'s of phenyl rings, $^3J(^{13}C-^{31}P)=9.8$Hz); 96.4(alkyne quaternary *C*); 72.7(-*C*H-); 72.4(alkyne *C*H); 32.3(-$CH_2$-); 10.6(-$CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2060(m), 2005(s), 1970(sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 587 (3) $C_{28}H_{22}O_5PCo_2$ $(M-OH)^+$; 559 (3) $(M-OH-CO)^+$; 548 (15) $(M-2CO)^+$; 531 (4) $(M-OH-2CO)^+$; 520 (30) $(M-3CO)^+$; 503 (6) $(M-OH-3CO)^+$; 492 (49) $(M-4CO)^+$; 475 (4) $(M-OH-4CO)^+$; 464 (100) $(M-5CO)^+$; 447 (9) $(M-OH-5CO)^+$; 397 (62) $(M-H_2O-4CO-C_6H_5)^+$; 321 (48) $(M-OH-4CO-2C_6H_5)^+$. (FAB-): 603 (15) $(M-H)^-$; 342 (100) $(M-PPh_3)^-$; 314 (27) $(M-PPh_3-CO)^-$; 286 (14) $(M-PPh_3-2CO)^-$; 258 (11) $(M-PPh_3-3CO)^-$.

$[(C_5H_5)Mo(CO)_2-Co(CO)_3][HC\equiv C-CH(OH)Et]$, **71**. A solution of $(C_5H_5)Mo(CO)_3^-Na^+$ and $[(OC)_3Co-Co(CO)_3][HC\equiv C-CH(OH)Et]$ **67** (0.556 g, 1.50 mmole) in THF (65 $cm^3$) was stirred at reflux for 0.5 hours under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 25/75) which showed the formation of the product as a red-orange band ($R_f$ 0.15). Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/pentane, 15/85) yielded the product **71** as a red-orange oily material (0.460 g, 1.04 mmole, 69.3%) containing an approximately 70:30 mixture of the diastereomers. $^{13}C$ NMR ($C_6D_6$): δ 226.5, 225.4(molybdenum CO's, 1:1 ratio); 204.6(cobalt CO's); 92.6, *92.2

(alkyne quaternary _C_); 90.3, *90.0(Cp ring _CH's_); 78.0, *79.2(alkyne _CH_); 77.0, *77.2(-_CH_-); 34.3, *33.1 -$CH_2$-); 11.1(-$CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2040(m), 1990(s), 1950 (sh), 1885(sh) $cm^{-1}$. Mass spectra: (FAB+): _m/z_ (%) 446 (17) $C_{15}H_{13}O_6CoMo$ $(M)^+$; 418 (40) $(M-CO)^+$; 390 (100) $(M-2CO)^+$; 362 (50) $(M-3CO)^+$; 334 (45) $(M-4CO)^+$; 306 (30) $(M-5CO)^+$; 288 (15) $(M-5CO-H_2O)^+$. (FAB-): 445 (95) $(M)^-$; 418 (100) $(M-CO)^-$; 389 (40) $(M-H-2CO)^-$. Analysis: Found: C, 40.36; H, 3.03. $C_{15}H_{13}O_6CoMo$ calcd.: C, 40.57; H, 2.95%.

$[(C_5H_5)W(CO)_2-Co(CO)_3][HC{\equiv}C-CH(OH)Et]$, **72**. A solution of $(C_5H_5)W(CO)_3^-Na^+$ and $[(OC)_3Co-Co(CO)_3][HC{\equiv}C-CH(OH)Et]$ **67** (0.715 g, 1.93 mmole) in THF (60 $cm^3$) was stirred at reflux for 1.0 hours under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/pentane, 20/80) which showed the formation of the product as a red-orange band ($R_f$ 0.14). Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/pentane, 20/80) yielded the product **72** as a reddish oily material (0.311 g, 0.58 mmole, 30.1%) containing an approximately 60:40 mixture of the diastereomers. [Note: The major diatereomer could be isolated by flash chromatography on silica gel (eluent, ether/pentane, 5:95)] $^{13}C$ NMR ($C_6D_6$): 212.4, *213.4(1 tungsten carbonyl); 211.0, *211.0 (1 tungsten carbonyl); 203.0(cobalt carbonyls); 88.0, *88.2 (Cp ring _CH's_); 85.9(alkyne quaternary _C_); 77.7, *77.2

(-*C*H-); 72.6, *71.3(alkyne *C*H); 33.4, *34.7(-$CH_2$-); 10.8, *11.2(-$CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2040(m), 2000(s), 1985(s,br), 1940(sh) $cm^{-1}$. Mass spectra: (FAB+): *m/z* (%) 532 (15) $C_{15}H_{13}O_6CoW$ $(M)^+$; 515 (7) $(M-OH)^+$; 504 (40) $(M-CO)^+$; 487 (10) $(M-OH-CO)^+$; 476 (100) $(M-2CO)^+$; 459 (10) $(M-OH-2CO)^+$; 448 (43) $(M-3CO)^+$; 431 (14) $(M-OH-3CO)^+$; 420 (22) $(M-4CO)^+$; 403 (21) $(M-OH-4CO)^+$; 392 (32) $(M-5CO)^+$; 375 (20) $(M-OH-5CO)^+$. (FAB-): 531 (100) $(M)^-$; 504 (95) $(M-CO)^-$; 476 (30) $(M-2CO)^-$; 448 (65) $(M-3CO)^-$; 419 (56) $(M-H-4CO)^-$; 392 (24) $(M-5CO)^-$. Analysis: Found: C, 33.30; H, 2.55. $C_{15}H_{13}O_6CoW$ calcd.: C, 33.86; H, 2.46%.

(2-$CH_3$-C≡C-norborn-2-ene)[$(C_5H_5)_2Mo_2(CO)_4$], **73**. A solution of $[(C_5H_5)Mo(CO)_3]_2$ (1.062 g, 2.17 mmole) in toluene (200 $cm^3$) was heated at reflux with a slow flow of $N_2$ passing over the surface for 24 hours. At that time, 2-*endo*-propynylborneol **43** (0.420 g, 2.18 mmole) dissolved in toluene/THF (15 $cm^3$/50 $cm^3$) was added and the mixture was stirred at reflux for a further 20 hours. The reaction was monitored by TLC on Kieselgel (eluent, ether/pentane, 2/98) which showed the formation of the product as a red band ($R_f$ 0.25). After cooling to room temperature, the solvent was removed and the residue extracted with pentane. Evaporation of the solvent and purification of the resultant solid by flash chromatography on silica gel (eluent, ether/pentane, 2/98) gave **73** as a red solid (0.453 g, 0.74 mmole, 34.1%).

$^1$H NMR ($C_6D_6$): δ 5.52(d, 1H, *H*-3, $J_{3-4}$=3.3Hz); 4.94(s, 5H), 4.93(s, 5H) (*H*'s of cyclopentadienyl rings); 2.77(d of d, 1H, *H*-4, $J_{4-3}$= 3.3, $J_{4-5x}$= 3.5Hz; 2.66(s, 3H, alkyne C*H*$_3$); 1.86(d of d of d of d, 1H, *H*-5*x*, $J_{5x-4}$=3.5Hz, $J_{5x-5n}$= 11.5 Hz, $J_{5x-6x}$=8.6Hz, $J_{5x-6n}$=3.6Hz; 1.45(d of d of d, 1H, *H*-6*x*, $J_{6x-5x}$=8.6Hz, $J_{6x-5n}$= 3.5Hz, $J_{6x-6n}$=11.7 Hz; 1.24(d of d of d, 1H, *H*-6*n*, $J_{6n-5x}$=3.6Hz, $J_{6n-5n}$=9.2Hz, $J_{6n-6x}$= 11.7Hz; 1.10(d of d of d, 1H, *H*-5*n*, $J_{5n-5x}$=11.5Hz, $J_{5n-6x}$= 3.5Hz, $J_{5n-6n}$=9.2Hz; 1.01(s, 3H), 0.73(s, 3H) (*H*-8 and *H*-9); 0.70 (s, 3H, *H*-10). $^{13}$C NMR ($C_6D_6$): δ 234.3, 233.9, 230.8, 230.0 (carbonyls); 151.9(*C*-2); 137.8(*C*-3); 108.2 (alkyne quaternary *C*); 92.8, 92.3(*C*H's of cyclopentadienyl rings); 60.8, 58.2, 57.2(alkyne quaternary *C*, *C*-1 and *C*-7); 52.0(*C*-4); 32.1(*C*-5); 26.2(*C*-6); 26.0(alkyne *C*H$_3$); 20.4, 20.2(*C*-8 and *C*-9); 14.0(*C*-10). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 1990(m), 1920(s) and 1830(m) cm$^{-1}$. Mass Spectrum (FAB+): (*m/z*) (%) 608 (12) $C_{27}H_{28}O_4Mo_2$ (M)$^+$; 552 (74) (M-2CO)$^+$; 524 (9) (M-3CO)$^+$; 496 (100) (M-4CO)$^+$; 450 (15) (M+H-norbornene-CO)$^+$; 421 (10) (M-norbornene-2CO)$^+$. Analysis: Found: C, 52.20; H, 4.65; $C_{27}H_{28}O_4Mo_2$ Calcd.: C, 53.30; H, 4.64%.

Protonation of (2-$CH_3$-C≡C-norborn-2-ene)[$(C_5H_5)_2$-$Mo_2(CO)_4$] **73** to give **74**. A solution of (2-$CH_3$-C≡C-norborn-2-ene)[$(C_5H_5)_2Mo_2(CO)_4$] **73** (0.30 g, 0.5 mmole) in $CD_2Cl_2$ (1.0 cm$^3$) was filtered into a 5mm NMR tube and cooled in a dry ice/ acetone bath. Under an atmosphere of $N_2$ in a glovebag, 4-5 drops of $HBF_4$-$Et_2O$ was added to the solution. The tube was then transferred to the spectrometer (AM 500) where the probe temperature had already been cooled to 0°C. After allowing the temperature of the NMR sample to warm up and stabilize at 0°C the spectra of the cation **74** were recorded. $^1H$ NMR ($CD_2Cl_2$, 0°C): $\delta$ 5.60(s, 5H), 5.56(s, 5H) (*H*'s of cyclopentadienyl rings); 2.89(s, 3H, alkyne $\mathit{CH}_3$); 2.29(m, 1H), 1.81(m, 1H) (*H*-3*x* and *H*-3*n*); 2.03(br, 1H), 1.23(br, 1H) (*H*-6*x* and *H*-6*n*); 2.00(br, 1H, *H*-4); 1.98(br, 1H), 1.36(br, 1H) (*H*-5*x* and *H*-5*n*); 0.92(s, 3H), 0.80(s, 3H) (*H*-8 and *H*-9); 0.82(s, 3H, *H*-10). $^{13}C$ NMR ($CD_2Cl_2$, 0°C): $\delta$ 227.1, 226.5, 223.0, 220.0(carbonyls); 181.7(*C*-2); 94.0, 92.8(*CH*'s of cyclopentadienyl rings); 63.3, 51.4(*C*-1 and *C*-7); 46.0 (*C*-3); 43.3(*C*-4); 41.9(*C*-6); 27.6(*C*-5); 27.4 (alkyne $\mathit{CH}_3$); 20.2, 19.3(*C*-8 and *C*-9); 14.2(*C*-10).

Protonation of (2-endo-propynylborneol)[$Co_2(CO)_6$] **44** to give **75**. A sample of (2-endo-$CH_3$-C≡C-borneol)[$Co_2(CO)_6$] **44** (0.20 g, 0.4 mmole) was dissolved in $CD_2Cl_2$ (1.0 $cm^3$), filtered into a 5mm NMR tube and cooled in a dry ice/acetone bath. Under an atmosphere of $N_2$ in a glovebag, 4-5 drops of $HBF_4$-$Et_2O$ were added to the sample. The tube was then transferred to the spectrometer (AM 500) where the probe temperature had already been cooled to -40°C. After allowing the temperature of the NMR sample to stabilize at -40°C, the spectra of the cation **75** were recorded. $^{13}C$ NMR

($CD_2Cl_2$, -40°C): δ 194.4, 192.2(carbonyls); 180.3(*C*-2); 103.9, 102.9(alkyne quaternary *C*'s); 64.5(*C*-1); 52.1(*C*-7); 44.5(*C*-3); 43.7(*C*-4); 39.8(*C*-6); 27.5(*C*-5); 21.4(alkyne $CH_3$); 20.3, 19.3(*C*-8 and *C*-9); 13.2(*C*-10). $^1H$ NMR ($CD_2Cl_2$, -40°C): δ 2.86(s, 3H, alkyne $CH_3$); 2.57(m, 1H, *H*-3*x*); 2.19 (m, 1H, *H*-4); 2.12(m, 1H, *H*-5*x*); 2.10(m, 1H; *H*-6*x*); 2.01(m, 1H, *H*-3*n*); 1.57(m, 1H, *H*-5*n*); 1.36(m, 1H, *H*-6*n*); 1.03(s, 3H), 0.94(s, 3H) (*H*-8 and *H*-9); 0.85(s, 3H, *H*-10). The sample was removed from the spectrometer, immediately quenched with $H_2O$ and allowed to warm to room temperature overnight. After decanting off the water layer, the solution was dried over $MgSO_4$ and then the solvent was removed. The $^{13}C$ NMR of the quenched sample was recorded and it was identified as the elimination product **78** analogous to **73**. $^{13}C$ NMR ($CD_2Cl_2$): δ 146.3(*C*-2); 139.7(*C*-3); 95.1, 86.9 (alkyne quaternary *C*'s); 57.5, 57.2(*C*-1 and *C*-7); 52.8(*C*-4); 32.1(*C*-5); 25.4(*C*-6); 21.8, 19.6, 19.5(alkyne $CH_3$, *C*-8 and *C*-9); 12.9(*C*-10).

Protonation of $(H\text{-}C{\equiv}C\text{-}CH_2OH)[(C_5H_5)Mo(CO)_2Co(CO)_3]$ **54** to give **83**. In a glove bag containing an atmosphere of $N_2$, a sample of $(H\text{-}C{\equiv}C\text{-}CH_2OH)[(C_5H_5)Mo(CO)_2Co(CO)_3]$ **54** (0.15 g, 0.36 mmole) was dissolved in $CD_2Cl_2$ (1 $cm^3$) and filtered into a 5mm NMR tube. $HBF_4\text{-}Et_2O$ (4-6 drops) was added to the solution and the NMR spectra of the cation **83** were recorded. $^1H$ NMR ($CD_2Cl_2$, ambient temperature): δ 6.42(s, 1H, alkyne

C*H*); 5.84(s, 5H, cyclopentadienyl ring *H′*s); 5.77(br, 1H) and 4.94(br, 1H) (C$H_2$). $^{13}$C NMR ($CD_2Cl_2$, ambient temperature): δ 216.2, 209.2(molybdenum carbonyls); 198.9(cobalt carbonyls); 132.0 (alkyne quaternary *C*); 92.1(cyclopentadienyl ring *C*H′s); 86.3($CH_2$); 83.1(alkyne *C*H).

Protonation of (H-C≡C-$CH_2OH$)[($C_5H_4CH_3$)W$(CO)_2$Co$(CO)_3$] **55** to give **84**. Under a $N_2$ atmosphere in a glovebag, a sample of (H-C≡C-$CH_2OH$)[($C_5H_4CH_3$)W$(CO)_2$Co$(CO)_3$] **55** (0.16 g, 0.34 mmole) was dissolved in $CD_2Cl_2$ (1 cm$^3$) and filtered into a 5mm NMR tube. $HBF_4$-$Et_2O$ (4-6 drops) was added to the solution and the NMR spectra of the cation **84** were recorded. $^1$H NMR ($CD_2Cl_2$, ambient temperature): δ 6.36(s, 1H, alkyne C*H*); 6.27(br, 1H) and 5.18(br, 1H) (C$H_2$); 5.92(br, 1H), 5.78 (br, 1H), 5.73(br, 1H), 5.68 (br, 1H) (ring *H′*s); 2.42(s, 3H, ring C$H_3$). $^{13}$C NMR ($CD_2Cl_2$, -20°C): δ 203.0, 194.9 (tungsten carbonyls); 197.3(cobalt carbonyls); 132.7(alkyne quaternary *C*); 107.8(ring quaternary *C*); 90.5, 89.0, 88.7, 87.9(ring *C*H′s); 84.9($CH_2$); 72.7 (alkyne *C*H).

Protonation of (H-C≡C-CH(OH)($CH_2CH_3$))[($C_5H_5$)W$(CO)_2$-Co$(CO)_3$] **72** to give **85**. A sample of (HC≡C-CH(OH)($CH_2CH_3$))-[($C_5H_5$)W$(CO)_2$Co$(CO)_3$] **72** (the major diastereomer isolated in the substitution reaction) was dissolved in $CD_2Cl_2$ (1 cm$^3$), filtered into a 5mm NMR tube and cooled in a dry ice/acetone bath. Under an atmosphere of $N_2$ in a glovebag, 4 drops of

$HBF_4$-$Et_2O$ were added to the solution. The tube was then transferred to the spectrometer where the probe had been cooled to -40°C. After allowing the temperature to stabilize, the $^{13}C$ NMR spectra of the cation **85** were recorded. $^{13}C$ NMR ($CD_2Cl_2$, -40°C): δ 202.3, *201.5(1 tungsten carbonyl); 194.9, *195.9(1 tungsten carbonyl); 197.7, *197.7 (cobalt carbonyls); 122.6, *123.2(alkyne quaternary *C*); 118.7, *121.0(-*C*HEt); 90.9, *88.9(ring *C*H's); 73.9, *71.6 (alkyne *C*H); 28.9, *37.3($CH_2$); 15.4, *17.2($CH_3$).

[$(C_5H_5)Mo(CO)_2Co_2(CO)_6CC(CH_3)=CH_2$], **87**. A sample of [$Co_3(CO)_9CC(CH_3)=CH_2$] **86** (0.964 g, 2.0 mmole) dissolved in THF (10 $cm^3$) was added to a solution of $(C_5H_5)Mo(CO)_3^-$ $Na^+$ in 50 $cm^3$ of THF and the mixture was stirred at reflux for 45 minutes under an atmosphere of $N_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/pentane, 5/95) which indicated the formation of the product as a green band ($R_f$ 0.32). After cooling the solution to room temperature and removing the solvent, the crude solid was purified by flash chromatography on silica gel (eluent, ether/pentane, 3/97) to give the product **87** as a green solid (0.681 g, 1.22 mmole, 61.0%). $^1H$ NMR ($C_6D_6$): δ 5.04(br, 1H) and 4.72(br, 1H) ($CH_2$); 4.48(s, 5H, ring *H*'s); 2.06(s, 3H, $CH_3$). $^{13}C$ NMR ($C_6D_6$): δ 163.5(alkene quaternary *C*); 111.3($CH_2$); 92.1(ring *C*H's); 28.6($CH_3$). I.R. ($CH_2Cl_2$): $\nu_{CO}$ at 2075(w), 2060 (w), 2020(m), 2010(s), 2005(s), 1940(br, sh), 1885(br) $cm^{-1}$.

Mass Spectra: (FAB+): (*m/z*) (%) 558 (4) $C_{17}H_{10}O_8Co_2Mo$ $(M)^+$; 530 (20) $(M-CO)^+$; 502 (57) $(M-2CO)^+$; 474 (100) $(M-3CO)^+$; 446 (75) $(M-4CO)^+$; 418 (48) $(M-5CO)^+$; 390 (28) $(M-6CO)^+$; 362 (17) $(M-7CO)^+$; 334 $(M-8CO)^+$ (24). (FAB-): (*m/z*) (%) 530 (100) $C_{17}H_{10}O_8Co_2Mo$ $(M-CO)^+$; 502 (83) $(M-2CO)^+$; 474 (72) $(M-3CO)^+$; 446 (63) $(M-4CO)^+$; 418 (23) $(M-5CO)^+$.

$[(C_5H_5)Mo(CO)_2Co_2(CO)_6CC(CH_3)_2]^+$ $PF_6^-$, **88**. Using a syringe, 60% $HPF_6$ (0.10 $cm^3$, 0.67 mmole) was added to a solution of $[(C_5H_5)Mo(CO)_2Co_2(CO)_6CC(CH_3)=CH_2]$ **87** (0.298 g, 0.53 mmole) in propionic anhydride (4 $cm^3$) under an $N_2$ atmosphere. The solution was stirred for 0.5 hours during which time a noticeable quantity of the desired precipitate was observed to form. In order to ensure maximum precipitation of the salt, dry ether (15 $cm^3$) was added. The mixture was filtered under nitrogen and the product was further washed with anhydrous ether (15 $cm^3$). After being dried *in vacuo* at room temperature for one hour, the solid was collected and transferred to a 10mm NMR tube. It was subsequently dissolved in a mixture of $SO_2$ (5 $cm^3$) and $CD_2Cl_2$ (1 $cm^3$) (the latter added to provide a lock signal) and the NMR tube was sealed. The sample was transferred to the spectrometer (WM250) where the probe had been cooled to 0°C and, after allowing time for the temperature to stabilize, the $^{13}C$ NMR spectra of **88** were recorded. $^{13}C$ NMR ($SO_2$/$CD_2Cl_2$): $\delta$ (0°C) 203.7(broad, molybdenum and cobalt carbonyls); 153.0(*C*Me$_2$); 96.0(ring *C*H's); 35.3(*C*H$_3$'s); (-90 °C) 296.0(alkylidyne quaternary *C*); 198.7(broad, molybdenum and cobalt carbonyls); 147.5(*C*Me$_2$); 95.4(ring *C*H's); 34.7(*C*H$_3$'s).

$[Co_3(CO)_9CC(CH_3)_2]^+ PF_6^-$. Under an atmosphere of $N_2$, 60% $HPF_6$ (0.14 cm$^3$, 0.95 mmole) was added to solution of $[Co_3(CO)_9CC(CH_3)=CH_2]$ (0.350 g, 0.73 mmole) in propionic anhydride (4cm$^3$). After stirring for 0.5 hours, ether (15 cm$^3$) was added to ensure complete precipitaion of the salt and then the mixture was filtered under nitrogen. After washing the solid with additional ether (20 cm$^3$), the sample was dried *in vacuo* for one hour at room temperature and then transferred into a 10mm NMR tube. The salt was dissolved in a mixture of $SO_2/CD_2Cl_2$ (5 cm$^3$/1 cm$^3$), the NMR tube was sealed and the spectra of the cation[95] recorded. $^{13}$C NMR ($SO_2/CD_2Cl_2$, -110 °C): δ 197.8(3 carbonyls), 191.5(6 carbonyls); 149.6(*C*Me$_2$); 33.2(*C*H$_3$'s).

Molecular Orbital Calculations: All calculations were carried out within the Extended Hückel formalism[105,106] using the weighted $H_{ij}$ formula.[107] The bond lengths and angles were taken from the X-ray crystal structure of $(C_5H_5)Mo(CO)_2Co_2(CO)_6C\text{-}Ph$.[42] The atomic parameters used were taken from reference 103.

# CHAPTER SIX

# X-RAY CRYSTALLOGRAPHY

Crystals of $[(HC(Ph_2P)_3)Co_3(CO)_6CCH_3]$, 34, were grown from $CH_2Cl_2$/pentane. The density was determined by suspension in an aqueous solution of $ZnCl_2$. Reddish/purple prismatic crystals were examined under a polarizing microscope for homogeneity. A well formed crystal, 0.3 x 0.3 x 0.4mm, was selected and mounted on the tip of a glass fibre with use of epoxy cement. Unit cell parameters were obtained at -80°C from a least squares fit of $\chi$, $\phi$, and $2\theta$ for 15 reflections in the range ($18.1° < 2\theta < 25.8°$) recorded on a Nicolet P3 diffractometer with use of graphite monochromated MoKα radiation ($\lambda$=0.71069Å at 22°C). Intensity data were also recorded on a Nicolet P3 diffractometer at -80°C with use of $w$-scans, for 5871 reflections in the quadrant ($h,k,\pm l$) with $2\theta \leq 45°$. The method of selection of scan rates and initial data treatment have been described.[108,109] Corrections for Lorentz-polarization effects were applied to all reflections. Two standard reflections (4,4,8;2.1% and -6, 4,8;1.85%) monitored every 48 reflections showed no sign of crystal decomposition or instrument instability. Systematically absent reflections (296) were excluded and 459 symmetry-equivalent data were then averaged ($R_{int}$ = 0.0147) to give 5116 unique reflections. A summary of crystal data is given in Table 3.

The coordinates of the cobalt atoms were found from a three-dimensional Patterson synthesis with use of the program SHELXS-86.[110] Full-matrix least-squares refinement of these coordinates followed by a three-dimensional electron density synthesis revealed all the non-hydrogen atoms and confirmed the positional assignments for the heavy atoms. After refinement the temperature factors of the non-hydrogen atoms, which were previously isotropic, were made anisotropic and further cycles of refinement revealed the positional parameters for all of the hydrogen atoms. These were included in subsequent cycles of refinement (U fixed at 0.08Å$^2$). Further refinement using full-matrix least-squares minimizing $\Sigma w(|F_o|-|F_c|)^2$ was terminated when the maximum shift/error reached 0.001. Correction for secondary extinction was made by the method in SHELX-76.[111] Final $R_1$=0.0682, $R_2$=0.0728 for 5116 reflections. Throughout the refinement, scattering curves were taken from Ref. 112 and anomalous dispersion corrections from Ref. 113 were applied to the curve for cobalt. All calculations were performed on a VAX 8650 computer. Programs used: XTAL,[114] data reduction; SHELXS-86,[110] structure solution; SHELX-76,[111] structure refinement: MOLGEOM,[115] molecular geometry and SNOOPI,[116] diagrams. Final atomic positional parameters are given in Table 4, selected bond lengths and bond angles are given in Table 5.

Crystals of $[(Co(CO)_3)_2(C_{13}H_{19}OH)]$, **44**, were grown from $CH_2Cl_2$/hexane. The density was determined by suspension in an aqueous solution of $ZnCl_2$. Reddish/black prismatic crystals were examined under a polarizing microscope for homogeneity. A well formed crystal, 0.64 x 0.42 x 0.26mm, was selected and mounted on the tip of a glass fibre with use of epoxy cement. Unit cell parameters were obtained from a least squares fit of $\chi$, $\phi$, and $2\theta$ for 15 reflections in the range ($21.6° < 2\theta < 28.7°$) recorded on a Nicolet P3 diffractometer with use of graphite monochromated MoK$\alpha$ radiation ($\lambda$=0.71069Å at 22°C). Intensity data were also recorded on a Nicolet P3 diffractometer with a coupled $\theta$(crystal)-$2\theta$(counter) scan, for 4269 reflections in the quadrant ($h,k,\pm l$) with $2\theta \leq 50°$. The method of selection of scan rates and initial data treatment have been previously described.[108,109] Corrections for Lorentz-polarization effects and absorption ($\psi$-scans)[117] were applied to all reflections. Two standard reflections (0,6,7;1.74% and -1,6,-3;1.93%) monitored every 48 reflections showed no sign of crystal decomposition or instrument instability. Systematically absent reflections (31) were excluded and 525 symmetry-equivalent data were then averaged ($R_{int}$ = 0.0175) to give 3713 unique reflections. A summary of crystal data is given in Table 6.

The coordinates of the cobalt atoms were found from a three-dimensional Patterson synthesis with use of the program SHELXS-86.[110] Full-matrix least-squares refinement of these coordinates followed by a three-dimensional electron density synthesis revealed all the non-hydrogen atoms and confirmed the positional assignments for the heavy atoms. After refinement the temperature factors of the non-hydrogen atoms, which were previously isotropic, were made anisotropic and further cycles of refinement revealed the positional parameters for all of the hydrogen atoms. These were included in subsequent cycles of refinement (U fixed at 0.08Å$^2$). Further refinement using full-matrix least-squares minimizing $\Sigma w(|F_o|-|F_c|)^2$ was terminated when the maximum shift/error reached 0.001. Correction for secondary extinction was made by the method in SHELX-76.[111] Final $R_1$=0.0546, $R_2$=0.0567 for 3713 reflections. Alternative refinement where coordinates x,y,z were replaced by -x,-y,-z gave $R_1$=0.0626, $R_2$=0.0667, and S=1.2812 (for definition see Table 6) for 3713 reflections, confirming the assignment for the correct hand of the structure. Throughout the refinement, scattering curves were taken from Ref. 112 and anomalous dispersion corrections from Ref. 113 were applied to the curve for cobalt. All calculations were performed on a VAX 8650 computer. Programs used: XTAL,[114] data reduction; TAPER,[117] absorption correction; SHELXS-86,[110] structure solution; SHELX-76,[111] structure refinement:

MOLGEOM,[115] molecular geometry and SNOOPI,[116] diagrams. Final atomic positional parameters are given in Table 7, selected bond lengths and bond angles are given in Table 8.

Crystals of (2-$CH_3$-C≡C-norborn-2-ene)[$(C_5H_5)_2Mo_2$-$(CO)_4$], **73**, were grown from hexane/$CH_2Cl_2$. The density was determined by suspension in an aqueous solution of $ZnCl_2$. Purple/black prismatic crystals were examined under a polarizing microscope for homogeneity. A well formed crystal, 0.23 x 0.32 x 0.35mm, was selected and sealed in a Lindemann capillary. Unit cell parameters were obtained from a least squares fit of $\chi$, $\phi$, and $2\theta$ for 15 reflections in the range ($20.8° < 2\theta < 27.4°$) recorded on a Nicolet P3 diffractometer with use of graphite monochromated MoKα radiation ($\lambda$ = 0.71069Å at 22°C). Intensity data were also recorded on a Nicolet $P2_1$ diffractometer with a coupled $\theta$(crystal)-$2\theta$ (counter) scan, for 5056 reflections in the quadrant ($h,k,\pm l$) with $2\theta \leq 50°$. The method of selection of scan rates and initial data treatment have been described.[108,109] Corrections for Lorentz-polarization effects and absorption ($\psi$-scans)[117] were applied to all reflections. Two standard reflections (0,-8,0;2.55% and -3,-6,1;2.36%) monitored every 48 reflections showed no sign of crystal decomposition or instrument instability. Systematically absent reflections (28) were excluded and 678 symmetry-equivalent data were then averaged ($R_{int}$ = 0.0098) to give 4350 unique reflections. A summary of crystal data is given in Table 9.

The coordinates of the molybdenum atoms were found from a three-dimensional Patterson synthesis with use of the program SHELXS-86.[110] Full-matrix least-squares refinement of these coordinates followed by a three-dimensional electron density synthesis revealed all the non-hydrogen atoms. After refinement the temperature factors of the non-hydrogen atoms, which were previously isotropic, were made anisotropic and further cycles of refinement revealed the positional parameters for all of the hydrogen atoms. These were included in subsequent cycles of refinement (U fixed at 0.08Å$^2$). Further refinement using full-matrix least-squares minimizing $\Sigma w(|F_o|-|F_c|)^2$ was terminated when the maximum shift/error reached 0.004. Correction for secondary extinction was made by the method in SHELX-76.[111] Final $R_1$=0.0290, $R_2$=0.0276 for 4350 reflections. Alternative refinement where coordinates x,y,z were replaced by -x,-y,-z gave $R_1$=0.0301, $R_2$=0.0286, and S=1.1661 (for definition see Table 9) for 4350 reflections, confirming the assignment for the correct hand of the structure. Throughout the refinement, scattering curves were taken from Ref. 112 and anomalous dispersion corrections from Ref. 113 were applied to the curve for molybdenum. All calculations were performed on a VAX 8650 computer. Programs used: XTAL,[114] data reduction; TAPER,[117] absorption correction; SHELX-86,[110] structure solution; SHELX-76,[111] structure refinement: MOLGEOM,[115] molecular geometry and SNOOPI,[116] diagrams. Final atomic positional parameters are given in Table 10, selected bond lengths and bond angles are given in Table 11.

Table 3: Crystal Data for $[(HC(Ph_2P)_3)Co_3(CO)_6CCH_3]$, **34**.

| | |
|---|---|
| Formula | $C_{45}H_{34}O_6P_3Co_3$ |
| f.w. | 940.48 |
| System | Monoclinic |
| Systematic absences | $h0l, h+l\neq 2n$, $0k0, k\neq 2n$, |
| Space group | $P2_1/n$ No-14 |
| a, Å | 16.359(4) |
| b, Å | 13.317(3) |
| c, Å | 18.728(4) |
| β, ° | 92.24(2) |
| V, $Å^3$ | 4076(2) |
| Z | 4 |
| Temp. °C | -80.0 |
| Dc, g $cm^{-3}$ | 1.53 |
| Dm, g $cm^{-3}$ | 1.49 |
| F(000) | 1917.27 (1912) |
| $\mu(MoK\alpha)$, $cm^{-1}$ | 14.19 |
| Final $R_1$, $R_2$ [a,d] | 0.0682, 0.0728 |
| Weighting scheme | $w=(\sigma^2F+0.002217F^2)^{-1}$ |
| Error in observation of unit weight [b] | 1.2222 |
| Highest peak, $eÅ^{-3}$; location | 0.92; 0.0249, 0.0896, 0.2386 [c] |
| Lowest peak, $eÅ^{-3}$ | -1.11 |

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_2=(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{½}$

[b] $S=(\Sigma w(|F_o|-|F_c|)^2/(m-n))^{½}$. m=No. of reflections, n=No. of variables

[c] 1.33Å from Co(1).

[d] $R_1$,$R_2$ for 3884 reflections with $I>2.5\sigma(I)$ 0.0527, 0.0566 respectively.

Table 4: Positional parameters (x$10^4$) and $U_{eq}$ (Å$^2$)(x$10^4$) for [(HC($Ph_2P$)$_3$)$Co_3$(CO)$_6$$CCH_3$], 34, with standard errors in parentheses.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Co(1) | 324.8(4) | 894.7(5) | 1681.0(4) | 240 |
| Co(2) | -437.5(4) | 157.6(5) | 2674.6(3) | 237 |
| Co(3) | 758.8(4) | 1272.6(5) | 2935.6(4) | 251 |
| P(1) | -373.6(8) | 2334.9(9) | 1563.7(7) | 233 |
| P(2) | -1420.8(8) | 1339.2(9) | 2621.3(7) | 227 |
| P(3) | -16.6(8) | 2629.2(9) | 3116.8(7) | 237 |
| C(1) | -132(3) | 68(4) | 1046(3) | 293 |
| O(1) | -412(3) | -488(3) | 642(2) | 423 |
| C(2) | 1230(4) | 1102(4) | 1193(3) | 347 |
| O(2) | 1802(3) | 1165(4) | 882(2) | 517 |
| C(3) | -507(3) | -348(4) | 3538(3) | 313 |
| O(3) | -566(3) | -724(3) | 4084(2) | 468 |
| C(4) | -757(3) | -961(4) | 2241(3) | 304 |
| O(4) | -872(3) | -1747(3) | 2001(2) | 492 |
| C(5) | 1055(3) | 811(4) | 3789(3) | 323 |
| O(5) | 1295(3) | 461(3) | 4321(2) | 493 |
| C(6) | 1716(4) | 1773(4) | 2732(3) | 344 |
| O(6) | 2357(3) | 2077(4) | 2605(3) | 546 |
| C(7) | -899(3) | 2563(4) | 2426(3) | 219 |
| C(8) | 681(3) | 24(4) | 2440(3) | 281 |
| C(9) | 1229(4) | -860(4) | 2461(3) | 371 |
| C(11) | -208(4) | 4332(4) | 1053(3) | 400 |

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| C(12) | 232(5) | 5177(5) | 881(3) | 506 |
| C(13) | 1074(5) | 5211(5) | 986(3) | 501 |
| C(14) | 1481(4) | 4358(5) | 1285(4) | 477 |
| C(15) | 1045(4) | 3514(4) | 1456(3) | 351 |
| C(16) | 189(3) | 3491(4) | 1349(3) | 279 |
| C(21) | -1894(3) | 2978(4) | 894(3) | 277 |
| C(22) | -2441(4) | 3060(4) | 304(3) | 327 |
| C(23) | -2261(4) | 2599(5) | -336(3) | 422 |
| C(24) | -1527(4) | 2087(5) | -397(3) | 404 |
| C(25) | -991(4) | 1989(4) | 194(3) | 313 |
| C(26) | -1168(3) | 2430(4) | 846(3) | 269 |
| C(31) | -2989(3) | 1784(4) | 2005(3) | 280 |
| C(32) | -3609(3) | 1717(4) | 1482(3) | 353 |
| C(33) | -3514(4) | 1087(4) | 901(3) | 382 |
| C(34) | -2822(4) | 510(4) | 847(3) | 338 |
| C(35) | -2206(3) | 570(4) | 1375(3) | 284 |
| C(36) | -2272(3) | 1216(4) | 1949(3) | 268 |
| C(41) | -2311(3) | 746(4) | 3774(3) | 305 |
| C(42) | -2811(4) | 854(5) | 4351(3) | 375 |
| C(43) | -3036(4) | 1803(5) | 4572(3) | 385 |
| C(44) | -2768(4) | 2645(4) | 4215(3) | 330 |
| C(45) | -2269(3) | 2528(4) | 3632(3) | 319 |
| C(46) | -2037(3) | 1585(4) | 3407(3) | 243 |
| C(51) | -538(3) | 3704(4) | 4323(3) | 289 |
| C(52) | -811(4) | 3779(4) | 5023(3) | 393 |

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| C(53) | -964(4) | 2935(5) | 5407(3) | 413 |
| C(54) | -826(4) | 1991(4) | 5116(3) | 364 |
| C(55) | -542(3) | 1917(4) | 4432(3) | 326 |
| C(56) | -418(3) | 2764(4) | 4018(3) | 267 |
| C(61) | -46(4) | 4708(4) | 2739(3) | 389 |
| C(62) | 302(5) | 5659(5) | 2691(4) | 545 |
| C(63) | 1091(6) | 5802(5) | 2941(4) | 653 |
| C(64) | 1535(5) | 5022(6) | 3256(4) | 693 |
| C(65) | 1191(4) | 4063(5) | 3287(3) | 432 |
| C(66) | 406(4) | 3896(4) | 3023(3) | 294 |

$U_{eq}=(U_{11}+U_{22}+U_{33}+2\cos a U_{23}+2\cos b U_{13}+2\cos c U_{12})/3$

Table 5: Selected bond lengths (Å) and bond angles (°) for $[(HC(Ph_2P)_3)Co_3(CO)_6CCH_3]$, 34, with estimated standard deviations in parentheses.

(i) Cobalt Coordination

| | | | |
|---|---|---|---|
| Co(1)-Co(2) | 2.483(1) | | |
| Co(1)-Co(3) | 2.480(1) | Co(1)-P(1) | 2.239(1) |
| Co(1)-C(1) | 1.765(5) | Co(1)-C(2) | 1.792(6) |
| Co(1)-C(8) | 1.907(5) | Co(2)-Co(3) | 2.490(1) |
| Co(2)-P(2) | 2.250(1) | Co(2)-C(3) | 1.761(6) |
| Co(2)-C(4) | 1.767(6) | Co(2)-C(8) | 1.908(5) |
| Co(3)-P(3) | 2.241(2) | Co(3)-C(5) | 1.762(6) |
| Co(3)-C(6) | 1.758(6) | Co(3)-C(8) | 1.906(5) |
| Co(3)-Co(1)-Co(2) | 60.2(1) | P(1)-Co(1)-Co(2) | 98.2(1) |
| P(1)-Co(1)-Co(3) | 92.6(1) | C(1)-Co(1)-Co(2) | 92.7(2) |
| C(1)-Co(1)-Co(3) | 149.7(2) | C(1)-Co(1)-P(1) | 105.5(2) |
| C(2)-Co(1)-Co(2) | 153.2(2) | C(2)-Co(1)-Co(3) | 103.9(2) |
| C(2)-Co(1)-P(1) | 104.3(2) | C(2)-Co(1)-C(1) | 95.1(3) |
| C(8)-Co(1)-Co(2) | 49.4(2) | C(8)-Co(1)-Co(3) | 49.4(2) |
| C(8)-Co(1)-P(1) | 137.2(2) | C(8)-Co(1)-C(1) | 103.4(2) |
| C(8)-Co(1)-C(2) | 103.8(2) | Co(3)-Co(2)-Co(1) | 59.8(1) |
| P(2)-Co(2)-Co(1) | 94.0(1) | P(2)-Co(2)-Co(3) | 98.4(1) |
| C(3)-Co(2)-Co(1) | 153.2(2) | C(3)-Co(2)-Co(3) | 97.2(2) |
| C(3)-Co(2)-P(2) | 103.7(2) | C(4)-Co(2)-Co(1) | 97.9(2) |
| C(4)-Co(2)-Co(3) | 144.1(2) | C(4)-Co(2)-P(2) | 111.8(2) |
| C(4)-Co(2)-C(3) | 94.1(3) | C(8)-Co(2)-Co(1) | 49.4(2) |

| | | | |
|---|---|---|---|
| C(8)-Co(2)-Co(3) | 49.2(2) | C(8)-Co(2)-P(2) | 138.2(2) |
| C(8)-Co(2)-C(3) | 105.9(2) | C(8)-Co(2)-C(4) | 94.9(2) |
| Co(2)-Co(3)-Co(1) | 59.9(1) | P(3)-Co(3)-Co(1) | 99.5(1) |
| P(3)-Co(3)-Co(2) | 93.7(1) | C(5)-Co(3)-Co(1) | 147.9(2) |
| C(5)-Co(3)-Co(2) | 99.0(2) | C(5)-Co(3)-P(3) | 106.4(2) |
| C(6)-Co(3)-Co(1) | 95.5(2) | C(6)-Co(3)-Co(2) | 152.1(2) |
| C(6)-Co(3)-P(3) | 104.0(2) | C(6)-Co(3)-C5) | 96.5(3) |
| C(8)-Co(3)-Co(1) | 49.5(2) | C(8)-Co(3)-Co(2) | 49.3(2) |
| C(8)-Co(3)-P(3) | 138.6(2) | C(8)-Co(3)-C5) | 98.5(2) |
| C(8)-Co(3)-C(6) | 105.5(2) | | |

(ii) Carbonyls

| | | | |
|---|---|---|---|
| C(1)-O(1) | 1.142(7) | C(2)-O(2) | 1.125(8) |
| C(3)-O(3) | 1.145(7) | C(4)-O(4) | 1.152(7) |
| C(5)-O(5) | 1.155(7) | C(6)-O(6) | 1.156(7) |
| Co(1)-C(1)-O(1) | 178.1(5) | Co(1)-C(2)-O(2) | 175.4(5) |
| Co(2)-C(3)-O(3) | 176.3(5) | Co(2)-C(4)-O(4) | 170.7(5) |
| Co(3)-C(5)-O(5) | 174.5(5) | Co(3)-C(6)-O(6) | 178.0(5) |

Table 6: Crystal Data for $[(Co(CO)_3)_2(C_{13}H_{19}OH)]$, **44**.

| | |
|---|---|
| Formula | $C_{19}H_{20}O_7Co_2$ |
| f.w. | 478.23 |
| System | Orthorhombic |
| Systematic absences | $h00, h \neq 2n$, $0k0, k \neq 2n$, $00l, l \neq 2n$ |
| Space group | $P2_12_12_1$ No-19 |
| a, Å | 12.136(6) |
| b, Å | 12.682(2) |
| c, Å | 13.652(3) |
| V, Å$^3$ | 2101(1) |
| Z | 4 |
| Dc, g cm$^{-3}$ | 1.51 |
| Dm, g cm$^{-3}$ | 1.49 |
| F(000) | 978.80 (976) |
| $\mu$(MoK$\alpha$), cm$^{-1}$ | 16.75 (15.37) |
| Final $R_1$, $R_2$$^{a,d}$ | 0.0546, 0.0567 |
| Weighting scheme | $w=(\sigma^2F+0.001833F^2)^{-1}$ |
| Error in observation of unit weight$^b$ | 1.0713 |
| Highest peak, eÅ$^{-3}$; location | 0.67; 0.2029, 0.0016, 0.9815$^c$ |
| Lowest peak, eÅ$^{-3}$ | -0.50 |

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_2=(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{1/2}$

[b] $S=(\Sigma w(|F_o|-|F_c|)^2/(m-n))^{1/2}$. m=No. of reflections, n=No. of variables

[c] 1.15Å from Co(2).

[d] $R_1$, $R_2$ for 2953 reflections with $I>2.5\sigma(I)$ 0.0437, 0.0463 respectively.

Table 7: Positional parameters (x$10^4$) and $U_{eq}$ ($Å^2$)(x$10^4$) for $[(Co(CO)_3)_2(C_{13}H_{19}OH)]$, 44, with standard errors in parentheses.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Co(1) | 1184.9(5) | 1375.9(5) | 9602.8(4) | 398 |
| Co(2) | 1291.6(5) | -564.2(5) | 9692.2(5) | 419 |
| C(1) | -1790(4) | -674(3) | 8905(3) | 355 |
| O(1) | -1448(3) | 662(3) | 10163(2) | 490 |
| C(2) | -1153(3) | 352(3) | 9183(3) | 326 |
| C(3) | -1609(4) | 1161(4) | 8417(4) | 450 |
| C(4) | -2415(4) | 500(4) | 7796(4) | 481 |
| C(5) | -1717(4) | -246(5) | 7168(4) | 531 |
| C(6) | -1311(4) | -1064(4) | 7930(3) | 457 |
| C(7) | -2939(4) | -233(4) | 8554(4) | 475 |
| C(8) | -3688(5) | -1081(5) | 8096(4) | 634 |
| C(9) | -3638(4) | 343(5) | 9314(4) | 613 |
| C(10) | -1828(5) | -1505(4) | 9715(4) | 569 |
| C(11) | 90(3) | 297(3) | 9134(3) | 338 |
| C(12) | 959(4) | 339(4) | 8545(3) | 402 |
| C(13) | 1330(5) | 329(5) | 7491(4) | 618 |
| C(14) | 406(4) | 2528(4) | 9272(4) | 492 |
| C(15) | 2570(5) | 1733(4) | 9211(4) | 527 |
| C(16) | 1169(5) | 1560(4) | 10914(4) | 570 |
| C(17) | 2781(5) | -616(5) | 9780(6) | 767 |
| C(18) | 1065(5) | -1843(4) | 9156(4) | 639 |
| C(19) | 802(5) | -822(4) | 10934(4) | 578 |
| O(2) | -102(3) | 3248(3) | 9080(3) | 660 |

Table 7 Continued.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| O(3) | 3421(3) | 1952(4) | 8926(4) | 803 |
| O(4) | 1211(5) | 1678(4) | 11737(3) | 947 |
| O(5) | 3701(4) | -634(5) | 9826(6) | 1259 |
| O(6) | 914(5) | -2638(3) | 8821(4) | 1072 |
| O(7) | 479(5) | -986(4) | 11693(4) | 985 |

$U_{eq}=(U_{11}+U_{22}+U_{33})/3$

Table 8: Selected bond lengths (Å) and bond angles (°) for $[(Co(CO)_3)_2(C_{13}H_{19}OH)]$, **44**, with estimated standard deviations in parentheses.

(i) Cobalt Coordination

| | | | |
|---|---|---|---|
| Co(1)-Co(2) | 2.467(1) | | |
| Co(1)-C(11) | 2.011(4) | Co(2)-C(11) | 1.976(4) |
| Co(1)-C(12) | 1.973(4) | Co(2)-C(12) | 1.982(5) |
| Co(1)-C(14) | 1.798(6) | Co(2)-C(17) | 1.814(6) |
| Co(1)-C(15) | 1.821(6) | Co(2)-C(18) | 1.801(6) |
| Co(1)-C(16) | 1.806(6) | Co(2)-C(19) | 1.825(4) |
| C(11)-Co(1)-C(12) | 38.9(2) | C(11)-Co(2)-C(12) | 39.2(2) |
| C(11)-Co(1)-C(14) | 97.2(2) | C(11)-Co(2)-C(17) | 141.5(2) |
| C(11)-Co(1)-C(15) | 133.3(2) | C(11)-Co(2)-C(18) | 103.3(2) |
| C(11)-Co(1)-C(16) | 113.3(2) | C(11)-Co(2)-C(19) | 102.6(2) |
| C(12)-Co(1)-C(14) | 106.5(2) | C(12)-Co(2)-C(17) | 106.1(3) |
| C(12)-Co(1)-C(15) | 94.6(2) | C(12)-Co(2)-C(18) | 99.7(2) |
| C(12)-Co(1)-C(16) | 144.2(2) | C(12)-Co(2)-C(19) | 140.5(2) |
| C(14)-Co(1)-C(15) | 102.1(2) | C(17)-Co(2)-C(18) | 98.3(3) |
| C(14)-Co(1)-C(16) | 98.0(2) | C(17)-Co(2)-C(19) | 104.8(3) |
| C(15)-Co(1)-C(16) | 105.6(3) | C(18)-Co(2)-C(19) | 99.6(3) |
| Co(2)-Co(1)-C(11) | 51.1(1) | Co(1)-Co(2)-C(11) | 52.4(1) |
| Co(2)-Co(1)-C(12) | 51.6(1) | Co(1)-Co(2)-C(12) | 51.2(1) |
| Co(2)-Co(1)-C(14) | 148.3(2) | Co(1)-Co(2)-C(17) | 95.3(2) |
| Co(2)-Co(1)-C(15) | 102.4(2) | Co(1)-Co(2)-C(18) | 150.5(2) |
| Co(2)-Co(1)-C(16) | 94.6(2) | Co(1)-Co(2)-C(19) | 102.0(2) |

Table 8 Continued

| | | | |
|---|---|---|---|
| Co(1)-C(11)-Co(2) | 76.4(1) | Co(1)-C(12)-Co(2) | 77.2(2) |
| Co(1)-C(11)-C(2) | 127.9(3) | Co(2)-C(11)-C(2) | 138.1(3) |
| Co(1)-C(11)-C(12) | 69.0(3) | Co(2)-C(11)-C(12) | 70.7(3) |
| Co(1)-C(12)-C(11) | 72.1(3) | Co(2)-C(12)-C(11) | 70.2(3) |
| Co(1)-C(12)-C(13) | 131.4(4) | Co(2)-C(12)-C(13) | 133.5(4) |

(ii) 1,7,7-trimethyl-2-propynyl-2-hydroxy-norbornyl

| | | | |
|---|---|---|---|
| C(2)-C(3) | 1.567(6) | C(6)-C(1) | 1.534(6) |
| C(2)-O(1) | 1.439(5) | C(1)-C(10) | 1.527(6) |
| C(2)-C(1) | 1.562(6) | C(1)-C(7) | 1.578(6) |
| C(2)-C(11) | 1.512(6) | C(7)-C(9) | 1.528(7) |
| C(3)-C(4) | 1.543(7) | C(7)-C(8) | 1.540(7) |
| C(4)-C(5) | 1.533(7) | C(11)-C(12) | 1.327(6) |
| C(4)-C(7) | 1.529(7) | C(12)-C(13) | 1.508(7) |
| C(5)-C(6) | 1.548(7) | | |
| O(1)-C(2)-C(3) | 110.7(3) | C(2)-C(1)-C(10) | 114.5(4) |
| O(1)-C(2)-C(1) | 109.3(3) | C(6)-C(1)-C(10) | 114.7(4) |
| C(3)-C(2)-C(1) | 102.1(3) | C(2)-C(1)-C(7) | 102.4(3) |
| O(1)-C(2)-C(11) | 107.6(3) | C(6)-C(1)-C(7) | 100.6(4) |
| C(3)-C(2)-C(11) | 110.6(3) | C(10)-C(1)-C(7) | 116.0(4) |
| C(1)-C(2)-C(11) | 116.4(3) | C(4)-C(7)-C(1) | 93.1(3) |
| C(2)-C(3)-C(4) | 103.5(4) | C(4)-C(7)-C(9) | 113.5(4) |
| C(3)-C(4)-C(5) | 107.0(4) | C(1)-C(7)-C(9) | 117.0(4) |

Table 8 continued

| | | | |
|---|---|---|---|
| C(3)-C(4)-C(7) | 102.9(4) | C(4)-C(7)-C(8) | 113.3(4) |
| C(5)-C(4)-C(7) | 103.4(4) | C(1)-C(7)-C(8) | 113.4(4) |
| C(4)-C(5)-C(6) | 102.3(4) | C(9)-C(7)-C(8) | 106.4(4) |
| C(5)-C(6)-C(1) | 104.3(4) | C(2)-C(11)-C(12) | 144.9(4) |
| C(2)-C(1)-C(6) | 107.0(3) | C(11)-C(12)-C(13) | 144.7(5) |

(iii) Carbonyls

| | | | |
|---|---|---|---|
| C(14)-O(2) | 1.134(6) | C(17)-O(5) | 1.118(7) |
| C(15)-O(3) | 1.141(6) | C(18)-O(6) | 1.122(7) |
| C(16)-O(4) | 1.134(6) | C(19)-O(7) | 1.127(7) |
| Co(1)-C(14)-O(2) | 178.4(5) | Co(2)-C(17)-O(5) | 178.8(6) |
| Co(1)-C(15)-O(3) | 177.1(5) | Co(2)-C(18)-O(6) | 179.2(6) |
| Co(1)-C(16)-O(4) | 176.8(6) | Co(2)-C(19)-O(7) | 178.5(6) |

Table 9: Crystal Data for $[(Mo(C_5H_5)(CO)_2)_2(C_{13}H_{18})]$, 73.

| | |
|---|---|
| Formula | $C_{27}H_{28}O_4Mo_2$ |
| f.w. | 608.40 |
| System | Orthorhombic |
| Systematic absences | $h00, h\neq 2n$, $0k0, k\neq 2n$, $00l, l\neq 2n$ |
| Space group | $P2_12_12_1$ No-19 |
| a, Å | 8.938(4) |
| b, Å | 14.074(4) |
| c, Å | 19.510(6) |
| V, $Å^3$ | 2454(1) |
| Z | 4 |
| Dc, g $cm^{-3}$ | 1.65 |
| Dm, g $cm^{-3}$ | 1.64 |
| F(000) | 1209.76 (1224) |
| $\mu$(MoK$\alpha$), $cm^{-1}$ | 10.36 |
| Final $R_1$, $R_2$[a,d] | 0.0290, 0.0276 |
| Weighting scheme | $w=(\sigma^2F+0.000342F^2)^{-1}$ |
| Error in observation of unit weight[b] | 1.0881 |
| Highest peak, e$Å^{-3}$; location | 0.55; 0.6776, -0.0217, 0.7422[c] |
| Lowest peak, e$Å^{-3}$ | -0.53 |

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_2=(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{½}$

[b] $S=(\Sigma w(|F_o|-|F_c|)^2/(m-n))^{½}$. m=No. of reflections, n=No. of variables

[c] 0.80Å from H(19).

[d] $R_1$,$R_2$ for 3846 reflections with $I>2.5\sigma(I)$ 0.0236, 0.0245 respectively.

Table 10: Positional parameters (x$10^4$) and $U_{eq}$ (Å$^2$)(x$10^4$) for [(Mo($C_5H_5$)(CO)$_2$)$_2$($C_{13}H_{18}$)], **73**, with estimated standard deviations in parentheses.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Mo(1) | 3192.7(3) | -126.4(2) | 7477.2(2) | 313 |
| Mo(2) | 2467.8(4) | 1430.7(2) | 6503.5(1) | 328 |
| C(1) | 4694(4) | -512(3) | 5158(2) | 353 |
| C(2) | 4727(4) | -467(2) | 5950(2) | 312 |
| C(3) | 5796(5) | -1063(3) | 6148(2) | 427 |
| C(4) | 6458(5) | -1532(3) | 5522(2) | 465 |
| C(5) | 5204(6) | -2207(3) | 5266(3) | 650 |
| C(6) | 4003(5) | -1505(3) | 5017(2) | 565 |
| C(7) | 6378(4) | -712(3) | 5002(2) | 392 |
| C(8) | 6696(5) | -1016(4) | 4257(2) | 601 |
| C(9) | 7411(6) | 101(3) | 5167(2) | 566 |
| C(10) | 3985(5) | 309(3) | 4778(2) | 497 |
| C(11) | 3608(4) | 5(3) | 6377(2) | 313 |
| C(12) | 2095(4) | -61(2) | 6449(2) | 334 |
| C(13) | 867(5) | -654(3) | 6142(2) | 450 |
| C(14) | 2760(5) | -1489(3) | 7292(2) | 455 |
| O(1) | 2521(6) | -2270(2) | 7205(2) | 754 |
| C(15) | 1038(5) | -83(3) | 7710(2) | 484 |
| O(2) | -231(4) | -84(3) | 7819(2) | 748 |
| C(16) | 4060(5) | 400(3) | 8536(2) | 524 |
| C(17) | 4230(6) | -599(3) | 8506(2) | 545 |
| C(18) | 5307(6) | -784(4) | 7986(2) | 573 |

Table 10 Continued

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| C(19) | 5807(5) | 74(4) | 7713(2) | 524 |
| C(20) | 5054(5) | 814(3) | 8050(2) | 525 |
| C(21) | 2473(5) | 1819(2) | 7456(2) | 450 |
| O(3) | 2338(5) | 2212(2) | 7986(2) | 707 |
| C(22) | 4603(5) | 1679(3) | 6415(2) | 451 |
| O(4) | 5864(4) | 1837(3) | 6348(2) | 711 |
| C(23) | 817(6) | 1602(3) | 5560(3) | 575 |
| C(24) | 1866(6) | 2325(3) | 5539(2) | 610 |
| C(25) | 1628(6) | 2911(3) | 6138(3) | 703 |
| C(26) | 429(6) | 2515(4) | 6491(3) | 702 |
| C(27) | -61(6) | 1704(4) | 6144(3) | 655 |

$U_{eq}=(U_{11}+U_{22}+U_{33})/3$

Table 11: Selected bond lengths (Å) and bond angles (°) for $[(Mo(C_5H_5)(CO)_2)_2(C_{13}H_{18})]$, 73, with estimated standard deviations in parentheses.

(i) Molybdenum Coordination

| | | | |
|---|---|---|---|
| Mo(1)-Mo(2) | 2.972(1) | | |
| Mo(1)-C(11) | 2.187(3) | Mo(2)-C(11) | 2.265(4) |
| Mo(1)-C(12) | 2.236(3) | Mo(2)-C(12) | 2.129(3) |
| Mo(1)-C(14) | 1.990(4) | Mo(2)-C(21) | 1.937(4) |
| Mo(1)-C(15) | 1.980(4) | Mo(2)-C(22) | 1.948(4) |
| Mo(1)-C(16) | 2.328(4) | Mo(2)-C(23) | 2.371(4) |
| Mo(1)-C(17) | 2.308(4) | Mo(2)-C(24) | 2.328(4) |
| Mo(1)-C(18) | 2.327(4) | Mo(2)-C(25) | 2.327(4) |
| Mo(1)-C(19) | 2.399(4) | Mo(2)-C(26) | 2.377(5) |
| Mo(1)-C(20) | 2.403(4) | Mo(2)-C(27) | 2.398(5) |
| Mo(1)-Ctd(1)¥ | 2.017 | Mo(2)-Ctd(2) | 2.036 |
| C(11)-Mo(1)-C(12) | 35.9(1) | C(11)-Mo(2)-C(12) | 36.0(1) |
| C(11)-Mo(1)-C(14) | 86.3(1) | C(11)-Mo(2)-C(21) | 110.7(1) |
| C(11)-Mo(1)-C(15) | 112.8(3) | C(11)-Mo(2)-C(22) | 73.0(1) |
| C(12)-Mo(1)-C(14) | 77.9(1) | C(12)-Mo(2)-C(21) | 109.1(1) |
| C(12)-Mo(1)-C(15) | 77.2(1) | C(12)-Mo(2)-C(22) | 109.0(1) |
| C(14)-Mo(1)-C(15) | 83.2(2) | C(21)-Mo(2)-C(22) | 91.8(2) |
| Mo(1)-C(11)-Mo(2) | 83.7(1) | Mo(1)-C(12)-Mo(2) | 85.8(1) |
| Mo(1)-C(11)-C(2) | 129.6(2) | Mo(2)-C(11)-C(2) | 140.6(2) |
| Mo(1)-C(11)-C(12) | 74.0(2) | Mo(2)-C(11)-C(12) | 66.6(2) |
| Mo(1)-C(12)-C(11) | 70.1(2) | Mo(2)-C(12)-C(11) | 77.4(2) |

Table 11 Continued

| | | | |
|---|---|---|---|
| Mo(1)-C(12)-C(13) | 131.0(3) | Mo(2)-C(12)-C(13) | 132.9(3) |
| C(11)-Mo(1)-Mo(2) | 49.2(1) | C(11)-Mo(2)-Mo(1) | 47.0(1) |
| C(12)-Mo(1)-Mo(2) | 45.5(1) | C(12)-Mo(2)-Mo(1) | 48.6(1) |
| C(14)-Mo(1)-Mo(2) | 123.5(1) | C(21)-Mo(2)-Mo(1) | 66.1(1) |
| C(15)-Mo(1)-Mo(2) | 85.0(1) | C(22)-Mo(2)-Mo(1) | 88.6(1) |
| C(16)-Mo(1)-Mo(2) | 113.9(1) | C(23)-Mo(2)-Mo(1) | 135.0(1) |
| C(17)-Mo(1)-Mo(2) | 148.9(1) | C(24)-Mo(2)-Mo(1) | 165.1(1) |
| C(18)-Mo(1)-Mo(2) | 138.0(1) | C(25)-Mo(2)-Mo(1) | 157.9(2) |
| C(19)-Mo(1)-Mo(2) | 104.3(1) | C(26)-Mo(2)-Mo(1) | 130.3(2) |
| C(20)-Mo(1)-Mo(2) | 92.4(1) | C(27)-Mo(2)-Mo(1) | 120.7(1) |
| Ctd(1)-Mo(1)-C(11) | 120.5 | Ctd(2)-Mo(2)-C(11) | 136.5 |
| Ctd(1)-Mo(1)-C(12) | 156.0 | Ctd(2)-Mo(2)-C(12) | 113.7 |
| Ctd(1)-Mo(1)-C(14) | 109.7 | Ctd(2)-Mo(2)-C(21) | 109.6 |
| Ctd(1)-Mo(1)-C(15) | 125.5 | Ctd(2)-Mo(2)-C(22) | 121.1 |

¥ Ctd(1) and Ctd(2) are the calculated centroids of the two cyclopentadienyl rings.

(ii) 1,7,7-trimethyl-2-propynyl-norbornene

| | | | |
|---|---|---|---|
| C(2)-C(3) | 1.329(5) | C(1)-C(6) | 1.553(6) |
| C(1)-C(2) | 1.546(5) | C(1)-C(10) | 1.513(6) |
| C(2)-C(11) | 1.461(5) | C(1)-C(7) | 1.561(5) |
| C(3)-C(4) | 1.509(5) | C(7)-C(9) | 1.505(6) |
| C(4)-C(5) | 1.552(6) | C(7)-C(8) | 1.542(5) |

| | | | |
|---|---|---|---|
| C(4)-C(7) | 1.539(5) | C(11)-C(12) | 1.363(5) |
| C(5)-C(6) | 1.537(7) | C(12)-C(13) | 1.502(5) |
| C(1)-C(2)-C(3) | 106.1(3) | C(2)-C(1)-C(7) | 100.6(3) |
| C(11)-C(2)-C(3) | 127.8(3) | C(6)-C(1)-C(7) | 100.8(3) |
| C(11)-C(2)-C(1) | 125.1(3) | C(10)-C(1)-C(7) | 116.4(3) |
| C(2)-C(3)-C(4) | 108.8(3) | C(4)-C(7)-C(1) | 92.9(3) |
| C(3)-C(4)-C(5) | 104.1(3) | C(4)-C(7)-C(9) | 113.6(3) |
| C(3)-C(4)-C(7) | 100.8(3) | C(1)-C(7)-C(9) | 114.4(3) |
| C(5)-C(4)-C(7) | 102.3(3) | C(4)-C(7)-C(8) | 113.8(3) |
| C(4)-C(5)-C(6) | 102.3(3) | C(1)-C(7)-C(8) | 114.4(3) |
| C(5)-C(6)-C(1) | 104.1(4) | C(9)-C(7)-C(8) | 107.5(4) |
| C(6)-C(1)-C(2) | 102.8(3) | C(2)-C(11)-C(12) | 134.9(3) |
| C(6)-C(1)-C(10) | 115.7(3) | C(11)-C(12)-C(13) | 136.2(3) |
| C(2)-C(1)-C(10) | 117.8(3) | | |

(iii) Carbonyls and cyclopentadienyl rings

| | | | |
|---|---|---|---|
| C(14)-O(1) | 1.133(5) | C(21)-O(3) | 1.179(5) |
| C(15)-O(2) | 1.154(5) | C(22)-O(4) | 1.157(5) |
| Mo(1)-C(14)-O(1) | 178.1(4) | Mo(2)-C(21)-O(3) | 166.8(3) |
| Mo(1)-C(15)-O(2) | 176.8(4) | Mo(2)-C(22)-O(4) | 178.4(4) |
| C(16)-C(17) | 1.417(6) | C(23)-C(24) | 1.385(7) |
| C(17)-C(18) | 1.421(6) | C(24)-C(25) | 1.445(7) |
| C(18)-C(19) | 1.395(7) | C(25)-C(26) | 1.390(8) |
| C(19)-C(20) | 1.404(6) | C(26)-C(27) | 1.397(7) |
| C(16)-C(20) | 1.423(6) | C(23)-C(27) | 1.391(7) |

| | | | |
|---|---|---|---|
| C(20)-C(16)-C(17) | 108.2(4) | C(27)-C(23)-C(24) | 109.3(4) |
| C(16)-C(17)-C(18) | 106.5(4) | C(23)-C(24)-C(25) | 107.2(5) |
| C(17)-C(18)-C(19) | 109.4(4) | C(24)-C(25)-C(26) | 106.6(5) |
| C(18)-C(19)-C(20) | 108.0(4) | C(25)-C(26)-C(27) | 109.3(5) |
| C(19)-C(20)-C(16) | 108.0(4) | C(26)-C(27)-C(23) | 107.6(5) |

## CHAPTER SEVEN

## PROPOSALS FOR FUTURE WORK

The results obtained for the three research projects discussed in the preceding chapters allowed us to successfully draw some specific conclusions regarding the behaviour of bi- and trimetallic organotransition metal clusters. In particular, the study on bimetallic μ-alkyne clusters demonstrated that it was possible to carry out either ligand or complete metal vertex substitution reactions with some degree of control over the ratio of the diastereomeric products formed. Although it is theoretically possible to generate only one diastereomer in such substitutions, i.e., 100% diastereoselectivity, the highest selectivity observed was 75:25 in this work. It is proposed that even greater selectivity could be obtained in these substitutions if one were to modify the enantiomerically pure dicobalt μ-alkyne clusters used as the starting materials. Outlined below are a number of suggestions for such investigations which could be carried out at some future time.

In his related work on bimetallic alkyne clusters, Nicholas[83] demonstrated that the incorporation of increasingly bulkier groups onto the alkyne carbon which did not contain the chiral entity caused a further enhancement in the diastereoselectivity observed for ligand substitution reactions. The three chiral dicobalt clusters used as starting materials in this thesis only had either a hydrogen atom or a methyl group attached to the alkyne carbon in question. By employing different alkyne reagents (with the same natural products), it would be possible to synthesize enantiomerically pure dicobalt clusters which differed only in the nature of the substituent at the second alkyne carbon atom. For example, by treating (1*R*)-(+)-camphor with the anion of 3,3-dimethyl-1-butyne, and then stirring this product with $Co_2(CO)_8$, it should be possible to generate a dicobalt μ-alkyne cluster containing borneol with a bulky *t*-butyl group at the second alkyne carbon, instead of the relatively small methyl group found in **44**. The influence of bulkier groups on the substitution reactions could then be investigated; it might be possible to obtain complete diastereoselectivity with the proper group.

Another point raised regarding the degree of diastereoselectivity observed in the ligand and vertex substitution reactions concerned the ability of the chiral entity to undergo rotation about the bond attaching it to the carbon atom in the tetrahedral core. Although the two cobalt tricarbonyl vertices remain diastereotopic in spite of this rotation, there was some apprehension about the extent to which the two sites were being differentiated because of the rotation. It is proposed, therefore, that some investigations involving diastereoselective substitution reactions be carried out on dicobalt μ-alkyne clusters in which the chiral moiety is unable to spin, i.e., it maintains a constant position with respect to the tetrahedral core. The most profitable route to synthesize the chiral dicobalt μ-alkyne clusters necessary for this investigation would likely involve attaching the chiral organic fragment directly to each of the two alkyne carbons which help to make up the tetrahedral core of the cluster. This could be accomplished either by treating dicobalt octacarbonyl with a chiral cyclic organic molecule possessing a carbon-carbon triple bond or by linking the two alkyne carbons in an existing dicobalt tetrahedral cluster. One specific idea for the latter approach would involve treating the dicobalt cluster stabilized dication analogous to the known[97] $[(OC)_2(C_5H_5)Mo-Mo(C_5H_5)(CO)_2][H_2C-C\equiv C-CH_2]^{2+}$ with natural products that contain at least two hydroxyl moieties, i.e., as found in sugars such as glucose, to generate linked "di-ether" species. These clusters would be entirely analogous to the chiral "mono-ether" clusters already used in this work. However, the inability of the chiral organic fragment to undergo rotations about the bonds to the alkyne carbons might enhance the differences between the two tricarbonyl cobalt sites. In turn, this might result in increased diastereoselectivity during ligand or metal vertex substitution reactions.

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