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Investigation into the uses of bimetallic alkyne complexes in organic synthesis

by

Andrew Michael Poulton

A Doctoral Thesis
Submitted in partial fulfilment of the requirements of
for the award of
Doctor of Philosophy of Loughborough University
(15th August 2005)

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Thanks also to my family for their support and encouragement without which I wouldn’t have had the confidence to progress so far with my studies

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Abstract.

This thesis describes the use of both heterobimetallic and novel desymmetrised homobimetallic metal alkyne complexes in organic chemistry.

A range of novel desymmetrised Co$_2$(CO)$_3$IPr-alkyne complexes have been synthesised and their reactivity investigated. This resulted in a highly diastereoselective thermal Pauson-Khand reaction. Previous protocols in the literature have had to use N-oxide promoters to achieve diastereoselectivity on desymmetrised bis-cobalt cores.

The use of substituted dihydrofurans as cyclopropane surrogates for the formation of novel homobimetallic 1,3-dipoles has been realised, although currently with high substrate specificity.

The zinc mediated addition of carbon nucleophiles to the inherently chiral Co(CO)$_3$MoCp(CO)$_2$-alkyne core has been investigated. This overcomes a previous lack of reactivity towards carbon nucleophiles, but expresses only low diastereoselectivity.

The use of the Co(CO)$_3$MoCp(CO)$_2$-alkyne core as a nucleophilic chiral auxiliary has been thoroughly investigated.

Chapter 1: An overview of the Pauson-Khand and Nicholas reaction and developments in the field.
Chapter 2: Highlights our research into the use of bimetallic-alkyne complexes in organic synthesis.
Chapter 3: Provides experimental data for our experiments.
Abbreviations

Ac = Acetyl
aq = aqueous
approx = approximately
Ar = aryl
Bn = benzyl
Bu = butyl
i-Bu (or i^Bu) = iso-butyl
n-Bu (or n^Bu) = normal butyl
t-Bu (or t^Bu) = tertiary butyl
CAN = ceric ammonium nitrate
cat = catalyst/catalytic
cm^{-1} = wavenumber
°C = degrees Celcius
Cp = cyclopentadienyl
Cy = cyclohexyl
δ = chemical shift
d = doublet
DCM = dichloromethane
dd = doublet of doublets
d.e. = diastereoisomeric excess
DME = dimethoxyethane
DMS = dimethylsulfide
d.r. = diastereoisomeric ratio
e.e. = enantiomeric excess
El = electron ionisation
eq (or equiv.) = equivalent
Et = ethyl
EtOH = ethanol
EWG = electron withdrawing group
FAB = fast atom bombardment
g = gram
h = hour(s)
n-hexane = normal hexane
Hz = Hertz
IR = infra-red
LDA = lithium diisopropylamine
m = multiplet
m-CPBA = meta-chlorobenzoic acid
MeOH = methanol
MeCN = acetonitrile
MHz = Megahertz
min = minutes
mL = millilitre
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<tr>
<td>mmol</td>
<td>millimole(s)</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
</tr>
<tr>
<td>Ms</td>
<td>mesyl</td>
</tr>
<tr>
<td>m/z</td>
<td>mass to charge ratio</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectroscopy</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NMO</td>
<td>N-methylmorpholine-N-oxide</td>
</tr>
<tr>
<td>Nu</td>
<td>nucleophile</td>
</tr>
<tr>
<td>P</td>
<td>protecting group</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>PKR</td>
<td>Pauson-Khand reaction</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>Pr</td>
<td>propyl</td>
</tr>
<tr>
<td>i-Pr</td>
<td>iso-propyl</td>
</tr>
<tr>
<td>IPr</td>
<td>1,3-bis-(2,6-diisopropylphenyl)-imidazolium</td>
</tr>
<tr>
<td>pTSA</td>
<td>para-toluene sulfonic acid</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>syn</td>
<td>synclinical</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>TBAF</td>
<td>tetra n-butyl ammonium fluoride</td>
</tr>
<tr>
<td>TBDMS</td>
<td>tert-butyldimethylsilyl</td>
</tr>
<tr>
<td>TBDPS'</td>
<td>tert-butyldiphenylsilyl</td>
</tr>
<tr>
<td>TBAHSO₄</td>
<td>tetra n-butyl ammonium hydrogen sulfate</td>
</tr>
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<td>tet</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>Tf</td>
<td>trifluoromethanesulfonyl</td>
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<tr>
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<td>terahydrofuran</td>
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<tr>
<td>Tips</td>
<td>tri-iso-propylsilyl</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
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<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>trig</td>
<td>trigonal</td>
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<tr>
<td>Ts</td>
<td>para-toluenesulfonate</td>
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### 1.0 INTRODUCTION

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### 2.0 RESULTS AND DISCUSSION

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1.0 Introduction

1.1 Bimetallic metal alkyne complexes

Several transition metals are able to form stable bimetallic complexes with alkynes.\(^{(1)}\) In general the alkyne acts as a four electron donor bridging ligand with a metal-metal bond perpendicular to this plane, forming a tetrahedral arrangement around the core (Figure 1). The number of other ligands varies with the metal used, satisfying the eighteen-electron rule for each metal atom.

![Figure 1](image.png)

The most studied of these complexes are the dicobalt hexacarbonyl analogues.\(^{(2)}\) These are air stable, and form in excellent yield by simply adding dicobalt octacarbonyl to a solution of the alkyne in a non-polar solvent (Scheme 1).

![Scheme 1](image.png)

Although this is by far the most studied complex, stable bimetallic complexes of molybdenum and tungsten are known.\(^{(1,3)}\) More interestingly, heterobimetallic complexes, of cobalt-molybdenum, cobalt-tungsten, and cobalt-nickel \(^{(1)}\) are also known. These
complexes are synthetically interesting as they are inherently chiral, and can be assigned $R$ or $S$ using the method illustrated. Placing a dummy atom at the centre of the complex, then following the Cahn-Ingold-Prelog convention. (Clu $R$ complex illustrated, order of priority is clockwise with the lowest priority group at the back) (Figure 2).

\[
\begin{align*}
\text{(OC)}_3\text{Co-MoCp(CO)}_2 & \quad \equiv \quad \text{Me} \\
\text{H~H}_3 & \quad \text{HC, j ::;MoCP(CO)}_2
\end{align*}
\]

Figure 2

Since their discovery in 1956, and initial use as a protecting group for the alkyne moiety in reduction and hydroboration processes, the synthesis and reactivity of bimetallic complexes has been well documented. While there are scattered reports of the uses of the heterobimetallic, dimolybdenum and ditungsten complexes, the dicobalt complexes have been the most intensively studied, resulting in the development of two synthetically significant reactions, the Pauson-Khand reaction (PKR) in 1971, and the Nicholas reaction in 1972.

1.2 The Pauson–Khand reaction

1.2.1 Discovery and mechanism

Pauson, Khand and co-workers discovered the PKR whilst investigating dicobalt hexacarbonyl complexes in the early 1970’s. They found that heating the alkyne complex in the presence of an alkene initiated a $[2+2+1]$ cycloaddition resulting in the formation of cyclopentenones (Scheme 2).
Since its initial discovery the reaction has been intensively researched with many variations and improvements made.\(^7\) However, the mechanism of the reaction has yet to be conclusively elucidated. The generally accepted pathway for the stoichiometric reaction, proposed by Magnus \(^8\) is shown below (Scheme 3).

1. Loss of CO and addition of alkene
2. Alkene insertion into least hindered Co-C bond
3. CO insertion
4. Reductive elimination
5. Decolplexation

Scheme 3
Pauson himself made some suggestions towards the mechanism based upon observations of the regioselectivity of reaction. However, Magnus is generally credited with the above mechanism.

Further evidence for the mechanism comes from several sources. Theoretical studies reveal that dissociative loss of carbon monoxide from the complex is the most energetic and hence rate limiting step. Experimental evidence comes from the fact that the reaction can be promoted by a range of hard bases and N-oxides (discussed in section 1.3.2), more significantly Krafft and co-workers found that while both homo- and bishomopropargylic sulfides accelerated the rate of the thermal reaction, bishomopropargylic sulfides greatly retarded the N-oxide mediated reaction, (27 h instead of 2 h). More significantly still, they were actually able to trap out an intermediate (Scheme 4).

Some retardation of the reaction was also seen with the homopropargylic sulfide and a more unstable intermediate was isolated. This was thought to be due to the greater bond strain in the 5-membered ring chelate formed in the latter case. Krafft suggested that in the case of the thermal reaction, although the association of the alkene to the complex (step 1 in Scheme 3) was retarded, co-ordination of the sulfide to the vacant site generated in subsequent steps actually enhances their rate, leading to an overall rate enhancement. At the lower reaction temperatures at which the NMO reactions are performed (rt. or below), the initially formed chelate is stable enough to greatly decrease the reaction rate.

In addition to the above, Gimbert used electrospray ionisation-tandem mass spectrometry in order to trap out the initially formed intermediate (Scheme 5).
The bis(diphenylphosphino)methane dicobalt hexacarbonyl phenylacetylene complex (4) was initially subject to electrospray ionisation. The M-H ion was then selectively allowed into the second cell where it was subject to low energy collisions with norbornene. The fact that no ion was found for the addition product gives strong evidence for loss of carbon monoxide as the initial step.

While the Magnus mechanism for the stoichiometric reaction is beginning to look increasingly plausible, the question of whether the catalytic reaction (see 1.4) goes via the same mechanism is still an area of intense debate. Few attempts have been made to propose a mechanism for this reaction. However, after the isolation of a pre-catalyst, and the successful development of an asymmetric catalytic system, Gibson (13) tentatively proposed a one-centre mechanism for this reaction (Scheme 6).
While the above mechanism has yet to be proven it demonstrates that there is still much to learn mechanistically about the PKR, and it should not be assumed that the catalytic version, although leading to the same general products, proceeds via the same mechanism.

1.2.2 Scope and limitations of the reaction

The PKR has developed into a very general method of forming cyclopentenones. The reaction is tolerant of a wide range of functionality, this has been enhanced by the development of new reaction conditions (vida infra) allowing the reaction to be tailored to protect reactive sites on sensitive substrates.

However, there are some inherent limitations. Terminal alkenes, and strained cyclic alkenes react much better than internal alkenes, presumably through steric considerations, and the relief of strain respectively. Tri- and tetra substituted alkenes react more slowly and in
many cases, not at all. Also electron deficient alkynes, and alkenes containing electron withdrawing groups, or \( \pi \)-conjugating groups are problematic, in some cases altering the reaction pathway to diene formation\(^{(14)}\) (Scheme 7).

![Scheme 7](image)

The above product presumably arises via a \( \beta \)-hydride elimination competing with the carbonyl insertion step after alkene insertion. This problem is brought to a head when styrene is used and both diene and cyclopentenones products are formed.\(^{(15)}\)

1.2.3 Stereo- and Regio-selectivity

Although Schore\(^{(16)}\) has shown that substituent effects can lead to \textit{exo} products in the intramolecular PKR, the intermolecular PKR generally leads to \textit{exo}-cyclopentenone adducts. However, products can sometimes be contaminated with some \textit{endo}-product. Pericás \textit{et al}\(^{(17a)}\) probed this effect \textit{via} the addition of electron withdrawing groups of gradually increasing strength to the propargylic carbon. He found that sequentially oxidising a \( p \)-tolylsulfonyl ethyne moiety to the sulfoxide then sulfone gave gradually increasing amounts of the \textit{endo}-product (0-16 \%) in the intermolecular PKR. Altering this functionality to an amide also gave some interesting results, in this case alkyl amides gave exclusively the expected \textit{exo} product but substituted aryl amides gave up to 26 \% of the \textit{endo} product. Although strong experimental evidence for the increase in \textit{endo} product with increasing electron withdrawing group strength was given in the paper, no theoretical rationale was suggested.
Recently the same group revealed that *endo* cyclopentenone adducts could be synthesised *via* the use of heterobimetallic cobalt-molybdenum complexes (Scheme 8). (17b)

A series of complexes derived from a range of N-(2-alkynoyl)oxazolidinones or sultams were synthesised and reacted in the thermal PKR with norbornadiene, all of the complexes gave good yields of the *endo*-adduct, with the oxazolidinone shown in Scheme 8 (formed as two diastereomers then separated by chromatography) giving the *endo*-adduct exclusively. Other analogues were contaminated with small amounts of exo-adduct (7-20 %). The selectivity is thought to arise through a reaction templated around the cobalt vertex, with the olefin co-ordinating from the *endo* face in order to alleviate steric interactions (Figure 3b).
The regioselectivity of the cobalt mediated PKR is determined mostly by steric effects. It was quickly determined experimentally (18) that the largest group on the alkyne becomes orientated α to the carbonyl group in the cyclopentenone product, this arises as a consequence of the initial insertion step of the alkene taking place between the cobalt and the least hindered carbon of the alkyne, thus forming the first C-C bond here. More recently Greene and Gimbert (19) have reported that stereoelectronic effects also play an important part in the regioselectivity, especially where the acetylene unit contains substituents of similar size but differing electronic properties. In this case the electronics make the carbon monoxide (CO) ligands on the cobalt inequivalent, leading to site discrimination for the loss of CO (Figure 4).
The differing electronic properties of the substituents on the acetylene lead to a build up of electron density on one of the acetylenic carbons. This discharges through the metal atoms onto the $\pi$-acceptor carbon monoxide ligands. The electron density is not distributed evenly and the CO in the trans pseudo-equatorial position is most receptive to back donation, which leads to the cis positioned CO being labile in comparison.\(^{(20)}\) After alkene co-ordination at this position the reaction proceeds as proposed earlier (Scheme 3) to give group A in the $\alpha$ to the ketone.

1.3 Reaction Promoters

The PKR was initially performed thermally, and although some substrates work well, results can be poor and the reactions often take a long time. The scope and applicability of the reaction has greatly developed since the mid 1980’s, in a large part due the use of milder, more efficient reaction conditions involving the use of promoters.

1.3.1 Dry state adsorption conditions

Smit and Caple \textit{et al} \(^{(21)}\) were the first to report encouraging new conditions when they applied dry state adsorption conditions to the synthesis of 3-oxabicyclo [3.3.0] oct-5-en-7-
one derivatives (Scheme 9). Previously these had only been synthesised in low to moderate yields (11-41 %) with long reaction times. (22)

Scheme 9

The authors found that SiO₂, Al₂O₃ and MgO·SiO₂ could be used as the adsorbent, although SiO₂ gave the best yields. Typically the enyne was dissolved in hexane, then the adsorbent added at 5-10 g adsorbent per mmol of substrate. The solution was rotary evaporated to dryness, then slowly rotated under a stream of oxygen whilst heating. Extraction of the product into ether followed by purification led to the desired products in good yield. During the course of their studies the authors also found that 10-15 % w/w of water was beneficial, and that the reaction must be performed in an oxygen atmosphere. Performing the reaction in an inert atmosphere led to cleavage of the cyclic ether and hence ring opened products. It was suggested that the observed rate enhancement came about via a template effect, where the hydrophilic moiety of the substrate was attracted to the adsorbent, and the hydrophobic ends were repelled leading to a coiling and concomitant decrease in the entropy barrier for the reaction.

A later report by Pérez-Castells and co-workers, (23) showed that 8 weight equivalents of molecular sieves could also promote previously slow reactions in the presence of trimethylamine-N-oxide (TMANO), with the yields for some substrates doubling from 40+ % to 90 %. They also found that sieves alone did promote the reaction, but that the combination of sieves and N-oxide worked better than either individually.
1.3.2 Tertiary amine-\(N\)-oxides

The addition of amine-\(N\)-oxides to metal carbonyl complexes had previously been reported to result in cleavage of the carbon monoxide ligand via oxidation to carbon dioxide.\(^{(24)}\) Schreiber\(^{(14)}\) reasoned that these could therefore be used as promoters for the PKR. He found that \(N\)-methylmorpholine-\(N\)-oxide (NMO) was able to promote the intramolecular reaction on a range of simple substrates and natural product intermediates in DCM at room temperature. He also found that the milder conditions improved both functional group tolerance and the stereoselectivity of the reaction when compared to thermal or ultrasound conditions (Scheme 10).

\[
\begin{array}{ccc}
\text{Conditions} & \text{Yield (\%)} & \text{Selectivity (10 : 11)} \\
\text{NMO, DCM, rt} & 68 & 11 : 1 \\
\text{MeCN, 82°C} & 75 & 4 : 1 \\
\text{MeCN, ))} & 45 & 3 : 1 \\
\end{array}
\]

Scheme 10

It is thought that the likely initial step in the mechanism is the loss of carbon dioxide. However it is also suggested that the residual amine may also act as a ligand co-ordinating to the vacant sites in the reaction intermediates influencing the steric and electronic course of the reaction, leading to the enhanced stereoselectivity.

Following the above report, Jeong \textit{et al.}\(^{(25)}\) investigated the reactivity of several oxidants in this procedure (Scheme 11).
As can be seen from the above results, the stronger oxidant, ceric ammonium nitrate (CAN) led to either poor yields of the cyclopentenone or complete decomplexation of the enyne. However both of the N-oxide oxidants resulted in excellent yields of the desired compound. Following these initial reports, N-oxide promoted reactions have become standard practice where mild reaction conditions are necessary.

One further significant advancement in the use of N-Oxides was reported by Kerr et al.\(^{(26)}\) in 2000 with the development of re-usable solid supported NMO (Scheme 12).

Oxidation of the commercially available Merryfield resin with N-phenyl-sulfonyl oxaziridine (Davis reagent) led to the solid phase NMO reagent (18) in good yield. The reagent was used with a variety of PKR substrates and found to be effective. More usefully,
the resin sequestered the cobalt residues, simplifying clean up, and was found to be recyclable after treatment. In addition the PKR and oxidation were compatible in one pot, allowing the use of just one equivalent of resin.

1.3.3 Hard Lewis bases

The earlier suggestion, (14) that when using N-oxides the residual tertiary amine stabilised the vacant sites on the reaction intermediates, prompted research into the use of hard Lewis bases (oxygen, nitrogen, sulfur) as reaction promoters. Amines and alcohols had already been shown to promote ligand substitution on low-valent organotransition metal carbonyls, (27) hence it was thought that these might play a dual catalytic role. Further encouragement for this area of investigation came from the report of Krafft (Scheme 4), where rate enhancements for the thermal reaction were observed in the presence of substrates containing homo- and bishomo-allylic sulphides. Krafft 11) successfully investigated the use of co-ordinating solvents as catalysts for the NMO mediated reaction (Scheme 13 and Table 1).

![Scheme 13](image-url)
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Reaction time</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>4 min</td>
<td>88</td>
</tr>
<tr>
<td>EtOAc</td>
<td>8 min</td>
<td>63</td>
</tr>
<tr>
<td>THF</td>
<td>10 min</td>
<td>72</td>
</tr>
<tr>
<td>acetone</td>
<td>10 min</td>
<td>78</td>
</tr>
<tr>
<td>THF / DCM (1 :1)</td>
<td>25 min</td>
<td>61</td>
</tr>
<tr>
<td>DCM</td>
<td>30 min</td>
<td>70</td>
</tr>
<tr>
<td>Et₂O</td>
<td>8 h</td>
<td>50</td>
</tr>
<tr>
<td>DMSO</td>
<td>14 h</td>
<td>71</td>
</tr>
</tbody>
</table>

Table 1

Krafft’s results clearly demonstrated that co-ordinating solvents not only catalysed the reaction but also increased yields. Interestingly, although dimethylsulfoxide (DMSO) appeared to retard the reaction when used as solvent, Stumphf, (28) found that 10 equivalents of this in combination with the same amount of dimethylsulfide (DMS) in benzene at 60 °C was the best promoter in the synthesis of 3-thia-bicyclo- [3.3.0-oct-5-en-7]-ones. This promoter gave yields of between 65% and 80 % for a range of substrates. For these substrates both dry state adsorption and NMO catalysis gave yields below 25 %.

Sugihara (29) took the Lewis base methodology a step further by investigating amines as solvent or co-solvent. It was postulated that amines could catalyse the reaction by first forming weak interactions with the carbonyl ligand (24) (Scheme 14).
It was found that amines did indeed catalyse the reaction with cyclohexylamine and amines containing secondary alkyl groups the most effective promoters. Ammonia was also found to catalyse the reaction, either by direct bubbling of the gas through the reaction mixture or via release of ammonia from aqueous ammonium hydroxide when used in a biphasic system with 1,4-dioxane as the co-solvent (Scheme 15 and Table 2).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CyNH₂</td>
<td>35</td>
<td>5</td>
<td>72</td>
</tr>
<tr>
<td>1,2-DCE / CyNH₂</td>
<td>83</td>
<td>5</td>
<td>99</td>
</tr>
<tr>
<td>2M NH₄OH / 1,4-dioxane</td>
<td>100</td>
<td>15</td>
<td>93</td>
</tr>
<tr>
<td>1M NH₄OH / 1,4-dioxane</td>
<td>100</td>
<td>45</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 2
Although amines did work, and were also successfully used by Rajesh and Perasamy\textsuperscript{(31)} to promote PKR's utilising \textit{in-situ} formation of the cobalt complex from CoBr\textsubscript{2}, they were poorer than N-oxides, and only worked with active alkenes. Reduction products were formed with less active alkenes in many cases. Sugihara\textsuperscript{(32)} decided to try and extend his earlier work, and overcome this problem by utilising alkyl and aryl methyl sulfides. These are poorer $\sigma$-donors and better $\pi$-acceptors than amines and therefore less likely to lead to reduction of the intermediates. In practice these did work better than the amines with both primary and secondary methyl sulfides, and aryl sulfides containing electron-donating groups e.g. thioanisole worked best. In addition the reaction proceeded at 35 °C allowing the use of low boiling point alkenes, they also appeared to be better promoters for sensitive substrates such as (23) (Scheme 16).

\begin{center}
\textbf{Scheme 16}
\end{center}

Noting the unfortunate problem associated with sulfides (smell and toxicity), Kerr and co-workers\textsuperscript{(33)} were again able to develop a polymer-supported analogue. This was found to be recyclable and showed good functional group tolerance for both the inter- and intramolecular reactions with a range of alkenes and alkynes (Scheme 17).

\begin{center}
\textbf{Scheme 17}
\end{center}
Other reagents including water, 1,2-dimethoxy ethane,\cite{34} and ionic liquids\cite{35} have also been shown to catalyse the PKR, although reports are more scattered and the reagents are possibly, generally less effective.

1.3.4 Physical and other methodology.

Ultrasound has previously been shown to promote the loss of carbon monoxide from metal carbonyls.\cite{36} When Kerr\cite{37} used this to promote N-oxide mediated reactions, he found that the use of high intensity ultrasound not only decreased reaction time but also increased the \textit{exo} selectivity of the reaction to 100\%. In addition non-activated alkenes were also found to be active under these conditions. Microwaves also promote the PKR when performed in DME, with good yields in several cases and reaction times as low as 100 s.\cite{38} Interestingly; the reaction can be performed semi-catalytically with 0.5 equivalents of cobalt used. Finally cobalt nanoparticles adsorbed onto silica can also catalyse the reaction, Chung \textit{et al}.\cite{39} exploited this in an elegant one pot catalytic allylic alkylation Pauson-Khand reaction using palladium and cobalt nanoparticles in the same pot (Scheme 18).

\begin{center}
\begin{tikzpicture}
\node (A) at (-3,0) {\text{\textit{exo}} selectivity\%};
\node (B) at (-3,-1) {100\%};
\end{tikzpicture}
\end{center}

![Scheme 18](image)


In conclusion, the development of effective promoters has enabled the PKR to develop from an academic research topic to a useful reaction widely used in many areas of natural product synthesis. In addition greater insight has been gained into the mechanism of the reaction.
1.4 Catalytic Reactions

Although the PKR is one of the most powerful methods for the synthesis of substituted cyclopentenones, the use of stoichiometric amounts of cobalt has retarded its progress and stopped its use outside of academic research institutions. Hence the development of good catalytic methods for the reaction are essential if it is to reach its full potential. Developments in this area over the last 10 years have lead to realistic catalytic turnovers, and more recently good progress has been made towards the development of asymmetric catalytic systems.

1.4.1 Initial developments and Co$_2$(CO)$_n$ systems

The first published report of a PKR, sub-stoichiometric with respect to cobalt was by Billington in 1983\(^{(40)}\) although Pauson did mention some investigations in his original papers. Billington used the reaction to synthesise substituted 3-oxabicyclo [3.3.0] oct-7-en-6-ones as intermediates in natural product synthesis. However, although sub-stoichiometric amounts of cobalt were used, the turnover was so low (1.5 turnovers) that the first generally accepted report of a truly catalytic PKR was by Rautenstrauch et al in 1990\(^{(41)}\). Catalytic turnovers of \(>220\) were achieved for the synthesis of the dihydrojasmonate precursor (31) (Scheme 19). It was noted in this report that high CO pressure and a low alkyne concentration was needed to increase catalytic turnover and suppress side product formation, of which cyclotrimerisation was found to be a major problem. This was not a problem associated with the stoichiometric reaction.

\[\text{CO}, 100 \text{ bar} \quad 0.22 \text{ mol} \% \text{ Co}_2(\text{CO})_8 \quad \text{30}\]
\[0.8 \text{ M Toluene, C}_2\text{H}_2, 40 \text{ bar} \quad \text{31}\]
\[(47 \%, >220 \text{ turnover)}\]

Scheme 19
Livinghouse (42) also reported a thermal catalytic PKR although it was suggested that a small thermal window of 50-80 °C existed, with catalyst degradation seen above this temperature and retardation of the reaction below. It was also suggested that high purity Co$_2$(CO)$_8$ was necessary for the reaction to proceed. The same group later reported (43) that high intensity light could be used to initiate the reaction at lower temperatures (50-55 °C) \textit{via} photochemical induced dissociation of the metal carbonyls. Krafft and co-workers (44) later published several significant developments from the Livinghouse publications, they found that base washing the reaction vessel obviated the need for high purity CO$_2$(CO)$_8$. This was useful as high purity CO$_2$(CO)$_8$ is both air sensitive and pyrophoric. In addition they found that the addition of cyclohexylamine to the reaction mixture led to both increased yields and reaction rates. It was suggested that the amine could act as a carrier, stabilising the active catalyst and inhibiting the formation of dead-end side products.

They further went on to demonstrate the efficiency of cyclohexylamine as an additive in the reaction by utilising both Co$_4$(CO)$_{12}$ (previously shown to be a dead end pathway in this reaction)\(^{(41,45)}\) and pre-complexed Co$_2$(CO)$_6$-alkynes as reaction catalysts (Scheme 20).

![Scheme 20](image)

A) 5 mol % Co$_4$(CO)$_{12}$, 30 mol % CyNH$_2$, 70 °C, 94 % yield
B) 5 mol % Co$_2$(CO)$_8$, 10 mol % CyNH$_2$, 70 °C, 89 % yield

In a similar vain, Hayashi \textit{et al} (46) found tributylphosphane sulfide to be another excellent additive for the catalytic reaction under mild conditions (70 °C, 1atm CO, 3 mol %
Interestingly this reaction proceeded best using benzene as the solvent instead of the generally accepted 1,2-DME, and was also effective with allyl propargyl ethers, which are poor substrates under many other conditions.

An interesting extension of the catalytic PKR was reported by Chung et al.\(^{(47)}\) who was able to perform a Co\(_2\)(CO)\(_8\)-catalysed tandem [2+2+1]/[2+2+2] cycloaddition of terminal diynes leading to the formation of tetracyclic systems such as (36) (Scheme 21).

![Scheme 21](image)

Mechanistic studies suggested that the reaction proceeds via the [2+2+1] cycloaddition to form an intermediate bicyclic cyclopentadienone which then participates in a [2+2+2] cycloaddition to form the tetracyclic product. Chung\(^{(48)}\) found that triynes also participated in tandem reactions, only this time, tandem PKR products such as compound (40) were formed. However propargyl ethers tended to cyclotrimerise instead (Scheme 22).
Although cobalt carbonyl species are the most investigated catalysts for the PKR, they are quite sensitive compounds, hence several other cobalt containing pre-catalysts have been developed in the hope of producing more efficient and easier to handle catalysts. Livinghouse et al. (49) following a report by Isobe (50) on the reductive decomplexation of hexacarbonyldicobalt complexes with triethylsilane, reasoned that the cobalt carbonyl species formed in the reaction could be regenerated into catalytic species (Scheme 23).
Catalytic yields for the above reactions with a range of enynes were comparable to cobalt carbonyl catalysed reactions, and this method had the advantage that the pre-catalyst is a stable crystalline compound. Krafft (51) later found that the reduction step of the above reaction was unnecessary. It was discovered that adding a catalytic amount of a pre-complexed enyne to a reaction vessel containing either the uncomplexed enyne or a different enyne led to good catalytic activity under mild conditions (Scheme 24 and Table 3).

![Scheme 24]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₂(CO)₈</td>
<td>15</td>
<td>80</td>
</tr>
<tr>
<td>42</td>
<td>2</td>
<td>78</td>
</tr>
<tr>
<td>43</td>
<td>5</td>
<td>79</td>
</tr>
<tr>
<td>44</td>
<td>1</td>
<td>92</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>75</td>
</tr>
</tbody>
</table>

Table 3
Other more exotic species have also been used to catalyse the reaction. Sugihara\(^{52}\) found alkylidienetricobalt nonacarbonyl clusters were better precatalysts than Co\(_2\)(CO)\(_8\), for the catalytic PKR without any additional promoters. These catalysts gave good yields for a range of inter and intra-molecular PKR's under just 1 atm of carbon monoxide. The reaction was sensitive to the bulk of the substituent on the alkylidine carbon, with bulkier groups being less effective. The most effective species was found to be the methylidyne-Co\(_2\)(CO)\(_9\) cluster.

Chung \textit{et al.,}\(^{53}\) reported the use of 1,5-cyclooctadiene(indenyl)cobalt(I) as a catalyst for a variety of intermolecular reactions with norbornene and norbornadiene, with yields of up to 96\% using 1 mol\% catalyst (Scheme 25).

\begin{equation}
\text{Scheme 25}
\end{equation}

The same group\(^{54}\) later disclosed the use of Co(acac)\(_2\)/NaBH\(_4\) as another alternative system under 30-40 atmospheres of CO, using as little as 0.02 mol\% catalyst. In some cases the reaction also proceeded quantitatively without the NaBH\(_4\). This catalyst was found to be more effective than the indenyl version.

The most recent work along the theme of active cobalt-carbonyl surrogates has come from the group of Gibson,\(^{55}\) who noted that despite phosphite and phosphine substituted alkyne complexes reducing the yield and efficiency of stoichiometric PKR's\(^{51}\) they improved the efficiency of the catalytic reaction.\(^{52}\) Following previous literature procedures a series of phosphine and phosphite catalysts were synthesised in moderate to good yield (58-96\%), of the catalysts tried the air stable triphenylphosphine substituted complex (45)\(^{56}\) gave the best results in the catalytic intramolecular PKR. (Scheme 26.)
Interestingly bis-phosphine substituted products were poorer than the mono-phosphine and phosphite analogues, this was tentatively attributed to their poorer solubility under reaction conditions. The group later published the first N-heterocyclic carbene-triphenylphosphine complex (48) (Figure 5), although this complex was unexpectedly more unstable, and less active than (45).
1.3.3 Environmentally friendly PKR's

While the move from stoichiometric to catalytic amounts of cobalt is undoubtedly the most environmentally friendly advancement made over the last few years, further developments focusing upon heterogeneous (i.e. recoverable) catalysts and performing the PKR in benign solvents are beginning to receive attention.

Gibson et al (58) investigated polymer supported cobalt carbonyl complexes. Stirring Co$_2$(CO)$_8$ at rt in THF followed by heating to 60 °C in 1,4-dioxane (Scheme 27), or alternatively stirring a pre-complexed alkyne with the polymer at 50 °C in THF formed a bis-phosphine substituted resin complex (49) along with a monosubstituted complex (50).

![Scheme 27](image)

The purple, air stable complexes were then subject to an intramolecular PKR. Yields of up to 66 % were achieved with 5 mol % catalyst under 1.05 bar of carbon monoxide at 70 °C. Interestingly THF proved to be the solvent of choice for this reaction, along with a static carbon monoxide atmosphere, rather than continuous flow. In addition stirring of the solution was found to degrade the catalyst. Some leaching of the cobalt (13 %) was seen, and the catalyst was not re-used.

Mesoporous silica and charcoal have both been exploited in heterogeneous supports for cobalt. Chung et al (60) has led the way in several developments in this field. An initial
report described the adsorption of cobalt onto mesoporous silica. Initially $\text{Co}_2(\text{CO})_8$ was decomposed onto the silica supports SBA-15 and MCM-41. Later they discovered that the relatively cheap cobalt nitrate could be used, with the catalyst prepared by calcination of impregnated cobalt nitrate then reduction at 650 °C. In both cases the silica contained 8-10 w/w % cobalt. Both catalysts were found to be active in the intramolecular PKR using a range of substrates, with yields comparable to $\text{Co}_2(\text{CO})_8$ catalysis under 20 atm of carbon monoxide at 130 °C. The catalyst was also recycled 4 times with no loss of efficiency. This initial catalyst was poor in the catalysis of intermolecular PKR. However later reports by the same group (61) where cobalt on charcoal and colloidal cobalt nanoparticles were developed overcame this problem, leading to effective, stable, easily removable heterogeneous catalysts.

Relatively high pressures of carbon monoxide are necessary for all of these systems and the mechanism of the reaction is not known, with the adsorption of the substrate and carbon monoxide onto metallic cobalt, followed by insertion a possibility. No leaching of cobalt into the reaction mixture was seen with these catalysts.

The reaction solvent for the catalytic PKR has also been investigated with respect to a greening of the PKR. Jong et al (62) has developed conditions for both inter and intramolecular reactions using supercritical fluids. While supercritical CO$_2$ was successful, a more interesting and novel development was the use of ethylene as a co-solvent and substrate. (Scheme 28).
While the yield of the cyclopentenone and the effectiveness of the respective catalysts varied from case to case, this is possibly the first useful PKR incorporating the unreactive and volatile ethylene substrate.

A final report along the theme of green solvent systems comes from the Krafft group (63), who were able to perform the intramolecular catalytic PKR in water using Co₄(CO)₁₂ and 0.5-0.6 equivalents of Triton® X-100 or CTAB (cetyltrimethyl ammonium bromide) (cf enyne) as co-solvent. In the case of Triton® X-100 20 mol % of Co₄(CO)₁₂ was sufficient to catalyse the reaction.

As can be seen the catalytic PKR is a rapidly developing reaction, recently asymmetric versions have begun to be developed (see sec 1.5.4). Hopefully this move away from the stoichiometric version of the PKR will stimulate interest in this powerful reaction in industrial settings outside of research institutions.
1.5 Stereoselective reactions

One of the most intensively studied areas of the Pauson-Khand reaction has been the stereoselective synthesis of chiral cyclopentenones. Several approaches to this problem have been investigated. Initial developments focused on the intramolecular reaction with the chirality of the starting substrates directing the stereocontrol. Latterly stereoselective intramolecular reactions have been investigated. Five approaches to this more difficult problem have been successfully utilised. 1) Substrate controlled intramolecular PKR’s. 2) The use of chiral auxiliaries or tethers attached to the alkyne, 3) Desymmetrisation of the bimetallic core, 4) The (limited) use of chiral promoters and finally 5) The use of chiral catalysts (asymmetric catalytic PKR). All approaches have their advantages although the majority of the currently used methods are stoichiometric.

1.5.1 Substrate controlled

Substrate controlled PKR’s have seen the most use in natural product synthesis. Although closely related to chiral auxiliary methods they are almost exclusively intramolecular and the chirality formed is utilised further in the synthetic route. In comparison, chiral auxiliaries are generally removed after the PKR.

Although some of the earliest reports on the PKR are related to the synthesis of natural products (40) recent advances in the efficiency and use of mild conditions for the use of the PKR (see sec 1.3) mean that the area is still really in the development stages.

In a seminal paper Magnus (8b) successfully utilised an asymmetric PKR in the synthesis of coriolin (51) and hirsutic acid (52) (Figure 6).
These compounds are both templated around the tricyclo[6.3.0.0^{2,6}]undecane system. Of note is stereochemistry around the central ring. Magnus achieved the required stereochemistry via an intramolecular PKR and in the process was able to hypothesise a mechanistic rational for both the stereochemistry achieved and the reaction mechanism (Scheme 29).
The desired epimer (55) was synthesised in 79% yield with a 23:1 (exo:endo) geometry. It was noted that the bulky protecting group on the alcohol, and on the terminal end of the alkyne was necessary in order to achieve high stereoselectivity. This was rationalised by invoking the previously mentioned mechanistic rational (Scheme 3) which leads to the following diastereotopic transition states. A strong 1,3-pseudo di axial interaction is seen in the transition state leading to the minor (endo) epimer (56) (Scheme 30). (CO’s omitted for clarity).

The above work by Magnus showed that the PKR could be exploited in stereoselective synthesis. This has been increasingly utilised by other groups.
Yoo and Lee,\(^{(64)}\) used a PKR as the key step in their synthesis of \((-\)-\(\alpha\)-Kanic acid, using the reaction to set up the \textit{trans}-C2-C3 stereochemistry in the final product (\textbf{Scheme 31}).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{scheme31.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 31}

Voelter et al\(^{(65)}\) used readily prepared carbohydrate precursors followed by a palladium-cobalt mediated double annulation process to stereoselectively access polysubstituted \textit{bis}-cyclopentenoids suitable for further elaboration (\textbf{Scheme 32}).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{scheme32.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 32}
The increase in the generality of the PKR mediated by different reaction conditions and also the subtleties of the actual reaction have been demonstrated by Alcaide et al (66) in the synthesis of a range of fused tricyclic β-lactam and azetidine systems. The β-lactam ring is an important but unstable ring system present in many active antibiotics and related compounds. Small variations in the PKR precursors significantly altered the reaction conditions needed; however stereoselectivity was high in all cases (Scheme 33).

Scheme 33
Many other PKR mediated asymmetric synthesis based upon the stereospecificity of the PKR continue to appear. However, most, if not all are stoichiometric in cobalt, with several mentioning the failure of attempts to perform the reaction catalytically. In order to develop further the reaction needed to be able to introduce stereoselectivity into the intermolecular version, and catalytic asymmetric variations need to be developed.

1.5.2 Use of Chiral auxiliaries attached to alkyne

As seen above, the highly ordered transition state for the PKR can lead to highly stereoselective reactions. The success of the intramolecular reaction in synthetic papers led to an interest in the use of removable chiral auxiliaries attached to the complexed alkyne.

An initial attempt by Pericas and Greene (68) arose from an initial report on the simple synthesis of chiral acetylenic ethers (69) (Scheme 34).

![Scheme 34]

The above one-pot procedure was found to be general. Several chiral acetylenic ethers were subject to the PKR with norbornene and cyclopentene. In general diastereomeric ratios were unspectacular to non-existent, however substituted trans-cyclohexanol derivatives gave reasonable product yields with d.r's of up to >10:1 (Scheme 35).
Although the 9-phenanthryl analogue gave the best d.r., it was found that the trans-2-phenylcyclohexanol diastereoisomers were easily separable and therefore, the suggested best auxiliary. The auxiliary could then be cleaved with samarium iodide in order to leave the chiral cyclopentenone for further elaboration.

In an interesting and unusual approach, Carreto \(^{(70)}\) was able to achieve extremely high diastereo- and enantioselectivity in the intramolecular PKR via the use of vinyl sulfoxides. Although the reaction was limited to terminal alkynes, and the reaction conditions to NMO in acetonitrile, high diastereoselectivities (86->96 %) were achieved for a range of substrates using 2-N,N-(dimethylamino)-phenyl vinyl sulfoxide. In order to illustrate the scope of this reaction the (R)- enantiomer of (68) was prepared in two steps from the sulfinyl derivative of norephedrine,\(^{(71)}\) then used in a 4-step synthesis of the antibiotic (−)-pentenomycin (69)(Scheme 36).
Following Krafft's earlier report of internal chelation via alkynyl sulfides,\(^\text{(11)}\) Pericás and Moyano\(^\text{(72)}\) developed and investigated a series of internally chelating chiral auxiliaries. An initial investigation\(^\text{(72a)}\) into the synthesis of angular triquinane systems using a range of enyne substrates generated from chiral alcohols (70-73) showed only the camphor derived auxiliary 10-methylthioisoborneol gave reasonable diastereoselectivity (Scheme 37 and Table 4).
<table>
<thead>
<tr>
<th>Enyne</th>
<th>Conditions</th>
<th>Time (h)</th>
<th>Prod</th>
<th>Yield (%)</th>
<th>d.r.</th>
</tr>
</thead>
<tbody>
<tr>
<td>74a</td>
<td>Isooctane, 80 °C</td>
<td>12</td>
<td>76a</td>
<td>43</td>
<td>1.6:1</td>
</tr>
<tr>
<td>74b</td>
<td>Isooctane, 80 °C</td>
<td>12</td>
<td>76b</td>
<td>46</td>
<td>2.6:1</td>
</tr>
<tr>
<td>74c</td>
<td>Isooctane, 80 °C</td>
<td>12</td>
<td>76c</td>
<td>52</td>
<td>3.3:1</td>
</tr>
<tr>
<td>74d</td>
<td>Isooctane, 80 °C</td>
<td>3</td>
<td>76d</td>
<td>32</td>
<td>9.5:1</td>
</tr>
<tr>
<td>74d</td>
<td>NMO, DCM, rt.</td>
<td>20</td>
<td>76d</td>
<td>20</td>
<td>8:1</td>
</tr>
<tr>
<td>75a</td>
<td>Isooctane, 100 °C</td>
<td>7</td>
<td>77a</td>
<td>42</td>
<td>1.4:1</td>
</tr>
<tr>
<td>75b</td>
<td>Isooctane, 100 °C</td>
<td>8</td>
<td>77b</td>
<td>32</td>
<td>1.5:1</td>
</tr>
<tr>
<td>75c</td>
<td>Isooctane, 100 °C</td>
<td>8</td>
<td>77c</td>
<td>29</td>
<td>2.8:1</td>
</tr>
<tr>
<td>75d</td>
<td>Isooctane, 80 °C</td>
<td>10</td>
<td>77d</td>
<td>34</td>
<td>12:1</td>
</tr>
</tbody>
</table>

**Table 4**

Although yields were moderate, several important points were noted. Firstly, during the reaction with the 10-methylthioisoborneol derived enyne another intermediate spot was seen during the reaction, secondly product (74d) was only one isolated under oxidative conditions. All other attempts at oxidative PKR led to destruction of the starting material and complex reaction mixtures. Finally, when the same auxiliary was used for the synthesis of diquinones, low diastereoselectivity was observed, and the presence of the previously noted intermediate was not seen. It was concluded from these results that the intermediate was a chelated species dependent upon the relative rates of formation of the sulfide vs alkene complexation. In the case of the less hindered enynes used for the diquinane synthesis, the intermediate sulfur chelated complex did not form. This was the first example of an internally chelating chiral auxiliary. The group then developed this work through the use of the more stable thio-alkynyl ethers, with their best results eventually being found via the use of N-(2-Alkynol) sultams, especially 10,2-camphorsultam (78a-c), with d.r's of 318 to > 800:1 found in the reaction with norbornadiene for several alkynes (Scheme 38).
Krafft \(^{(73)}\) following an initial report by de Meijere \(^{(72)}\) approached the area via the synthesis of a C\(_2\)-symmetric chiral acetal, derived from (+)-dimethyl-L-tartrate \((90)\). The optimised reaction gave d.r.'s of 15-20:1 and a 68 % yield (Scheme 39).

It was noted during these studies that, i) the bulky R group attached to the alkyne was necessary for high stereoselectivity, ii) the best results were achieved when the NMO was added as a solution, with concentration also a factor affecting stereoselectivity, and iii) that the methylenecyclopropane terminator was essential in the reaction. Enynes without this group failed to give any discernible product, even under more harsh reaction conditions. The use of chiral auxiliaries attached to the alkyne is becoming a useful method for the synthesis of chiral cyclopentenones. However, in many cases the diastereoisomeric products still have to be separated after the PKR. Another successful approach is the use of desymmetrised bimetallic cores.
1.5.3 Stereoselective synthesis utilising chiral bimetallic cores

The dicobalt hexacarbonyl-alkyne core usually used to perform the PKR is achiral, however the metal-alkyne complex forms an exploded tetrahedron, hence, when one of the carbon monoxide ligands, or cobalt vertices is replaced with another ligand, or metal, the complex is rendered chiral (Figure 7).

In general this methodology has several advantages and disadvantages over the previously discussed routes. On the plus side, the reaction can be performed with complete stereocontrol under the correct conditions. Mechanistic studies can give insight into the mechanism of the PKR, leading to possible developments towards asymmetric catalytic versions of the reaction. On the down side, diastereoselectivities of the various desymmetrisation reactions are generally low, leading to the often difficult separation of diastereoisomers prior to the PKR. Also under some conditions, intermolecular epimerisation of the complexes is observed at elevated temperatures, rendering the thermal PKR unusable. Finally, the electronic properties of the ligand and/or metallic vertex effects the reactivity of the system, often lowering the reactivity.

Pauson et al\(^{75,76}\) was the first to attempt this methodology. He reported the use of glyphos (82) a chiral phosphine ligand. Kerr\(^{76b}\) developed this work via the use of NMO conditions. (Scheme 40). He found that the diastereomeric complexes (85-87a and 85-87b) formed when the phosphine ligand was stirred with the parent hexacarbonyl dicobalt
complexes at 60-70 °C could be separated into the single diastereoisomers by preparative HPLC. Although results for the thermal PKR using norbornene as the alkene were poor with a best e.e. of only 14%. However, when amine-N-oxides were used at lower temperatures good e.e.’s were achieved in all cases (69-90 % e.e.), along with yields in excess of 75 %.

Along a similar theme, Chung et al.\(^{(77)}\) realised that he could apply his recently developed NMO mediated reaction conditions to the asymmetric PKR via another route. The l-Menthol derivatives of dicobalt hexacarbonyl-propargyl alcohol (84) were reacted with trimethylphosphite or triphenylphosphine. These gave separable diastereoisomers that reacted with 100 % enantioselectivity under NMO mediated conditions (Scheme 41).
It may be noted that the reaction occurred in 80-98 % yield in the mixed THF / DCM system but DCM alone gave a poor 40 % yield, a result supporting Krafft's earlier report on hard Lewis basic solvents.

Christie and Rutherford (78) took this methodology a step further utilising heterobimetallic cobalt-molybdenum complex (92), once again the Menthol-derived diastereisomers were separable by chromatography. The reactivity of these complexes varies from that of the phosphine and phosphite analogues in that once separated the diastereoisomers are configurationally stable, hence these are amenable to the thermal PKR with 100% diastereoselectivity observed (Scheme 42).
The mechanism of the reactions using the desymmeterised cores was investigated by Kerr, (79) who utilised commercially available chiral alkynols as core substrates. After complexation with octacarbonyl dicobalt, the complexes were reacted with triphenylphosphine leading to two diastereoisomeric complexes. Nicholas, (80) who was able to obtain X-ray crystal structures, had previously established the relative configuration of these complexes. After separation and identification the diastereoisomers were subject to PKR with norbornene under NMO mediated conditions (only diastereoisomer 93a illustrated). The reactions were found to be stereoselective, and it was possible to obtain a crystal structure of the cyclopentenone product. From this a mechanistic pathway based upon the previously described Magnus mechanism (Scheme 3) was deduced. The products were found to have been formed by decarbonylation of the unsubstituted cobalt vertex (Scheme 43).
The only product seen was cyclopentenone (94) arising from the illustrated pathway. It can be suggested that the strong σ-donation and poor π-acceptor characteristics of the triphenylphosphine ligand lead to an increase in the π-back bonding of the metal carbonyls (evidenced by a decrease in the IR bands of the CO stretching frequency of 30-50 cm⁻¹, along with decreased reactivity towards N-oxides). This increase is felt most strongly on the cobalt vertex directly bonded to triphenylphosphine, leading to the observed selectivity.

As stated earlier, replacement of one of the CO ligands by a more electron donating species alters the reactivity of the complexes, usually for the worse. Pericás and Riera investigated the idea of using bidentate ligands to moderate the reactivity. Previous studies using diphosphine ligands had led to reports of extremely poor reactivity (81) so they decided to utilise mixed heteroatomic ligands. The first ligands used successfully were
phosphino-oxazoline ligands (95 and 96). These formed diastereomeric complexes with high d.r.'s, (Scheme 44) however when subject to the PKR reaction under several conditions they gave only moderate e.e.'s (up to 51 %).

![Scheme 44]

Changing the R group to t-butyl resulted in non-chelated complexes formed with no diastereoselectivity. These underwent the NMO mediated PKR with 100 % enantioselectivity after separation. However as has been discussed, this can be performed with much simpler ligands.

A later report (83) changing the chelating group to sulfur via the synthesis of the PuPHOs ligand (protected as its borane) (101), (Scheme 45) provided the first bidentate ligands to give high ee’s in the thermal PKR (up to 99%). However the d.r. for the diastereoisomeric cobalt complexes was low (up to 4.5: 1 in the best case).
A final report by the group (at the time of writing)\cite{84} appeared to achieve respectable diastereoselectivity in the complexation and enantioselectivity in the PKR. The MeCamPHOS ligand (102) when reacted with several dicobalt hexacarbonyl complexes then isomerised by heating led to excellent diastereoselectivity (Table 5). The diastereoisomers were not separable, however when reacted in the NMO mediated PKR the stereochemical integrity was maintained (Scheme 46 and Table 5) with significant levels of enantioselectivity observed. X-ray crystallography showed that the ligands bridged the two cobalt atoms, this had been the rational behind the design of these ligands, as it was thought that this would increase diastereoselectivity and reaction rate. Interestingly, the closely related CamPHOS ligand, (from which the X-ray was obtained) while exhibiting much lower diastereoselectivity, gave the cyclopentenone of the opposite absolute configuration as its major product when reacted with norbornene.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>d.r</th>
<th>e.e. PKR (%)</th>
<th>Yield PKR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>103a,b</td>
<td>65</td>
<td>48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>104a,b</td>
<td>65</td>
<td>18</td>
<td>80</td>
<td>20 : 1</td>
<td>79</td>
<td>72</td>
</tr>
<tr>
<td>105a,b</td>
<td>80</td>
<td>19</td>
<td>64</td>
<td>12 : 1</td>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>106a,b</td>
<td>65</td>
<td>18</td>
<td>99</td>
<td>13 : 1</td>
<td>50</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 5

Green and co-workers, (85) approached the same area through the use of chiral phosphoramidate ligands. However they found that monophosphine Binol derived phosphoramidates were significantly better that the diphosphinoamidates they initially synthesised. E.e.’s of up to 56 % were observed for the intermolecular PKR with norbornene at 60 °C in DME.

In an elegant alternative to the above methods, Kerr (86) used brucine-N-oxide (107) (Figure 8) as a promoter of the asymmetric PKR. Using chiral propargylic alcohols as substrates in DME with norbornene as the alkene at -60° C, e.e.’s of up to 78 % were achieved. It is believed that the chiral N-oxide discriminates between the two-enantiotopic faces of the complex, leading to an enantioselective decarbonylation. It was thought that the chiral alcohols increased the selectivity via H-bonding to polar groups on the N-oxide. Isosteric groups in the same position led to decreased selectivity.

![Figure 8](image-url)
The elegance of the above chemistry was demonstrated in another communication, where it was found that phosphines and phosphites could be introduced into the complexes using the same methodology. When later subjected to the N-oxide promoted PKR, the opposite enantiomers to those previously seen were synthesised, with little loss of selectivity; hence either enantiomer of a complex could be successfully synthesised.

1.5.4 Cobalt mediated catalytic asymmetric PKR and other metals

The cobalt mediated catalytic asymmetric PKR is only just being realised. Other metals can catalyse this reaction. However the generality of the cobalt mediated reaction means that this is an area of high interest.

Hiroi and co-workers were the first to develop a catalytic asymmetric version of the reaction, although with limited applicability. Following the screening of a large number of commonly used asymmetric phosphine ligands, the group found that (S)-Binap was able to induce selectivity in the cyclisation of 1,6-enynes in certain cases (Scheme 47 and Table 6).

Scheme 47
As can be seen, both yields and stereoselectivities were very dependent upon the substrate. Occasionally one of the other ligands screened would give an improved result, however (S)-Binap was the most general. All of the other ligands that showed any selectivity also expressed axial chirality. One point of interest was that 0.2 equivalents of ligand were found to be optimum, any more and selectivity surprisingly dropped off.

Hiroi proposed a mechanistic rational for his results based upon the ligand bridging the alkyne onto both cobalt atoms. However in a more recent investigation Gibson (13) was able to isolate a pre-catalyst using this ligand. Surprisingly both phosphine atoms were bound to the same cobalt atom. Furthermore attempts to use a pre-prepared bridged diphosphine catalyst in a stoichiometric PKR failed. These results led to the hypothesis that the catalytic PKR in this case is templated around the unsubstituted cobalt atom only (See Scheme 6).

In the only other report of a catalytic cobalt based PKR, Buchwald and Sturla (88) were able to achieve e.e's of up to 75 % using chiral-biaryl phosphites, although once again extreme substrate specificity was observed.
Although the stoichiometric PKR has been performed using bimetallic-alkyne complexes of metals other than cobalt, e.g. tungsten and molybdenum, these are generally less reactive than the cobalt analogues and the regioselectivity seen in the cobalt mediated PKR is lost. Of more interest are the PKR-type reactions using a range of other metals as catalysts. These reactions couple an alkene, alkyne and CO to form a cyclopentenone, although mechanistically the reactions are different to the PKR. Reports of these reactions are rapidly increasing, and were recently reviewed by Gibson, Lewis and Mainolfi. Some of the more interesting will be discussed below. Rhodium is one of the most interesting of these alternatives. Morimoto and Shibata independently published the first reports of Rh mediated intramolecular PKR-type reaction, with the most interesting point being that aldehydes could be used as both the CO source and solvent (solvent free conditions). Morimoto found [RhCl(COD)]₂ to be the best catalyst, with aromatic aldehydes containing electron withdrawing groups as the best CO source (especially C₆F₅CHO). Shibata found the combination of Rh(dppp)₂Cl and cinnamaldehyde worked best. Yields were in the 75-95 % range for a variety of enynes, and both groups were able to induce high enantioselectivity via the addition of the TolBINAP ligand (up to 95 % e.e.). Labelling studies suggested direct CO transfer, and Shibata proposed the mechanism below based on these findings (Scheme 48).

![Scheme 48](image)
The dual catalytic cycle was proposed as an alternative catalytic cycle in which the complex (121) co-ordinates directly to the enyne would result in dissociation of the phosphine ligand, and hence no enantioselectivity would have been achieved with the chiral ligand. Negishi (94) successfully developed a Zr mediated PKR type reaction, however it was found that in this case only internal alkynes underwent the cyclisation. Takahashi (95) investigated this methodology further and was able to couple trisubstituted alkenes containing two electron withdrawing groups with internal alkynes using isocyanates as the CO source. Hence these Zr mediated reactions exhibit completely dichotomous behaviour to the traditional PKR. Other metals including titanocene complexes, (96) ruthenium complexes, (97) iridium, (98) molybdenum hexacarbonyl (99) and palladium (100) have all been found to participate in PKR-type cyclisations, often with enantioselectivity, however the cobalt mediated PKR remains the most general, and most frequently used variant.

1.6 The Nicholas reaction

1.6.1 Discovery and reactivity

Nicholas and Pettit (7) first reported the facile acid catalysed dehydration of hexacarbonyl dicobalt complexes of propargylic alcohols in 1972 (Scheme 49). They subsequently reported the isolation of the dark red stable cationic salts formed by addition of HBF4 or HF.SbF5 to the parent alkynols. (101) Schreiber (102) later introduced the Lewis acid mediated version of the reaction. Since this time the Nicholas reaction has developed into a useful synthetic tool, allowing substitution α to an alkyne with no competition from allenic side products.

\[
\begin{align*}
\text{H} & \quad \text{R}_1 \text{OH} \quad \text{R}_2 \\
\text{(OC)}_3 \text{Co} & \quad \text{Co}(\text{CO})_3 \\
\text{H} & \quad \text{R}_1 \quad \text{R}_2
\end{align*}
\]

\[
\text{Scheme 49}
\]
Although the isolated salts were reported soon after their discovery, it took until 1998 for a crystal structure of the cationic complexes to be elucidated. Melikyan\textsuperscript{(103)} obtained a crystal structure of (123). The crystallinity and stability of the complex was enhanced by the incorporation of two stabilising dicobalt hexacarbonyl moieties (Scheme 50).

The effect of the cation formation can be seen in the structures. In the parent alcohol (122), the central carbon is $sp^3$-hybridised with all of the covalent bonds essentially equal. Upon protonation to cation (123), the central carbon becomes $sp^2$ hybridised with all bond angles of almost 120°, however the metal complexed alkynes now become non-equivalent, with one adopting a twist of 7.7° from perpendicular. More importantly the central carbon now lies significantly closer to one of the metal atoms indicating the charge stabilisation via the metal d-orbitals. This correlates to the observed shift to 30-50 cm$^{-1}$ wavenumbers higher frequency for the CO ligands seen in going from the parent alkynol to the cationic salt. Mayr \textit{et al} \textsuperscript{(104)} undertook a quantitative study of the electrophilicity of these ions and concluded that they were of a similar reactivity to the xanthylum and ferrocenylmethylium ions (Figure 9).
Mayr also found that, although the substitution pattern on the alkyne caused little variation in the nucleophilicity (less than a factor of 10), substitution of one CO ligand by PPh$_3$ lowered the reactivity by $10^5$. This result is supported by the fact, that while the parent Nicholas ions react with a host of carbon nucleophiles (see later sections). Attempts to react the PPh$_3$ substituted complexes with a host of soft and harder carbon nucleophiles failed, with either hydrolysis products or degradation seen after work up.$^{(105)}$ (Although Mayr did report the successful addition of a silyl enol ether to this complex).$^{(104)}$

1.6.2 Reactions with aromatic nucleophiles

Nicholas$^{(106)}$ was the first to report the reaction of the cobalt-alkyne cations with aromatic nucleophiles. Addition of BF$_3$.OEt to a solution of the parent propargylic alcohol and anisole at 0°C led to the formation of the substituted aromatics as a mixture of regioisomers in good yield, with the least hindered para-anisole isomer predominant.

Grove et al$^{(107)}$ used the dicobalt hexacarbonyl moiety as a stereocontrolling element in the synthesis of synthetically useful tricyclic fused ring systems (Scheme 51).
The above synthesis is stereoconvergent, with the cis-isomer almost the exclusive product. Grove postulated that in the conformer leading to the trans-isomer there is a steric interaction between 3 hydrogen’s of the ring being formed, and the dicobalt hexacarbonyl moiety, whereas in the conformer for the less stable cis-isomer, there is only one hydrogen giving a steric interaction, hence this is the predominant product. Roth (108) found that indoles were also excellent nucleophiles for these substrates. As expected reaction occurs at the 3-position of the indole core, and in the case of N-protected indoles, the incipient cation can be quenched with a suitable nucleophile (Scheme 52).
Roth found that the best way to perform this reaction was to add the indole to a slurry of the pre-formed cation at -20 °C. Nakagawa and Hino\(^{109}\) suffered both from substitution on the aromatic ring and N-propargylation when they attempted to activate the complexes \textit{in-situ} using BF\(_3\).OEt\(_2\).

In an early report on the use of hexacarbonyl dicobalt complexes (1975), Seyferth\(^{110}\) was able to \textit{mono-} and \textit{bis-}acylate complexed diarylacetylenes using standard Lewis acid conditions (acid chloride and AlCl\(_3\)). At the time the complex was used as a protecting group as these substrates cannot be directly acylated normally, however the substrates were active and this could be postulated to the incipient propargylic cation formed during the acylation. \textit{Para-}substituted products were formed exclusively in good yield and the products could be decomplexed smoothly.

1.6.3 Reactions of complexed enynes

As mentioned earlier (Scheme 49) Nicholas\(^4\) first reported the facile hydration/dehydration of the complexed propargylic alcohols. The reactivity of these alkenes has been explored. Nagasawa \textit{et al}\(^{111}\) found that the complexed enynes were good donors for the carbonyl-ene reaction with a variety of aldehydes. This reaction can usually
only be performed with active aldehydes, however in this case a wide variety of aromatic and aliphatic aldehydes were active (Scheme 53 and Table 7).

\[
\begin{array}{c}
RCHO + \overset{\text{Me}_2\text{AlCl}_3, \text{Tol, } 0 \degree \text{C}}{\text{(OC)}_3\text{Co-Co(CO)}_3} \\
\text{H} \\
\text{H} \\
\text{(OC)}_3\text{Co-Co(CO)}_3 \\
\end{array}
\]

\text{Scheme 53}

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCHO</td>
<td>79</td>
</tr>
<tr>
<td>CCHO</td>
<td>73</td>
</tr>
<tr>
<td>CHO</td>
<td>57</td>
</tr>
<tr>
<td>CCHO</td>
<td>69</td>
</tr>
<tr>
<td>CCHO Cl</td>
<td>83</td>
</tr>
</tbody>
</table>

\text{Table 7}

The cobalt complexed enynes also successfully participate in Ad_{E} type reactions where a nucleophile can be added discretely to the intermediate formed after the addition of an electrophile (Scheme 54). Smit and Caple \textsuperscript{(112)} were the first to observe this reaction; however, Mayr was once again able to quantify the nucleophilicity of these complexes.\textsuperscript{(113)}}
Mayr reached some interesting conclusions; co-ordination to the metals increased the nucleophilicity of the enynes by $>10^6$, a reactivity similar to 1,3-butadiene. However in this case substitution of one of the CO ligands by PPh$_3$ had little effect on the activity of the eneyne. This indicates that the enhanced stabilisation of the cation is not involved in the transition state of the first step of the reaction. Hence the reactions follow second-order rate kinetics.

1.6.4 Reactions with alkenes and enolate nucleophiles

Krafft (114) first investigated the addition of the Nicholas cations to unactivated terminal alkenes. She found that in addition to a simple addition-elimination reaction leading to regioisomeric olefins appropriately placed oxygen moiety could act as a second nucleophile leading to a small range of cyclic ethers and lactones (Scheme 55).
Tyrell (115) further exploited this work in the one pot synthesis of substituted benzopyrans. In both of the above cases disubstituted alkenes reacted poorly or not at all, suggesting that the reactions are reversible with the lower stability of secondary cations and/or the lower nucleophilicity of disubstituted alkenes pushing the reaction back towards the starting material.

Allyl silanes are also active nucleophiles in the Nicholas reaction, once again Nicholas himself published the first report. (116) However Schreiber et al (117) developed then exploited this in tandem with the PKR in an elegant synthesis of (+)-epoxydictytmene (136) (Scheme 56).
The Nicholas step in the reaction is noteworthy for several reasons; firstly the reaction is chemoselective in that the least hindered oxygen of the acetal is removed. Secondly the reaction is stereoselective in that the C10 ether linkage (134) occupies the $\beta$-configuration exclusively in either case. Finally, this step obviously sets up the correct configuration in order to obtain the desired isomer from the PKR reaction.
Although, as mentioned earlier, desymmetrised cobalt-alkyne complexes are generally unreactive towards soft carbon nucleophiles, the parent hexacarbonyl dicobalt complexes are reactive in many cases. Nicholas found that \( \beta \)-dicarbonyl compounds were readily alkylated by the cationic complexes. Simply adding HBF\(_4\) to a solution of the complexed alkynol and \( \beta \)-dicarbonyl in DCM at -78 °C resulted in yields of up to 95 % of the desired compounds, with none of the problems of allenic, elimination or other by-products seen when propargyl halides were used under similar conditions. Silyl enol ethers have been shown to be good nucleophiles for the complexes with both intra- and intermolecular reactions reported. In-situ generation of the cation via Lewis acid catalysis of a variety of functionalities is successful. In many cases syn selectivity predominates with moderate to high levels of diastereoselectivity seen. Interestingly the stereoselectivity is controlled by the remote acetylenic substituent, with bulkier groups leading to higher levels of stereoselectivity, although the structure of the enol-ether also has a significant effect. (Scheme 57).

\[
\begin{align*}
R_1 = \text{Me}, & \quad R_2 = \text{H} & 18 : 1 & \text{syn} : \text{anti} \\
R_1 = \text{H}, & \quad R_2 = \text{Me} & 9 : 1 & \text{syn} : \text{anti}
\end{align*}
\]

Scheme 57
Schreiber (102) proposed a transition state invoking a *synclinal* alignment of the two $\pi$-systems as a rationale for this result. This explains the influence of the terminal substituent R, as this transition state minimises van der Waals strain between the methyl group of the enol ether and the R group (Figure 10).

![Figure 10](image)

Carbon centred nucleophiles have been used in combination with the Nicholas reaction and have received a significant amount of attention in natural product and related syntheses. Perhaps the most comprehensive and interesting use has been by the Magnus group in their development of routes to enediyne natural products. This group of pharmacologically active compounds were first reported in 1987 when structure of *calicheamicin* $\gamma_1^{(122)}$ was revealed. This compound contained the previously unprecedented Z-enediyne moiety. This fragment is the active part of the compound, however it is unstable and synthetically challenging. Since that time several other compounds of this family have been isolated with many being some of the most potent antitumor antibiotics known.

Magnus *et al* (123) synthesised several of these compounds using the dicobalt hexacarbonyl fragment both as an alkyne protecting group and synthetic tool in setting up the enediyne fragment. The group were able to devise a general strategy to this moiety in this way illustrated by their synthesis of the bicyclo[7.3.1]tridecadienediyne ring core during their synthesis of protected calicheamicinone (124)(Scheme 58).
Conjugate addition to complex (143) using PhSAIMe₂ forms 2 diastereomeric β-sulfides, one of which cyclises following transmetallation with Ti(O'Pr)_4 to form compound (146). Oxidation of the sulfide, followed by decomplexation with CAN leads to the free enediyne (147).

1.6.6 Heteroatom Nucleophiles

Nicholas chemistry is amenable to many hard and soft heteratomic nucleophiles. Fluoride\(^{125}\) and sulfur \(^{126}\) are both active although little used. Suprisingly nitrogen nucleophiles have also only been lightly investigated; azide is active \(^{127}\) as are primary and secondary amines. Roth and Muller \(^{128}\) found that secondary amines only added to the
complexes once, whereas primary amines formed dimeric cobalt-alkyne complexes in good yield. Yeh et al.\textsuperscript{(129)} utilised this in a short synthesis of substituted pyrrole derivatives in moderate yield, although side products were a problem (Scheme 59).

![Scheme 59](image)

Oxygen nucleophiles have received a lot of attention in the literature; these will be briefly reviewed here as the area is discussed in more detail in sec (2.6).

The majority of the work in the area is focused on the synthesis of cyclic ether systems. Martin et al.\textsuperscript{(130)} found that medium sized cyclic ethers (6-9 membered rings) could be formed in good yield from the corresponding alkynols (Scheme 60).

![Scheme 60](image)

Where defined stereogenic centres were present in the linear precursor, the reaction was found to be stereoselective allowing the synthesis of enantiomerically enhanced cyclic ethers. Along a similar theme Hanaoka et al.\textsuperscript{(131)} was able to selectively form cis or trans tetrahydropyrans via a 6-endo cyclisation of cis or trans-4,5-epoxy-6-heptyn-1-ols. (Scheme 61).
The retention of stereochemistry and the fact that the cyclisation is exclusively 6-endo rather than 5-exo suggests the intermediacy of a stabilised propargylic cation. Subjecting a pre-formed tetrahydrofuran derivative to the reaction conditions led to no rearrangement to the tetrahydropyran, suggesting that this is in fact the kinetic product of the reaction. Hanaoka finding that the above methodology only worked for rings of up to seven members extended this methodology to form the more difficult oxocane and oxononane ring systems (Scheme 62).
Interestingly this reaction failed in the presence of Lewis acids giving intractable mixtures, hence the activation of the alcohol under basic conditions. In the same way that Magnus developed the Nicholas reaction in the synthesis of the enedyines, Isobe et al has applied the Nicholas reaction to the synthesis of gambiertoxin (133) and ciguatoxin (153), one of the large polycyclic ether marine toxins, in this case the cause of ciguatera poisoning (Figure 11).

![Figure 11](image1)

In the case of ciguatoxin the cobalt chemistry used by Isobe was a vital part of the synthesis of the B-C-D-E (134) and H-I-J (135) ring fragments. In the synthesis of the B-C-D-E fragment illustrated, both the D (155) and E (157) rings were formed as single isomers via the intramolecular trapping of a Nicholas carbocation with an alcohol nucleophile (Scheme 63).
1.6.7 Miscellaneous Reactions
There have been several reactions published using dicobalt hexacarbonyl complexes that do not fit fully into the earlier sections, nevertheless they are useful and of synthetic significance. There have been several reports on the radical chemistry of complexed enynes. Both Melikyan\(^{136}\) and McGlinchey\(^{137}\) have reported the radical coupling of preformed cationic salts, either by using zinc, or more interestingly by simply stirring the complexes, i.e. spontaneous generation of the radical. Of more synthetic interest are the reports by Salazar and Nicholas\(^{138}\) on the radical cyclisations of these species (Scheme 64).

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Scheme 63

---
While attempting to use the propargyl bromide complex (159) as an intermediate, the authors found that it spontaneously cyclised in the presence of light at rt. to give the bromine transfer product (160), presumably through a radical 5-exo-trig cyclisation. This reaction was found to be quite general for a variety of similar substrates. Harrity et al,\textsuperscript{(139)} published a novel synthesis of α-functionalised β-alkynyl cyclohexanones prepared via a cobalt mediated rearrangement (Scheme 65).
The rearrangement under the above conditions was found to be stereoselective, with the E alkene giving the cis product (163) and the Z alkene the trans (164). However, changing the remote functionality (terminal alkyne group) to phenyl resulted in the failure of the reaction in several cases, altering the Lewis acid to Bu₂BOTf enabled substrates to react, but unfortunately, both E and Z alkenes gave the trans product.

Finally, Jamison et al (140) reported a three component coupling for the highly diastereoselective synthesis of tetrahydrofurans (Scheme 66). The reaction and stereoselectivity were found to be general for a range of dipolarophiles.
In conclusion, the field of cobalt alkyne complexes in organic synthetic chemistry is still developing and growing. The multiple carbon-carbon bond forming power of the PKR, along with its stereoselective mechanism makes it an attractive reaction to academic chemists, its power has been demonstrated in a growing number of natural product synthesis. However, until good catalytic asymmetric systems for the reaction have been developed it will remain an academic reaction. Nicholas methodology is also still in development and offers another powerful tool for the academic synthetic chemist.
2.0 Results and Discussion

2.1 Chiral heterobimetallic alkyne systems

2.1.1 Background

The application of homobimetallic alkyne systems in the Nicholas reaction has been extensively explored and reported in the literature.(7,11-140) Although in some cases diastereoselectivity has been reported (116, 117) there has been relatively little research into the use of desymmetrised systems as chiral auxiliaries,(142) although these systems have been successfully used in several asymmetric variations of the Pauson-Khand reaction.(75-84) Furthermore, no research has been published into the possible stabilisation of a negative charge to the complexed alkyne although this is known with $\eta^6$Cr(CO)$_3$-arene complexes. (143)

Following on from the successful utilisation of desymmetrised bimetallic and heterobimetallic cores as electrophilic chiral auxiliaries within the group,(142) an investigation into their possible use as nucleophilic chiral auxiliaries seemed appropriate. In addition, the group had not previously been successful in forming carbon-carbon bonds using the heterobimetallic cobalt-molybdenum Nicholas salts, although they were responsive to heteroatom nucleophiles. It was thought we may be able to overcome this by forming the propargylic anion, hence this was the initial area of research.

2.1.2 Rationale for stereocontrol induced by the heterobimetallic core

The metal alkyne complex initially investigated was a heterobimetallic cobalt-molybdenum species. These complexes are inherently chiral when an unsymmetricaly-substituted alkyne is used and don’t suffer from possible intramolecular epimerisation as seen with complexes desymmetrised with ligands, which replace a carbon monoxide.(73) X-ray crystallography data reveals an “exploded tetrahedron” configuration about the metal-alkyne core, with the metal-metal bond lying perpendicular to the alkyne carbon-carbon bond (Figure 12).(144)
As can be seen from the above scheme, the alkyne is no longer linear, with the R groups having a bond angle of around 142° giving a bond order of almost 2.5. The cyclopentadiene ring on the molybdenum vertex effectively blocks off one face of the complex, leading to diastereoisomeric transition states under reaction conditions. In addition the two metal vertices are electronically different, and X-ray analysis of the Nicholas salts of these structures (144) suggests that the cation is stabilised via the more electron rich molybdenum vertex (168) (Figure 13).
2.1.3 Synthesis of heterobimetallic core

Although molybdenum cyclopentadienyl tricarbonyl dimer is commercially available, its price means it is generally made within the group. The previous route to this compound used the method described by Manning et al.\(^{(145)}\) (Scheme 67).

Freshly distilled cyclopentadiene (170) was deprotonated with NaH in THF at 0 °C. This was then added to a solution of molybdenum hexacarbonyl in diglyme and heated to reflux for 3 h in order to form the cyclopentadienyl molybdenum tricarbonyl anion. After cooling the reaction mixture was treated with a filtered solution of acetic acid, iron sulphate and water. After cooling the air stable purple crystalline product (171) precipitated out of solution.

While this method gave reasonable yields (50-70 %) of the desired product they were variable, and, in addition the distillation of the high boiling diglyme makes the process somewhat time consuming. Hence another preparation by Curtis and Hay\(^{(146)}\) was investigated (Scheme 68).
Molybdenum hexacarbonyl was refluxed in MeCN for 4 h in order to form the molybdenum tricarbonyl-triacetonitrile complex (172). The excess acetonitrile was then removed under vacuum, followed by the addition of excess freshly distilled cyclopentadiene (170). This was refluxed for a further 2 h, then left to cool, during which the product precipitated out of solution.

Unfortunately, despite several attempts, yields using this method were very poor; however it could be seen from the presence of a yellow solid in the reaction flask that the triacetonitrile intermediate was being formed. As a last attempt to improve the synthesis it was decided to combine the methods by adding the pre-formed cyclopentadienyl anion rather than cyclopentadiene itself the triacetonitrile complex (172) (Scheme 69).
In practice this method worked well, with comparable or better yields than the traditionally used method, in addition dry MeCN and THF were always readily available, making the synthesis comparably simple.

The method used to form the heterobimetallic core (47) (Scheme 70) has been developed within the group, and is based upon initial research by Gladysz et al (148) who reported the reductive cleavage of metal carbonyl dimers using trialkylborohydrides in the late 1970's.

K, or L-Selectride® (lithium, or potassium tri-sec-butyl borohydride), was added to a solution of the molybdenum cyclopentadienyl tricarbonyl dimer (171) in THF at room temperature. An immediate loss of hydrogen was seen and the purple solution turned an orange/green colour as the molybdenum anion was formed. After 20-30 min, the dicobalt hexacarbonyl- alkyne complex was added then the solution was brought to reflux for 1-2 h depending upon the selectride used and the alkyne. (K- Selectride® is generally quicker than L-Selectride, and alkynes that contain electron withdrawing groups take longer to react). After purification by column chromatography the cobalt-molybdenum-alkyne complexes were usually isolated as bright orange oils in moderate to good yield (50-85 %).

\[
\text{Mo}_2\text{Cp}_2(\text{CO})_6 \xrightarrow{\text{K or L-Selectride \[ THF, rt}} \text{MoCp(CO)}_3 \\ \Theta \\
\text{M} \\
\xrightarrow{\text{THF, heat}} \text{OC}_3\text{Co} \text{Co(OC)}_3 \text{MoCp(CO)}_2 \\
\text{R}_1 \\
\text{R}_2 \\
50-85 \%
\]

Scheme 70

This methodology was already well established within the group. However, although in most cases this reaction is a more convenient method for the synthesis of the heterobimetallic core, it gives poor yields with alkynols. In this situation protection of the alkynol as its methoxy or ethoxy ether was found to give a better overall yield over the two steps, than displacement of the parent alkynol, while still being significantly more convenient than using older methodology for the displacement reaction (Scheme 71 and Table 8).
The ether protection can be performed in one pot. Addition of dicobalt octacarbonyl to the alkynol in DCM, followed by stirring for 4 h leads to the dicobalt hexacarbonyl alkynol. Either a Lewis acid (BF₃·OEt₂) and alcohol, or protic acid (HBF₄) followed by the alcohol was then added to the reaction mixture, along with 4Å molecular sieves. This was then left to stir at rt for 4 – 12 h (Scheme 72). In either case, the mass balance of the reaction was residual starting material, along with some expected loss due to degradation of the complex. Following the above results all alkynols displaced during this work were protected as their ethoxy ethers (undistilled absolute ethanol was pure enough).
2.2 Phenylsulfone as a nucleophilic chiral auxiliary

2.2.1 Synthesis of the sulfone

While it was hoped that the bimetallic complex would show some amphiphilic behaviour comparable to the $\eta^6$ Cr(CO)$_3$-arene complexes. It was thought that a strong electron-withdrawing group attached to the $\alpha$-carbon would facilitate this reaction. After some consideration we decided upon the phenylsulfone group. This is known for its versatility as an intermediate in organic synthesis, and with the pKa values for the $\alpha$ hydrogen's ranging from 24-29, enables the use of the majority of the generally used bases. In addition this complex is easy to synthesise using the readily available benzene sulfonic acid sodium salt, while synthetic routes to place a carbonyl group at this position are difficult to propose.

The sulfone was synthesised by a simple 3-step route (Scheme 73)
Isolobal displacement of dicobalt hexacarbonyl-propynol (173), or its ethoxy derivative, formed the cobalt-molybdenum core. This complex was then dissolved in diethyl ether and HBF$_4$ added slowly. The orange air stable salt (177) precipitated out of solution. This salt was then dissolved in acetonitrile along with a slight excess of benzene sulfinic acid sodium salt. After 10 min the product (178) was isolated as a bright orange oily solid in a 75-90% yield after chromatographic purification.

With the complex in hand the electrophilic substitution reaction was attempted (Scheme 74).

2.2.2 Attempts at electrophilic substitution using the phenylsulfone

![Scheme 74](image)
Initially a range of secondary amine and hydride bases were tried (Table 9).

<table>
<thead>
<tr>
<th>Base (equiv.)</th>
<th>Electrophile (equiv.)</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHDMS (1.4)</td>
<td>MeI (5.0)</td>
<td>THF</td>
<td>-78</td>
<td>S/M</td>
</tr>
<tr>
<td>LHDMS (1.4)</td>
<td>MeI (5.0)</td>
<td>THF</td>
<td>-78</td>
<td>S/M</td>
</tr>
<tr>
<td>LDA (1.4)</td>
<td>MeI (5.0)</td>
<td>THF</td>
<td>-78 (1 h), then -78 to rt (1 h)</td>
<td>S/M</td>
</tr>
<tr>
<td>LHMDS / DMPU  (1.4)</td>
<td>MeI (5.0)</td>
<td>THF</td>
<td>-78 (40 min) then -78 to rt (1 h)</td>
<td>S/M</td>
</tr>
<tr>
<td>NaH (1.5)</td>
<td>MeI (5.0)</td>
<td>THF</td>
<td>-78</td>
<td>S/M</td>
</tr>
<tr>
<td>NaH (1.5)</td>
<td>Allyl bromide (5.0)</td>
<td>THF</td>
<td>-78 (10 min) then -78 to rt (1 h)</td>
<td>decomposed</td>
</tr>
</tbody>
</table>

Table 9

Only starting material in various amounts were ever recovered from these reactions. No spots of possible product were ever seen despite careful TLC analysis and column purification. The actual yields of recovered starting material are not given as these complexes suffer from some decomposition during work up and purification and are therefore not accurate, however they generally ranged from 50-70 % recovery.

Previous work within the group (1142a) had shown that these complexes were stable towards n-butyllithium at low temperature (alkyllithiums were added to complexed aldehydes in excess and good yields of the secondary alcohols were isolated), hence we decided to try a range of alkyllithium bases. It was thought that these would be less sterically hindered than the secondary amine bases, and would be stronger than both the amine and hydride bases. These were used under the following conditions (Table 10).
<table>
<thead>
<tr>
<th>Base (equiv.)</th>
<th>Electrophile (equiv.)</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-BuLi (1.4)</td>
<td>MeI (5.0)</td>
<td>THF</td>
<td>-78</td>
<td>S/M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-78 (1 h) then</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-78 to rt (1h)</td>
<td></td>
</tr>
<tr>
<td>n-BuLi (1.2)</td>
<td>MeI (5.0)</td>
<td>THF</td>
<td>-78 (30 min) then</td>
<td>S/M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-78 to rt (1 h)</td>
<td></td>
</tr>
<tr>
<td>t-BuLi (1.2)</td>
<td>MeI (5.0)</td>
<td>THF</td>
<td>-78 (30 min) then</td>
<td>S/M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-78 to rt (1 h)</td>
<td></td>
</tr>
<tr>
<td>n-BuLi /</td>
<td>BnBr (5.0)</td>
<td>THF</td>
<td>-78 (30 min) then</td>
<td>S/M</td>
</tr>
<tr>
<td>TMEDA (1.5)</td>
<td></td>
<td></td>
<td>-78 to rt (1 h)</td>
<td></td>
</tr>
<tr>
<td>n-BuLi /</td>
<td>MeI (5.0)</td>
<td>Diethyl ether</td>
<td>-78 (30 min) then</td>
<td>S/M</td>
</tr>
<tr>
<td>TMEDA (1.5)</td>
<td></td>
<td></td>
<td>-78 to rt (1 h)</td>
<td></td>
</tr>
<tr>
<td>t-BuLi /</td>
<td>MeI (5.0)</td>
<td>Diethyl ether</td>
<td>-78 (30 min) then</td>
<td>S/M</td>
</tr>
<tr>
<td>TMEDA (1.5)</td>
<td></td>
<td></td>
<td>-78 to rt (1 h)</td>
<td></td>
</tr>
<tr>
<td>n-BuLi /</td>
<td>D₂O (5.0)</td>
<td>Diethyl ether</td>
<td>-78 (30 min) then</td>
<td>S/M</td>
</tr>
<tr>
<td>TMEDA (1.5)</td>
<td></td>
<td></td>
<td>-78 to rt (1 h)</td>
<td></td>
</tr>
<tr>
<td>*sec-BuLi (2)</td>
<td>Allyl bromide (5.0)</td>
<td>THF</td>
<td>-78 (30 min) then</td>
<td>decompos</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-78 to rt (1 h)</td>
<td>cd</td>
</tr>
</tbody>
</table>

* Performed on phenylsulfide complex (182)

Table 10

As can be seen from the above tables this reaction was completely unsuccessful. In addition to none of the expected product, no ortho-alkylation of the phenyl ring was seen, as might have been expected with some of the conditions used. A darkening of the solution was sometimes seen upon addition of the base (possibly suggesting a delocalised species). However, had any significant deprotonation occurred one would expect to have formed some product unless the anionic species decomposed immediately.

Every effort was taken to ensure that all reactions were as anhydrous as possible, and the electrophiles chosen were picked because of their small size and reactivity, therefore it
could be concluded that this reaction was fundamentally unfeasible. Two possible reasons are immediately apparent. 1) The phenylsulfone is simply too bulky in this situation, the lack of ortho-alkylation possibly supports this argument. However, one would have expected some small amount of product to be seen, especially with the smaller bases (i.e. hydride, n-BuLi) and methyl iodide. 2) The formation of an anion at this site is simply unfeasible for electronic reasons with deprotonation leading to immediate decomposition of the anionic species. The slight darkening of the reaction mixture seen in some situations may have been some of the complex being deprotonated then decomposing. Unfortunately the slight instability of these complexes during work up and on silica means that no real conclusions can be drawn from recovered mass balances.

Following on from the failure of the sulfone route we had to assess whether to try alternative electron withdrawing groups, or whether to try and form a formal negative charge on the carbon via an indirect route.

With respect to electron withdrawing groups, the only obvious alternative was the nitro-group, with sodium nitrite (NaNO₂) as the nucleophile. This group was considered. However, these species are ambident nucleophiles, which would lead to problems, with two possible linkage isomers (179 and 180), probably seen as a mixture (Scheme 75).
Although the nitroso ligand should have a different IR spectrum to the nitro, evidence from previous studies on these salts suggests that this would be the predominant isomer, the salts are very oxaphillic\(^{(150)}\) and responsive to hard nucleophiles, although nitrogen nucleophiles do add in reasonable yields. However soft nucleophiles e.g. malonate do not add to the cobalt-molybdenum salts, although they are active with respect to the dicobalt hexacarbonyl analogues.\(^{(118)}\)\(^{\text{NO}_2}\) has been found to react with hard electrophiles at O and soft electrophiles at N.\(^{(151)}\) With this in mind it was decided it would be more profitable to go down the indirect route.

2.2.3 Grignard formation and reductive lithiation

Grignard reagents are some of the most versatile nucleophiles in organic synthesis. Although these can often be directly compared to organolithiums the carbon-magnesium bond has more covalency and they are formed via a radical insertion into a carbon-halogen bond rather than via the direct formation of an anionic charge on the carbon. Hence it was hoped that this would be an alternative less harsh method of forming the nucleophilic species.

\(\alpha\)-halo dicobalt hexacarbonyl complexes are known in the literature,\(^{(138, 152)}\) however they rapidly decompose, hence the displacement route via these complexes can be rapidly
discounted. We thought that the simplest way to try and synthesise these compounds would be from the corresponding salt (Scheme 76).

Dissolving the parent salt (177) in a saturated solution of sodium bromide in acetone did produce a new complex in 10-30% yield along with residual alcohol. The new complex was much less polar than the alcohol, and \(^1\)H NMR spectroscopy showed a complex with two \(\alpha\)-protons and little else. However these complexes appeared unstable and quickly decomposed and attempts at further analysis failed.

As the unstable product could possibly have been the desired complex (181), the Grignard reaction was attempted (for completion purposes). The salt was stirred in a saturated solution of NaBr, then quickly purified and the product fraction frozen under N\(_2\). This was then transferred to a flask containing magnesium turnings in dry THF, along with a catalytic amount of iodine. The reaction was left to stir for 1h before benzaldehyde was added however no product was isolated, and TLC analysis showed only decomposition.

One final route used in an attempt to synthesise the anion at the \(\alpha\)-carbon was a brief investigation into reductive lithiation (Scheme 77).
A 1M solution of lithium naphthalenide was made according to literature procedure by dissolving lithium metal in a solution of THF and naphthalene at ambient temperature. The formation of the \( \text{Li}^+ (\text{C}_{10}\text{H}_8)^- \) species. The formation of this single electron transfer intermediate was indicated by the solution turning a green/black colour. It was found in practice that this could take some time (4-12 h). This solution was then added to a cooled solution of the cobalt-molybdenum complex in THF. The reaction was attempted under the following conditions (Table 11).

<table>
<thead>
<tr>
<th>Reducing agent ( (\text{equiv.}) )</th>
<th>Electrophile ( (\text{equiv.}) )</th>
<th>Temp ( (^\circ \text{C}) )</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>*( \text{Li}^+ (\text{C}_{10}\text{H}_8)^- ) (3)</td>
<td>MeI (5.0)</td>
<td>-78 (0.5 h) then -78 to rt (3 h)</td>
<td>?</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-78 (2 h) then -78 to rt (12 h)</td>
<td>decomposition</td>
</tr>
<tr>
<td>Li(^{+})(C(_{10})H(_8))(^{-}) (6)</td>
<td>Ally bromide (5.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>**( \text{Li}^+ (\text{C}_{10}\text{H}_8)^- ) (6)</td>
<td>Allylbromide (5.0)</td>
<td>-78 (30 min) then -78 to rt (1 h)</td>
<td>S/M + decomposition</td>
</tr>
</tbody>
</table>

** Performed on phenylsulfone complex (178)
* In one case a small amount of possible reduction product was isolated. However the result could not be repeated.

Table 11

The reductive lithiation reaction was quickly abandoned for several reasons. 1) The complexes appeared to be attacked by the reducing agent. Although a small amount of reduction product was identified from the first attempt at the reaction, subsequent attempts to repeat this result failed completely. Only small amounts of starting material or degradation were seen by TLC depending upon how long the reaction was left. Allyl bromide was used as the quench after this first result due to the possibility of this product being the result of a radical reduction. 2) The formation of the lithium naphthalenide itself proved to be difficult and not always repeatable, the dark colour of the solution made monitoring whether all of the lithium had dissolved impossible.
An attempt to use catalytic naphthalene to form the 2Li.\(^+\)C\(_{10}\)H\(_8\)\(^2-\) complex (a purple complex with a higher reduction potential)\(^{(154)}\) also failed.

### 2.2.4 Functionalised acetylenes.

The formation of a negative charge at the alkynyl \(\alpha\)-carbon appeared to be increasingly improbable. With several routes tried and no hint of success we decided to try an alternative pathway, namely forming the negative charge on the acetylenic carbon itself.

There was some precedent for this reaction in the literature. Magnus \textit{et al}, \(^{(155)}\) was able to deprotonate dicobalt hexacarbonyl trimethylsilyl ethyne (183) with both LDA and LHMDS, although dimeric lithium species were implicated. Only dimeric and single electron transfer products were isolated in moderate or poor yields after work up with a proton source or radical trap. (Scheme 78).
Scheme 78

In addition Green et al (156) was able to add lithium acetylides to the dimolybdenum core (Mo2Cp2(CO)4) (187) and to deprotonate complexed terminal acetylene’s on the same system with t-BuLi. However these didn’t behave as complexed acetylide anions, and reactions with electrophiles such as trifluoromethane sulfonate instead formed vinylidene systems such as (188)(Figure 14).

Figure 14
There had already been a small attempt to repeat this work on the heterobimetallic cobalt-
molybdenum system within the group.\textsuperscript{(157)} However this had failed, with only baseline
decomposition seen. In addition it could be suggested that were this proton acidic enough to
remove then some related products (possibly dimers) should have seen during the initial
studies on the sulfone. A more circumspect route was therefore undertaken.

The initial route was proposed via lithium-halogen exchange (Scheme 79).

![Scheme 79](image)

The bromination of the phenylacetylene (189) proceeded well using a literature procedure,
\textsuperscript{(158)} with yields of 1-bromo-2-phenylacetylene (190) of 60-80 %. However, although an
initial product was formed during the complexation reaction, it rapidly decomposed after
purification. (\textsuperscript{1}H NMR analysis and IR seemed to show the formation of the complex, but
the compound decomposed too rapidly for further analysis). An attempt was made to
perform the halogen-lithium exchange without isolating the intermediate (191). The
reaction mixture containing (191) was evaporated under vacuum, then immediately re-
dissolved in dry THF. This solution was cooled to \(-78 \, ^\circ\text{C}\) under \(\text{N}_2\) then 1 equivalent of \(\text{n-}
butyllithium\) added. After 10 min 5 equivalents of methyl iodide were added. TLC analysis
after a further 10 min at \(-78 \, ^\circ\text{C}\) showed only baseline degradation.
It was also discovered that bromo-acetylenes are explosive, however a report by Ku et al.,\(^\text{159}\) suggested that 1-iodo acetylenes were significantly more stable than their chloro- or bromo- analogues, therefore we decided to investigate these compounds.

The cleanest synthesis of iodo-acetylenes was via a tri-\(n\)-butyltin intermediate (192) (Scheme 80).

\[
\text{Ph} 
\xrightarrow{\text{i) } n\text{-BuLi, THF, } 0\,^\circ\text{C}} 
\xrightarrow{\text{ii) } \text{Sn(Bu)}_3\text{Cl, } 0\,^\circ\text{C}} 
\text{Ph} \equiv \text{Sn(Bu)}_3 
\xrightarrow{\text{i) } I_2, \text{THF, } 0\,^\circ\text{C}} 
\xrightarrow{\text{ii) } \text{Co}_2\text{(CO)}_8, \text{THF, } 0\,^\circ\text{C}} 
\text{Ph} \equiv \text{Sn(Bu)}_3 \equiv \text{Co} \equiv \text{CO}_3
\]

**Scheme 80**

As the iodo-acetylenes were still apparently unstable, the complexation was attempted *in situ*. The formation of tributyl-phenylethynyl-stannane (192) using a literature method,\(^\text{160}\) proceeded cleanly in 66 % yield. The iodination was monitored visually by watching the yellow colour of the iodine disappear. The characteristic evolution of CO was seen after addition of the dicobalt octacarbonyl and a new product was seen by TLC. However, once again, although products were isolated they rapidly decomposed and hence couldn’t be identified.

As tributyl-phenylethynyl-stannane was stable and already formed, a new route was immediately apparent; tin-lithium metathesis. Hence this alkyne was complexed. This time the product (194) was successfully isolated in 80-90 % yield as a black solid. An attempt to displace this complex failed. However, a brief investigation the reactivity of the dicobalt species with respect to tin-lithium metathesis and Stille couplings was carried out (Scheme 81).
Neither reaction gave the desired product, leaving the reactions on for extended periods led only to several unidentifiable degradation products. As the above dicobalt hexacarbonyl complex has no inherent chirality, and hence no real synthetic utility apart from academic interest this work was not continued as both reactions can be performed on the uncomplexed alkynes, using \( n\)-Buli in the first case, and a Sonogoshira or Castro-Stevens coupling in the second.

The above chemistry represents a significant attempt at forming anionic complexes. Most of the generally used methods for forming these species were attempted. Although there may be possible routes to this system, one would have reasonably expected some success were this reaction feasible. After consideration it was decided to halt this work in favour of more profitable research.

### 2.3 Conjugate addition reactions

#### 2.3.1 Background. Asymmetric conjugate addition

Conjugate addition reactions (Michael, or 1,4-addition) are an important step in many organic syntheses. Asymmetric variations of this reaction are the focus of much interest.

Although much progress has been made in this area there remains many unanswered questions and room for improvement.
There are several different approaches to introducing asymmetry into this reaction (Scheme 82). (161-163)

Scheme 82

Currently, the area receiving the most interest is the use of chiral catalysts, with well over 300 different catalysts already known. (164) However these reactions virtually always involve the use of organocuprates, and hence carbon-carbon bond formation (although this is obviously the most important reaction). In addition substrate specificity is still observed with all of the available catalysts, meaning the screening of several (probably expensive)
catalysts may well be needed. However, chiral auxiliaries placed on either $R_1$, $R_2$ (shown above), or $R_3$ can be used to control the chirality of the reaction.

Although sometimes considered a little old fashioned, and with the obvious extra steps added to the synthesis, where feasible these do have advantages. 1) The chirality comes from the substrate itself allowing a greater range of nucleophiles. 2) Chiral auxiliaries are often cheaper than the chiral catalysts. 3) Where only one stereocentre is involved the initial products are diastereoisomers, allowing for easier separation (hopefully). 4) The auxiliary may be used to control more than one-step in the reaction (for example in our case, conjugate addition followed by PKR). With this in mind it was decided to investigate the possibility of using the heterobimetallic cobalt-molybdenum complexes as chiral auxiliaries for this reaction.

2.3.2 Conjugate additions to complex

Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-methyl-(E)-hex-2-en-4-ynoate (201) was synthesised in good yield in a 3-step route (Scheme 83).

![Scheme 83](image-url)
2-Butynal diethylacetal (198) was complexed with dicobalt octacarbonyl, then a spatula full of p-toluenesulfonic acid and a few drops of water were added to deprotect the aldehyde (199) in situ. The stable methoxycarbonyl methyl triphenylphosphonium bromide ylid was pre-formed as a white solid by deprotonation with sodium hydroxide in water, followed extraction into DCM then rotary evaporation. The two compounds were then stirred overnight in dry THF to form dicobalt hexacarbonyl-methyl-(E)-hex-2-en-4-ynoate (200) in excellent yield. This was then displaced to the cobalt molybdenum complex (201) under the standard conditions in reasonable yield. Both homo- and heterobimetallic alkyne complexes (200 and 201) were used for the conjugate addition reactions in order to monitor whether any differences in reactivity were caused by the different cores.

It is worth noting that the Wittig reaction only works on the dicobalt analogue. In order to obtain better yields attempts were made to displace the aldehyde then perform the Wittig reaction on the cobalt-molybdenum core. It was found that the cobalt-molybdenum complex is virtually unreactive in this reaction, only traces of product are seen after extended periods at ambient temperature (48 h), and heating the reaction destroyed the complex rather than form any product. This is another example of the inherent difference in reactivity of the different analogues first discussed in relation to the Nicholas reaction.

With the complex in hand, we started to investigate the chemistry. We hoped to utilise Nicholas chemistry using protic acid catalysis if non-catalysed systems failed (Scheme 84).
The conjugate additions were attempted under the following conditions (Table 12)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Nucleophile</th>
<th>Solvent / additive</th>
<th>Temp (time)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>dicobalt</td>
<td>NaHC(CO₂Et)₂</td>
<td>MeOH</td>
<td>-78 (1 h)</td>
<td>S/M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-78 to rt (1 h)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>reflux (48 h)</td>
<td></td>
</tr>
<tr>
<td>cobalt –</td>
<td>PhSLi(165)</td>
<td>DCM / Benzaldehyde</td>
<td>-78 to rt (16 h)</td>
<td>S/M</td>
</tr>
<tr>
<td>molybdenum</td>
<td></td>
<td>THF / TBAF</td>
<td>rt (48 h)</td>
<td>S/M</td>
</tr>
<tr>
<td>cobalt –</td>
<td>PhSH(166)</td>
<td>HBF₄ / MeCN</td>
<td>rt (3 h)</td>
<td>decomp</td>
</tr>
<tr>
<td>molybdenum</td>
<td></td>
<td>i) Hünigs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cobalt –</td>
<td>PhSH</td>
<td>HBF₄, Et₂O</td>
<td>rt (3 h)</td>
<td>S/M</td>
</tr>
<tr>
<td>molybdenum</td>
<td></td>
<td>i) Hünigs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cobalt –</td>
<td>MeOH</td>
<td>HBF₄ / Et₂O</td>
<td>rt (5 h)</td>
<td>S/M</td>
</tr>
<tr>
<td>molybdenum</td>
<td></td>
<td>ii) TEA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cobalt –</td>
<td>MeONa</td>
<td>MeOH</td>
<td>0 to rt (16 h)</td>
<td>S/M</td>
</tr>
<tr>
<td>molybdenum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cobalt –</td>
<td>EtOH</td>
<td>EtOH</td>
<td>0 to rt (16 h)</td>
<td>S/M</td>
</tr>
<tr>
<td>molybdenum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cobalt –</td>
<td>EtONa</td>
<td>EtOH</td>
<td>0 to rt (16 h)</td>
<td>Trans-</td>
</tr>
<tr>
<td>molybdenum</td>
<td></td>
<td></td>
<td></td>
<td>esterification</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48 %</td>
</tr>
</tbody>
</table>

Table 12

As can be seen from above a broad range of conditions were tried, including some more unusual additives and acid catalysis. When a good oxygen nucleophile is used it appears that trans-esterification occurs at the carbonyl (as could be expected). However, no trace of conjugate addition was ever seen. Carbon nucleophiles including organocuprates were not
used in these reactions, as forming carbon-carbon bonds on the cobalt-molybdenum complex had at this point failed. We therefore reasoned that heteroatomic-nucleophiles, which we knew were active in the Nicholas reaction, and were known to be active in conjugate addition reactions, would be better initial substrates. Although different Michael acceptors could have been tried (aldehyde, nitro or cyano groups), these were unlikely to make any difference, as under acid conditions the ester should be significantly in the enol form during the reaction, with a large amount of cationic character at the desired carbon. It seems that although the site of attack is only a disubstituted alkene, steric hindrance in these complexes overcomes any stereoelectronic effects that favour this addition. It is suggested that the site of attack is too hindered for attack by soft nucleophiles, and that hard nucleophiles preferentially attack the carbonyl group. It is well known that increasing steric bulk is one of the best ways of shutting down conjugate addition, it appears that in this case this overrides any stereoelectronic advantages derived from the metallation of the alkyne. A sample of complex (201) was demetallated using ammonium cerium nitrate [Ce(NH₄)₂(NO₃)₆] in acetone, then the IR and ¹H NMR spectra analysed in order to try and see whether complexation to the metals was having any stereoelectronic effect upon the alkene(Figure 15 and Table 13).
The results show no real discernible trend apart from that of the carbonyl stretching frequency, which seems to indicate greater electron donation from the cobalt-molybdenum core as would be expected. Hence no conclusions could be drawn.

As discussed earlier (sec 2.2.1) the cobalt-molybdenum complexes form isolable cationic salts, attempts were made to form the salt of (201) using the standard conditions of diethyl ether and HBF₄. Despite several different attempts varying the reaction temperature and concentrations of the reagents no isolable salt was ever formed, as indicated in table 12, attempts were also made to form the salt then react it in situ, once again these failed.
Further investigation indicated that no Nicholas salts had ever been formed on complexes with two Lewis acid binding sites.\(^{(152)}\)

The absence of any traces of product in the above reactions led us to review the situation, it was decided to no longer pursue the above chemistry, as it appears that the steric hindrance makes the reaction unfeasible.

Following the termination of the above work, the problem of carbon-carbon bond formation on the cobalt-molybdenum Nicholas salts was addressed. Although the parent dicobalt complexes respond well to carbon nucleophiles, including malonates, and are even active in Friedel-Krafts reactions,\(^{(106)}\) both the triphenylphosphine substituted and cobalt-molybdenum complexes suffer from a lack of reactivity towards carbon nucleophiles. We hoped to solve this problem via the use of soft organometallic species.

### 2.4 Zinc mediated additions to Nicholas salts

#### 2.4.1 Background Radical investigations

Our investigations into the zinc mediated reactions initially started with an interest into developing radical chemistry on these complexes. Although there are scattered reports of radical reactions on these species, most notably by Nicholas and Melikyan\(^{(136-138)}\) there is much scope for further chemistry, and we had hoped to utilise the chirality of the cobalt-molybdenum core. Initial work focussed on a report of coupling of Nicholas salts in DCM in the presence of zinc\(^{(136)}\) (Scheme 85).

![Scheme 85](image-url)
The reaction was repeated using the previously isolated cobalt-molybdenum salts. When the parent primary salt (177) was used, very little was isolated except starting material, probably due to the insolubility of the salt in DCM.

When the secondary salt (202), (R = Ph) was used in the reaction a small amount of material was isolated (up to 30%). This was found to be the reduced product (203) (Scheme 86). No dimer was ever isolated. Exclusive formation of the reduction product is in agreement with the results of Gruselle (144) who also attempted this reaction using the cobalt-molybdenum salts. The use of a mixed THF/DCM solvent system gave only starting material, as did leaving the salt in DCM without zinc for an extended period (Melikyan has shown that the dicobalt system can spontaneously dimerise under these conditions). (136b)

Scheme 86
2.4.2 Xanthate investigations

Initial work focused on the homobimetallic dicobalt core. It was thought that based upon previous knowledge and the above reaction, new chemistry would be more likely to work on this core before transfer to the less reactive cobalt-molybdenum core. The previous literature reports were limited in that the best substrate was the highly unstable propargyl bromide species, it was reasoned that a replacement which gave similar reactivity but a more stable precursor would be advantageous, even before the switch to the heterobimetallic core.

One functionality, which immediately appealed, was the sparingly used xanthate moiety. This is relatively non-toxic, participates in radical reactions including atom transfer,\(^{(167)}\) and is available as its sodium salt allowing an easy preparation. Hence dicobalt hexacarbonyl propyn-1-O-Ethylxanthate (204) was prepared in a 90 % yield from dicobalt hexacarbonyl propynol (84) using ethyl xanthic acid sodium salt (Scheme 87).

![Scheme 87](image)

The complex was then reacted under several conditions (Table 14).
Complex Reagent Conditions Result
---
(204) HSn(Bu)$_3$ Et$_3$B, air, toluene S/M
0 °C- rt, 12 h
(204) IPA Et$_3$B, air, IPA S/M
0 °C- rt, 12 h
(204) THP Et$_3$B, air, DCM S/M
rt, 12 h
(204) Zn DCM S/M

Table 14

The complex appeared unreactive under the (admittedly limited) reaction conditions tried. Unfortunately the complex also appeared unstable when not in the reaction and purification and recovery of starting material proved to be problematic. Ideally other radical initiators such as AIBN would have been tried; however the thermal instability of the cobalt complex prohibits the use of even the lower temperature radical initiators. This area of research was not pursued further as results observed simultaneously led research along a different pathway (*vida infra*).

2.4.3 Barbier additions

Although not really synthetically useful, the reduction reaction observed earlier (Scheme 86) demonstrated that a radical could be formed using the cobalt-molybdenum core (unless one suggests that the DCM somehow reacts with Zn in order to form a hydride species in solution, or that an anionic charge is formed *via* 2 successive electron transfer reactions). This led our thoughts to using activated Zn (eventually in the form of a Zn/Cu couple) (205) in order to facilitate carbon-carbon bond forming reactions in these complexes. Previously, attempts within the group to add Grignard reagents and organolithiums to the
salts had met with failure. However while browsing through some literature reports we came across a case of the addition of Zn and Cu species to cationic π-allyl molybdenum complexes,\(^{(168)}\) a situation where harder organometallic reagents had also failed.

With several routes available, the problem became deciding where to start. The literature is resplendent with different methods and conditions for reacting and forming organozinc and organocuprate species. With the results of the radical chemistry in mind we decided to start with the simplest reaction possible, Barbier reactions using zinc-copper couple (Zn/Cu).

\(\text{Zn/Cu (205) couple was synthesised according to literature procedure,}^{(169)} \text{ this was chosen as the active metal species as it is simple to make and can be stored for long periods under nitrogen. The reactions were then performed as below (Scheme 88 and Table 15).}\)

\[
\begin{align*}
\text{(177)} & \quad R = H, R_2 = H \\
\text{(202)} & \quad R = \text{Ph}, R_2 = H \\
\text{(206)} & \quad R = \text{Me}, R_2 = H \\
\text{(207)} & \quad R = \text{Et}, R_2 = \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{BF}_4^- & \quad \text{Zn/Cu, } R'\text{Br, } \text{THF, } 60 \degree \text{C} \\
\text{R} & \quad \text{R'} \quad \text{R} \\
\text{(OC)}_3\text{MoCp(CO)}_2 & \quad 208-213 \\
\end{align*}
\]

\text{Scheme 88}

Initial attempts at the reaction using the parent salt (177) gave small traces of something by TLC, but no identifiable product; once again due to the insolubility of the salt in THF even at 60 °C. However, upon changing to a secondary cation the reaction began to work. Although isolated yields range from moderate to good (Table 14), the reaction is usually quantitative by TLC within 10-15 min, with some product apparently being lost during work up, or decomposing under reaction conditions. \(^1\)H, \(^{13}\)C, COSY and HMQC NMR and mass spectrometry [FAB] analysis confirmed the product structures.
Table 15

The reactions were carried out using 5 equivalents of ZnClCu and 5 equivalents of the nucleophile. The ZnClCu and nucleophile were left to stir at ambient temperature for 5 min before addition of the salt. The solution was then lowered into a pre-heated oil bath at 60°C and monitored by TLC.

Two things are immediately apparent from the above table. Firstly, the reaction gives good, although somewhat variable yields, and secondly stereochemical control is poor to non-existent.

As the cation is known to sit closer to the molybdenum vertex, and no flipping of the cation has been seen in these species, it can be postulated that the lack of stereocontrol is due to rotation around the C- C⁺ bond. This process has been identified by Gruselle (144) (Figure 16).
Gruselle noted that the two rotomers were in equilibrium at room temperature, i.e. although the rotation occurs the isomeric ratios stay the same. At the elevated reaction temperatures one could possibly expect this process to be much quicker with a change in the thermodynamic ratio of the isomers resulting in the observed loss of stereocontrol. Alternatively, the minor diastereoisomer of the salt may be reacting much faster than the major, once again resulting in the loss of selectivity.

Following the above results, research focused on maintaining the diastereoselectivity of the reaction. It was immediately apparent that a lowering of the reaction temperature provided a possible answer. Performing the reaction as above but at lower temperatures failed, so an attempt to pre-form the organozinc reagent was made.

Initially this was approached by forming the organozinc reagents using literature procedures (usually heating in THF for 1-2 h),\(^{(170)}\) then cooling the solution before addition of the salt. The reaction failed in these cases. When the salt was added to a pre-formed organozinc reagent at 60 °C the reaction also failed, possibly providing evidence that these are not the reactive species in the reaction (the speed of the reactions also suggests this as the Reformatsky reagents generally take 1-2 h to form at elevated temperature and would therefore not be expected to be present in the reaction mixture in any reasonable concentration over the 10 min it takes).
Mixed solvent systems were also tried using a MeCN/THF mixture, as we knew that the salts are soluble in MeCN. Once again several variations on this theme failed. Finally the reaction was attempted using indium in MeCN (indium forms complexes with allyl bromide in very polar solvents such as water). Once again this failed.

Attempts to add 3,3-dimethyl allyl bromide gave a mixture of unidentifiable products, however, benzyl bromide did appear to add, although it was not possible to purify the product in order to obtain clean analysis.

In conclusion of this work, a new method for the formation of carbon-carbon-bonds on the bimetallic cobalt-molybdenum core has been demonstrated. However, despite further investigation of reaction conditions, we were unable to overcome the accompanying lack of stereocontrol. Due to time constraints it was not possible to take this work further.

2.5 Cobalt-carbene complexes

2.5.1 Background. Desymmetrised dicobalt complexes and N-heterocyclic carbenes

As previously described (see 1.5.3) the dicobalt hexacarbonyl core has been desymmetrised in several ways, the most investigated being the replacement of one of the carbonyl groups by triphenylphosphine (Scheme 89). (76,77)

\[
\begin{align*}
\text{R}_1 \quad \text{R}_2 & \quad \xrightarrow{\text{PPh}_3, \text{THF, } 60^\circ C} & \quad \text{R}_1 \quad \text{R}_2 \\
\text{(OC)}_3 \text{Co} - \text{Co(OC)}_3 & & \quad \text{(OC)}_3 \text{Co} - \text{Co(OC)}_2 \text{PPh}_3 \\
\end{align*}
\]

60-75%

Scheme 89

Phosphites, and various other phosphines have also been used, (75,77) in each case the complex express different reactivity to the parent complex. Tris-Pyrrole phosphine has been
shown to behave electronically as a bulky CO mimic,\(^{(172)}\) however because of this there are serious problems with oversubstitution of the complex core leading to mixtures of complexes with very little monosubstituted product.

Phosphines and related compounds have also been the ligand of choice for many other reactions involving transition metals, with numerous variations on this theme including chiral, monodentate, bidentate and other more exotic species.\(^{(173)}\) In recent years the dominance of phosphine related ligands has been challenged by \(N\)-heterocyclic carbenes. These ligands are extremely strong \(\sigma\) donors with the general structure as shown (Figure 17).

![Figure 17](image.png)

Wanzlic\(^{(174)}\) first recognised that the imidazole/imidazolium core could possibly stabilise a carbene at the central carbon via \(\pi\)-electron donation from the adjacent nitrogen atoms. Although unable to isolate a free carbene, he was able to infer the species via functional group associated reactions (cyclopropanation etc). However in 1990 Arduengo\(^{(175)}\) after the development of a simple synthetic route, was able to isolate the first free carbene (Figure 18).
The adamantane carbene 1,3-bis(1-adamantyl)imidazole-2-ylidene (214) was isolated as a stable crystal, and this revealed its single carbene nature, with the important point being the N-C-N bond angle of 102° (the theoretically calculated angle for a singlet carbene). A lengthening of the C-N bonds was also seen in comparison with the parent salt, indicating that although there is formally a vacant 2p orbital on the central carbon, there is actually little π-bonding between this and the adjacent nitrogen atoms, hence the imidazolium core does not express the expected aromaticity. However this is still an area of debate.\(^{(176)}\)

Since the above development, the metal co-ordination chemistry and synthetic utility of these ligands have been (and is still being) rigorously investigated. Studies of the transition metal complexes of these ligands have revealed some interesting characteristics. The M-C bond is relatively long, and in some cases rotation around the M-C bond is seen, indicating little or no back bonding, with the ligand acting as a 2-electron σ donor.\(^{(177)}\) In addition thermal investigations by Nolan\(^{(178)}\) and others show that these compounds are very effective electron donors, that form stronger, more thermally stable bonds than the phosphine ligands they have been used to replace.

Synthetically these ligands have been used to replace tertiary phosphines or phosphites in the majority of the generally used transition metal catalysed reactions. In virtually all cases they have significantly altered reactivity with yields, functional group tolerance, catalyst stability, and general versatility of the catalyst often being improved. Examples include, Suzuki, Heck, Stille and Sonogoshira couplings,\(^{(176,179)}\) aryl amination, hydroxylation,
hydrogenation, hydroformylation\textsuperscript{(180)} and perhaps most significantly metathesis catalysts,\textsuperscript{(181)} where the second generation Grubbs catalyst and variants have enabled whole new areas of chemistry to be investigated.

2.5.2 Synthesis of the cobalt-carbene complexes

With the above introduction in mind, we were surprised that no imidazolium substituted dicobalt-alkyne complexes had been published. We were intrigued as to possible applications of these complexes in our chemistry. Firstly, we wondered whether they would be easier to handle and more stable than phosphine substituted analogues, secondly the sheer size of the ligands provides a virtual “wall” across one side of the complex (highly desirable for stereoselective reactions) and thirdly, we were hoping to investigate the reactivity of the complexes in catalytic PKRs with one eye on the applications of chiral versions of the ligand in this case. The ligand investigated was the 1,3-\textit{bis-(2,6-diisopropylphenyl)}imidazolium (IPr) ligand (216). This was synthesised using literature methods\textsuperscript{(182)} \textit{via} the following route (Scheme 90).
The synthesis of 1,4-bis-(2,6-diisopropylphenyldiazabutadiene) (215) proceeded smoothly. Two equivalents of 2,6-diisopropylaniline were added to a solution of aqueous glyoxal in ethanol along with a few drops of formic acid. Within a few minutes the product precipitated out of solution as a bright yellow solid. This was then filtered with cold methanol to give the product as a bright yellow crystalline solid in a 75-95 % yield.

The second step of the reaction proved to be a little more difficult. Paraformaldehyde and 1,4-bis-(2,6-diisopropylphenyl)diazabutadiene (215) were added to a solution of toluene then heated to 100 °C in order to start to dissolve the paraformaldehyde, this solution was then cooled to 40 °C before addition of the acid (either HBF₄, or HCl). The solution was then left to stir at ambient temp for 24-36 h before washing with THF, to give the product as an off white solid. Prior to filtration the product is a dark purple sludge, which was often
difficult to extract from the flask. However, eventually yields of between 35-45 % were obtained on a multigram scale.

It was found that although the initial product was supposed to be analytically pure, poor yields were obtained when using it in the following reactions (10-20 %) with starting material still visible by TLC analysis, and recovered after purification. However, dissolving the salt in DCM, followed by drying over MgSO₄, then filtration and concentration in vacuo gave a pure white solid (in the case of the HBF₄ salt), which, when used in reactions under the same conditions, enabled them to go to completion by TLC.

The method for the synthesis of the cobalt-alkyne complexes was developed from a previous report by Nolan et al (182) (Scheme 91).

![Scheme 91](image)

While Nolan's synthesis worked at a range of temperatures from ambient to 60 °C, it was found that the cobalt analogue had a very small thermal window of between 60 and 70 °C. Any lower and the reaction proceeded slowly with a lot of recovered starting material, any higher and the product decomposed as it formed.

A mechanistic rationale behind the difference in reaction conditions can be suggested. In the case of the synthesis of the metathesis catalysts two mechanisms can be proposed. Firstly, the phosphine ligands are hemilabile in solution. The strongly nucleophilic carbene can attack the vacant site on this complex, as the carbene ligand is much more strongly
bonded the reverse reaction doesn’t occur; hence even at low temperatures the reaction is driven towards the carbene product. Secondly complex (217) is an unsaturated 16 Ve complex, hence an associative mechanism can be proposed for the formation of (218) with a saturated 18 Ve intermediate decomposing to give the more thermodynamically stable product (Scheme 91).

In the case of the dicobalt hexacarbonyl complexes, in common with the PKR one can strongly suggest that the first step is dissociation of a CO ligand. This is essentially the rate limiting step and occurs at elevated temperatures (Scheme 92). In this case an associative mechanism is not viable.

When the reaction temperature is too low the loss of CO is retarded, however at too high a temperature further dissociation of CO (or alternative pathways) takes place in the newly formed complexes leading to decomposition.

After much optimisation, a general method for the synthesis of imidazolium dicobalt pentacarbonyl–alkyne complexes was developed, with moderate to good yields (Scheme 93 and Table 15).
During the optimisation studies both the HBF$_4$ and HCl imidazolium salts were used. However in test reactions on dicobalt hexacarbonyl diphenylacetylene (220), the HBF$_4$ salt gave a significantly better yield than the HCl salt (67 % vs 46 %), using identical conditions in simultaneous reactions. It was therefore decided to use this salt as the carbene precursor.

In practice the reaction was simple to perform, although it does exhibit some sensitivity and solvents must be degassed. The carbene precursor (216) was dissolved in hexane at a concentration of 30 ml/g (due to its low solubility in this solvent), K-tert pentoxide (K-amylate), was then added and the solution left to stir for 20-40 min, occasionally the solution become viscous and more hexane was added. The cobalt complex was then added, either as a solid, or hexane solution, and the reaction left to stir at 65°C for 40 min-1 h. The product was then filtered through a pad of celite and silica before purification. As stated
earlier, when performed carefully the reaction goes to completion by TLC. However the products are slightly unstable, and the moderate isolated yields can be attributed to loss during purification. The products appeared to be slightly unstable on silica even under nitrogen, and when the silica had been neutralised with triethylamine. They don’t crystallise from reaction liquor, as in the case of the metathesis catalysts so chromatography was necessary. Once purified the products were generally dark purple to black solids. An X-ray crystal structure of the aldehyde (224) was obtained (Figure 19).

![Figure 19](image)

The sheer steric bulk of the ligand is immediately apparent from the crystal structure, it sits in the apical position one side of the complex and forms a wall across that side. It is noticeably more bulky than either the triphenylphosphine ligand, or the cyclopentadiene ligand used on the cobalt-molybdenum complex (which actually sits in a basal position). Both the crystal structure and spectroscopic details of the complex were compared with...
other known complexes of the same alkyne on the different metal cores in order to investigate any measurable electronic differences (Table 16).

<table>
<thead>
<tr>
<th>Bimetallic core</th>
<th>$\delta^1$H</th>
<th>$\delta^{13}$C</th>
<th>$\nu_{\text{max}}$ M-CO</th>
<th>$\nu_{\text{max}}$ CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_2$(CO)$_6$</td>
<td>10.30</td>
<td>191.1</td>
<td>2100, 2058, 2029</td>
<td>1669</td>
</tr>
<tr>
<td>CoMo(CO)$_5$Cp</td>
<td>10.11</td>
<td>194.0</td>
<td>2057, 1992, 1959</td>
<td>1648</td>
</tr>
<tr>
<td>(Co)$_2$(CO)$_5$PPh$_3$</td>
<td>9.72</td>
<td>191.7</td>
<td>2066, 2010, 1968</td>
<td>1653</td>
</tr>
<tr>
<td>(Co)$_2$(CO)$_5$IPr</td>
<td>8.68</td>
<td>186.7</td>
<td>2060, 2007, 1960</td>
<td>1632</td>
</tr>
</tbody>
</table>

Table 16

The table appears to show that the IPr substituted core is the most electron rich, in particular the aldehyde carbonyl stretching frequency is particularly low, indicating the delocalisation of the electron density throughout the complex in a synergistic bonding process. The M-CO stretching frequencies of the cobalt-molybdenum core cannot be directly compared as the ligands are attached to a different metal. Within the group we have the crystal structures of the same alkyne on both the cobalt-molybdenum and PPh$_3$ substituted cores, we were therefore able to closely compare the structures.

Disappointingly, little insight could be gained as to the electronic differences between the complexes from the respective crystal structures, the only significant difference seen was a lengthening of the alkyne-carbonyl bond (C3 – C4) in the case of the Ipr substituted complex.

With the complexes in hand their reactivity was investigated

2.5.3 Pauson–Khand reactions
The first reaction investigated was the PKR. Taking the phenylacetylene complex (222) and reacting with 5 equivalents of norbornadiene at 70 °C in dimethoxy ethane (DME) gave an 89 % yield of the cyclised product (226) (Scheme 94).

Interestingly, use of the imidazolium dicobalt pentacarbonyl-diphenylacetylene complex (223) under the same conditions resulted in a maximum yield of 11 % of compound (227), with decomplexed diphenylacetylene being the major product isolated. This was unexpected, as while the phenylacetylene complex itself was one of the most sensitive and gave the lowest isolated yield (39 %), the diphenylacetylene complex was one of the easiest to handle and gave consistently good yields for its synthesis. It was later discovered that the complexes react extremely quickly under the above conditions (the reactions are complete in under 1 h). It is therefore suggested that in the above case steric interactions hinder the alkene complexation step of the PKR, leading to decomposition of the complex as the major pathway.

Of more interest was the possibility of an asymmetric PKR using the separated diastereoisomers of the menthyl substituted complex (225). The complex could be consistently synthesised in reasonable yields (50 - 65 %) on a 1-2 g scale. Interestingly there appeared to be some diastereoselectivity in the synthesis of this complex, the alkynyl protons of the two diastereoisomers, and the alkene protons of the imidazolium ligand have slightly different shifts in the \(^1\)H NMR spectra. From these a diastereomeric ratio (d.r.) which varied between 2 : 1 and 3 : 2 for the products was seen (it was later found that the earlier eluting isomer was the major product).
An attempt was then made to separate the diastereoisomers, a solvent system of 5 : 1 petroleum ether/DCM was found to give the best separation. Unfortunately the isomers did not completely separate, therefore the product had to be repeatedly chromatographed. Pure samples of the early eluting isomer were easily harvested. However due to its instability on silica and co-elution, obtaining useful amounts of the minor (later eluting) isomer proved to be both difficult and time consuming. Eventually clean pure diastereoisomers were obtained. The separated isomers were then reacted in a PKR under the following conditions (Scheme 95 and Table 17).

![Diagram of reaction](image)

**Scheme 95**

<table>
<thead>
<tr>
<th>Solvent / additive</th>
<th>Temp (°C)</th>
<th>Time</th>
<th>Yield (%)</th>
<th>d.e</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCM / THF / NMO</td>
<td>25</td>
<td>3 days</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>DME / NMO #</td>
<td>40</td>
<td>24 h</td>
<td>43</td>
<td>-</td>
</tr>
<tr>
<td>DME *</td>
<td>45</td>
<td>24 h</td>
<td>65</td>
<td>90</td>
</tr>
<tr>
<td>DME *</td>
<td>70</td>
<td>1 h</td>
<td>95</td>
<td>87</td>
</tr>
<tr>
<td>DME ∞</td>
<td>70</td>
<td>1 h</td>
<td>87</td>
<td>92</td>
</tr>
<tr>
<td>DME ♦</td>
<td>70</td>
<td>1 h</td>
<td>85</td>
<td>35</td>
</tr>
</tbody>
</table>

# racemic mixture
* First eluting diastereomer
∞ Second eluting diastereomer
♦ diastereomers not separated after complexation

**Table 17**

114
The complex reacted well under the standard thermal conditions outlined earlier (10 equivalents norbornadiene) with the spectra of products obtained conforming to the literature. The diastereoselectivity of the reaction was good, although complete stereocontrol was not obtained. Attempts at increasing the diastereoselectivity by lowering the reaction temperature and adding N-methylmorpholine-N-oxide (NMO) were generally unsuccessful. At ambient temperature only 20% starting material was recovered after 3 days, although this was still one diastereoisomer. At 40 °C a low yield was obtained after 24 h.

The fact that the complex appeared inert to N-oxide activation was interesting. Daresburg and Daresburg (184) suggested that stronger electron donors increased the amount of back bonding on CO ligands thus reducing the electrophilicity of the CO carbon. As NMO had been successfully used to perform low temperature asymmetric PKR on triphenylphosphine (PPh₃) substituted complexes (77) this result suggests that, although not immediately apparent from the M-CO IR frequency, the Ipr ligand is significantly more electron donating than PPh₃. It is also worth noting that N-oxide activation failed to work on the cobalt-molybdenum complexes used previously within the Christie group. (157) Stronger N-oxides could have been tried in the above reaction, but as mentioned earlier this has already been achieved using the more readily available PPh₃ substituted complexes, and is therefore of little synthetic interest. However diastereomerically pure PPh₃ complexes epimerise under thermal conditions (75, 149) making this reaction the first thermal highly stereoselective bis-cobalt PKR.

The final entry in Table 17 is also interesting, as mentioned earlier a d.r. is seen for the complexation. When the mixture of complexed diastereomers is taken through into the PKR this selectivity is retained. This effect is due to the complex and not to the presence of the chiral menthol group as the dicobalt hexacarbonyl complex (88) forms a racemic mixture of cyclopentenones (91a and b) under the same conditions. (185) The mechanism of epimerisation was then addressed (Scheme 96).
Under the reaction conditions the menthol complex slowly epimerises. The 3:1 d.r seen in the product doesn’t indicate a thermodynamic ratio as the complex also slowly decomposes. At ambient temperature in DCM no epimerisation was seen, although the complex did slowly decompose (entry 1 in Table 17). When a crossover reaction was attempted by mixing the IPr-menthol complex (225) with dicobalt hexacarbonyl ethoxy complex (173) no inter-complex ligand crossover was seen. These results indicate a slow intramolecular epimerisation at elevated temperatures.

It is suggested that the stereoselectivity occurs via preferential cyclisation around one of the metal vertices, most probably the unsubstituted one. As one would expect the carbonyl ligands on this vertex to be the most labile and the IPr ligand to form a very strong M-L bond (this was almost always the parent ion for the MS spectra of these complexes) (Scheme 97).
Scheme 97
2.5.4 Grignard additions to aldehyde

The group had previously successfully exploited the desymmetrised cobalt-molybdenum and Co$_2$(CO)$_5$PPh$_3$ alkynyl aldehydes for diastereoselective addition of Grignard reagents. (142) This was attempted using the IPr substituted complex (Scheme 98).

![Scheme 98](image)

Unfortunately, despite several attempts the reaction failed completely. When the reaction was quenched at −78 °C starting material was recovered. When it was allowed to warm up only degradation products along with a little residual starting material were recovered. Due to time constraints, and as we already had two successful systems for this reaction it was decided not to pursue it further. Under the conditions used some product should have been isolated. The reason for the failure was possibly partly steric but also electronic. The aldehyde stretching frequency for this complex is very low (1632 cm$^{-1}$) much lower than either the Co$_2$(CO)$_5$PPh$_3$ or cobalt-molybdenum complexes (1653 and 1648 cm$^{-1}$ respectively) suggesting a very electron rich aldehyde, this coupled with the steric bulk around the carbonyl (see X-ray) possibly accounts for the observed lack of reactivity.
2.5.5 Nicholas chemistry of the complex

The Nicholas carbocation chemistry of the complex was also investigated. Addition of HBF₄ to the propargyl alcohol complex (221) led to the formation of a red/purple solid Nicholas salt similar to those formed from the cobalt-molybdenum complexes. Unfortunately it was also discovered that these salts do not have the stability of the cobalt-molybdenum salts and decompose fairly rapidly in air, although they are stable for short periods (Scheme 99).

\[
\begin{align*}
\text{HBF}_4, \text{diethylether} & \quad \text{rt} \quad \begin{array}{c}
\text{H} \\
\text{(OC)}_3\text{Co} \\
\text{Co(CO)}_2\text{Ip} \\
\text{221}
\end{array} \\
& \quad \begin{array}{c}
\text{H} \\
\text{(OC)}_3\text{Co} \\
\text{Co(CO)}_2\text{Ip} \\
\text{228}
\end{array} \\
& \quad \begin{array}{c}
\text{BF}_4^- \\
\text{228}
\end{array} \\
\end{align*}
\]

Scheme 99

It was initially hoped to use this salt to access more of the minor menthol diastereoisomer unfortunately this reaction worked poorly with a maximum 16% yield from several attempts (see Table 18), however the salt was responsive to smaller heteroatom nucleophiles giving respectable isolated yields (Table 18).
NUcleophile | Conditions | Yield (%) | Product
---|---|---|---
MeOH | MeCN / Hünigs | 50 | (229)
NaSO₂Ph | MeCN | 94 | (230)
benzotriazole | MeCN / Hünigs | 71 | (231)
diallylamine | MeCN / Hünigs | 70 | (232)
L-menthol | MeCN / Hünigs | 16 | (225)
L-menthol | BF₃ / DCM *(in situ)* | 0 | 

Table 18

The salt was added to a flame-dried flask under an atmosphere of nitrogen, solid nucleophiles were also added at this time. Dry acetonitrile was then added followed by the nucleophile in the case of liquids and the solution stirred for 5-10 min. For neutral nucleophiles Hünigs base was then added before the solution was filtered through a pad of celite then purified. The poor yields for menthol can possibly be blamed on steric interactions. The PKR work was completed while the Nicholas work was being performed, therefore the menthol addition was not pursued further, however the addition of pre-formed sodium mentholate would possibly give better yields.

The above work represents the first synthesis of and investigation into the reactivity of dicobalt imidazolium carbene complexes. While completing the work, Gibson et al.⁵⁸ᵇ published a report which used a related analogue in catalytic PKR reactions. However in their case the complexed alkyne was never isolated and characterised. While the complexes have expressed some interesting characteristics and reactivity, it was increasingly found that in the majority of circumstances, the phosphine substituted or cobalt-molybdenum analogues worked as well, and were significantly easier to handle. Therefore it was decided to move on to potentially more profitable areas, with the intention of revisiting this chemistry if we found a situation where it was advantageous. Our findings
on the robustness of the complexes are in agreement with Gibson, who also found the other systems more robust in her catalytic studies.

2.6 Cascade reactions leading to biomimetic studies

Inspired by the work of W.S. Johnson, \(^{186}\) and more recently F. McDonald \(^{187,188}\) on the biomimetic synthesis of polycarbocycles and polycyclic ethers, we were intrigued as to whether Nicholas carbocations could a) initiate these reactions and b) whether any stereocontrol could be achieved with the use of the desymmetrised systems.

2.6.1 Opening of epoxides via Nicholas chemistry.

We initially wondered whether we could use Nicholas chemistry to form polycyclic ethers via the opening of epoxides. Although the use of oxygen nucleophiles for the formation of cyclic ethers using this methodology was well known \(^{130-135, 2a}\) at the time of starting the work, epoxides had not been reported. However they are found in the literature for other systems e.g. Corey's synthesis of glabrescol\(^{189}\) and several papers by McDonald (illustrated) \(^{188}\) (Scheme 100).
The polycarbonate substrates used in the above syntheses are readily synthesised from commercial polyalkenes using asymmetric epoxidation catalysts such as those developed by Shi.\(^{(190)}\) It was envisaged that using Nicholas chemistry we could develop this methodology towards synthetic fragments, leaving the alkyne available for further elaboration (PKR or removal of metals).

In order to begin the research, reactions on simpler test substrates derived from citronellal (236) were instigated (Scheme 101).
Deprotonation of (235) in THF at −78 °C, followed by a quench with citronellal (236) gave compound (237), in a 92 % yield. This was then epoxidised with 1.5 equivalents of meta chloro perbenzoic acid (mCPBA) in DCM at 0 °C, with the reaction going to completion in around 2 h. After a standard work up the epoxide (238) was isolated in a good yield, although it appeared to be unstable (the colour rapidly changed from colourless to yellow in air), therefore it was immediately complexed giving (239) in a 71 % yield over the two steps.

The methoxy version of the compound (240) was also synthesised in good yield, with the methoxy group being formed by a Williamson ether synthesis (NaH, MeI quench at 0 °C in THF) before epoxidation.

It was then hoped to form the cyclic ether by a Lewis or protic acid mediated Nicholas reaction, followed by elimination of H⁺ (Scheme 102).

The reaction was performed under the following conditions (Table 19).
<table>
<thead>
<tr>
<th>Complex</th>
<th>Conditions</th>
<th>Prod</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(239)</td>
<td>HBF₄, DCM, rt, 12 h</td>
<td>(241)</td>
<td>52</td>
</tr>
<tr>
<td>(240)</td>
<td>BF₃.OEt₂, DCM, 0 °C, 1 h</td>
<td>(241)</td>
<td>51</td>
</tr>
<tr>
<td>(240)</td>
<td>HBF₄, 0 °C, 5 min, DCM</td>
<td>(241)</td>
<td>58</td>
</tr>
<tr>
<td>(240)</td>
<td>HBF₄, 0 °C, 5 min, Hünigs, MeCN</td>
<td>decomposed</td>
<td>-</td>
</tr>
<tr>
<td>(240)</td>
<td>BF₃.OEt₂, MeCN, 0 °C, 1 h</td>
<td>decomposed</td>
<td>-</td>
</tr>
<tr>
<td>(239)</td>
<td>TsCl, Et₃N, DCM, rt</td>
<td>decomposed</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 19

Unfortunately non of the desired product was ever identified, the only product isolated was the ketonic compound (241), possibly formed as below (Scheme 103).

As can be seen, after the oxepane ring formation a 1,2-hydride shift can occur, followed by elimination to give compound (241). Alternatively, the ketone formation can occur initially.
followed by elimination. While both mechanisms would be valid, the fact that Martin et al (191) later published a very similar reaction forming a cyclic ether using BF$_3$.OEt$_2$ supports the above hypothesis. Martin found that a functional group capable of stabilising the incipient cation was required and that yields and products (cis/trans and exo/endo selectivity) were sensitive to the stabilising group used. He proposed several mechanistic models for the results, one of which is shown below (Scheme 104).

![Scheme 104](image)

2.6.2 Polycarbocycles

Following the report by Martin, and the failure of our initial system we faced a dilemma. It was obvious that Martins work on the formation of polycyclic epoxides was far more advanced than that within the group and that the formation of these systems was more complicated than first envisaged. Rather than try and catch up in an area already occupied, at the risk of inadvertently repeating unpublished work, we began to work on our primary target, polycarbocycles. Nicholas methodology has been used frequently to form carbocycles and bicycles (107-110) However, we were most interested in two reports. Firstly
the publication by Krafft\(^{(114)}\) who was able to form lactones \textit{via} reaction with a terminal alkenyl acid (Scheme 105).

\[ \text{Scheme 105} \]

Secondly, the work of Tyrrel \textit{et al}\(^{(115)}\) on the synthesis of trans-benzopyrans (Scheme 106). This chemistry provided the initial test substrates.

\[ \text{Scheme 106} \]
Although not ideal, it was thought that Tyrrell's methodology could be used to quickly test whether attempts at cascade reactions were feasible. Geranyl and farnesyl bromides were substituted for the 3,3-dimethyl allyl bromide (prenyl bromide) used by Tyrrel in order to form the polyalkenyl substrates (Scheme 107).

The synthesis of the precursors was achieved in high yield. Adding the polyalkenyl bromide to a solution of salicylaldehyde (248) in DMF, followed by K₂CO₃ and a catalytic amount of potassium iodide (KI), resulted in virtually quantitative isolated yields of the desired product (249 or 250) after aqueous work up followed by chromatographic purification. These were then dissolved in dry THF at 0 °C, then alkynyl magnesium bromide (1.5 equivalents) added. After aqueous work up and chromatographic purification the alkynes (251 and 252) were isolated as pale yellow oils in 90 % + yields. The product
of the first step was later found to be clean enough to take through without purification with no loss of overall yield. Complexation of the alkynes under standard conditions (DCM, \( \text{Co}_2(\text{CO})_8 \), ambient temperature) proceeded with the expected good yields (80 % + isolated in all cases). With the complexes in hand the cyclisations were attempted (Scheme 108).

Unfortunately, although the complexes did appear to cyclise under either protic (HBF\(_4\)), or Lewis acid activation (BF\(_3\).OEt\(_2\)), the products were a complex mixture of isomers and/or
products and we were unable to characterise the spectra. Attempts to improve the analytical data by removal of the metals (methanolic ceric ammonium nitrate (CAN) in DCM) also failed to help. However, the spectra for the compounds after cyclisation did not appear to have any alkenyl protons suggesting that the cascade had indeed worked, although this was obviously of little use as the compounds were not characterisable. A test reaction using the prenyl-derived substrate gave the fluorinated product in a 76% yield using Tyrrell's *in-situ* demetallation methodology, proving that the reaction worked in our hands.

As the test reactions did not give us the desired results, it was decided to instead proceed with a more novel approach to polycarbocyclic systems, using an extension of our recently developed 1,3-dipolar Nicholas methodology. The dipole is formed via Lewis acid catalysed opening of an alkynyl cyclopropane, and has already been used to form substituted tetrahydrofuran and pyrrolidine rings in moderate to good yields (Scheme 109).

We realised that in order to form fused carbocycles we needed to have several structural features in place. Firstly, a good terminating group. Secondly, the alkenes had to be spaced appropriately in order to form the carbocyclic rings and finally the carbocation formed during the cyclisation should be tertiary in order to drive the cyclisation and control the
regiochemistry (we could foresee problems with competitive 5-exo vs 6-endo ring formation).

It was suggested that by using the isoprene derived polyalkynols geraniol and farnesol we could turn the alcohol into the prerequisite leaving group, then selectively functionalise the opposite end, forming the carbocycle precursor (Scheme 110).

\[
\text{geraniol} \xrightarrow{\text{(BOC)}_2\text{O, pyridine, THF}} \text{activation of OH} \xrightarrow{\text{SeO}_2, \text{H}_2\text{O}_2} \text{Lg} \xrightarrow{\text{OH}} \text{O}^{\text{c}}\text{Bu}
\]

Scheme 110

The majority of this work has literature precedent. The BOC protection of the allylic alcohol is a literature procedure\(^{(188b)}\) and the regioselective selenium dioxide oxidation of a terminal alkene on these structures is known.\(^{(193)}\) Manipulation of the intermediate alcohol formed (activation by tosylation or mesylation, or alternatively formation of the bromo compound), would then yield the desired intermediate.

Based upon the suggested mechanism for the cycloadditions, it was hoped that by using the above systems we could effect the synthesis of fused polcarboxylic fragments as below (Scheme 111).
This work was to be initially performed on the *bis*-cobalt system, but eventually it was hoped to desymmetrise the system and hopefully achieve some stereocontrol.

Previous attempts to cyclise 3,3-dimethyl allyl bromide by R.Davoile \(^{(150)}\) using the above chemistry had failed, therefore we decided to look towards tuning the alcohol into a tosyl or triflate leaving group.

Allyl triflates are unstable at high temperatures. However they can be made at low temperatures and are extremely reactive.\(^{(194)}\) As a test reaction it was decided to form the
triflate of 3,3-dimethylallyl alcohol and react this with the cyclopropane complex at low temperature then allow to gradually warm up (Scheme 112).

Scheme 112

The above reaction was attempted twice on a small scale. Within 5 min of the addition of the cobalt complex a single new product was seen. Unfortunately it decomposed during work up. An attempt at an aqueous work up also failed to yield any product. The decomposed complex was extracted into ether in order to hopefully isolate any decomplexed organic fraction, but once again nothing was isolated.

Although the product from this reaction was unstable, the formation of a new product was promising and this work will be continued within the group. However, problems with the synthesis of the alkynyl cyclopropane moved the project slightly sideways and due to time constraints, no further work in this area was undertaken at this time.

2.7 Alkynyl cyclopropane surrogates

The problem found with the alkynylcyclopropane was a low yielding and expensive step in the synthesis of the complex. This led to difficulty in getting significant quantities of the complex for use in cascade reactions. Therefore, while using the old method to make small quantities of the cyclopropane, we were actively seeking another route. The discovery of a possible surrogate complex available cheaply and in two high yielding steps took the work in this direction.
2.7.1 Formation of the alkynyl cyclopropane complex.

The route to the cyclopropane complex was originally developed by R. Davoile,\(^{(150)}\) and was synthesised as below (Scheme 113).

Deprotonation of dimethylmalonate (258) with sodium methoxide, followed by the addition of \textit{trans}-1,4-dibromobutene (259), led to the formation of vinyl cyclopropane (2-ethenylcyclopropane-1,1-dicarboxylic acid dimetyl ester) (260) as a colourless oil in a 90\% yield. Ozonolysis of this formed 2-formylcyclopropane-1,1-dicarboxylic acid dimethyl ester (261) as a colourless oil in a 91\% yield after breakdown of the secondary ozonide with dimethylsulfoxide (DMS) followed by the extraction of DMS into water. The crude product was found to be clean enough for immediate reaction with dimethyl 1-diazo-2-oxopropylphosphonate (262) (Bestmann reagent)\(^{(195)}\) in the so called Seyferth procedure.
formed the 2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (alkyne cyclopropane) (258). Although, R. Davoile reported yields of up to 45 % for this step, the yields were variable and in my hands only 15-30 % was achieved In addition the phosphonate used is quite an expensive reagent. The complexation with Co₂(CO)₈ in DCM gave an 80 % yield of dicobalt hexacarbonyl -2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (255).

As the synthesis of the alkyne had been a problem we constantly investigated different synthetic routes as they arose, although as a side project to the main research.

The first alternative method tried was the Fritsch-Buttenberg-Wiechell rearrangement (196) in order to form the alkyne from the same common intermediate 2-formylcyclopropane-1,1-dicarboxylic acid dimethyl ester (261) (Scheme 114).

\[
\begin{align*}
\text{CBr}_4 & \quad \text{i) PPh}_3, \text{DCM, 0 °C} \\
& \quad \text{ii) MeO}_2\text{C} \quad \text{CO}_2\text{Me} \\
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{CO}_2\text{Me} & \quad \text{LDA, THF, -78 °C} \\
& \quad (6 \text{ equiv}) \\
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{261} & \quad \text{264} \\
& \quad 89 \% \\
\text{261} & \quad \text{264} \\
\end{align*}
\]

\[\text{Scheme 114}\]

Triphenylphosphine was added to a solution of carbon tetrabromide in DCM resulting in a golden yellow solution. Aldehyde (261) was then added and the solution left to stir. The addition of a large excess of hexane, followed by vigorous stirring resulted in the precipitation of triphenylphosphine oxide. Filtration through a pad of celite, followed by rotary evaporation gave (2,2)-dibromo-1-methyl-vinyl)cyclopropane-1,1-dicarboxylic acid dimethyl ester (264) as a colourless oil in an 89 % yield. The dibromoolefin was then dissolved in THF and 6 equivalents of freshly prepared LDA added. Although the solution turned purple as suggested in the literature no product was isolated after work up. Adding fewer equivalents of LDA, or leaving the reaction for longer before quenching also failed.
The next route attempted was a rather ambitious use of Nicholas chemistry. Although the desired reaction failed the product actually formed was also of synthetic interest (Scheme 115).

Two equivalents of ethynyl magnesium bromide were added to a solution of 2-formylcyclopropane-1,1-dicarboxlic acid diethyl ester in THF at −78 °C then the solution allowed to warm giving 2-(1-hydroxy-prop-2-ynyl)-malonic acid diethyl ester (266) as a colourless oil in 63 % yield. This was then complexed with Co₂(CO)₈ to give dicobalt hexacarbonyl 2-(1-hydroxy-prop-2-ynyl)-malonic acid diethyl ester (267) as a purple oil (quantitative). The initial product appeared slightly unstable, as despite several attempts adequate NMR data was not obtained. However upon addition of tetrafluoroboric acid, followed by Hünigs base, dicobalt hexacarbonyl 3-(ethoxycarbonyltetrahydrofuran-2-on-5-yl) ethyne (268) was obtained in a 40 % yield. Although not the desired product, this compound was isolated as a side product by R. Davoile during his cycloaddition reactions (150) and we wanted to investigate whether this compound was active in the cycloaddition
reaction. Test reactions using the previously described conditions for the formation of the tetrahydrofuran complexes (192) showed that this was an inactive side product in the reaction, as only starting material was ever isolated.

At this point it was thought that we were stuck with the previous route to the cyclopropane. However a publication by Melikyan et al. (197) on some novel radical cyclisations it became apparent that a cyclopropane surrogate was available.

2.7.2 New Cyclopropane surrogate

Melikyan (197) formed dihydrofurans in good yields from the corresponding dicobalt hexacarbonyl enyne and 1,3-dicarboxyls mediated by a manganese(III) radical reaction. It was suggested that if opened by a Lewis acid, these formed the same intermediate in principle as the alkynyl cyclopropane (Scheme 116).
Previously developed work and proposed intermediate

Dihydrofuran and new proposed intermediate

Scheme 116

The dihydrofurans were synthesised from the corresponding dicobalt hexacarbonyl alkynols in 2 steps. (Scheme 117).
The alkynol was dissolved in DCM along with 4Å molecular sieves, a catalytic amount of p-TSA was added then the solution left to stir for 12 - 24 h. After purification the dicobalt hexacarbonyl enynes (269 - 272) were obtained in good yields (Table 20).
One problem found with the formation of the enynes was the failure of the synthesis of the monosubstituted alkene \( (R_1 = R_2 = H) \). After the failure of the original conditions different conditions were tried. The addition of HBF\(_4\) in DCM, followed by Hünigs base also failed, as did repeating the reaction on a more dilute scale. Interestingly, in his original paper on the formation of these compounds Nicholas was also unable to isolate this complex\(^{(7)}\) as the reaction gave a mixture of products. Although in the original paper it was suggested that the desired enyne formed a large part of this mixture no evidence of it seen in the above reactions.

An attempt to synthesise vinylacetylene using literature methods,\(^{(198)}\) followed by immediate complexation also failed.

Initial attempts at the Mn(III) mediated reaction following the literature procedure failed. Here a solution of the cobalt complex and the 1,3-dicarbonyl in acetic acid were added to the Mn(OAc)\(_3\) and the resulting solution stirred for 40 min – 2 h at 35 °C depending upon the substrate. In our hands this method only resulted in recovered starting material.
However, stirring the Mn(OAc)$_3$ for 30 – 40 min in acetic acid at 40 – 45 °C before addition of the complex and 1,3- dicarbonyl, followed by extraction into ether, neutralisation with saturated NaHCO$_3$, then column chromatography resulted in the formation of complexes (273 - 276) generally in reasonable yields (Table 21).

<table>
<thead>
<tr>
<th>dihydrofuran</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Complex 273" /></td>
<td>58</td>
</tr>
<tr>
<td><img src="image" alt="Complex 274" /></td>
<td>57</td>
</tr>
<tr>
<td><img src="image" alt="Complex 275" /></td>
<td>15</td>
</tr>
<tr>
<td><img src="image" alt="Complex 276" /></td>
<td>31</td>
</tr>
</tbody>
</table>

Table 21

We found that the reactivity of the enynes in this reaction was as suggested in the literature. The α monosubstituted enyne (269) reacted fastest and gave the best yields, the cyclic dihydrofuran complex (276) was also obtained in reasonable yield, however the tri-substituted enyne complex (270) was unreactive in the reaction, and the β- monosubstituted enyne complex (271) gave very poor yields. This particular enyne also appeared to be slightly more unstable than the others. The proton NMR spectra appeared to be a slight mess with both cis and trans alkenes present (confirmed by the carbon NMR), and although
the complex appeared stable on silica, and one product was obtained from the column, the compound isolated after concentration always contained another degradation product. The instability of this complex may be the cause of the low yields in the dihydrofuran formation as no starting material was ever recovered.

With the compounds in hand we proceeded to attempt the cycloaddition reactions. Complex (274) was used with a range of Lewis acids and 4-nitrobenzaldehyde as the trap. Initially no product was seen. However changing the aldehyde to 2 equivalents of ethylglyoxylate (277), along with 4 equivalents of tetrafluoroboric acid in DCM resulted in the formation of a new compound within 10 min. This compound was found to be the desired product (278) (Scheme 118). The conditions for the reaction were then optimised using ethyl glyoxolate and acetaldehyde and a range of Lewis acids (Table 22).

![Scheme 118]

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>d.r</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF₃.OEt₂</td>
<td>rt</td>
<td>10</td>
<td>71</td>
<td>1:2:4:2</td>
</tr>
<tr>
<td>BF₃.OEt₂</td>
<td>45</td>
<td>10</td>
<td>56</td>
<td>1:2:4:2</td>
</tr>
<tr>
<td>ZnBr₂</td>
<td>rt</td>
<td>90</td>
<td>95</td>
<td>7:5:3:1</td>
</tr>
<tr>
<td>Cu(OTf)₂</td>
<td>rt</td>
<td>10</td>
<td>98</td>
<td>1:2:4:2</td>
</tr>
<tr>
<td>BF₃.OEt₂</td>
<td>rt</td>
<td>45</td>
<td>60*</td>
<td>-</td>
</tr>
<tr>
<td>ZnBr₂</td>
<td>rt</td>
<td>90</td>
<td>-*</td>
<td>-</td>
</tr>
<tr>
<td>Cu(OTf)₂</td>
<td>rt</td>
<td>10</td>
<td>-*</td>
<td>-</td>
</tr>
</tbody>
</table>

* acetaldehyde used

Table 22
The best conditions for the ethyl glyoxolate reaction were found to be using zinc bromide or copper triflate at ambient temperature. Interestingly although not diastereoselective the diastereomeric ratio for ZnBr₂ was different to both BF₃·OEt₂ and Cu(OTf)₂ with different products as the major diastereoisomer (unfortunately inseparable). The zinc-mediated reaction also took significantly longer to go to completion. It is suggested that the lower recovered yields in the presence of BF₃·OEt₂ are due to some degradation of the complex in the presence of the stronger Lewis acid during the reaction. R.Davoile [150] also noticed that the complexes exhibited some sensitivity towards strong Lewis acids while screening a range for the previously mentioned cycloadditions. With several different usable reaction conditions ready, other aldehydes were used in the reaction. ZnBr₂ proved to be ineffective with aldehydes other than ethylglyoxylate, as did Cu(OTf)₂, with only starting material recovered for both ambient and reflux conditions. BF₃·OEt₂ also proved to be effective in the addition of acetaldehyde to complex (274) giving compound (279). However, other aldehydes gave low to moderate yields of what was found to be another product (Scheme 119).
Under ambient conditions, the above products were seen in very low yield, however upon heating, the formation of a much more polar product was seen. After extensive analysis these were found to be the above compounds (280 and 281). A mechanistic rational can be shown for the above compounds by invoking a Prinz-type addition, already known for these complexes (Scheme 120). (112)
Unfortunately no identifiable product was isolated when the dihydrofurans (273, 275 and 276) were subject to the reaction conditions developed for complex (274), even when the reaction mixture was heated to reflux for extended periods.

The above results, although synthetically disappointing show that the original hypothesis works. The high yield achieved for the ethyl glyoxylate addition using the mild Lewis acid ZnBr$_2$ or Cu(OTf)$_2$, suggests that the ring opening is a facile process. The failure of most of the other reagents is possibly due to steric crowding in the transition state. Hence, when a strong enough Lewis acid is used, the elimination reaction can occur, leading to the unwanted side products. In the case of the cyclohexane derived product (276), the 6,5 fused ring system may have disfavoured ring opening, when pushed (refluxed for an extended period) this complex did show some possible product or degradation products although the amounts made analysis impossible. The failure of the diketone derived complex (273) is interesting, one would have thought that this compound would have been as reactive as complex (274), it may be possible that some bidentate chelation to the Lewis acid occurs, or that more than one Lewis acid molecule is associated with the complex in the transition state.
As stated earlier an attempt to synthesise dicobalt hexacarbonyl vinylacetylene failed. However, the unsubstituted enynes have been shown to form the dihydrofurans in good yield,\(^{(197)}\) and the cycloaddition reaction should be more facile, as the proposed transition state now mimics that of the cyclopropane more closely.

A brief attempt was made to transfer this chemistry to the cobalt-molybdenum core. This could be useful for several reasons. Firstly the chirality of the core may help with some diastereoselectivity. Secondly, the cation in these systems is more stable, possibly facilitating easier opening of the dihydrofuran, and finally the unsubstituted enyne can be made from the corresponding alcohol in good yields on this system by adding HBF\(_4\) then Hüning's base (Scheme 121).

![Scheme 121]

Unfortunately, despite extended reaction times and higher temperatures the Mn(OAc)\(_3\) mediated reaction only starting material was recovered.

The dicobalt hexacarbonyl complex (274) was successfully displaced to the cobalt molybdenum complex however an attempt to perform the cycloaddition reaction was inconclusive (a very small product spot was isolated but decomposed before analysis). This is an area for further investigation.
2.8 Conclusion

A range of novel bimetallic-alkyne complexes, desymmetrised with an N-heterocyclic carbene ligand have been successfully synthesised in moderate to good yield. The chemistry of these complexes has been investigated, and resulted in the first highly diastereoselective thermal PKR on a bis-cobalt alkyne complex (Scheme 122). In addition the mechanism of epimerisation has been investigated.

\[
\text{Scheme 122}
\]

The problem of the addition of carbon nucleophiles to the cobalt-molybdenum-alkyne complex has been partially solved via the use of zinc mediated Barbier type couplings. However this reaction unfortunately scrambles the stereochemistry of the complexes leading to poor diastereoselectivity (Scheme 123). The mechanism of the reaction is still unknown with both ionic and radical mechanisms possible, however; the speed of the reaction suggests it may be radical rather than proceeding by the formation of discreet
organozinc intermediates as these are suggested to form slowly under the reaction conditions.\(^{(170)}\)

\[
\begin{array}{c}
\text{Zn/Cu, R'Br, THF, 60 °C, 10 to 15 min} \\
\begin{array}{c}
\text{(OC)_{3}Co} \\
\text{MoCp(CO)_{2}} \\
\end{array}
\end{array}
\rightarrow
\begin{array}{c}
\text{(OC)_{3}Co} \\
\text{MoCp(CO)_{2}} \\
\end{array}
\]

\text{BF}_{4}^{\ominus}

\text{Scheme 123}

The possibility of forming an anion at the site \(\alpha\) to the complexed alkyne has been thoroughly explored; it is suggested that this is intrinsically unfavoured on these complexes (Scheme 124).

\[
\begin{array}{c}
\text{(OC)_{3}Co} \\
\text{MoCp(CO)_{2}} \\
\end{array}
\xrightarrow{\text{Base}}
\begin{array}{c}
\text{(OC)_{3}Co} \\
\text{MoCp(CO)_{2}} \\
\end{array}
\]

\text{Scheme 124}

The use of dihydrofurans as an alternative to the cyclopropane methodology has been shown to work in principle (Scheme 125).
Preliminary research into the use of Nicholas methodology as an initiator for biomimetic cascade reactions has been performed. Although currently unsuccessful it is suggested that with the correct choice of substrate this work could yield some interesting results, with the possibility of diastereoselective cascade reactions being performed via the use of a desymmetrised bimetallic core.

2.9 Further work

Currently the reactivity of the disubstituted dihydrofurans is being investigated by E. Allart following the successful formation via a Sonogashira coupling (Scheme 126).
These substrates should be less sterically crowded in the (proposed) transition state and hopefully they will elucidate whether these complexes are a viable alternative to the alkynyl cyclopropane complex (255).

The biomimetic cascade reactions may yield some results, particularly when used in conjunction with the 1,3-dipolar cycloaddition methodology developed by R. Davoile\(^{(149)}\) using the substrates proposed in schemes (110 and 111).

Although organocuprate species were not thought to suitable substrates for the attempted Michael addition reactions (sec 2.3.2). The later successful use of organozinc reagents suggests that these substrates may be worth further investigation, particularly as a radical or ionic mechanisms can be proposed for conjugate addition with these reagents with initial \(\pi\)-complexation a proposed intermediate (Scheme 127).\(^{(205)}\)

![Scheme 127](image-url)
### 3.0 Experimental

#### General information

All reactions herein were carried out in one of the following solvents, which were dried and purified, or purchased in the following procedures.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Processing Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Stirred over anhydrous potassium carbonate, followed by distillation over anhydrous calcium sulphate.</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>Purchased from Aldrich (99.8 %), Sure/Seal™ anhydrous quality.</td>
</tr>
<tr>
<td>Benzene</td>
<td>Purchased from Aldrich (99+ %) and used without further purification.</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Purchased from Fischer Scientific (99+ %) used without purification for general use or distilled over CaH₂ for anhydrous reactions.</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>For general use DCM was distilled over boiling chips or CaH₂ for anhydrous reactions.</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>Purchased from Fischer Scientific (99+ %) used without purification for general use or distilled over sodium and benzophenone for anhydrous reactions.</td>
</tr>
<tr>
<td>Diglyme</td>
<td>Distilled over sodium.</td>
</tr>
<tr>
<td>1,2-Dimethoxyethane</td>
<td>Purchased from Lancaster (99+ %) degassed by purging under a flow of nitrogen before use.</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>Purchased from Aldrich, Sure/Seal™ anhydrous quality.</td>
</tr>
<tr>
<td>Dimethysulfide</td>
<td>Purchased from Aldrich (99+ %) and used without further purification.</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>Distilled over CaCl₂ for general use.</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>Purchased from Fischer Scientific (99+ %) and used without further purification.</td>
</tr>
<tr>
<td>Light petroleum</td>
<td>Distilled over boiling chips for general use, collecting the fraction distilling below 60 °C.</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>Distilled over sodium and benzophenone.</td>
</tr>
</tbody>
</table>
Mo(CO)\textsubscript{6} was purchased from Fluka and Co(CO)\textsubscript{8} from Strem (stabilised by 1-5 % hexane), both were used without any further purification.

Anhydrous reactions were extensively flame-dried under an atmosphere of nitrogen. All metal carbonyl complexes were stored under a nitrogen atmosphere and kept at \(-18\) °C in a freezer.

Analysis of the compounds created herein was made using a number of the following instruments and procedures.

High resolution mass spectroscopy was carried out on a Jeol SX 102 machine, used for both electron ionisation [El] and fast atom bombardment [FAB] ionisation techniques. For FAB spectroscopy a matrix of 1,3-nitrobenzylalcohol was used to dissolve the compounds under investigation prior to ionisation. Nuclear magnetic resonance spectroscopy was acquired using a Bruker DPX 400 instrument. The spectra were calibrated where possible to the signals of tetramethylsilane or the small quantity of CHCl\textsubscript{3} present in CDCl\textsubscript{3}, typically used as the solvent for these experiments. Where possible coupling constants (\(J\)) are shown denoting the multiplicity as a singlet (s), doublet (d), triplet (t), quarter (q), multiplet (m) or broad signal (br) etc. The size of the coupling constants is given in Hertz (Hz). Elemental analysis was carried out using a Perkin Elmer CHN 2400 elemental analyser. Fourier transform Infra Red spectroscopy was recorded using a Paragon 1000 Perkin Elmer FT-IR spectrophotometer in the range of 3500-600 cm\(^{-1}\) following a standard background correction. Melting points of solid products were recorded using a Stuart Scientific SMP3 instrument.

Flash silica column chromatography was used as a standard purification procedure using Fluka Kiesel gel 60, 0.04-0.063 mm particle size. Thin layer chromatography was used where possible as a standard procedure for monitoring the course and rate of a given reaction. TLC plates used were Merk aluminium backed sheets with Kiesel gel 60 F\textsubscript{254} silica coating.
Dicobalt hexacarbonyl-phenylacetylene (83)\(^{(4)}\)

Phenylacetylene (0.270 g, 2.66 mmol) was added to a solution of dicobalt octacarbonyl (0.917 g, 2.66 mmol) in DCM (20 mL) under an atmosphere of nitrogen. After 12 h the dark purple solution was filtered through a plug of celite and silica, concentrated in vacuo then purified via flash silica chromatography (18 : 1 petroleum ether : diethyl ether), to yield the title compound as a dark red viscous oil (0.885 g, 86 %); \(v_\text{max}\) (thin film)/\(\text{cm}^{-1}\) 3075, 3023 (CH), 2093, 2052, 2020 (M-CO), 1443, 877, 690 (selected fingerprint); \(\delta\)H (400 MHz; CDCl\(_3\)) 7.57-7.61 (2H, m, H5), 7.34-7.40 (3H, m, H4, H6), 6.39 (1H, s, H1); \(\delta\)C (100.6 MHz; CDCl\(_3\)) 199.3 (q, M-CO), 137.4 (q, C3), 130.2 (2 x CH, C5), 128.8 (2 x CH, C4), 128.0 (CH, C6), 90.2 (q, C2), 72.5 (CH, C1).

Dicobalt hexacarbonyl-prop-2-ynol (84)\(^{(4,42)}\)

Prop-2-ynol (0.66 mL, 11.22 mmol) was added to a solution of dicobalt octacarbonyl (3.837 g, 11.22 mmol) in DCM (40 mL) under an atmosphere of nitrogen. After 12 h the dark purple solution was filtered through a plug of celite and silica then concentrated in vacuo to yield the title compound as a dark red solid (3.730 g, 97 %); mp 49-50 °C (Lit 52 °C); \(v_\text{max}\) (thin film)/\(\text{cm}^{-1}\) 3376 (OH), 2918, 2850 (CH), 2096, 2052, 2020 (M-CO), 1031, 987 (selected fingerprint); \(\delta\)H (250 MHz; CDCl\(_3\)) 6.07 (1H, t, \(J 1.0\) Hz, H1), 4.80 (2H, dd, \(J 2.0\) Hz, C4, C5).
6.2 Hz, J 1.0 Hz, H3), 1.88 (1H, t, J 6.2 Hz, H4); δC (100.6 MHz; CDCl3) 199.4 (q, M-CO), 95.1 (q, C2), 71.2 (CH, C1), 63.4 (CH2, C3).

Dicobalt hexacarbonyl -1-isopropyl-4-methyl-2-prop-2-ynyloxycyclohexane (88)

L-menthol (11.900 g, 76.30 mmol), was added to a solution of dicobalt hexacarbonyl propynol (5.222 g, 15.20 mmol) and 4Å molecular sieves in dry DCM (200 mL). BF3.OEt (3.80 mL, 30.40 mmol) was then added and the solution stirred for 12 h at ambient temperature under an atmosphere of nitrogen. The solution was filtered through a plug of celite and silica then concentrated in vacuo before purification via flash silica chromatography (100 % petroleum ether), to yield the title compound as a dark red oil (6.078 g, 83 %); [α]D = +7.3° (C= 0.111, CHCl3); νmax (thin film)/cm⁻¹ 2957, 2925, 2870 (CH), 2095, 2057, 2020 (M-CO), 1456, 1090 (selected fingerprint); δH (400 MHz; CDCl3) 6.01 (1H, s, H1), 4.70 (1H, d, J 12.7 Hz, H3), 4.47 (1H, d, J 12.7 Hz, H3), 3.22 (1H, dt, J 10.7 Hz, J 4.1 Hz, H4), 2.29 (1H, d sept, J 7.2 Hz, J 2.8 Hz, H10), 2.11 (1H, m, H9), 1.56-1.71 (2H, m, H5), 1.46-1.56 (2H, m, H7/H8), 0.82-1.08 (3H, m, H7/H8 and H6), 0.93 (3H, d, J 6.8 Hz, H11/H13), 0.88 (3H, d, J 6.8 Hz, H12/H13), 0.78 (3H, d, J 6.9 Hz, H11); δC (100.6 MHz; CDCl3) 200.1 (q, M-CO), 93.4 (q, C2), 79.8 (CH, C1), 71.5 (CH, C4), 68.7 (CH2, C3), 48.6 (CH, C10), 40.7 (CH2, C8), 34.9 (CH2, C7), 32.0 (CH, C6), 25.7 (CH, C9), 23.6 (CH2, C5), 21.3, 22.7 (CH3, C12, C10), 16.4 (CH3, C13).
4-[[5-Methyl-cyclohexyl]oxy]methyl]tricyclo[5.2.1.0\(^{26}\)deca-4,8-diene-3-one (91)\(^{(77,78)}\)

First eluting diastereoisomeric complex

Pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazoliumdicobaltpentacarbonyl propargylmenthoether (0.184 g, 0.23 mmol) and norbornadiene (0.25 mL, 23 mmol), were added to dimethoxyethane (10 mL) in around bottomed flask fitted with a reflux condenser. The solution was stirred at 70 °C for 2 h while being monitored for the disappearance of the starting material by TLC. The resulting solution was filtered through a pad of celite, rotary evaporated to dryness then purified via flash silica chromatography (9 : 1 petroleum ether : diethyl ether) to yield the title compound as a colourless oil (0.068 g, 95 %, (87 % d.e.));  \(\nu_{\text{max}}\) (thin film)/cm\(^{-1}\) 3056, 2974, 2938, (CH), 1695 (CO), 1617 (C=C), 1591, 1442, 1347, 1167, 911 (selected fingerprint);  \(\delta\)H (400 MHz; CDCl\(_3\))  7.41-7.43 (1H, m, H5), 6.29 (1H, dd, J 5.6 Hz, J 2.8 Hz, H8/H9), 6.21 (1H, dd, J 5.6 Hz, J 2.8 Hz, H8/H9), 4.32 (1H, m, 1 x H11), 3.97-4.02 (1H, m, 1 x H11), 3.09 (1H, dt, J 4.1 Hz, J 9.9 Hz, H12), 2.93 (1H, s, H6), 2.77 (1H, s, H7), 2.76 (1H, s, H1), 2.33 (1H, dd, J 3.3 Hz, J 1.2 Hz, H2), 2.26-2.27 (2H, m, H17, H18), 1.55-1.59 (2H, m, H10), 1.19-1.43 (4H, m, H15, H16), 0.81-1.02 (8H, m, H13, H14, H19, H19'), 0.77 (3H, d, J 7.2 Hz, H20);  \(\delta\)C (100.6 MHz; CDCl\(_3\)) 209.8 (q, C3), 160.6, 160.2 (CH, C5), 148.9 (q, C4), 138.9 (CH, C8/C9), 137.5 (CH, C8/C9), 80.5, 80.2 (CH, C12), 62.8, 62.4 (CH, C11), 53.5 (CH, C2), 48.6 (2 x CH, C7, C18), 44.0 (CH, C6/C1), 43.4 (CH, C6/C1), 41.7 (CH, C10), 40.7 (CH, C15/C16), 34.9 (CH, C15/C16), 31.9 (CH, C14), 26.2 (CH, C17), 23.8 (CH, C13), 22.7 (CH, C19/C19'), 21.2 (CH, C19/C19'), 16.8 (CH, C20). (peaks for major diastereoisomer underlined)
Later eluting diastereoisomeric complex

Pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazoliumdicobaltpentacarbonyl propargylinmethylether (0.227 g, 0.28 mmol) and norbornadiene (0.31 mL, 28 mmol), were added to dimethoxyethane (12 mL) in around bottomed flask fitted with a reflux condenser. The solution was stirred at 70 °C for 2 h while being monitored for the disappearance of the starting material by TLC. The resulting solution was filtered through a pad of celite, rotary evaporated to dryness then purified via flash silica chromatography (9 : 1 petroleum ether : diethyl ether) to yield the title compound as a colourless oil (0.077 g, 87 %, (92 % d.e)); ν<sub>max</sub> (thin film)/cm<sup>-1</sup> 3056, 2974, 2938, (CH), 1695 (CO), 1617 (C=C), 1591, 1442, 1347, 1167, 911 (selected fingerprint); δH (400 MHz; CDCl<sub>3</sub>) 7.41-7.43 (1H, m, H5), 6.29 (1H, dd, J 5.6 Hz, J 2.8 Hz (H8/H9)), 6.21 (1H, dd, J 5.6 Hz, J 2.8 Hz, H8/H9)), 4.32 (1H, m, 1 x H11), 3.97-4.02 (1H, m, 1 x H11), 3.09 (1H, dt, J 4.1 Hz, J 9.9 Hz, H12), 2.93 (1H, s, H6), 2.77 (1H, s, H7), 2.76 (1H, s, H1), 2.33 (1H, dd, J 3.3 Hz, J 1.2 Hz, H2), 2.26-2.27 (2H, m, H17,H18), 1.55-1.59 (2H, m, H10), 1.19-1.43 (4H, m, H15,H16), 0.81-1.02 (8H, m, H13,H14,H19,H19'), 0.77 (3H, d, J 7.2 Hz, H20); δC (100.6 MHz; CDCl<sub>3</sub>) 209.1 (q, C3), 160.7, 160.3 (CH, C5), 148.8 (q, C4), 138.9 (CH, C8/C9), 137.4 (CH, C8/C9), 80.7, 80.3 (CH, C12), 62.8, 62.4 (CH<sub>2</sub>, C11), 53.5 (CH, C2), 48.6 (2 x CH, C7,C18), 43.9 (CH, C6/C1), 43.3 (CH, C6/C1), 41.7 (CH<sub>2</sub>, C10), 40.7 (CH<sub>2</sub>, C15/C16), 34.8 (CH<sub>2</sub>, C15/C16), 31.9 (CH, C14), 26.2 (CH, C17), 23.8 (CH<sub>2</sub>, C13), 22.7 (CH<sub>3</sub>, C19/C19'), 21.2 (CH<sub>3</sub>,C19/C19'), 16.8 (CH<sub>3</sub>,C20). (Major peaks for diastereoisomer underlined)

Hexacarbonyl bis-(cyclopentadienyl) dimolybdenum (171)<sup>145,146</sup>

Molybdenum hexacarbonyl (8.800g, 33.3 mmol) was dissolved in anhydrous acetonitrile (100 mL) under an atmosphere of nitrogen and heated to reflux for 2 h. The acetonitrile was
then removed *in vacuo*, under a to leave the yellow solid molybdenum tricarbonyl-
triacetonitrile complex.

30 min before the finish of the above preparation, freshly distilled cyclopentadiene (6.00
mL, 70 mmol) was added dropwise to a solution of NaH (65 % disp in mineral oil) (2.00 g,
50 mmol) in dry THF at 0 °C, the solution was then warmed to ambient temperature, with
the formation of the cyclopentadiene anion visible as a colour change of the solution from
colourless to deep red. This solution was then added *via* cannular to the unstable solid
molybdenum tricarbonyl-triacetonitrile complex. The solution was then heated to reflux for
2 h with the colour altering to a deep yellow. After cooling to ambient temperature,
methanol (5 ml) was added followed by distilled water (5 mL). A pre-filtered solution
containing distilled water (250 mL), concentrated acetic acid (15 mL) and iron (III)
sulphate (20.00 g) was then added to the solution, after which a purple precipitate was seen
to form. This was filtered and washed with distilled water (250 mL), cold methanol (50
mL) then cold hexane (50 mL). The product was then dried to yield the title complex as a
dark purple powder (5.518 g, 67 %); $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 2951 (CH), 1950, 1900,
1884 (M-CO), 1417, 1264, 863 (selected fingerprint; $\delta$H (400 MHz; CDCl$_3$) 5.29 (10H, s, CH);
$\delta$C (100.6 MHz; CDCl$_3$) 229.5, 229.3 (M-CO), 92.4 (5 x CH).

**Dicobalt hexacarbonyl-propynol ethylether (173)**

![Diagram of Dicobalt hexacarbonyl-propynol ethylether]

Tetrafluoroboric acid (0.63 mL, 4.60 mmol) was added dropwise to a solution of dicobalt
hexacarbonyl propynol (1.298 g, 3.80 mmol) in dry DCM (70 mL) and 4 Å mol sieves at
ambient temperature under an atmosphere of nitrogen. The solution was then left to stir for
5 min, then dry ethanol (3 mL) added. This solution was left to stir for 1 h then filtered
through a plug of celite and silica, before purification via flash silica chromatography (15 : 1 petroleum ether: diethyl ether) to yield the title compound as a dark red oil (1.183 g, 85 %); C_{11}H_{18}Co_{2}O_{7}, HRMS [FAB](M^+-CO), required 369.8934, found 369.8926; \( \nu_{\text{max}} \) (thin film)/cm\(^{-1}\) 2980, 2932, 2870 (CH), 2051, 2095, 2021, 1975 (M-CO), 1548, 1331, 1100 (selected fingerprint); \( \delta \)H (400 MHz; CDCl\(_3\)) 6.04 (1H, s, H1), 4.63 (2H, s, H3), 3.64 (2H, q, J 7.0 Hz, H4), 1.24 (3H, t, J 7.0 Hz, H5); \( \delta \)C (100.6 MHz; CDCl\(_3\)) 199.6 (q, M-CO), 91.7 (q, C2), 72.1 (CH, C1), 71.2 (CH\(_2\), C2), 66.2 (CH\(_2\), C4), 14.9 (CH\(_3\), C5); \( m/z \) 370 (M\(^{+}\), 23 %), 342 (68 %), 314 (58 %), 286 (76 %), 258 (67 %), 230 (54 %), 202 (38 %).

**Dicobalt hexacarbonyl-1-ethoxy-prop-2-ynyl-benzene (174)**

Tetrafluoroboric acid (0.75 mL, 5.50 mmol) was added dropwise to a solution of dicobalt hexacarbonyl 1-phenyl-2-propynol (2.075 g, 5.00 mmol) in dry DCM (200 mL) and 4 Å mol sieves at ambient temperature. The solution was then left to stir for 10 min then dry ethanol (3 mL) added, followed by Hünigs base after a further 20 min. After another 10 min the solution was filtered through a plug of celite and silica, before purification via flash silica chromatography (8 : 1 petroleum ether: diethyl ether) to yield the title compound as a dark red oil (2.214 g, 93 %); C\(_{17}\)H\(_{12}\)Co\(_{2}\)O\(_{7}\), HRMS [FAB](M^+-CO), required 417.9298, found 417.9306; \( \nu_{\text{max}} \) (thin film)/cm\(^{-1}\) 3086, 3028, 2977, 2930, 2869 (CH), 2093, 2052, 2026 (M-CO), 1451, 1100, 702 (selected fingerprint); \( \delta \)H (400 MHz; CDCl\(_3\)) 7.35-7.27 (5H, m, H5-H7), 5.99 (1H, s, H1), 5.39 (1H, s, H3), 3.61 (2H, q, J 6.8 Hz, H8), 1.26 (3H, t, J 6.8 Hz, H9); \( \delta \)C (100.6 MHz; CDCl\(_3\)) 199.4 (q, C10), 142.8 (q, C4), 128.5 (2 x CH, C6), 127.9 (CH, C7), 126.1 (2 x CH, C5), 99.4 (q, C2), 81.4 (CH, C3), 71.8 (CH, C1), 65.0
(CH₂, C8), 15.1 (CH₃, C9); m/z 418 (M⁺-CO, 27 %), 390 (11 %), 362 (100 %), 334 (63 %), 306 (56 %), 278 (11 %).

Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-propynyl ethyl ether

(175)

K-selectride® (3.51 mL, 3.51 mmol), was added dropwise to a solution of hexacarbonyl bis-(cyclopentadienyl) dimolybdenum (0.7840 g, 1.60 mmol) in dry THF (20 mL) under a nitrogen atmosphere. The solution was left to stir at ambient temperature for 1 h, with a colour change from red to orange observed. Dicobalt hexacarbonyl propynol (1.1826 g, 3.19 mmol) was then added and the solution heated under reflux for 2 h. The crude product was then filtered through a plug of celite and silica, before purification via flash silica chromatography (10 : 1 petroleum ether: diethyl ether) to yield the title compound as a dark red oil (0.1230 g, 87 %); C₁₅H₁₃CoMoO₆, HRMS [FAB](M⁺), required 445.9098, found 445.9014; v max (thin film)/cm⁻¹ 2974, 2927, 2861 (CH), 2048, 1992, 1942 (M-CO), 1097, 815 (selected fingerprint); δH (400 MHz; CDCl₃); 5.68 (1H, s, H1), 5.43 (5H, s, H6), 4.61 (2H, m, H3), 3.50-3.62 (2H, m, H4), 1.21 (3H, t, J 7.0 Hz, H5); δC (100.6 MHz; CDCl₃); 225.4, 225.2 (q, M-CO), 90.4 (5 x CH, C6), 88.4 (q, C2), 74.9 (CH, C1), 73.6 (CH₂, C3), 66.1 (CH₂, C4), 15.1 (CH₃, C5); m/z 445 (M⁺, 18 %), 417 (32 %), 389 (100 %), 361 (73 %), 333 (36 %), 305 (14 %).
L-Selectride® (2.92 mL, 2.92 mmol) was added dropwise to a solution of hexacarbonyl bis-
(cyclopentadienyl) dimolybdenum (0.573 g, 1.17 mmol) in dry THF (25 mL) under a
nitrogen atmosphere. The solution was left to stir at ambient temperature for 1 h, with a
colour change from red to yellow observed. Dicobalt hexacarbonyl prop-2-ynol (0.800 g,
2.34 mmol) was then added and the solution refluxed for 2 h. The crude product was then
filtered through a plug of celite and silica, before purification via flash silica
chromatography (6.5 : 3.5 petroleum ether / diethyl ether) to yield the title compound as a
dark red oil (0.350 g, 36 %); ν\text{max} (thin film)/cm\text{-}1 3394 (OH), 2919 (CH), 2049, 1974,
1983, 1884 (M-CO) 1420, 1014, 817 (selected fingerprint); δH (250 MHz; CDCl\text{3}) 5.68
(1H, s, H1), 5.45 (5H, s, H5), 4.95-4.88 (1H, m, 1 x H3), 4.74-4.66 (1H, m, 1 x H3), 1.59
(1H, m, H4); δC (100.6 MHz; CDCl\text{3}) 224.9, 203.5 (q, M-CO), 90.2 (5 x CH, C5), 88.6
(CH, C2), 75.2 (CH, C1), 67.3 (CH\text{2}, C3).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-l-ethoy-prop-2-vnvl-
benzene (176)**
K-selectride® (4.98 mL, 4.98 mmol), was added dropwise to a solution of hexacarbonyl bis-(cyclopentadienyl) dimolybdenum (0.975 g, 1.99 mmol) in dry THF (60 mL) under a nitrogen atmosphere. The solution was left to stir at ambient temperature for 1 h, with a colour change from red to dark green observed. Dicobalt hexacarbonyl 1-ethoxy-prop-2-ynyl-benzene (2.144 g, 4.80 mmol) was then added and the solution heated under reflux for 45 min. The crude product was then filtered through a plug of celite and silica, before purification via flash silica chromatography (9 : 1 petroleum ether: diethyl ether) to yield the title compound as a dark red oil (1 : 1 mixture of inseparable diastereoisomers (1.522 g, 73 %); C_{21}H_{17}CoMoO_{6}, HRMS [FAB](M^+-CO), required 493.9462, found 493.9470; ν_{max} (thin film)/cm^{-1} 3110, 3025, 2973, 2972, 2868 (CH), 2049, 1982, 1936 (M-CO), 1490, 1095, 815 (selected fingerprint); δH (250 MHz; CDCl₃) 7.25-7.30 (5H, m, H₅,6,7), 5.75 (1H, s, H1), 5.32 (5H, s, H10), 5.18 (1H, s, H3), 3.37-3.60 (2H, m, H₈), 1.21 (3H, t, J 7.0Hz); δC (100.6 MHz; CDCl₃) 226.1, 224.9 (q, M-CO), 143.8 (q, C₄), 128.5 (2 x CH, C₆), 128.2 (CH, C₇), 127.5 (2 x CH, C₅), 94.9 (q, C₂), 90.2, 89.9 (5 x CH, C₁₀), 85.1, 84.9 (CH, C₃), 79.2 (CH, C₁), 64.6, 64.5 (CH₂, C₈), 15.2 (CH₃, C₉); m/z 494 (8 %), 466 (12 %), 449 (18 %).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-propyne tetrafluoroborate (177)^{(147,157)}**

\[
\begin{array}{c}
\text{H} \\
(\text{OC})_{3}\text{Co-MoCp(CO)₂} \\
\text{BF₄}^-
\end{array}
\]

Tetrafluoroboric acid (0.13 mL, 0.92 mmol) was added dropwise to a solution of cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-propynol (0.350 g, 0.84 mmol) in diethyl ether (15 mL) at ambient temperature under a nitrogen atmosphere. The solution was stirred for 15 min during which a bright orange precipitate formed. The solution was then filtered and washed with further portions of diethyl ether until the
washings remained colourless. The solid was then dried to yield the \textit{title compound} as a bright orange solid (0.290 g, 71 %); mp 123-135 °C; C\textsubscript{13}H\textsubscript{8}CoMoO\textsubscript{5}BF\textsubscript{4}, required C 32.1 \%, H1.7 \%, found C 30.9 \%, H 1.7 \%; HRMS [FAB](M\textsuperscript{+}-BF\textsubscript{4}), required 400.8758, found 400.8762; \(\nu_{\text{max}}\) (thin film)/cm\textsuperscript{-1} 2096, 2053, 1899, 1890 (M-CO), 1420, 1061, 1035 (selected fingerprint); m/z 401 (M\textsuperscript{+}-BF\textsubscript{4}, 31 \%), 373 (52 \%), 345 (35 \%), 317 (30 \%), 289 (22 \%), 261 (22 \%).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-(prop-2-yn-1-sulfonyl)-benzene (178)**

![Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-(prop-2-yn-1-sulfonyl)-benzene (178)](image)

Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-propyne tetrafluoroborate (0.170 g, 0.35 mmol) and benzenesulphinic acid sodium salt (0.115 g, 0.70 mmol), were added to a flame dried flask under an atmosphere of nitrogen. Anhydrous acetonitrile (10 mL) was then added and the resulting solution stirred for 20 min. The solution was then filtered through a pad of celite and silica the concentrated \textit{in vacuo} to yield the \textit{title complex} as an orange oil (0.180 g, 95 %); C\textsubscript{19}H\textsubscript{13}CoMoO\textsubscript{7}S, HRMS [FAB](M\textsuperscript{+}-2CO), required 485.8869, found 485.8866; \(\nu_{\text{max}}\) (thin film)/cm\textsuperscript{-1} 3114 (CH), 2052, 1984, 1887 (M-CO), 1316, 1307, 1149, 1085, 1023 (selected fingerprint); \(\delta\)H (400 MHz; CDCl\textsubscript{3}); 7.93 (2H, d, \(J\) 7.8, H5), 7.55-7.67 (3H, m, H6 and H7), 5.95 (1H, s, H1), 5.47 (5H, s, H8), 4.44 (2H, s, H3); \(\delta\)C (100.6 MHz; CDCl\textsubscript{3}); 203.4, 201.2 (q, M-CO), 139.9 (q, C4), 133.8 (CH, C7), 129.3 (2 \(x\) CH, C5), 127.9 (2 \(x\) CH, C6), 91.5 (5 \(x\) CH, C8), 90.4 (q, C2), 81.7 (CH, C1), 61.6 (CH, C3); m/z 514 (M\textsuperscript{+, 7 \%}), 486 (22 \%), 458 (100 \%), 430 (9 \%), 402 (18 \%).
Cyclpentadienyl molybdenum dicarbonyl cobalt tricarbonyl propynyl phenylsulfide

(182)\(^{157}\)

\[
\begin{array}{c}
\text{H} \\
\text{S} \\
\text{OC}_{3}\text{Co-MoCp(CO)_{2}}
\end{array}
\]

Cyclpentadienyl molybdenum dicarbonyl cobalt tricarbonyl-propyne tetrafluoroborate salt (0.366 g, 0.75 mmol) was dissolved in anhydrous acetonitrile (15 mL) then sodium thiophenolate (0.120 g, 0.90 mmol) was added and the resulting solution stirred for 10 min. The solution was then filtered through a pad of celite and silica then concentrated in vacuo to yield the title complex as an orange oil (0.223 g, 58 %); \text{C}_{19}\text{H}_{13}\text{CoMoO}_{6}\text{S}, \text{HRMS [FAB]}(\text{M}^{+}-\text{CO}), \text{required } 481.8921, \text{found } 481.8921; \nu_{\text{max}}\text{ (thin film)/cm}^{-1} 2048, 1979, 1939 (\text{M}^{+}-\text{CO}), 1581, 1417, 816 \text{ (selected fingerprint); } \delta\text{H (400 MHz; CDCl}_{3}\text{); } 7.34-7.14 (5\text{H, m, Ar-H}), 5.56 (1\text{H, s, H1}), 5.29 (5\text{H, s, H8}), 4.36 (1\text{H, d, } J 14.4 \text{ Hz, 1 x H3}), 4.21 (1\text{H, d, } J 14.4 \text{ Hz, 1 x H3}); \delta\text{C (100.6 MHz; CDCl}_{3}\text{); } 226.2, 225.7 \text{ (q, M-CO), } 136.4 \text{ (q, C4), } 129.1 \text{ (2 x CH, C6), } 128.9 \text{ (2 x CH, C5), } 126.2 \text{ (CH, C7), } 90.8 \text{ (5 x CH, C8), } 83.4 \text{ (q, C2), } 79.8 \text{ (CH, C1), } 40.0 \text{ (CH}_{2}\text{, C3) }; m/z 482 \text{ (M}^{+}-\text{CO, } 7 \text{ %), } 426 \text{ (100 %), } 398 \text{ (18 %), } 370 \text{ (53 %).}

1-Bromo-2-phenyl acetylene (190)\(^{158}\)

\[
\begin{array}{c}
\text{Ph} \\
\equiv 
\end{array}
\]

TBAHSO\text{4} (6.11 g, 18.0 mmol), was added to a solution of NaBr (5.56 g, 54.0 mmol) in NaOCl (8 % available, 32 mL) and stirred until a yellow semi-solid precipitate and red oily layer became visible. Phenylacetylene (0.92 g, 9.0 mmol) in hexane (20 mL) was then
added and the solution stirred vigorously for 1h at ambient temperature. The reaction mixture was then allowed to separate, then the hexane layer removed. The orange interfacial layer was then extracted with hexane (2 x 20 mL). The combined hexane layers were then washed sequentially with saturated brine, 10 % NaHCO₃ then 5 % NaHSO₄.

After drying over MgSO₄ the product was concentrated in vacuo to yield the title complex (1.23 g, 75 %) as a pale yellow oil. No further purification was required; δH (250 MHz; CDCl₃) 7.36-7.54 (5H, m, Ar-H); νmax (thin film)/cm⁻¹ 3061, 2923, 2360, 2200.

The product corresponded to the literature values. No further analysis was undertaken as these compounds were found to be explosive.

Dicobalt hexacarbonyl-1-bromo-2-phenylacetylene (191)

1-bromo-2-phenylacetylene (1.46 g, 8.1 mmol) was added to a solution of dicobalt octacarbonyl (2.80 g, 8.1 mmol) in DCM (50 mL) under an atmosphere of nitrogen. After 12 h the black solution was filtered through a plug of celite and silica, concentrated in vacuo then purified via flash silica chromatography (4 : 1 petroleum ether : diethyl ether), to yield the title compound as a black solid (3.09 g, 83 %); δH (250 MHz; CDCl₃) 7.41-7.54 (5H, m, Ar-H); νmax (thin film)/cm⁻¹ 2095, 2058 (M-CO), 759, 691 (selected fingerprint).

Further analysis was found to be impossible as the product rapidly decomposed.
n-butyllithium (1.58 mL, 2.53 mmol) was added dropwise to a solution of phenylacetylene (0.93 mL, 1.95 mmol) in dry THF under an atmosphere of nitrogen at 0 °C. The mixture was left to stir at 0 °C for 1 h then n-tributyltin chloride (0.63 mL, 2.34 mmol) added. The mixture was the left to stir for 12 h while gradually warming to ambient temperature. The reaction was quenched with water (2.0 mL) then concentrated in vacuo. The product was then extracted into petroleum ether, washed with water and dried over MgSO₄. The product was purified via flash silica chromatography (8 : 1 petroleum ether : diethyl ether) to yield the title compound (1.530 g, 66 %) as a pale yellow oil. νₘₐₓ (thin film)/cm⁻¹ 3053, 2957, 2852, 2143 (CH); δH (250 MHz; CDCl₃) 7.42-7.45 (2H, m, H₂), 7.25-7.28 (3H, m, H₁, H₃), 0.88-1.69 (27H, qm, H₆).

Dicobalt hexacarbonyl-1-(n-Tributyltin)-2-phenylacetylene (193)

1-(n-Tributyltin)-2-phenylacetylene (0.35 mL, 1.00 mmol) was added to a solution of dicobalt octacarbonyl (0.342 g, 1.00 mmol) in DCM (20 mL) under an atmosphere of nitrogen. After 4 h the black solution was filtered through a plug of celite and silica, concentrated in vacuo then purified via flash silica chromatography (100 % petroleum
ether), to yield the title compound as a black solid (0.730 g, 96 %); \( \nu_{\text{max}} \) (thin film)/cm\(^{-1} \) 3073, 2957, 2927, 2831, 2803 (CH), 2080, 2041, 2011 (M-CO), 1596, 1570, 1484, 1071 (selected fingerprint); \( \delta \)H (250 MHz; CDCl\(_3\)) 7.48-7.46 (2H, m, H2), 7.33-7.30 (3H, m, H1, H3), 1.64-1.56 (m, 6H, H7), 1.40-1.34 (6H, m, H8), 1.34-1.32 (6H, m, H9), 0.89 (9H, t, J 6.3Hz); \( \delta \)C (100.6 MHz; CDCl\(_3\)) 200.6 (q, M-CO), 138.3 (q, C4), 130.1 (2 x CH, C2), 128.7 (2 x CH, C3), 127.8 (CH, C1), 107.0 (q, C5), 29.1 (CH\(_2\), C7), 27.4 (CH\(_2\), C8), 14.4 (CH\(_2\), C9), 14.4 (CH\(_3\), C10) (C6 missing).

Mass ion not found

**Dicobalt hexacarbonyl-butynal (199)**

\[
\begin{align*}
\text{(OC)}_3\text{Co} & \quad \text{Co(OC)}_3 \\
\end{align*}
\]

2-butynal diethyl acetal (0.730 g, 5.10 mmol) was added to a solution of dicobalt octacarbonyl (1.920 g, 5.61 mmol) in DCM (40 mL) under an atmosphere of nitrogen. The solution was left to stir at ambient temperature for 4 h then \( p \)-toluenesulfonic acid (a spatula measure, approx. 0.150 g), and distilled water (a few drops) were added. The solution was then stirred at ambient temperature for a further 12 h. Magnesium sulphate was then added and the deep red solution filtered through a plug of celite and silica. The product was purified via flash silica chromatography (20 : 1 petroleum ether : diethyl ether) to yield the title compound (1.400 g, 78 %) as a deep red oil; C\(_{10}\)H\(_4\)Co\(_2\)O\(_7\), HRMS [FAB](M\(^{+}\)) required 353.8621, found 353.8623; \( \nu_{\text{max}} \) (thin film)/cm\(^{-1} \) 2101, 2858, 2028 (M-CO), 1670 (CHO), 1428, 1074 (selected fingerprint); \( \delta \)H (400 MHz; CDCl\(_3\)) 10.30 (1H, s, H4), 2.73 (3H, s, H1); \( \delta \)C (100.6 MHz; CDCl\(_3\)) 198.0 (q, M-CO), 190.6 (CH, C4), 94.9 (q, C3), 87.5 (q, C2), 20.6 (CH\(_3\), C1); \( m/z \) 354 (M\(^{+}\), 3 %), 326 (75 %), 298 (84 %), 270 (92 %).
Dicobalt hexacarbonyl-methyl-(E)-hex-2-en4-ynoate (200)

\[
\begin{align*}
\text{(OC)}_3\text{Co} & \quad \text{Co(OC)}_3 \\
\end{align*}
\]

Methoxycarbonylmethyltriphenylphosphonium bromide (1.270 g, 3.06 mmol) was dissolved in water (100 mL). Solid sodium hydroxide (2 pellets) was then added and the solution stirred until a white precipitate formed. This was then extracted into DCM (3 x 10 mL), dried over magnesium sulphate then concentrated in vacuo to yield an off white solid. The solid was then dissolved in dry THF (30 mL) then added to a flame dried 3-necked flask containing a solution of dicobalt hexacarbonyl-2-butynal (0.903 g, 2.55 mmol) in dry THF (10 mL). The solution was then stirred at ambient temperature under an atmosphere of nitrogen for 12 h. The solution was filtered through a plug of celite and silica then purified via flash silica chromatography (20 : 1 petroleum ether : diethyl ether) to yield the title compound (0.957 g, 92 %) as a deep red oil; C_{13}H_8Co_2O_8, HRMS [FAB](M+) required 409.8883, found 409.8818; \nu_{max}\ [\text{thin film}]/\text{cm}^{-1} 2953, 2905, 2842 (CH), 2093, 2053, 2021 (M-CO), 1719, 1635 (CO_2CH_3), 1434, 1297, 1271, 1166 (selected fingerprint); \delta H (400 MHz; CDCl_3); 7.87 (1H, d, J 15.2 Hz, H5), 6.15 (1H, d, J 15.2 Hz, H4), 3.78 (3H, s, H7), 2.69 (3H, s, H1); \delta C (100.6 MHz; CDCl_3); 199.5, 198.9, 198.8, (q, M-CO), 169.7 (q, C6), 144.2 (CH, C5), 122.5 (CH, C4), 97.2 (q, C3), 86.3 (q, C2), 51.7 (CH_3, C7), 20.5 (CH_3, C1); m/z 410 (M^+, 21 %), 382 (54 %), 354 (71 %), 326 (100 %).
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-methyl-(E)-hex-2-en-4-ynoate (201)\(^{150,200}\)

K-Selectride\(^{®}\) (4.32 mL, 4.32 mmol), was added dropwise to a solution of hexacarbonyl bis-(cyclopentadienyl) dimolybdenum (0.848 g, 1.73 mmol) in dry THF (30 mL) under a nitrogen atmosphere. The solution was stirred at ambient temperature for 1 h, with a colour change from red to orange observed. Dicobalt hexacarbonyl-methyl-(E)-hex-2-en-4-ynoate (1.420 g, 3.46 mmol) was then added and the solution refluxed for 2 h. The crude product was then filtered through a plug of celite and silica, before purification via flash silica chromatography (15 : 1 petroleum ether: diethyl ether) to yield the title compound as a dark red oil (0.907 g, 54 %); \(\text{C}_{17}\text{H}_{13}\text{CoMoO}_{7}\), HRMS [FAB](M\(^+\)), required 485.9052, found 485.9053; \(\nu_{\text{max}}\) (thin film)/\(\text{cm}^{-1}\) 2939 (CH), 2050, 1981, 1973 (M-CO), 1708, 1614 (CO\(_2\)CH\(_3\)); \(\delta\)H (400 MHz; CDCl\(_3\)); 7.85 (1H, d, J 15.3 Hz, H5), 5.81 (1H, d, J 15.3 Hz, H4), 5.35 (5H, s, H8), 3.75 (3H, s, H7), 2.69 (3H, s, H1); \(\delta\)C (100.6 MHz; CDCl\(_3\)); 224.9, 223.2 (q, M-CO), 167.1 (q, C6), 149.7 (CH, C5), 119.1 (CH, C4), 101.4 (q, C3), 91.1 (5 x CH, C8), 82.0 (q, C2), 51.4 (CH\(_3\), C7), 20.8 (CH\(_3\), C1); \text{m/z} 486 (M\(^+\), 21 %), 458 (10 %), 430 (25 %), 402 (30 %), 374 (60 %).
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-ethyl-(E)-hex-2-en-4-ynoate

Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-ethyl-(E)-hex-2-en-4-ynoate (0.310 g, 0.64 mmol) in freshly distilled ethanol (10 mL), was added via cannular to a freshly prepared solution of sodium ethoxide (0.020 g, 0.76 mmol sodium in 20 mL ethanol) at 0 °C under an atmosphere of nitrogen. The solution was warmed to ambient temperature and stirred for 12 h. The crude product was then filtered through a plug of celite and silica, before purification via flash silica chromatography (5:1 petroleum ether: diethyl ether) to yield the title compound as a dark red oil (0.152 g, 48%); C_{18}H_{15}CoMoO_{7}, HRMS [FAB](M^+-CO), required 471.9254, found 471.9245; \nu_{\text{max}}\text{(thin film)}/\text{cm}^{-1} 2982, 2938, 2903 (CH), 2051, 1981, 1940 (M-CO), 1704, 1615 (CO_{2}CH_{3}), 1292, 1146, 817 (selected fingerprint); \delta H (400 MHz; CDCl_{3}); 7.77 (1H, d, J 15.1 Hz, H5), 5.73 (1H, d, J 15.1 Hz, H4), 5.28 (5H, s, H9), 4.14 (2H, q, J 6.8 Hz, H7), 2.63 (3H, s, H1), 1.25 (3H, t, J 6.8 Hz, H8); \delta C (100.6 MHz; CDCl_{3}); 224.8, 223.0, 202.5 (q, M-CO), 166.6 (q, C6), 150.1 (CH, C5), 119.3 (CH, C4), 101.3 (q, C3), 90.9 (5 x CH, C9), 81.8 (q, C2), 60.1 (CH_{2}, C7), 20.7 (CH_{3}, C1), 14.1 (CH_{3}, C8); m/z 472 (M^+-CO, 22%), 444 (64%), 416 (37%), 388 (100%).
Tetrafluoroboric acid (0.10 mL, 0.75 mmol) was added dropwise to a solution of cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-1-ethoxy-prop-2-ynyl-benzene (0.388 g, 0.75 mmol) in diethyl ether (30 mL) at ambient temperature. The solution was stirred for 15 min during which a bright orange precipitate formed. The solution was then filtered and washed with further portions of diethyl ether until the washings remained colourless. The solid was then dried to yield the title compound as a bright orange solid (0.381 g, 91 %); C_{19}H_{12}CoMoO_{5}BF_{4}, required: C 40.1 %, H 2.1 %, found: C 40.3 %, H 2.3 %; HRMS [FAB] (M^+\text{-BF}_4) required 476.9071, found 476.9077; v_{\text{max}} (\text{thin film})/\text{cm}^{-1} 2099, 2062, 2037, 2014 (M-CO), 1085, 1048, 1033 (selected fingerprint); m/z 477 (M^+, 23 %), 449 (33 %), 393 (18 %), 365 (18 %), 337 (16 %).
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-prop-2-ynyl benzene

(203)

Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-prop-2-ynyl-benzene tetrafluoroborate (0.150 g, 0.26 mmol) and zinc powder (activated by washing with HCl) were dissolved in dry DCM (10 mL) under an atmosphere of nitrogen at ambient temperature. The reaction mixture was stirred for 12 h then filtered through a plug of celite and silica, before purification via flash silica chromatography (10 : 1 petroleum ether: diethyl ether) to yield the title compound as a dark red oil (0.047 g, 36 %); C_{11}H_{13}CoMoOs,

HRMS [FAB](M⁺-CO), required 449.9200, found 449.9198; ν\text{max} (thin film)/cm⁻¹ 3422(CH), 2045, 1974, 1934, (M-CO), 1418, 1014, 813 (selected fingerprint); δ\text{H} (400 MHz; CDCl₃); 7.18-7.31 (5H, m, C₅-C₇), 5.84 (1H, s, H₁), 5.26 (5H, s, H₈), 4.02 (2H, d, J 6.2Hz, H₃); δ\text{C} (100.6 MHz; CDCl₃); 141.4 (q, C₄), 128.9 (2 x CH, C₆), 128.3 (2 x CH, C₅), 126.6 (CH, C₇), 94.2 (q, C₂), 90.6 (5 x CH, C₈), 81.3 (CH, C₁), 41.8 (CH₂, C₃); m/z 450 (M⁺-CO, 11 %), 422 (12 %), 394 (100 %), 366 (35 %), 338 (55 %).
Dicobalt hexacarbonyl-dithiocarbonic acid O-ethyl ester S-prop-2-vynyl ester (204)

\[\text{H} \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \]
\[\text{(OC)}_3\text{Co} \quad \text{Co(OC)}_3\]

Tetrafluoroboric acid (1.02 mL, 7.40 mmol) was added dropwise to a solution of dicobalt hexacarbonyl-propynol (2.299 g, 6.70 mmol) in dry DCM (100 mL) under a nitrogen atmosphere. The solution was stirred for 5 min then dithiocarbonic acid O-ethylester sodium salt (1.184 g, 7.40 mmol) was added as a solid. The solution was then stirred for 1 h, filtered through a plug of celite and silica, then purified via flash silica chromatography (19 : 1 petroleum ether: diethyl ether) to yield the title compound as a black oil (2.631 g, 90 %); C\text{_{12}}\text{H}_6\text{Co}_2\text{O}_7\text{S}_2, \text{HRMS [FAB]}(\text{M}^+\text{-2CO}) \text{ required } 389.8477, \text{obtained } 389.8471; \nu_{\text{max}} (\text{thin film})/\text{cm}^{-1} 2094, 2052, 2020 (\text{M-CO}), 1242, 1213, 111, 1047 (\text{selected fingerprint}); \delta\text{H} (400 MHz; CDCl}_3) 6.01 (1H, s, H1), 4.70 (2H, q, J 7.0 Hz, H5), 4.46 (2H, s, H3), 1.44 (3H, t, J 7.0 Hz, H6); \delta\text{C} (100.6 MHz; CDCl}_3) 213.5 (q, C4), 199.5 (q, M-CO), 90.8 (q, C2), 74.5 (CH, C1), 72.5 (CH\text{2}, C3), 40.8 (CH\text{2}, C5), 14.7 (CH\text{3}, C6); \text{m/z } 390 (\text{M}^+\text{-2CO, 44 %}), 362 (25 %), 334 (20 %), 306 (25 %).
Dicobalt hexacarbonyl-3-ethoxy-but-2-yne

Method 1
3-butyne-2-ol (0.65 mL, 8.77 mmol) was added to solution of octacarbonyl dicobalt (3.00 g, 8.77 mmol) and 4 Å mol sieves in DCM (100 mL). This solution was stirred for 4 h at ambient temperature. Dry ethanol (2.0 mL) was then added followed by boron trifluoride diethyl etherate (2.20 mL, 17.54 mmol). The solution was then left to stir for 1 h, filtered through a plug of celite and silica, then purified via flash silica chromatography (19:1 petroleum ether: diethyl ether) to yield the title compound as a dark red oil (2.742 g, 81%); C₁₂H₁₀Co₂O₇, HRMS [FAB](M⁺-CO) required 355.9141, obtained 355.9146; νₘₐₓ (thin film)/cm⁻¹ 2980, 2932, 2970 (CH), 2051, 2095, 2021, 1975 (M-CO), 1548, 1331, 1100 (selected fingerprint); δH (400 MHz; CDCl₃) 6.06 (1H, s, H1), 4.54 (1H, q, J 6.4 Hz, H3), 3.68-3.75 (1H, m, 1 x H5), 3.54-3.60 (1H, m, 1 x H5), 1.50 (3H, d, J 6.4 Hz, H4), 1.21 (3H, t, J 6.4 Hz, H6); δC (100.6 MHz; CDCl₃) 199.8, 199.1 (q, M-CO), 97.8 (q, C2), 75.2 (CH, C3), 72.6 (CH₂, C1), 64.6 (CH₂, C5), 23.5 (CH₃, C4), 15.2 (CH₃, C6); m/z 356 (M⁺-CO, 47%), 328 (83%), 300 (100%), 272 (57%), 244 (33%).

Method 2
Tetrafluoroboric acid (1.7 mL, 13.06 mmol), was added to a solution of hexacarbonyl dicobalt 3-butyne-2-ol (3.10 g, 8.71 mmol) and 4Å mol sieves in dry DCM (150 mL). The solution was left to stir for 5 min then dry ethanol (3 mL) added. This was then left to stir for 12 h, then dried with MgSO₄, filtered through a plug of celite and silica, then purified via flash silica chromatography (19:1 petroleum ether: diethyl ether) to yield the title compound as a dark red oil (2.979 g, 89%). The spectroscopic data was identical to the above compound.
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-3-ethoxy-but-2-yne

\[ \text{H}_1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \]
\[ \text{(OC)}_3\text{Co-MoCp(CO)}_2 \]

K-selectride\textsuperscript{®} (3.33 mL, 3.33 mmol), was added dropwise to a solution of hexacarbonyl bis-(cyclopentadienyl) dimolybdenum (0.650 g, 1.33 mmol) in dry THF (30 mL) under a nitrogen atmosphere. The solution was left to stir at ambient temperature for 40 min, with a colour change from red to orange observed. Dicobalt hexacarbonyl-3-ethoxy-2-butyne (1.022 g, 2.66 mmol) in THF (10 mL) was then added and the solution refluxed for 1 h. The crude product was then filtered through a plug of celite and silica, before purification via flash silica chromatography (6: 1 petroleum ether: diethyl ether) to yield the title compound (2 separable diastereoisomers 1.2: 1 d.r) as a dark red oil (1.057 g, 86 % (combined yield)); C\textsubscript{17}H\textsubscript{19}CoMoO\textsubscript{6}, HRMS [FAB](M\textsuperscript{+}-CO), required 447.9619, found 447.9618; \( \nu_{\text{max}} \) (thin film)/cm\textsuperscript{-1} 2974, 2927, 2866 (CH), 2048, 1976, 1936 (M-CO), 1443, 1081, 812 (selected fingerprint); m/z 448 (M\textsuperscript{+}-CO, 16 %), 420 (52 %), 405 (18 %), 392 (45 %), 364 (11 %).

NMR Data:
First eluting major diastereoisomer
\( \delta \text{H} \) (400 MHz; CDCl\textsubscript{3}); 5.71 (1H, s, H1), 5.48 (5H, s, H7), 4.51 (1H, q, J 6.2Hz, H3), 3.56 (2H, dq, J 7.0 Hz, J 2.2 Hz, H4), 1.29 (3H, d, J 6.2Hz), 1.19 (3H, t, J 7.0Hz, H5); \( \delta \text{C} \) (100.6 MHz; CDCl\textsubscript{3}) 225.2, 225.1, 217 (q, M-CO), 90.20 (CH, C7), 79.0 (CH, C3), 78.2 (CH, C1), 64.4 (CH\textsubscript{2}, C4), 23.4 (CH\textsubscript{3}, C6), 15.3 (CH\textsubscript{3}, C5), (C2 not seen)

Later eluting minor diastereoisomer
\( \delta \text{H} \) (400 MHz; CDCl\textsubscript{3}); 5.81 (1H, s, H1), 5.44 (5H, s, H7), 4.42 (1H, q, J 6.2Hz, H3), 3.56 (2H, dq, J 7.0 Hz, J 2.2 Hz, H4), 1.30 (3H, d, J 6.2Hz), 1.19 (3H, t, J 7.0Hz, H5); \( \delta \text{C} \)
(100.6 MHz; CDCl₃) 225.9, 225.2 (M-CO), 90.18 (5 x CH, C7), 78.5 (CH, C3), 78.5 (CH, C1), 64.4 (CH₂, C4), 23.6 (CH₃, C6), 15.3 (CH₃, C5), (C2 not seen).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-but-2-yn-2 tetrafluoroborate (206)**

\[
\begin{array}{c}
\text{(OC)₃Co-MoCp(CO)₂} \\
\text{BF₄⁻}
\end{array}
\]

Tetrafluoroboric acid (0.22 mL, 1.58 mmol) was added dropwise to a solution of cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-3-ethoxy-but-2-yn (0.726 g, 1.58 mmol) in diethyl ether (50 mL) at ambient temperature. The solution was stirred for 15 min during which a bright orange precipitate formed. The solution was then filtered and washed with further portions of diethyl ether until the washings remained colourless. The solid was then dried to yield the **title compound** as a bright orange solid (0.5208 g, 65 %); mp 118 °C (decomposed); C₁₄H₁₀CoMoO₅, HRMS [FAB] (M⁺-BF₄), required 414.8914, found 414.8921; v_max (thin film)/cm⁻¹ 2094, 2044, 2007 (M-CO), 1067, 1033 (selected fingerprint); m/z 415 (M⁺, 43 %), 387 (72 %), 359 (40 %), 331(31 %).

**Zinc-copper couple**

Zinc powder (24.600 g, 375 mmol) was placed on a round-bottomed flask containing a magnetic stirrer bar. The zinc was washed with 1M HCl (3 x 20 mL) and the supernatant decanted, the zinc was then washed with water (4 x 50 mL) then aqueous copper(II)sulphate (2 x 38 mL, 2 % w/w) added. The solution was stirred for 1 min then the supernatant decanted. This product was washed with water (4 x 50 mL), ethanol (3 x 50
mL), then finally diethyl ether (4 x 50 mL). The product was then filtered under suction and dried in a dessicator to yield the title compound as a light grey metallic solid (quant).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-4-methyl-hex-1-en-5-yne (208)**

![Chemical structure](image)

Allyl bromide (0.056 mL, 0.49 mmol) was added to a solution of Zn/Cu couple (0.063 g, 0.49 mmol), in dry THF (5 mL) under an atmosphere of nitrogen. Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-but-2-yn-3 tetrafluoroborate (0.050 g, 0.40 mmol) was then added and the solution was stirred at 60 °C for 10 min while following by TLC. The solution was then filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (9 : 1 petroleum ether : diethyl ether), to give the title compound as an orange oil (2 inseparable diastereoisomers (0.038 g, 80 %, 2 : 1 d.r); C_{17}H_{15}CoMoO_5, HRMS [FAB](M^+-2CO), required 399.9407, found 399.9408; ν_max (thin film)/cm^{-1} 2967 (CH), 2044, 1969, 1934 (M-CO), 1449, 1369, 813 (selected fingerprint); m/z 400 (M^+-2CO, 21 %), 372 (100 %), 344 (15 %), 316 (10 %).

**NMR Data:**

**Major isomer**

δH (400 MHz; CDCl_3) 5.86 (1H, s, H1), 5.71-5.85 (1H, m, H5), 4.40 (5H, s, H8), 5.01-5.1 (2H, m, H6), 2.75-2.84 (1H, m, H3), 2.22-2.39 (1H, m, H4), 1.92-2.04 (1H, m, H4), 1.09 (3H, d, J 6.7 Hz, H7); δC (100.6 MHz; CDCl_3) 226.1, 226.3, 226.5 (q, C9), 137.2 (CH, C5), 116.5 (CH2, C6), 90.9 (5 x CH, C8), 88.4 (q, C2), 78.8 (CH, C1), 43.9 (CH2, C4), 39.1 (CH, C3), 22.8 (CH3, C7).
Minor isomer

δH (400 MHz; CDCl₃) 5.87 (1H, s, H1), 5.71-5.85 (1H, m, H5), 4.41 (5H, s, H8), 5.01-5.1 (2H, m, H6), 2.75-2.84 (1H, m, H3), 2.22-2.39 (1H, m, H4), 1.92-2.04 (1H, m, H4), 1.09 (3H, d, J 6.7 Hz, H7); δC (100.6 MHz; CDCl₃) 226.1, 226.3, 226.5 (q, C9), 137.0 (CH, C5), 116.4 (CH2, C6), 90.7 (5 x CH, C8), 88.3 (q, C2), 78.8 (CH, C1), 43.8 (CH2, C4), 39.2 (CH, C3), 22.6 (CH3, C7).

Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-3-methyl-pent-4-ynoic acid ethyl ester (209)

![Chemical structure of the title compound](image)

Ethyl bromoacetate (0.17 mL, 1.50 mmol), was added to a solution of Zn/Cu couple (0.193 g, 1.50 mmol), in dry THF (15 mL) under an atmosphere of nitrogen then left to stir for 10 min. Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-but-2-yn-3-tetrafluoroborate (0.150 g, 0.30 mmol) was then added and the solution was stirred at 60 °C for 20 min while following by TLC. The solution was then filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (5 : 1 petroleum ether : diethyl ether), to give the title compound as a orange oil (2 inseparable diastereoisomers) (0.077 g, 51 %, 3 : 1 d.r); C₁₈H₁₇CoMoO₅S, HRMS [FAB](M⁺-3CO), required 417.9541, found 417.9541; νmax (thin film)/cm⁻¹ 2974, 2932 (CH), 2045, 1973, 1935, 1889 (M-CO), 1733 (CO₂Et), 1272, 1173, 815 (selected fingerprint); m/z 418 (M⁺-3CO, 53 %), 390 (36 %), 286 (40 %).
NMR Data:

Major isomer
\[ \delta H (400\text{ MHz}; \text{CDCl}_3) \] 5.73 (1H, d, \( J 0.7 \text{ Hz}, H1 \)), 5.41 (5H, s, H9), 4.14 (2H, q, \( J 7.2 \text{ Hz}, H6 \)), 3.21-3.52 (1H, m, H3), 2.47 (1H, m, H4), 2.28 (1H, m, H4), 1.27 (3H, t, \( J 7.2 \text{ Hz}, H7 \)), 1.17 (3H, d, \( J 6.9 \text{ Hz}, H8 \)); \( \delta C \) (100.6 MHz; CDCl\(_3\)) (M-CO missing), 172.3 (q, C5), 94.9 (q, C2), 90.5 (5 x CH, C9), 78.8 (CH, C1), 60.5 (CH\(_2\), C6), 44.2 (CH\(_2\), C4), 36.3 (CH, C3), 23.3 (CH\(_3\), C8), 14.2 (CH\(_3\), C7).

Minor isomer
\[ \delta H (400\text{ MHz}; \text{CDCl}_3) \] 5.80 (1H, d, \( J 0.7 \text{ Hz}, H1 \)), 5.42 (5H, s, H9), 4.14 (2H, q, \( J 7.2 \text{ Hz}, H6 \)), 3.21-3.52 (1H, m, H3), 2.47 (1H, m, H4), 2.28 (1H, m, H4), 1.27 (3H, t, \( J 7.2 \text{ Hz}, H7 \)), 1.17 (3H, d, \( J 6.9 \text{ Hz}, H8 \)); \( \delta C \) (100.6 MHz; CDCl\(_3\)) (M-CO missing), 172.3 (q, C5), 94.8 (q, C2), 90.3 (5 x CH, C9), 78.8 (CH, C1), 60.5 (CH\(_2\), C6), 44.0 (CH\(_2\), C4), 36.4 (CH, C3), 23.3 (CH\(_3\), C8), 14.2 (CH\(_3\), C7).

\textbf{Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-4-ethyl-hept-en-5-yne}

(209)

Allyl bromide (0.17 mL, 1.50 mmol) was added to a solution of Zn/Cu couple (0.193 g, 1.5 mmol), in dry THF (15 mL) under an atmosphere of nitrogen. Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-1-yne-2-tetrafluoroborate (0.150 g, 0.28 mmol) was then added and the solution was stirred at 60 °C for 15 min while following by TLC. The solution was then filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (9 : 1 petroleum ether : diethyl ether), to give the title compound as a orange oil (2 inseparable diastereoisomers)
(0.115 g, 79 %, 1 : 1 d.r); \(\nu_{\text{max}}\) (thin film)/cm\(^{-1}\) 2961, 2932, 2847 (CH), 2039, 1967, 1925 (M-CO), 1430, 1377, 811 (selected fingerprint); \(\delta\)H (250 MHz; CDCl\(_3\)) 5.72-5.91 (1H, m, H6), 5.34, 5.35 (5H, s, H10), 5.03-5.13 (2H, m, H7), 2.75 (3H, s, H1), 2.62-2.72 (1H, m, H4), 2.11-2.38 (2H, m, H5), 1.38-1.69 (2H, m, H8), 0.94 (3H, t, \(J\) 7.6 Hz, H9); \(\delta\)C (100.6 MHz, CDCl\(_3\)) 205.4 (q, M-CO), 137.0 (CH, C6), 116.2 (CH\(_2\), C7), 98.9 (q, C2), 94.3 (q, C3), 90.5, 90.6 (5 x CH, C10), 46.3 (CH, C4), 39.7, 39.9 (CH\(_2\), C5), 28.1, 28.8 (CH\(_2\), C8), 21.5 (CH\(_3\), C1), 11.7, 12.0 (CH\(_3\), C9); \(m/z\) [FAB](low res) 428 (M\(^+\)-2CO, 15 %), 400 (100 %), 372 (24 %).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-3-ethyl-hex-4-ynoic acid ethyl ester (211)**

![Structural Diagram](image)

Ethyl bromoacetate (0.17 mL, 1.50 mmol), was added to a solution of Zn/Cu couple (0.193 g, 1.50 mmol), in dry THF (15 mL) under an atmosphere of nitrogen then stirred for 10 min. Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-2-yne-2-tetrafluoroborate (0.150 g, 0.30 mmol) was then added and the solution was stirred at 60 °C for 20 min while following by TLC. The solution was then filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (5 : 1 petroleum ether : diethyl ether), to give the title compound as a orange oil (2 inseparable diastereoisomers (0.125 g, 84 %, 1 : 1 d.r). \(\nu_{\text{max}}\) (thin film)/cm\(^{-1}\) 2963, 2933, 2874 (CH), 2041, 1969, 1927 (M-CO), 1733 (CO\(_2\)Et), 1369, 1162, 814 (selected fingerprint); \(\delta\)H (400 MHz; CDCl\(_3\)) 5.37, 5.36 (5H, s, H11), 4.14 (2H, q, \(J\) 7.2 Hz, H7), 3.15-3.18 (1H, m, H4), 2.70, 2.71 (3H, s, H1), 2.38-2.48 (2H, m, H5), 1.33-1.60 (2H, m, H9), 1.20-1.25 (3H, m, H8), 0.94-1.05 (3H, m, H10); \(\delta\)C (100.6 MHz; CDCl\(_3\)
225.0, 225.4, 226.5, 226.7, 205.0 (q, M-CO), 172.7, 172.8 (q, C6), 98.8 (q, C3), 94.9 (q, C2), 90.6, 90.5 (5 x CH, C11), 60.5 (CH2, C7), 42.9, 43.0 (CH, C4), 40.4, 40.6 (CH2, C5), 30.0, 30.3 (CH2, C9), 21.11, 21.14 (CH3, C1), 14.2, 14.1 (CH3, C8), 12.0, 12.1 (CH3, C10).

No mass ion found.

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-1-(ethynyl-but-3-enyl)-benzene (212)**

![Diagram](image)

Allyl bromide (0.06 mL, 0.53 mmol) was added to a solution of Zn/Cu couple (0.84 g, 10.53 mmol), in dry THF (6 mL) under an atmosphere of nitrogen. Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-prop-2-ynyl benzene-tetrafluoroborate (0.059 g, 0.10 mmol) was then added and the solution was stirred at 60 °C for 10 min while following by TLC. The solution was then filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (10 : 1 petroleum ether : diethyl ether), to give the title compound as a orange oil (2 inseparable diastereoisomers (0.027 g, 50 %, 4 : 3 d.r); C22H17CoMoOs, HRMS [FAB](M+2CO) required 461.9564, found 461.9570; νmax (thin film)/cm⁻¹ 3078, 3026, 2976, 2926 (CH), 2045, 1975, 1936, 1860 (M-CO), 1638, 1492, 1452, 816 (selected fingerprint); m/z 462 (M+2CO, 17 %), 434 (84 %), 376 (62 %).

**NMR Data:**

**Major isomer**

δH (400 MHz; CDCl3) 7.10-7.32 (5H, m, H8-H10), 5.99 (1H, s, H1), 5.57-5.62 (1H, m, H5), 5.23-5.25 (1H, m, H3), 5.23 (5H, s, H11), 4.87-5.01 (2H, m, H6), 3.72 (1H, dd, J 9.5
Hz, \( J = 5.6 \text{ Hz, H4} \), 2.51 (1H, m, H4); \( \delta C \) (100.6 MHz; CDCl\textsubscript{3}) 225.8, 226.4 (q, M-CO), 145.1 (q, C7), 136.7 (CH, C5), 128.3 (2 x CH, C8), 128.0 (2 x CH, C9), 126.9 (C10), 116.3 (CH\textsubscript{2}, C6), 94.0 (q, C2), 90.6 (5 x CH, C11), 81.9 (CH, C1), 51.7 (CH, C3), 42.8 (CH\textsubscript{2}, C4).

**Minor isomer**

\( \delta H \) (400 MHz; CDCl\textsubscript{3}) 7.10-7.32 (5H, m, H8-H10), 5.93 (1H, s, H1), 5.57-5.62 (1H, m, H5), 5.23-5.25 (1H, m, H3), 5.12 (5H, s, H11), 4.87-5.01 (2H, m, H6), 3.84 (1H, dd, \( J = 9.5 \text{ Hz, } J = 5.6 \text{ Hz, H4} \)), 2.63 (1H, m, H4); \( \delta C \) (100.6 MHz; CDCl\textsubscript{3}) 225.8, 226.4 (q, C12), 144.4 (q, C7), 136.6 (CH, C5), 128.2 (2 x CH, C8), 128.1 (2 x CH, C9), 126.7 (C10), 116.5 (CH\textsubscript{2}, C6), 94.0 (q, C2), 90.5 (5 x CH, C11), 81.5 (CH, C1), 51.9 (CH, C3), 42.6 (CH\textsubscript{2}, C4).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-3-phenyl-pent-4-ynoic acid ethyl ester (213)**

![Chemical Structure](image)

Ethyl bromoacetate (0.10 mL, 0.90 mmol), was added to a solution of Zn/Cu couple (0.115 g, 0.90 mmol), in dry THF (12 mL) under an atmosphere of nitrogen then stirred for 10 min. Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-prop-2-ynl benzene tetrafluoroborate (0.101 g, 0.18 mmol) was then added and the solution was stirred at 60 °C for 20 min while following by TLC. The solution was then filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (4 : 1 petroleum ether : diethyl ether), to give the title compound as a orange oil (2 inseparable diastereoisomers (0.045 g, 45 %, 3 : 2 d.r). C\textsubscript{23}H\textsubscript{19}CoMoO\textsubscript{7};
HRMS [FAB](M⁺-2CO), required 507.9618, found 507.9615; νmax (thin film)/cm⁻¹ 2917 (CH), 2046, 1974, 1935 (M-CO), 1734 (CO₂Et), 1255, 1155, 1030 (selected fingerprint); m/z 508 (M⁺-2CO, 5 %), 480 (39 %), 452 (10 %).

NMR Data:

**Major isomer**

δH (400 MHz; CDCl₃) 7.17-7.34 (5H, m, H₉-H₁₁), 5.92 (1H, s, H₁), 5.26 (5H, s, H₁₂), 4.28 (1H, 7, J 6.8 Hz, H₃), 4.14 (2H, m, H₆), 2.77-2.85 (2H, m, H₄), 1.09-1.53 (3H, m, H₇); δC (100.6 MHz; CDCl₃) 223.6, 224.7, 225.5, 225.8 (q, M-CO), 171.5 (q, C₅), 144.4 (q, C₈), 128.33 (2 x CH, C₉), 127.72 (2 x CH, C₁₀), 127.1 (CH, C₁₁), 91.5 (q, C₂), 90.3 (5 x CH, C₁₂), 81.8 (CH, C₁), 60.5 (CH₂, C₆), 47.6 (CH, C₃), 42.9 (CH₂, C₄), 14.0 (CH₃, C₇).

**Minor isomer**

δH (400 MHz; CDCl₃) 7.17-7.34 (5H, m, H₉-H₁₁), 5.88 (1H, s, H₁), 5.20 (5H, s, H₁₂), 4.39 (1H, 7, J 6.8 Hz, H₃), 4.14 (2H, m, H₆), 2.88-2.93 (2H, m, H₄), 1.09-1.53 (3H, m, H₇); δC (100.6 MHz; CDCl₃) 223.6, 224.7, 225.5, 225.8 (q, M-CO), 171.5 (q, C₅), 143.8 (q, C₈), 128.3 (2 x CH, C₉), 127.7 (2 x CH, C₁₀), 127.0 (CH, C₁₁), 91.5 (q, C₂), 90.4 (5 x CH, C₁₂), 80.9 (CH, C₁), 60.4 (CH₂, C₆), 47.7 (CH, C₃), 42.9 (CH₂, C₄), 14.0 (CH₃, C₇).
1,4-bis-(2,6-diisopropylphenyl)-diazabutadiene (215)\(^{(182)}\)

![Structure of 1,4-bis-(2,6-diisopropylphenyl)-diazabutadiene](image)

Formic acid (0.5 mL), was added to a solution of 2,6-diisopropylphenylamine (10.00 g, 56.0 mmol) and glycol (3.15 mL, 28.0 mmol) in ethanol (50 mL). After a short while stirring at room temperature a bright yellow precipitate appeared. The solution was stirred for 24 h then the yellow solid collected by filtration and washed with cold methanol to give the title compound as bright yellow crystals (8.422 g, 80 %); mp 72-73 °C (lit 71-73 °C); \(\nu_{\text{max}}\) (thin film)/cm\(^{-1}\) 3062 (Ar CH), 2961, 2924, 2871 (CH) 1627 (C=N), 1456, 1432, 117, 758 (selected fingerprint); \(\delta H\) (400 MHz; CDCl\(_3\)) 8.14 (2H, s, H1), 7.28-7.19 (6H, m, H4, H5), 2.97 (4H, sept, J 6.8 Hz, H6), 1.24 (24H, d, J 6.8 Hz, H7); \(\delta C\) (100.6 MHz; CDCl\(_3\)) 163.0 (2 x CH, C1), 147.9 (2 x q, C2), 135.3 (4 x q, C3), 125.2 (2 x CH, C5), 124.3 (4 x CH, C4), 27.9 (4 x CH, C6), 23.2 (8 x CH\(_3\), C7).

1,3-Bis-(2,6-diisopropylphenyl)-imidazolium tetrafluoroborate, (IPrHBF\(_4\)) (216a)\(^{(182b)}\)

![Structure of 1,3-Bis-(2,6-diisopropylphenyl)-imidazolium tetrafluoroborate](image)
Solid paraformaldehyde (1.140 g, 38.00 mmol) was added to a solution of 1,4-bis-(2,6-diisopropylphenyl)-diazabutadiene (14.250 g, 38.00 mmol) in toluene (150 mL). The reaction mixture was heated to 100 °C for 15 min until most of the paraformaldehyde had dissolved. The solution was then cooled to 40 °C and tetrafluoroboric acid (5.20 mL, 38.0 mmol) was added dropwise over a 10 min period. The reaction mixture turned from orange to brown and a white precipitate slowly appeared. The solution was stirred for 48 h at ambient temperature then the purple precipitate filtered and washed with THF until the off white solid product appeared. This was then dissolved in DCM, dried over MgSO₄, filtered through celite then concentrated in vacuo to yield the title compound as a white solid (6.859 g, 37 %); mp 264 °C; C₂₇H₃₇N₂, HRMS [EI](M⁺-BF₄) required 389.29567, found 389.29619; νmax (thin film)/cm⁻¹ 3167, 3119, 3048 (Ar CH), 2966, 2930, 2872 (CH), 1536, 1083, 1058 (selected fingerprint); δH (400 MHz; CD₂Cl₂) 8.65 (1H, s, H2), 7.65 (2H, s, H1), 7.57 (2H, t, J 7.6Hz, H6), 7.33 (4H, d, J 7.6Hz, H5), 2.31 (4H, sept, J 6.8Hz, H7), 1.20, 1.13 (12H, 2 x d, J 6.8Hz, H8); δC (100.6 MHz; CD₂Cl₂) 144.7 (2 x q, C3), 136.6 (CH, C2), 131.6 (2 x CH, C6), 128.4 (4 x q, C4), 125.4 (2 x CH, C1), 124.1 (4 x CH, C5), 28.4 (4 x CH, C7), 23.4, 22.8 (8 x CH₃, C8); m/z 389 (M⁺, 19%), 387 (100%), 201 (48%), 186 (74%).

1,3-Bis-(2,6-diisopropylphenyl)-imidazolium chloride (IPrHCl) (216b)\(^{(182b)}\)

![1,3-Bis-(2,6-diisopropylphenyl)-imidazolium chloride (IPrHCl) (216b)\(^{(182b)}\)](image)

Solid paraformaldehyde (0.400 g, 13.4 mmol) was added to a solution of 1,4-bis-(2,6-diisopropylphenyl)-diazabutadiene (5.032 g, 13.4 mmol) in Toluene (60 mL). The reaction...
mixture was heated to 100 °C for 15 min until most of the paraformaldehyde had dissolved. The solution was then cooled to 40 °C and anhydrous HCl (4 M sol'n in dioxane (3.35 mL, 13.4 mmol) added dropwise over a 10 min period. The reaction mixture turned from orange to brown and a white precipitate slowly appeared. The solution was left to stir for 36 h at ambient temperature then the precipitate filtered and washed with THF until the pale pink solid product appeared. This was then dissolved in DCM, dried over MgSO₄, filtered through celite then concentrated in vacuo to yield the title compound as a pale pink solid (5.695 g, 42 %); mp 271-273 °C (lit > 255 °C) \( \nu_{\text{max}} \) (thin film)/cm\(^{-1}\) 3154, 3061 (Ar CH), 2966, 2930, 2874 (CH), 1533, 811 (selected fingerprint); \( \delta H \) (400 MHz; CD₂Cl₂) 10.9 (1H, s, H2), 7.26 (2H, s, H1), 7.52 (2H, t, \( J \) 7.6 Hz, H6), 7.29 (4H, d, \( J \) 7.6 Hz, H5), 2.32 (4H, sept, \( J \) 6.8 Hz, H7), 1.19, 1.12 (12H, 2 x d, \( J \) 6.8 Hz, H8); \( \delta C \) (100.6 MHz; CD₂Cl₂) 145.9 (2 x q, C3), 136.6 (2 x CH, C2), 131.6 (2 x CH, C6), 128.8 (4 x q, C4), 125.4 (CH, C1), 124.1 (4 x CH, C5), 28.4 (4 x CH, C7), 23.4, 22.8 (8 x CH₃, C8).

**Dicobalt hexacarbonyl-diphenylacetylene (220)**

![Dicobalt hexacarbonyl-diphenylacetylene](image)

Diphenylacetylene (0.520 g, 2.91 mmol) was added to a solution of dicobalt octacarbonyl (0.997 g, 2.91 mmol) in DCM (20 mL) under an atmosphere of nitrogen. After 12 h the dark purple solution was filtered through a plug of celite and silica, concentrated in vacuo then purified via flash silica chromatography (100 % petroleum ether), to yield the *title compound* as a black solid (1.23 g, 91 %); mp 109-110 °C (lit, 109-110 °C); \( \nu_{\text{max}} \) (thin film)/cm\(^{-1}\) 3075, 3023 (CH), 2095, 2034, 1995 (M-CO), 1593, 1495, 1440 (selected fingerprint); \( \delta H \) (400 MHz; CDCl₃) 7.58-7.62 (4H, m, H4), 7.26-7.38 (6H, m, H3, H5); \( \delta C \)
Potassium tert-pentoxide (K-amylate) (3.20 mL, 5.70 mmol) was added to a suspension of 1,3-bis-(2,6-diisopropylphenyl)-imidazolium.HBF$_4$ (2.70 g, 5.70 mmol) in hexane (150 mL) under an atmosphere of nitrogen at ambient temperature. After 30 min dicobalt hexacarbonyl propynol (1.500 g, 4.38 mmol) in hexane (10 mL) was added and the solution heated to 68 °C for 1 h while following by TLC. The solution was filtered through a pad of celite and silica, then concentrated in vacuo before purification by flash silica chromatography (4 : 1, petroleum ether : diethyl ether), to yield the title complex (2.120 g, 71 %) as a dark red solid; mp 158-161°C; C$_{33}$H$_{40}$Co$_2$N$_2$O$_6$, required: C 59.83 %, H 5.74 %, N 4.00 %, found: C 59.74 %, H 5.77 %, N 4.07 %; HRMS [FAB](M$^+$-CO), required 674.16012, found 674.16138; $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 3483 (OH), 3175, 3071, 2966, 2929, 2870 (CH), 2053, 1997 (M-CO), 1467, 1299, 735 (selected fingerprint); $\delta$H (400 MHz; CDCl$_3$ ) 7.57 (2H, t, J 7.6 Hz, H9), 7.39 (4H, d, J 7.6 Hz, H8), 7.02 (2H, s, H5), 4.31 (2H, dd, J 13.1 Hz, J 7.7 Hz, 1 x H3), 4.39 (2H, dd, J 13.1 Hz, J 7.7 Hz, 1 x H3), 4.14 (1H, s, H1), 2.59 (2H, sept, J 6.7 Hz, H10), 2.57 (2H, sept, J 6.7 Hz, H10), 1.43 (6H, d, J 6.7 Hz, H11), 1.41 (6H, d, J 6.7 Hz, H11), 1.13 (6H, d, J 6.7 Hz, H11), 1.10 (6H, d, J 6.7 Hz, H11) (H 12 not visible); $\delta$C (100.6 MHz; CDCl$_3$) 201.8 (q, CM-CO), 146.3, 146.0 (4 x q, C7), 137.1 (2 x q, C6), 130.5 (2 x CH, C9), 125.6 (2 x CH, C5), 124.2, 123.8 (4 x CH, C8), 91.1
Dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium phenylacetylene

Potassium tert-pentoxide (K-amylate) (1.87 mL, 3.23 mmol) was added to a suspension of 1,3-bis-(2,6-diisopropylphenyl)-imidazolium.HBF₄ (1.36 g, 2.85 mmol) in hexane (50 mL) under an atmosphere of nitrogen at ambient temperature. After 45 min dicobalt hexacarbonyl phenylacetylene (0.737 g, 1.9 mmol) in hexane (15 mL) was added and the solution heated to 68 °C for 1 h while following by TLC. The solution was filtered through a pad of celite and silica, then concentrated in vacuo before purification by flash silica chromatography (9 : 1, petroleum ether : diethyl ether), to yield the title complex (0.553 g, 39 %), as a dark red solid; mp 165-169 °C; C₃₆H₄₂C₀₂N₂O₅, required: C 64.18 %, H 5.65 %, N 3.74 %, found: C 64.77 %, H 5.95 %, N 3.61 %; HRMS [FAB](M⁺-CO), required 636.1960, found 636.1960; νmax (thin film)/cm⁻¹ 3140, 3071, 2966, 2930, 2869 (CH), 2050, 1997, 1950 (M-CO), 1593, 1465, 1296 (selected fingerprint); δH (400 MHz; CDCl₃) 7.52-7.58 (2H, m, Ar-H), 7.07-7.41 (9H, m, Ar-H), 7.02 (2H, s, H8), 4.47 (1H, s, H1), 2.70 (2H, sept, J 6.7 Hz, 2 x H13), 2.43 (2H, sept, J 6.7 Hz, 2 x H13), 1.40 (6H, d, J 6.7 Hz, H14), 1.06 (6H, d, J 6.7 Hz, H14), 1.05 (6H, d, J 6.7 Hz, H14), 1.04 (6H, d, J 6.7 Hz, H14); δC (100.6 MHz; CDCl₃) 208.0, 204.1 (M-CO), 146.4, 146.4 (4 x q, C10), 140.4 (q, C3), 137.3 (q, C9), 130.4, 130.3 (2 x CH, C12), 127.8 (C6), 125.9 (2 x CH, C4), 125.4 (CH, C8), 186
124.1, 124.0 (6 x CH, C11, C5), 85.2 (q, C2), 67.5 (CH, C1), 28.7 (4 x CH, C13), 26.1, 25.8, 22.7, 22.2 (8 x CH3, C14) C7 not seen; m/z 636 (M⁺-4CO, 35 %), 608 (79 %), 476 (66 %), 405 (100 %), 398 (94 %).

**Dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium**

**diphenylacetylene (223)**

Potassium tert-pentoxide (K-amylate) (0.40 mL, 0.68 mmol) was added to a suspension of 1,3-bis(2,6-diisopropylphenyl)-imidazolium.HBF₄ (0.295 g, 0.62 mmol) in hexane (20 mL) under an atmosphere of nitrogen at ambient temperature. After 45 min dicobalt hexacarbonyl diphenylacetylene (0.144 g, 0.31 mmol) in hexane (3 mL) was added and the solution heated to 68 °C for 1 h while following by TLC. The solution was then filtered through a pad of celite and silica, then concentrated in vacuo before purification by flash silica chromatography (20 : 1, petroleum ether : diethyl ether), to yield the title complex (0.175 g, 67 %), as a black solid; mp 169-172 °C; C₄₆H₅₆C₀₂N₂O₅, required: C 66.99 %, H 5.62 %, N 3.40 %, found: C 66.86 %, H 5.82 %, N 3.33 %; HRMS [FAB](M⁺-CO), required 796.7495, found 796.7494; \( \nu_{\text{max}} \) (thin film)/cm⁻¹: 3143, 3076, 3026, 2967, 2932, 2869 (CH), 2048, 1994, 1948 (M-CO), 1460, 1441, 908, 692 (selected fingerprint); δH (400 MHz; CDCl₃) 7.29-7.41 (6H, m, Ar-H), 7.13-7.17 (10H, m, Ar-H), 7.00 (2H, s, H7), 2.82 (4H, sept, J 6.7 Hz, H12), 1.28 (12H, d, J 6.7 Hz, H13), 1.08 (12H, d, J 6.7 Hz, H13); δC (100.6 MHz; CDCl₃) 208.3, 202.8 (q, M-CO), 145.5 (4 x q, C9), 141.2 (2 x q, C4), 137.2 (2 x q, C8), 130.4 (2 x CH, C11), 129.4 (2 x CH, C1), 127.8 (4 x CH, C2), 126.1 (4 x CH,
C3), 125.2 (2 x CH, C7), 123.9 (4 x CH, C10), 85.4 (2 x q, C5), 28.7 (4 x CH, C12), 26.1,
22.1 (8 x CH3, C13) (C6 not seen); \textit{m/z} 797 (M⁺-CO, 4 %), 769 (8 %), 712 (22 %), 684 (80
%); 476 (100 %).

\textbf{Dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium butynal (224)}

Potassium tert-pentoxide (K-amylate) (1.80 mL, 3.00 mmol) was added to a suspension of
1,3-bis(2,6-diisopropylphenyl)-imidazolium.HBF₄ (1.290 g, 2.70 mmol) in hexane (50 mL)
under an atmosphere of nitrogen at ambient temperature. After 30 min dicobalt
hexacarbonyl butynal (0.645 g, 1.80 mmol) dissolved in hexane (10 mL) was added and the
solution heated to 68 °C for 45 min while following by TLC. The solution was then
filtered through a pad of celite and silica and concentrated in vacuo before purification by
flash silica chromatography (9 : 1, petroleum ether : diethyl ether) to yield the \textit{title complex}
(0.693 g, 54 %), as a dark red solid. Recrystallisation from cold hexane produced dark
purple crystals; mp 175-180 °C; C₃₆H₄₀C₀₂N₂₀₆, required: C 60.51 %, H 5.64 %, N 3.92
%, found: C 60.21 %, H 5.65 %, N 3.95 %; HRMS [FAB](M⁺), required 715.16283, found
715.16447; νₘₐₓ (thin film)/cm⁻¹ 3125, 3103, 2964, 2930, 2837 (CH), 2060, 2015, 1959 (M-
CO), 1632 (CHO), 1464, 1295, 758 (selected fingerprint); δH (400 MHz; CDCl₃) 8.69 (1H,
s, H4), 7.53 (2H, t, J 7.6 Hz, H10), 7.34 (4H, d, J 7.6 Hz, H9), 7.00 (2H, s, H6), 2.67 (2H,
sept, J 6.6 Hz, H11), 2.59 (2H, sept, J 6.8 Hz, H11), 2.44 (3H, s, H1), 1.45 (6H, d, J 6.8 Hz,
H12), 1.49 (6H, d, J 6.8 Hz, H12), 1.10 (12 H, dd, J 6.8 Hz, J 4.0 Hz, H12); δC (100.6
MHz; CDCl₃) 208.2, 199.9 (q, M-CO), 186.1 (CH, C4), 145.7, 145.8 (4 x q, C8), 137.6 (2
x q, C7), 130.4 (2 x CH, C10), 125.7 (2 x CH, C6), 124.1, 123.6 (4 x CH, C9), 88.6 (q, C3), 79.8 (q, C2), 28.3, 28.2 (4 x CH, C11), 25.7, 25.3, 22.6, 22.4 (8 x CH3, C12), 21.3 (CH3, C1) (C5 not seen); m/z 715 (M+, 1 %), 631 (4 %), 603 (28 %), 575 (19 %), 547 (72 %), 476 (100 %).

An X-ray crystal structure of the above complex was also obtained (see appendix)

**Dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium -1-isopropyl-4-methyl-2-prop-2-ynyloxy-cyclohexane (225)**

![Chemical structure](image)

Potassium tert-pentoxide (K-amylate) (1.80 mL, 3.10 mmol) was added to a suspension of 1,3-bis-(2,6-diisopropylphenyl)-imidazolium·HBF4 (1.29 g, 2.70 mmol) in hexane (60 mL) under an atmosphere of nitrogen at ambient temperature. After 45 min dicobalt hexacarbonyl-1-isopropyl-4-methyl-2-prop-2-ynyloxy-cyclohexane (0.820 g, 11.80 mmol) in hexane (10 mL) was added and the solution heated to 68 °C for 1 h while following by TLC. The solution was filtered through a pad of celite and silica, then concentrated in vacuo before purification by flash silica chromatography (5:1, petroleum ether: diethyl ether), to yield the title complex (0.927 g, 60 %), as a dark red solid; C45H54Co2N2O6, HRMS [FAB](M+H) required 813.3088, found 813.3070; νmax (thin film)/cm⁻¹ 3176, 3137,
3070, 2961, 2867 (CH), 2051, 1982, 1946 (M-CO), 1457, 1296, 936 (selected fingerprint); m/z 813 (M+H, 5%), 729 (90%), 701 (80%), 476 (100%).

NMR data:

First eluting isomer

mp 142 °C

δH (400 MHz; CDCl₃) 7.54 (2H, t, J 7.8 Hz, H19), 7.36 (4H, d, J 7.8 Hz, H18), 6.92 (2H, s, H15), 4.17 (1H, d, J 11.6 Hz, 1 x H3), 4.06 (1H, s, H1), 3.97 (1H, d, J 11.6 Hz, 1 x H3), 2.99 (1H, m, H4), 2.57 (2H, sept, J 6.8 Hz, H20), 2.56 (2H, sept, J 6.8 Hz, H20), 2.41 (1H, m, H6), 1.97 (1H, m, H9), 1.47-1.49 (3H, m, H10/H5), 1.41 (6H, d, J 6.8 Hz, H21), 1.39 (6H, d, J 6.8 Hz, H21), 1.12 (6H, d, J 6.8 Hz, H21), 1.11 (6H, d, J 6.8 Hz, H21), 0.90 (3H, d, J 6.8 Hz, H12/H13), 0.80 (3H, d, J 6.8 Hz, H12/H13), 0.67 (3H, d, J 6.8 Hz, H11), (0.90-1.10) (4H, m, H7/H8); δC (100.6 MHz; CDCl₃) 206.2, 202.4 (q, M-CO), 146.6, 146.63 (4 x q, C17), 137.6 (2 x q, C16), 130.7 (2 x CH, C19), 125.7 (2 x CH, C15), 124.5, 125.5 (4 x CH, C18), 88.4 (q, C2), 79.2 (CH, C1), 68.8 (CH₂, C3), 65.6 (CH, C4), 48.8 (CH, C10), 40.8 (CH₂, C8), 34.9 (CH₂, C7), 32.0 (CH, C6), 29.0, 29.2 (4 x CH, C20), 26.0, 26.2 (4 x CH₃, C21), 25.0 (CH₃, C11), 23.3 (CH₂, C5), 23.2, 23.3 (4 x CH₃, C21), 22.8 (CH₃, C12/C13), 21.5 (CH₃, C12/C13), 16.3 (CH, C9).

Later eluting isomer

mp 136-138 °C

δH (400 MHz; CDCl₃) 7.54 (2H, t, J 7.8 Hz, H19), 7.36 (4H, d, J 7.8 Hz, H18), 7.10 (2H, s, H15), 4.54 (1H, d, J 11.6 Hz, 1 x H3), 4.07 (1H, s, H1), 3.75 (1H, d, J 11.6 Hz, 1 x H3), 3.00 (1H, m, H4), 2.57 (2H, sept, J 6.8 Hz, H20), 2.56 (2H, sept, J 6.8 Hz, H20), 2.29 (1H, m, H6), 1.97 (1H, m, H9), 1.53-1.57 (3H, m, H10/H5), 1.42 (6H, d, J 6.8 Hz, H21), 1.40 (6H, d, J 6.8 Hz, H21), 1.12 (6H, d, J 6.8 Hz, H21), 1.11 (6H, d, J 6.8 Hz, H21), 0.89 (3H, d, J 6.8 Hz, H12/H13), 0.77 (3H, d, J 6.8 Hz, H12/H13), 0.64 (3H, d, J 6.8 Hz, H11), (0.90-1.10) (4H, m, H7/H8); δC (100.6 MHz; CDCl₃) 206.2, 202.4 (q, M-CO), 146.6, 146.63 (4 x q, C17), 137.6 (2 x q, C16), 130.7 (2 x CH, C19), 125.7 (2 x CH, C15), 124.5, 125.5 (4 x CH, C18), 87.9 (q, C2), 79.6 (CH, C1), 69.9 (CH₂, C3), 66.0 (CH, C4), 48.5 (CH, C10), 40.1 (CH₂, C8), 34.7 (CH₂, C7), 31.9 (CH, C6), 28.86, 29.90 (4 x CH, C20), 26.0,
Pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium dicobalt pentacarbonyl phenylacetylene (0.374 g, 0.50 mmol) and norbornadiene (0.77 mL, 2.5 mmol), were added to dimethoxyethane (10 mL) in a round bottomed flask fitted with a reflux condenser. The solution was stirred at 70 °C for 2 h while being monitored for the disappearance of the starting material by TLC. The resulting solution was filtered through a pad of celite, concentrated in vacuo then purified via flash silica chromatography (9 : 1 petroleum ether : diethyl ether) to yield the title compound as a white solid (0.991 g, 89 %); mp 65-67 °C (lit 70-71°C); C_{16}H_{14}O, HRMS [EI](M^+), required 222.1045, found 222.1046; ν_{max} (thin film)/cm\(^{-1}\) 3059, 2974, 2942, 2874 (CH), 1699 (CO), 1492, 1323, 1142 (selected fingerprint); δH (400 MHz; CDCl\(_3\)); 7.59-7.63 (3H, m, H12, H14), 7.24-7.30 (3H, m, H13, H5), 6.25 (1H, dd, J 5.2 Hz, J 2.4 Hz, H8/H9), 6.16 (1H, dd, J 5.2 Hz, J 2.4 Hz, H8/H9), 2.93 (1H, br s, H6), 2.74-2.76 (1H, m, H1), 2.69-2.7 (1H, m, H7), 2.37-2.39 (1H, m, H2), 1.32-1.33 (1H, m, 1 x H10), 1.24-1.26 (1H, m, 1 x H10); δC (100.6 MHz; CDCl\(_3\)); 207.7 (q, C3), 159.8 (CH, C5), 147.1 (q, C4), 138.5, 137.1 (CH, C8 and C9), 131.6 (q, C11), 128.38 (2 x CH, C12), 128.32 (CH, C14), 127.0 (2 x CH, C13), 53.4 (CH, C2), 47.1 (CH, C7), 44.1 (CH, C1), 43.3 (CH, C6), 41.3 (CH\(_2\), C10); m/z 222 (M\(^+\), 79 %), 156 (100 %), 128 (44 %).
Pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium dicobalt pentacarbonyldiphenylacetylene (0.796 g, 0.93 mmol) and norbornadiene (0.5 mL, 4.67 mmol), were added to dimethoxyethane (20 mL) in a round bottomed flask fitted with a reflux condenser. The solution was stirred at 70 °C for 2 h while being monitored for the disappearance of the starting material by TLC. The resulting solution was filtered through a pad of celite, rotary evaporated to dryness then purified via flash silica chromatography (9 : 1 petroleum ether : diethyl ether) to yield the title compound as a white solid (0.032 g, 11 %); mp 114-117 °C (lit 117-118 °C); \( \nu_{\text{max}} \) (thin film)/cm\(^{-1} \) 3056, 2974, 2938, (CH), 1694 (CO), 1591, 1442, 1347, 1167, 911 (selected fingerprint); \( \delta^H \) (250 MHz; CDCl\(_3\)) 7.17-7.37 (10H, m, Ar-H), 6.32-6.35 (2H, m, H8, H9), 3.36 (1H, d, \( J \) 5.4 Hz, H6), 3.13-3.17 (1H, m, H7), 2.62-2.67 (2H, m, H1, H2), 1.46-1.54 (2H, m, H10); \( \delta^C \) (100.6 MHz; CDCl\(_3\)) 207.3 (q, C3), 170.0 (q, C5), 143.8 (q, C4), 138.5 (CH, C8/C9), 138.1 (CH, C8/C9), 135.2 (q, C11/C15), 132.2 (q, C11/C15), 129.8, 129.5, 128.7, 128.6, 128.0, (10 x ArCH, C12-14 and 16-18), 52.8 (CH, C2), 50.4 (CH, C7), 44.2 (CH, C1), 43.3 (CH, C6).
Dicobalt pentacarbonyl-1,3-bis(2,6-diisopropylphenyl)-imidazolium propyne
tetrafluoroborate (228)

Tetrafluoroboric acid (0.10 mL, 0.60 mmol), was added dropwise to a solution of dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium propynol (0.386 g, 0.55 mmol) in diethyl ether (10 mL) at ambient temperature. The solution was stirred for 10 min during which a purple precipitate formed. The solution was then filtered and washed with further portions of diethyl ether until the washings remained colourless. The solid was then dried to yield the title compound as a purple solid (0.189 g, 44 %); mp 123 °C (decomposed); C_{34}H_{39}Co_2N_2O_4, HRMS [FAB](M^+-CO,-BF_4), required 657.16247, found 657.16165; ν_{max} (thin film)/cm\(^{-1}\) 3176, 3103, 2967, 2930, 2871 (CH), 2112, 2068, 2003, (M-CO), 1460, 1059 (selected fingerprint); m/z 657 (M^+-CO,-BF_4, 5 %), (573, 9 %), 545 (28 %), 476 (100 %).
Dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium 3-methoxy-propyne (229)

Methanol (0.3 mL) was added to a solution of dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium propyne tetrafluoroborate (0.051 g, 0.065 mmol) in anhydrous MeCN (3.0 mL) at ambient temperature under an atmosphere of nitrogen. After 5 min Hünigs base (0.02 mL, 0.13 mmol) was added to the solution. The solution was then filtered through a pad of celite and silica and concentrated in vacuo before purification by flash silica chromatography (8 : 1 petroleum ether : diethyl ether), to yield the title complex (0.023 g, 50 %), as a dark purple solid. $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 2965, 2925, 2866, 2813 (CH), 2055, 2001, 1967, 1942 (M-CO), 1456, 1093 (selected fingerprint); $\delta$H (400 MHz; CDCl$_3$) 7.56 (2H, t, J 7.6 Hz, H10), 7.36 (4H, d, J 7.6 Hz, H9), 7.01 (2H, s, H6), 4.17 (2H, s, H3), 4.10 (1H, s, H1), 3.39 (3H, s, H4), 2.59 (2H, sept, J 6.8 Hz, H11), 2.56 (2H, sept, J 6.8 Hz, H12), 1.43 (6H, d, J 6.8 Hz, H12), 1.39 (6H, d, J 6.8 Hz, H11), 1.12 (6H, d, J 6.8 Hz, H12), 1.10 (6H, d, J 6.8 Hz, H12); $\delta$C (100.6 MHz; CDCl$_3$) 146.2 (4 x q, C8), 137.2 (2 x q, C7), 130.3 (2 x CH, C10), 125.4, 124.1 (4 x CH, C9), 73.2 (CH$_2$, C3), 65.4 (CH, C1), 58.1 (CH$_3$, C4), 28.6 (4 x CH, C11), 25.9, 25.7, 22.6 (8 x CH$_3$, C12), (M-CO, C5 not seen).

Mass ion not found.
Dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium-(prop-2-yne-sulfonyl)-benzene (230)

Dicobaltpentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazoliumpropyne tetrafluoroborate (0.111 g, 0.14 mmol) and benzenesulphinic acid sodium salt (0.035 g, 0.21 mmol) were dissolved in anhydrous MeCN (10 mL) at ambient temperature under an atmosphere of nitrogen. After 10 min the solution was then filtered through a pad of celite and silica, then concentrated in vacuo before purification by flash silica chromatography (1:1, petroleum ether : diethyl ether), to yield the title complex (0.113 g, 94%), as a dark purple solid; \( \nu_{\text{max}} \) (thin film)/cm\(^{-1}\) 3136, 3069, 2963, 2928, 2868 (CH), 2058, 2004, 1992, 1947 (M-CO), 1692, 1467, 1446, 1147 (selected fingerprint); \( \delta \)H (400 MHz; CDCl\(_3\)) 7.84 (2H, d, J 7.6 Hz, H5), 7.24-7.63 (9H, m, H6/H7/H12/H13), 7.01 (2H, s, H9), 4.48 (1H, s, H1), 4.11 (1H, d, J 14.4 Hz, 1 x H3), 3.89 (1H, d, J 14.4 Hz, 1 x H3), 2.58 (2H, sept, J 6.8 Hz, H14), 2.55 (2H, sept, J 6.7 Hz, H14), 1.43 (6H, d, J 6.7 Hz, H15), 1.33 (6H, d, J 6.7 Hz, H15), 1.09 (6H, d, J 6.7 Hz, H15), 1.07 (6H, d, J 6.7 Hz, H15); \( \delta \)C (100.6 MHz; CDCl\(_3\)) 205.1, 200.5 (q, M-CO), 147.4 (q, C4), 146.0, 146.1 (4 x q, C11), 137.0 (2 x q, C10), 125.6 (2 x CH, C9), 130.5, 129.0, 127.8, 124.2, 124.1 (11 x CH, C5/C6/C7/C12/C13), 70.8 (q, C2), 69.0 (CH, C1), 60.1 (CH\(_2\), C3), 28.6 (2 x CH, C14), 25.9, 25.8 (4 x CH\(_3\), C15), 22.8, 22.7 (4 x CH\(_3\), C15).

Mass ion not found
Dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium propyne-

$H$-benzatriazole (231)

Dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium propyne-
tetrafluoroborate (0.050 g, 0.07 mmol) and benzatriazole (0.015 g, 0.13 mmol) were
dissolved in anhydrous MeCN (3.0 mL) at ambient temperature under an atmosphere of
nitrogen. After 5 min Hünigs base (0.023 mL, 0.13 mmol) was added to the solution. The
solution was then filtered through a pad of celite and silica, then concentrated in vacuo
before purification by flash silica chromatography (3:1, petroleum ether:diethyl ether),
to yield the title complex (0.037 g, 71 %), as a red solid; $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 3069, 2964,
2928, 2868 (CH), 2055, 2001, 1951 (M-CO), 1686, 1296 (selected fingerprint); $\delta$H (400
MHz; CDCl$_3$) 7.60 (2H, t, $J$ 7.6 Hz, H12), 7.23-7.31, 7.37-7.45 (8H, 2 x m, H5, H6, H11),
7.10 (2H, s, H8), 5.46 (1H, d, $J$ 7.7 Hz, H3), 5.28 (1H, d, $J$ 7.7 Hz, H3), 4.38 (1H, s, H1),
2.71 (2H, sept, $J$ 6.7 Hz, H13), 2.66 (2H, sept, $J$ 6.7 Hz, H13), 1.50 (6H, d, $J$ 6.7 Hz, H14),
1.45 (6H, d, $J$ 6.7 Hz, H14), 1.17 (6H, d, $J$ 6.7 Hz, H14), 1.15 (6H, d, $J$ 6.7 Hz, H14); $\delta$C
(100.6 MHz; CDCl$_3$) 201.2 (M-CO), 47.6, 45.8 (2 x q, C4), 146.5, 146.4 (4 x q, C10),
137.4 (2 x q, C9), 130.2 (2 x CH, C12), 125.9 (2 x CH, C8), 126.9, 124.6, 124.0, 123.7,
109.9 (8 x CH, C11/C5/C6), 82.7 (q, C2), 67.1 (CH, C1), 49.7 (CH$_2$, C3), 29.0, 28.7 (4 x
CH, C13), 26.5, 25.9, 23.2, 23.0 (8 x CH$_3$, C14). Mass ion not found
Dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium diallyl-prop-2-ynyl-amine (232)

Diallylamine (0.016 mL, 0.13 mmol) was added to a solution of dicobalt pentacarbonyl-1,3-bis-(2,6-diisopropylphenyl)-imidazolium propyne tetrafluoroborate (0.050 g, 0.065 mmol) in anhydrous MeCN (3.0 mL) at ambient temperature under an atmosphere of nitrogen. After 5 min Hünigs base (0.023 mL, 0.13 mmol) was added to the solution. The solution was then filtered through a pad of celite and silica, then concentrated in vacuo before purification by flash silica chromatography (8:1, petroleum ether: diethyl ether), to yield the title complex (0.035 g, 70%), as a red solid. mp 151-153 °C; C_{39}H_{49}Co_{2}N_{3}O_{4}, HRMS [FAB](M+2CO), required 725.2646, found 725.2651; $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 3071, 2964, 2926, 2867 (CH), 2047, 1992, 1942 (M-CO), 1465, 1294, 919 (selected fingerprint); $\delta$H (400 MHz; CDCl$_3$) 7.54 (2H, t, $J_{7.8}$ Hz, H12), 7.37 (2H, d, $J_{7.8}$ Hz, H11), 7.29 (2H, d, $J_{7.8}$ Hz, H11), 7.00 (2H, s, H8), 5.65-5.76 (2H, m, H5), 5.00-5.09 (4H, m, H6), 4.18 (1H, s, H1), 3.50 (1H, d, $J_{14.3}$ Hz, H3), 3.16 (2H, dd, $J_{13.9}$ Hz, $J_{5.2}$ Hz, H4), 3.03 (1H, d, $J_{14.2}$ Hz, H3), 2.72 (2H, dd, $J_{13.9}$ Hz, $J_{6.2}$ Hz, H4), 2.67 (2H, sept, $J_{6.8}$ Hz, H13), 2.54 (2H, sept, $J_{6.8}$ Hz, H13), 1.41 (6H, d, $J_{6.8}$ Hz, H14), 1.38 (6H, d, $J_{6.8}$ Hz, H14), 1.12 (6H, d, $J_{6.8}$ Hz, H14), 1.11 (6H, d, $J_{6.8}$ Hz, H14); $\delta$C (100.6 MHz; CDCl$_3$) 146.3, 146.2 (4 x q, C10), 137.3 (2 x q, C9), 137.3. 136.4 (2 x CH, C5), 130.3 (2 x CH, C12), 197
n-Butyllithium (1.76 mL, 4.0 mmol), was added dropwise to a solution of 3,3-dimethyl-1-butyne (0.50 mL, 4.0 mmol) in THF (10 mL) at –78 °C under an atmosphere of nitrogen. After stirring for 15 min citronellal (0.84 mL, 4.40 mmol) was added then the mixture warmed to ambient temperature over a 1 h period. The resulting solution was quenched with water (10 mL), extracted into diethyl ether, dried over MgSO₄, then concentrated in vacuo. The crude product was purified via column chromatography to yield the title compound (0.843 g, 92 %) as a colourless oil. \( \nu_{\text{max}} \) (thin film)/cm\(^{-1} \) 3335 (OH), 2966, 2962, 2867 (CH), 2238 (alkyne), 1457, 1367, 1361, 1263 (selected fingerprint); \( \delta H \) (250 MHz; CDCl₃) 5.01-5.23 (1H, br t, H₈), 4.40 (1H, m, H₂), 1.97-2.2 (1H, m, H₃), 1.67 (3H, s, H₉), 1.60 (3H, s, H₁₀), 1.31-1.70 (7H, m, H₄-H₇), 1.21 (9H, s, H₁), 0.81-0.93 (3H, m, H₁₁).

The compound was immediately epoxidised.
9-(3,3-Dimethyl-oxiranyl)-2,2,7-dimethyl-non-3-yn-5-ol (238)

meta-chloroperbenzoic acid (0.464 g, 2.7 mmol), was added slowly to a solution of 2,2,7,11-Tetramethyl-dodec-10-en-3-yn-5-ol (0.41 g, 1.8 mmol) and NaHCO₃ (3.02 g, 3.6 mmol) in dry DCM (30 mL) at 0 °C over a 10 min period. The resulting mixture was warmed to ambient temperature while stirring for 2.5 h. After this time TLC analysis showed complete loss of the starting material. The product was then partitioned between DCM and 2M NaOH, the organic fraction dried over MgSO₄, then concentrated in vacuo. The resulting pale yellow oil was analysed by ¹H NMR and IR then immediately complexed to dicobalt octacarbonyl as it appeared unstable (depth of yellow colour increased significantly). The epoxidation was evidenced by the disappearance of the alkene peak at 5.1 ppm, and the appearance of an epoxide CH peak at 2.6 ppm. ν_max (thin film)/cm⁻¹: 3420 (OH), 2946, 2927, 2867 (CH), 2235 (alkyne), 1457, 1387, 1262, 1119, 1031 (selected fingerprint); δH (250 MHz; CDCl₃) 4.36 (1H, t, J 6.7 Hz, H2), 2.63-2.68 (lH, m, H7), 2.40-2.59 (1H, m, H12), 1.35 (3H, s, H9), 1.26 (3H, s, H8), 1.21-1.90 (7H, m, H3-H6), 1.20 (9H, s, H1), 0.79-0.92 (3H, m, H10).
Dicobalt hexacarbonyl-9-(3,3-Dimethyl-oxiranyl)-2,2,7-dimethyl-non-3-yn-5-ol (239)

9-(3,3-Dimethyl-oxiranyl)-2,2,7-dimethyl-non-3-yn-5-ol (0.54 g, 1.80 mmol) was added to a solution of dicobalt octacarbonyl (0.677 g, 1.80 mmol) in DCM (30 mL) under an atmosphere of nitrogen. The solution was left to stir for 4 h, then filtered through a pad of celite and silica then concentrated in vacuo. The product was purified *via* flash silica chromatography (5 : 1 petroleum ether : diethyl ether) to yield the *title compound* (0.54 g, 71 % over 2 steps) (4 inseparable diastereoisomers) as a deep red oil; \( \text{C}_{22}\text{H}_{28}\text{Co}_{2}\text{O}_8 \), HRMS [FAB](M\(^{+}\)-2CO), required 482.0549, found 482.0544; \( \nu_{\text{max}} \) (thin film)/cm\(^{-1}\) 3447 (OH), 2965, 2929, 2869 (CH), 2085, 2043, 2016 (M-CO), 1473, 1458, 1379, 1360 (selected fingerprint); \( \delta \)H (400 MHz; CDCl\(_3\)) 4.79-4.82 (1H, m, H5), 2.73-2.78 (1H, m, H10), 1.45-1.89 (8H, m, H6-H9 and H15), 1.33 (9H, s, H1), 1.31 (3H, d, \( J = 1.7 \) Hz, H13), 1.28 (3H, d, \( J = 0.7 \) Hz, H12), 1.00-1.06 (3H, m, H14); \( \delta \)C (100.6 MHz; CDCl\(_3\)) 200.2 (q, M-CO), 110.7 (q, C4), 102.7 (q, C3), 69.6, 69.8 (CH, C5), 64.54, 64.5, 64.64, 64.66 (CH, C10), 58.3, 58.4, 58.5, 58.6 (q, C11), 46.8, 47.6, 47.7, 47.9 (CH\(_2\), C6), 36 2 (q, C2), 34.6, 34.7 (CH\(_2\) C9), 32.77, 32.81, 32.84 (3 x CH\(_3\), C1), 29.2, 29.8, 28.9, 30.3 (CH, C7), 25.9, 26.0, 26.46, 26.48, (CH\(_2\), C8), 24.9 (CH\(_3\), C12), 19.0, 19.6, 20.5, 20.7 (CH\(_3\), C14), 18.61, 18.64, 18.7 (CH\(_3\), C13); \( m/z \) 482 (M\(^{+}\)-2CO, 27 %), 454 (64 %), 426 (100 %), 398 (10 %), 370 (50 %).
2,2,7,11-Tetramethyl-dodec-10-en-3-yn-5-ol (0.43 g, 1.94 mmol), was dissolved in dry THF under an atmosphere of nitrogen. The solution was then cooled to 0 °C. Sodium hydride (1.160 g, 2.91 mmol), was then added and the mixture left to stir at 0 °C for 10 min. MeI (0.36 mL, 5.82 mmol) was then added and the solution warmed to ambient temperature over 1 h. The product was then partitioned between diethyl ether and water, the organic fraction dried over MgSO₄ then concentrated in vacuo to give the title compound as a colourless oil. ¹H NMR and IR analysis of the crude product showed the disappearance of the OH peak (3335 cm⁻¹) and the appearance of a methoxy proton peak at 3.5 ppm. The crude product was immediately epoxidised.

**3-(5-Methoxy-3,8,8-trimethyl-non-6-ynyl)-2,2-dimethyl-oxirane**

*meta*-chloroperbenzoic acid (0.498 g, 2.90 mmol), was added slowly to a solution of crude 8-methoxy-2,6,11,11-tetramethyl-dodec-2-en-9-yne (1.94 mmol) and NaHCO₃ (0.327 g,
2.90 mmol) in dry DCM (30 mL) at 0 °C over a 10 min period. The resulting mixture was warmed to ambient temperature while stirring for 2.5 h. After this time TLC analysis showed complete disappearance of the starting material. The product was then partitioned between DCM and 2M NaOH, the organic fraction dried over MgSO4, then concentrated in vacuo. 1H NMR analysis of the crude product showed the disappearance of the alkenyl proton (5.1 ppm) and the corresponding appearance of the epoxide proton (2.6 ppm). The crude product was immediately complexed with dicobalt octacarbonyl.

Dicobalt hexacarbonyl-3-(5-methoxy-3,8,8-trimethyl-non-6-ynyl)-2,2-dimethyl-oxirane (240)

![Diagram of the compound]

3-(5-Methoxy-3,8,8-trimethyl-non-6-ynyl)-2,2-dimethyl-oxirane (1.94 mmol) was added to a solution of dicobalt octacarbonyl (0.73 g, 1.94 mmol) in DCM (30 mL) under an atmosphere of nitrogen. The solution was left to stir for 4 h then filtered through a pad of celite and silica and concentrated in vacuo. The product was purified via flash silica chromatography (9 : 1 petroleum ether : diethyl ether) to yield the title compound (0.594 g, 56 % over 3 steps) (4 inseparable diastereoisomers) as a deep red oil; C23H30C02Og, HRMS [FAB](M+-2CO), required 496.0706, found 496.0700; \( \nu_{\text{max}} \) (thin film)/cm\(^{-1} \) 2964, 2929, 2823 (CH), 2086, 2044, 2020 (M-CO), 1460, 1377, 1360, 1090 (selected fingerprint); \( \delta \)H (400 MHz; CDCl\(_3\)) 4.38-4.41 (1H, m, H5), 3.57, 3.55 (3H, 2 x s, H15), 2.73-2.76 (1H, m, H10), 1.46-1.92 (7H, m, H6-H9), 1.34 (9H, s, H1), 1.31-1.33 (3H, m, H13), 1.26-1.30 (3H, m, H12), 1.06 (1.5H, d, J 6.5 Hz, H14), 1.02 (1.5H, d, J 6.5 Hz, H14); \( \delta \)C (100.6 MHz; CDCl\(_3\)) 200.4 (q, M-CO), 111.0, 110.8 (q, C4), 98.9, 98.8 (q, C3), 79.94, 79.99, 80.24, 80.28 (CH, C5), 64.42, 64.44, 64.46, 64.50 (CH, C10), 59.1, 59.3, 59.4, 59.5 (CH, C15), 58.3, 58.4, 58.5, 58.6 (q, C11), 47.14, 47.18, 47.25, 47.38 (CH2, C6), 36.21, 36.25 (q, C2), 34.5, 34.6 (CH2, C9), 32.9, 32.8 (CH3, C1), 29.7, 30.0, 30.1, 30.4 (CH, C7), 26.1, 202
26.4, 26.5 (CH$_2$, C8), 24.9 (CH$_3$, C12), 19.1, 19.2, 20.3, 20.4 (CH$_3$, C14), 18.6, 18.7 (CH$_3$, C13); m/z 496 (M$^+$-2CO, 13%), 468 (26%), 440 (100%), 384 (53%).

[El]-2,6,11,11-Tetramethyldodec-7-en-9-yn-3-one (241)

Dicobalt hexacarbonyl 9-(3,3-Dimethyl-oxiranyl)-2,2,7-dimethyl-non-3-yn-5-ol (0.601 g, 1.11 mmol) was dissolved in dry DCM (10 mL) and cooled to 0 °C under an atmosphere of nitrogen. Tetrafluoroboric acid (0.16 mL, 0.14 mmol) was then added dropwise and the solution left to stir at 0 °C for 1 h while following by TLC. The solution was then filtered through a plug of celite and silica, concentrated in vacuo then purified via column chromatography to give an initial product as a dark purple oil (0.303 g, 52%). Due to difficulty with analysis this product was then dissolved in acetone and cerium ammonium nitrate (0.99 g, 1.80 mmol) added, along with a few drops of methanol. After 1h no starting material remained. The solution was partitioned between diethyl ether and water, the organic layer dried over MgSO$_4$, concentrated in vacuo, then purified via flash silica chromatography (9 : 1 petroleum ether : diethyl ether), to yield the title product (0.113 g, 81%) as a colourless oil; C$_{16}$H$_{26}$O, HRMS [EI], required 234.1984, found 234.1985; $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 2966, 2928, 2869 (CH), 1712 (CO), 1455, 1361, 1265, 959 (selected fingerprint); $\delta$H (400 MHz; CDCl$_3$) 5.77 (1H, dd, $J$ 15.8 Hz, $J$ 6.8 Hz, H6), 5.37 (1H, d, $J$ 15.8 Hz, H5), 2.51 (1H, sept, $J$ 6.8 Hz, H11), 2.35 (2H, t, $J$ 6.7 Hz, H9), 2.03-2.10 (1H, m, H7), 1.18-1.55 (2H, m, H8), 1.17 (9H, s, H1), 1.01 (6H, d, $J$ 6.8 Hz, H12), 0.79 (3H, d, $J$ 6.7 Hz, H13); $\delta$C (100.6 MHz; CDCl$_3$) 214.6 (q, C10), 147.4 (CH, C6), 109.2 (CH, C5), 97.3 (q, C4), 77.3 (q, C3), 40.9 (CH, C11), 38.3 (CH$_2$, C9), 37.1 (CH, C7), 30.8 (CH$_3$, C1), 30.2 (CH$_2$, C8), 27.8 (q, C2), 20.3 (CH$_3$, C13), 18.3, 18.2 (CH$_3$, C12); m/z 234 (M$^+$, 6%), 191 (38%), 163 (37%), 148 (79%), 133 (100%).
2-(3-Methyl-but-2-enyloxyl-benzaldehyde

K₂CO₃ (6.90 g, 50.00 mmol), and potassium iodide (0.410 g, 2.50 mmol) were added to a solution of 3,3-dimethylallyl bromide (1.50 mL, 12.50 mmol) and salicylaldehyde (1.07 mL, 10.40 mmol) in dry DMF (30 mL) at ambient temperature. After a few minutes the solution became a bright yellow colour. This solution was then stirred for 4 h while monitoring by TLC. The solution was decanted into water (40 mL) and the aqueous phase extracted into diethyl ether (6 x 10 mL), the organic layer was then washed sequentially with 10 % aqueous HCl (30 mL), 10 % aqueous K₂CO₃ (30 mL), then dried over MgSO₄, and concentrated in vacuo. It was then purified via flash silica chromatography (18 : 1 petroleum ether : diethyl ether), to yield the title compound (1.932 g, 98 %) as a pale yellow oil; C₁₂H₁₄O₂ HRMS [El], required 190.09938, found 190.09973; νmax (thin film)/cm⁻¹ 3073, 3031, 2973, 2914, 2859 (CH), 1683 (CO), 1597, 1479, 1160, 991 (selected fingerprint); δH (400 MHz; CDCl₃) 10.49 (1H, s, H1), 7.83 (1H, d, J 7.6 Hz, H3), 7.53 (1H, t, J 7.6 Hz, H5), 8.85-7.02 (2H, m, H6, H4), 5.51 (1H, t, J 4.1 Hz, H9), 4.64 (2H, d, J 4.1 Hz, H8), 1.81 (3H, s, H11), 1.76 (3H, s, H12); δC (100.6 MHz; CDCl₃) 189.9 (CH, C1), 161.3 (q, C7), 138.7 (q, C10), 135.7 (CH, C5), 128.2 (CH, C3), 125.1 (q, C2), 120.5 (CH, C4), 119.0 (CH, C9), 112.9 (CH, C6), 65.5 (CH₂, C8), 25.7 (CH₃, C12), 18.2 (CH₃, C11); m/z 190 (M+, 3 %), 122 (79 %), 69 (100 %).
2-Methyl-4-(2-(1-hydroxyprop-2-yn-1-yl)-phenoxy)-but-2-ene

Ethynylmagnesium bromide (32.0 mL, 16.0 mmol) (0.5 M solution in THF) was added dropwise to a solution of 2-(3-methoxy-but-2-enyloxy)-benzaldehyde (2.029 g, 10.7 mmol) in dry THF (10 mL) under an atmosphere of nitrogen at 0 °C. The solution was stirred at this temperature for 10 min then warmed to ambient temperature over a 1 h period. The mixture was quenched with aqueous ammonium chloride (10 mL) then the THF removed in vacuo. The aqueous layer was then extracted into ether (4 x 10 mL) then dried over MgSO₄, concentrated in vacuo, then purified via flash silica chromatography (3 : 1 cyclohexane : diethyl ether), to yield the title compound (1.881 g, 82 %) as a pale yellow oil; C₁₄H₁₆O₂, HRMS [El], required 216.1150, found 216.1146; νₘₐₓ (thin film)/cm⁻¹ 3423 (OH), 3290 (CC), 3062, 3035, 2972, 2913 (CH), 1675, 1600, 1487, 1233, 1016 (selected fingerprint); δH (400 MHz; CDCl₃); 7.52 (1H, dd, J 7.8 Hz, J 1.0 Hz, H5), 7.27 (1H, dt, J 7.8 Hz , J 1.0 Hz, H7), 6.95 (1H, t, J 7.8 Hz, H6), 6.90 (1H, d, J 7.8 Hz, H8), 5.70 (1H, dd, J 8.0 Hz, J 4.0 Hz, H3), 5.48 (1H, t, J 4.0 Hz, H11), 4.58 (2H, d, J 4.0 Hz, H10), 3.20 (1H, d, J 8.0 Hz, H15), 2.58 (1H, d, J 4.0 Hz, H1), 1.77 (3H, s, H13), 1.72 (3H, s, H14); δC (100.6 MHz; CDCl₃) 156.9 (q, C9), 138.5 (q, C12), 129.7 (CH, C7), 128.6 (q, C4), 127.9 (CH, C5), 120.8 (CH, C6), 119.3 (CH, C11), 112.1 (CH, C8), 83.6 (q, C2), 74.1 (CH, C1), 65.3 (CH₂, C10), 61.4 (CH, C3), 25.7 (CH₃, C13), 18.2 (CH₃, C14); m/z 216 (M⁺, 2 %), 130 (100 %), 102 (27 %), 69 (65 %).
2-Methyl-4-[2-(1-hydroxyprop-2-yn-1-yl)-phenoxy]-but-2-ene (245) (115)

2-Methyl-4-[2-(1-hydroxyprop-2-yn-1-yl)-phenoxy]-but-2-ene (1.00 g, 4.60 mmol) was added to a solution of dicobalt octacarbonyl (1.570 g, 4.60 mmol) in DCM (40 mL) under an atmosphere of nitrogen. After 4 h the deep red solution was filtered through a plug of celite and silica, concentrated in vacuo then purified via flash silica chromatography (4 : 1 petroleum ether : diethyl ether), to yield the title compound as a dark red oil (2.076 g, 90 %); C20H16Co2O8, HRMS [FAB] (M+ - CO), required 473.9561, found 473.9568; v_max (thin film)/cm⁻¹ 3439 (OH), 2976, 2916 (CH), 2092, 2054, 2020 (M-CO). 1598, 1231 (selected fingerprint); δH (400 MHz; CDCl3) 7.36 (1H, dd, J 7.5 Hz, J 1.7 Hz, H5), 7.24 (1H, dt, J 7.5 Hz, J 1.7 Hz, H7), 6.96 (1H, dt, J 7.5 Hz, J 1.7 Hz, H6), 6.87 (1H, dd, J 7.5 Hz, J 1.7 Hz, H8), 5.99 (1H, d, J 7.4 Hz, H3), 5.98 (1H, s, H1). 5.49-5.56 (1H, m, H11), 4.58 (2H, d, J 6.8 Hz, H10), 3.44 (1H, d, J 7.4 Hz, H15), 1.79 (3H, s, H13), 1.75 (3H, s, H14); δC (100.6 MHz; CDCl3) 199.4 (q, M-CO), 155.4 (q, C9), 138.5 (q, C12), 131.4 (q, C4), 128.8 (CH, C7), 127.1 (CH, C5), 120.8 (CH, C6), 119.2 (CH, C11), 111.7 (CH, C8), 100.1 (CH, C1), 72.5 (CH, C3), 65.8 (q, C2), 64.8 (CH2, C10), 25.7 (CH3, C13), 18.2 (CH3, C14); m/z 474 (M+ - CO, 5 %), 446 (17 %), 418 (100 %), 390 (73 %), 334 (29 %).

2-(3,7-Dimethyl-octa-2,6-dienyloxy)-benzaldehyde (249)
K₂CO₃ (1.120 g, 8.11 mmol), and potassium iodide (0.070 g, 0.40 mmol) were added to a solution of geranyl bromide (0.50 mL, 2.43 mmol) and salicylaldehyde (0.22 mL, 2.03 mmol) in dry DMF (9 mL) at ambient temperature. After a few minutes the solution became a bright yellow colour. This solution was then stirred 12 h. The solution was then decanted into water (20 mL) and the aqueous phase extracted into diethyl ether (6 x 5 mL) the organic layer was then washed sequentially with 10 % aqueous HCl (15 mL), 10 % aqueous K₂CO₃ (15 mL) then dried over MgSO₄, concentrated in vacuo, and purified via flash silica chromatography (18 : 1 petroleum ether : diethyl ether), to yield the title compound (0.516 g, 97 %) as a pale yellow oil; C₁₇H₂₂O₂, HRMS [EI], required 258.1619, found 258.1623; ν max (thin film)/cm⁻¹ 3073, 2966, 2919, 2856 (CH), 1687 (CO), 1597 (C=C), 1456, 1235, 988 (selected fingerprint); δH (400 MHz; CDCl₃) 10.51 (1H, s, H1), 7.84 (1H, d, J 7.6 Hz, H3), 7.53 (1H, t, J 7.6 Hz, H5), 7.00 (2H, m, H6, H4), 5.50 1H, t, J 4.1 Hz, H9), 5.09 (1H, t, J 4.2 Hz, H13), 4.67 (2H, d, J 4.1 Hz, H8), 2.09-2.15 (4H, m, H11, H12), 1.76 (3H, s, H15), 1.68 (3H, s, H16), 1.61 (3H, s, H17); δC (100.6 MHz; CDCl₃) 190.1 (CH, C1), 161.4 (q, C7), 141.9 (q, C10), 135.8 (CH, C5), 131.9 (q, C2), 128.3 (CH, C3), 125.2 (q, C14), 123.6 (CH, C9), 120.5 (CH, C4), 118.8 (CH, C13), 65.5 (CH₂, C8), 39.5, 26.2 (CH₂, C11, C12), 25.6 (CH₃, C15), 17.7 (CH₃, C16), 16.7 (CH₃, C17) ; m/z 258 (M⁺, 1 %), 137 (14 %), 122 (18 %), 93 (14 %), 81 (28 %), 69 (100 %).
K$_2$CO$_3$ (0.730 g, 5.28 mmol), and potassium iodide (0.044 g, 0.26 mmol) were added to a solution of farnesyl bromide (0.50 mL, 1.58 mmol) and salicylaldehyde (0.14 mL, 1.32 mmol) in dry DMF (6 mL) at ambient temperature. After a few minutes the solution became a bright yellow colour. The solution was stirred for 12 h then decanted into water (20 mL) and the aqueous phase extracted into diethyl ether (6 x 5 mL). The organic layer was washed sequentially with 10 % aqueous HCl (15 mL), 10 % aqueous K$_2$CO$_3$ (15 mL), then dried over MgSO$_4$, concentrated in vacuo, then purified via flash silica chromatography (18 : 1 petroleum ether : diethyl ether), to yield the title compound (0.401 g, 93 %) as a pale yellow oil; C$_{22}$H$_{30}$O$_2$, HRMS [EI], required 326.2247, found 326.2253; $\nu$$_{max}$ (thin film)/cm$^{-1}$ 3073, 2924, 2756 (CH), 1692 (CO), 1590 (C=C), 1479, 1382, 1160, 990, 756 (selected fingerprint); $\delta$H (400 MHz; CDCl$_3$) 10.51 (1H, s, H1), 7.83 (1H, d, 17.8 Hz, H3), 7.53 (1H, t, J 7.8 Hz, H5), 6.89-7.03 (2H, m, H4/H6), 5.51 (1H, t, J 4.1 Hz, H9), 6.8-5.13 (2H, m, H13/H17), 4.67 (2H, d, J 4.1 Hz, H8), 1.96-2.16 (8H, m, H11/H12/H15/H16), 1.66 (3H, s, H19), 1.68 (3H, s, H20), 1.51 (3H, s, H21/H22), 1.60 (3H, s, H21/H22); (100.6 MHz; CDCl$_3$) 189.9 (CH, C1), 161.3 (q, C7), 141.8 (q, C10), 135.7 (CH, C5), 135.5 (q, C14), 131.3 (q, C2), 128.3 (CH, C3), 125.2 (q, C18), 124.3 (CH, C13), 123.5 (CH, C9), 120.5 (CH, C4), 118.8 (CH, C17), 112.9 (CH, C6), 65.5 (CH$_2$, C8), 39.7, 39.6 (2 x CH$_2$, C11, C12), 26.1, 25.8 (2 x CH$_2$, C15, C16), 25.6 (CH$_3$, C19), 17.6 (CH$_3$, C20), 16.7 (CH$_3$, C21), 16.0 (CH$_3$, C22); m/z 326 (M$^+$, 1 %), 204 (6 %), 137 (17 %), 122 (17 %), 93 (28 %), 81 (60 %), 69 (100 %).
1-[2-(3,7-Dimethyl-octa-2,6-dienyloxy)-phenyl]-propyn-3-ol

(251)

Ethynylmagnesium bromide (13.0 mL, 6.50 mmol) (0.5 M solution in THF) was added dropwise to a solution of 2-(3,7-Dimethyl-octa-2,6-dienyloxy)-benzaldehyde (1.590 g, 5.60 mmol) in dry THF (10 mL) under an atmosphere of nitrogen at 0 °C. The solution was stirred at this temperature for 10 min then warmed to ambient temperature over a 1 h period. The mixture was quenched with aqueous ammonium chloride (10 mL), and then the THF removed in vacuo. The aqueous layer was then extracted into ether (4 x 10 mL), then dried over MgSO₄, concentrated in vacuo, then purified via flash silica chromatography (3 : 1 cyclohexane : diethyl ether), to yield the title compound (1.351 g, 94 %) as a pale yellow oil; ν_max (thin film)/cm⁻¹ 3432 (OH), 3294 (CC), 2965, 2920 (CH), 1669, 1600, 1490, 1232, 1017, 751 (selected fingerprint); δH (400 MHz; CDCl₃); 7.52 (1H, dd, J 7.8 Hz, J 1.5 Hz, H5), 7.27 (1H, dt, J 7.0 Hz, J 1.5 Hz, H7), 6.95 (1H, t, J 7.8 Hz, H6), 6.90 (1H, d, J 7.8 Hz, H8), 5.68 (1H, dd, J 8.0 Hz, J 4.0 Hz, H3), 5.48 (1H, t, J 4.0 Hz, H11), 5.07 (1H, t, J 4.0 Hz, H15), 4.61 (2H, d, J 4.0 Hz, H10), 3.20 (1H, t, J 8.0 Hz, H20), 2.58 (1H, d, J 4.0 Hz, H1), 2.05-2.12 (4H, m, H13, H14), 1.72 (3H, s, H17), 1.66 (3H, s, H18), 1.59 (3H, s, H19); δC (100.6 MHz; CDCl₃) 156.1 (q, C9), 141.6 (q, C12), 131.9 (q, C16), 129.6 (CH, C7), 128.6 (q, C4), 127.9 (CH, C5), 123.6 (CH, C15), 120.8 (CH, C6), 119.2 (CH, C11), 112.1 (CH, C8), 83.1 (q, C2), 74.0 (CH, C1), 65.3 (CH₂, C10), 61.4 (CH, C3), 39.4 (CH₂, C13), 26.2 (CH₂, C14), 25.6 (CH₃, C17), 17.7 (CH₃, C18), 16.6 (CH₃, C19).

No mass ion found.
Ethynylmagnesium bromide (15.0 mL, 7.50 mmol) (0.5 M solution in THF) was added dropwise to a solution of 2-(3,7,11-trimethyl-dodeca-2,6,10-trienyloxy)-benzaldehyde (1.630 g, 5.00 mmol) in dry THF (10 mL) under an atmosphere of nitrogen at 0 °C. The solution was left to stir at this temperature for 10 min then warmed to ambient temperature over a 1 h period. The mixture was quenched with aqueous ammonium chloride (10 mL) then the THF removed *in vacuo*. The aqueous layer was then extracted into ether (4 x 10 mL), then dried over MgSO₄, concentrated *in vacuo*, then purified *via* flash silica chromatography (3 : 1 cyclohexane : diethyl ether), to yield the *title compound* (1.602 g, 91 %) as a pale yellow oil; ν<sub>max</sub> (thin film)/cm<sup>-1</sup> 3444 (OH), 3304 (CC), 2995, 2922 (CH), 1667, 1600, 1488, 1232, 1017, 751 (selected fingerprint); δH (400 MHz; CDCl₃); 7.52 (1H, dd, J 7.8 Hz, J 1.5 Hz, H5), 7.29 (1H, dt, J 7.0 Hz, J 1.5 Hz, H7), 6.97 (1H, t, J 7.8 Hz, H6), 6.93 (1H, d, J 7.8 Hz, H8), 5.69 (1H, dd, J 8.0 Hz, J 4.0 Hz, H3), 5.50 (1H, t, J 4.0 Hz, H11), 5.10 (2H, m, H15, H19), 4.63 (2H, d, J 4.0 Hz, H10), 3.20 (1H, d, J 8.0 Hz, H25), 2.59 (1H, d, J 4.0 Hz, H11), 1.98-2.19 (8H, m, H13/H14/H17/H18), 1.74 (3H, s, H21), 1.69 (3H, s, H22), 1.61 (6H, s, H23/H24); δC (100.6 MHz; CDCl₃) 156.2 (q, C9), 141.7 (q, C12), 135.5 (q, C16), 131.9 (q, C20), 129.7 (CH, C7), 128.6 (q, C4), 127.9 (CH, C5), 124.3 (CH, C15), 123.6 (CH, C19), 120.8 (CH, C6), 119.2 (CH, C11), 112.2 (CH, C8), 83 1 (q, C2), 74.1 (CH, C1), 65.4 (CH, C10), 61.4 (CH, C3), 39.8, 39.5 (CH₂, C13/C17), 26.7, 26.2 (CH₂, C14/C18), 25.7 (CH₃, C21), 17.7 (CH₃, C22), 16.7 (CH₃, C24), 16.0 (CH₃, C23).

Mass ion not found.
Dicobalt hexacarbonyl-1-[2-(3,7-dimethyl-octa-2,6-dienyloxy)-phenyl]-propyn-3-ol

(253)

1-[2-(3,7-Dimethyl-octa-2,6-dienyloxy)-phenyl]-propyn-3-ol (1.00 g, 3.50 mmol) was added to a solution of dicobalt octacarbonyl (1.90 g, 3.50 mmol) in DCM (40 mL) under an atmosphere of nitrogen. After 4 h the deep red solution was filtered through a plug of celite and silica, concentrated in vacuo then purified via flash silica chromatography (5 : 1 petroleum ether : diethyl ether), to yield the title compound as a dark red oil (1.519 g, 76%); C_{25}H_{24}Co_{2}O_{8}, HRMS [FAB](M^+-3CO), required 486.0288, found 4486.0290; ν_{max} (thin film)/cm^{-1} 3461 (OH), 3073, 2967, 2924, 2857 (CH), 2091, 2054, 2022 (M-CO), 1487, 1453, 1231, (selected fingerprint); δH (400 MHz; CDCl₃); 7.36 (1H, dd, J 7.6 Hz, J 1.7 Hz, H5), 7.23 (1H, dt, J 7.6 Hz, J 1.7 Hz, H7), 6.96 (1H, t, J 7.6 Hz, H6), 6.87 (1H, d, J 7.6 Hz, H8), 5.99 (1H, d, J 7.4 Hz, H3), 5.97 (1H, s, H1), 5.51 (1H, t, J 6.5 Hz, H11), 5.05-5.08 (1H, m, H15), 4.61 (2H, d, J 6.5 Hz, H10), 3.39 (1H, d, J 7.4 Hz, H20), 2.04-2.17 (4H, m, H13,H14), 1.75 (3H, s, H17), 1.61 (3H, s, H18), 1.59 (3H, s, H19); 8C (100.6 MHz; CDCl₃) 199.4 (q, M-CO), 155.4 (q, C9), 141.6 (q, C12), 132.4 (q, C4), 131.9 (q, C16), 128.9 (CH, C7), 127.1 (CH, C5), 123.7 (CH, C15), 120.8 (CH, C6), 119.2 (CH, C11), 111.7 (CH, C8), 104.7 (q, C2), 100.1 (CH, C1), 72.4 (CH, C3), 65.2 (CH₂, C10), 39.5 (CH₂, C13), 26.3 (CH₂, C14), 25.7 (CH₃, C17), 17.7 (CH₃, C18), 16.7 (CH₃, C19); m/z 514 (M^+-2CO, 30%), 486 (59%), 430 (55%), 402 (79%).
Dicobalt hexacarbonyl-1-[2-(3,7,11-Trimethyl-dodeca-2,6,10-trienyloxy)-phenyl]-propan-3-ol (254)

1-[2-(3,7,11-Trimethyl-dodeca-2,6,10-trienyloxy)-phenyl]-propan-3-ol (1.00 g, 2.84 mmol) was added to a solution of dicobalt octacarbonyl (0.97 g, 2.84 mmol) in DCM (40 mL) under an atmosphere of nitrogen. After 4 h the deep red solution was filtered through a plug of celite and silica, concentrated in vacuo then purified via flash silica chromatography (8:1 petroleum ether:diethyl ether), to yield the title compound as a dark red oil (1.644 g, 90%); C$_{30}$H$_{32}$C$_{02}$O$_{8}$ HRMS [FAB](M$^+$-3CO), required 554.0914, found 554.0904; $\nu_{\text{max}}$ (thin film)/cm$^{-1}$: 3443 (OH), 2995, 2924 (CH), 2091, 2054, 2021 (M-CO), 1599, 1453, 1230 (selected fingerprint); $\delta$H (400 MHz; CDCl$_3$): 7.52 (1H, dd, J 7.8 Hz, J 1.7 Hz, H5), 7.29 (1H, dt, J 7.8 Hz, J 1.7 Hz, H7), 6.97 (1H, t, J 7.8 Hz, H6), 6.93 (1H, d, J 7.8 Hz, H8), 5.69 (1H, dd, J 8.0 Hz, J 4.0 Hz, H3), 5.50 (1H, t, J 4.0 Hz, H11), 5.08-5.13 (2H, m, H15, H19), 4.63 (2H, d, J 4.0 Hz, H10), 3.20 (1H, d, J 8.0 Hz, H25), 2.59 (1H, d, J 4.0 Hz, H1), 1.98-2.19 (8H, m, H13, H14, H17, H18), 1.74 (3H, s, H21), 1.69 (3H, s, H22), 1.61 (6H, s, H23, H24); $\delta$C (100.6 MHz; CDCl$_3$): 199.5 (q, M-CO), 156.2 (q, C9), 141.7 (q, C12), 135.5 (q, C16), 131.9 (q, C20), 129.7 (CH, C7), 128.6 (q, C4), 127.9 (CH, C5), 124.3 (CH, C15), 123.6 (CH, C19), 120.8 (CH, C6), 119.2 (CH, C11), 112.2 (CH, C8), 83.1 (q, C2), 74.1 (CH, C1), 65.4 (CH$_2$, C10), 61.4 (CH, C3), 39.8, 39.5 (CH$_2$, C13/C17), 26.7, 26.2 (CH$_2$, C14/C18), 25.7 (CH$_3$, C21), 17.7 (CH$_3$, C22), 16.7 (CH$_3$, C24), 16.0 (CH$_3$, C23) m/z 582 (4%), 554 (M$^+$-3CO, 22%), 498 (31%), 470 (100%), 453 (34%).
4-Ethynyl-3-(1-fluoro-1-methylethyl)chromane

Tetrafluoroboric acid (0.14 mL, 1.00 mmol), was added dropwise to a solution of dicobalt hexacarbonyl-2-Methyl-4-[2-(1-hydroxyprop-2-yn-1-yl)phenoxy]-but-2-ene (0.500 g, 1.00 mmol) in DCM (12 mL) at −10 °C under an atmosphere of nitrogen. After 20 min a methanolic solution of cerium ammonium nitrate (3.39 g, 6.00 mmol, in 30 mL), was added dropwise until the evolution of gas stopped and no trace of cobalt complex was visible by TLC. The reaction mixture was then quenched with aqueous NaHCO3, then extracted into diethyl ether and dried over MgSO4. The crude product was purified via flash silica chromatography (100 %, petroleum ether), then concentrated in vacuo, to give the title compound (0.1474 g, 68 %) as a colourless oil; C14H15FO, HRMS [El] required 218.11069, found 218.1169; νmax (thin film)/cm⁻¹ 3292, 2981 (CH), 1585, 1489, 1228 (selected fingerprint); δH (400 MHz; CDCl3) 7.38 (1H, d, J7.7 Hz, H8), 7.15 (1H, dt, J7.7 Hz, J 1.6 Hz, H7), 6.92 (1H, dt, J 7.7 Hz, J 1.6 Hz, H6), 6.81 (1H, dd, J 7.7 Hz, J 1.6 Hz, H5), 4.42 (1H, dd, J 11.8 Hz, J 2.8 Hz, 1 x H10), 4.15 (1H, dd, J 11.8 Hz, J 6.0 Hz, 1 x H10), 3.91 (1H, Br s, H3), 2.29-2.33 (1H, m, H11), 2.26 (1H, d, J 2.5 Hz, H1), 1.50 (3H, d, JHF 22.0 Hz, 1 x H13), 1.40 (3H, d, JHF 22.0 Hz, 1 x H13); δC (100.6 MHz; CDCl3) 153.8 (q, C9), 142.7 (q, C4), 129.9 (CH, C8), 128.3 (CH, C7), 121.3 (CH, C6), 117.0 (CH, C5), 90.6 (CF, d, JCF 168 Hz, C12), 86.6 (q, C2), 70.5 (CH, C1), 64.2, 64.1 (CH3, C10), 47.4 (CH, d, 3JCF 22.7 Hz C11), 27.8 (CH, C3), 25.7 (CH3, d, 2JCF 24.3 Hz, 1 x C13), 25.4 (CH3, d, 2JCF 97.0 Hz, 1 x C13), m/z (218 M⁺, 60 %), 155 (100 %), 102 (34 %).

A small amount of the degradation product 4-Ethynyl-3-(1-methylethynyl)chromane was visible in the 1H spectra, but at too low a level to characterise.
Dicobalt hexacarbonyl-2-ethylnylcyclopropane-1,1-dicarboxylic acid dimethyl ester

\[(255)\]^{(150)}

\[
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{CO}_2\text{Me} \\
\text{H} \\
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{6} \\
\text{7} \\
\text{(OC)}_3\text{Co} \rightarrow \text{Co(CO)}_3
\end{array}
\]

2-Ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.580 g, 3.20 mmol) was added to a solution of dicobalt octacarbonyl (1.200 g, 3.50 mmol) in DCM (20 mL) under an atmosphere of nitrogen. After 6 h the dark purple solution was filtered through a plug of celite and silica then concentrated \textit{in vacuo} then purified via flash silica chromatography (10:1 petroleum ether : diethyl ether) to yield the \textit{title compound} as a dark red solid (1.550 g, 85 %); C\textsubscript{15}H\textsubscript{10}Co\textsubscript{2}O\textsubscript{10}, HRMS [FAB] (M$^+$-2CO), required 411.9040 found 411.9036; $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 2094, 2053, 2020 (M-CO), 1736 (CO$_2$Me); $\delta$H (400 MHz; CDCl$_3$) 5.68 (1H, d, J 0.8 Hz, H1), 3.78, 3.77 (2 x 3H, s, H7), 3.34 (1H, ddd, J 0.8 Hz, 7.6 Hz, 9.2 Hz, H3), 1.90 (1H, dd, J 4.6 Hz, 9.2 Hz, 1 x H4), 1.77 (1H, dd, J 4.6 Hz, 7.6 Hz, 1 x H4); $\delta$C (100.6 MHz; CDCl$_3$) 199.5 (q, M-CO), 169.5, 167.6 (q, C6), 90.9 (q, C2), 69.2 (CH, C1), 53.4, 53.2 (CH$_3$, C7), 41.5 (q, C5), 31.6 (CH, C3), 27.0 (CH$_2$, C4); m/z 412 (M$^+$-2CO, 9 %), 384 (24 %), 356 (100 %), 328 (63 %), 300 (42 %).
2-Ethenylcyclopropane-1,1-dicarboxylic acid dimethyl ester (260)²⁰¹

![Chemical Structure](2-Ethenylcyclopropane-1,1-dicarboxylic acid dimethyl ester (260)²⁰¹)

Dimethyl malonate (5.89 mL, 51.50 mmol) was added dropwise to a solution of freshly prepared sodium methoxide (1.150 g, 50.00 mmol sodium in 20 mL methanol). (E)-1,4-dibromobutene (5.350 g, 25.00 mmol) in methanol (20 mL) was then added and the reaction mixture refluxed for 2.5 hr. After cooling to ambient temperature the white precipitate was filtered then the filtrate concentrated in vacuo to leave an oily residue. This was then partitioned between diethyl ether (30 mL) and distilled water (3 x 20 mL), dried over MgSO₄, filtered then concentrated in vacuo to leave a pale yellow oil. The product was then purified via flash silica chromatography (5:1 petroleum ether: diethyl ether) to yield the title compound as a colourless oil (6.700 g, 90%); C₉H₁₂O₄, HRMS [EI], required 184.0736, found 184.0738; ν max (thin film)/cm⁻¹ 2955 (CH), 1730 (CO₂Me), 1638, 1438, 1331, 1274 (selected fingerprint); δH (400 MHz; CDCl₃); 5.41 (1H, m, H₃), 5.27 (1H, d, J 17.0 Hz, H1), 5.13 (1H, d, J 10.5 Hz H2), 3.74 (6H, s, H8), 2.57-2.59 (1H, m, H₄), 1.72 1H, dd, J 5.0 Hz, 7.5 Hz, 1 x H₅), 1.58 (1H, dd, J 5.0 Hz, 9.0 Hz, 1 x H₅); δC (100.6 MHz; CDCl₃); 170.3, 168.1 (2 x q, C7); 133.3 (CH, C3), 119.0 (CH₂, C1), 52.9, 53.0 (2 x CH₃, C8), 36.1 (q, C6), 31.8 (CH, C4). 20.9 (CH₂, C5); m/z 184 (M⁺) (15%), 152 (65%), 124 (65%), 93 (50%), 71 (65%).
2-Formyl-cyclopropane-1,1-dicarboxylic acid dimethyl ester (261)\(^{(202)}\)

![Chemical structure of 2-Formyl-cyclopropane-1,1-dicarboxylic acid dimethyl ester](image)

2-Ethenyl-cyclopropane-1,1-dicarboxylic acid dimethyl ester (4.300 g, 186.20 mmol) in DCM (35 mL) was added to a flame dried 3-necked flask fitted with a stopper, cone adapter and gas inlet. Oxygen was bubbled through the solution for 15 min at -78 °C then ozone was bubbled through until the solution turned pale blue. At this point the ozone source was turned off and oxygen was again allowed to bubble through while dimethylsulfide (10 mL) was added. The solution was then allowed to warm to ambient temperature and left to stir for 12 h. The reaction mixture was then concentrated in vacuo and the crude product partitioned between DCM (100 mL) and water (3 x 50 mL) before drying, filtering and reducing in vacuo to yield the title compound as a colourless oil (4.00 g, 91 %); \( \nu_{\text{max}} \) (thin film)/cm\(^{-1} \) 2958 (CH), 1735, 1719 (CO and CO\(_2\)Me), 1438, 1272, 1134 (selected fingerprint); \( \delta \)H (400 MHz; CDCl\(_3\)); 9.36 (1H, d, \( J = 4.2 \) Hz, H1), 3.77 (6H, s, H6), 2.74-2.78 (1H, m, H2), 2.08 (1H, dd, \( J = 5.0, 6.9 \) Hz, 1 x H3), 1.82 (1H, dd, \( J = 5.0, 8.9 \) Hz, 1 x H3); \( \delta \)C (100.6 MHz; CDCl\(_3\)); 196.7 (CH, C1), 168.7, 166.7, (2 x q, C5), 53.6, 53.7 (2 x CH\(_3\), C6), 37.9 (q, C4), 35.1 (CH, C2), 20.0 (CH\(_2\), C3)

**Dimethyl-1-diazo-2-oxopropylphosphonate (262)\(^{(203)}\)**

![Chemical structure of Dimethyl-1-diazo-2-oxopropylphosphonate](image)

Dimethyl-2-oxopropylphosphonate (4.400 g, 26.30 mmol) in benzene (20 mL) was added to a suspension of NaH (1.150 g, 28.90 mmol) in benzene (50 mL) and THF (10 mL) at 0
°C. The suspension was stirred for 30 min, then tosyl azide (5.700 g, 28.90 mmol) in benzene (10 mL) added. The reaction mixture was then stirred for 2 h whilst warming to room temperature. The solution was then filtered through a pad of celite and concentrated in vacuo to yield the crude product as an orange oil. The product was purified by separation of the red/orange (product) lower layer from the colourless upper layer to give the title compound (4.332 g, 86 %); \( \nu_{\text{max}} \) (thin film)/cm\(^{-1} \) 2125 (C=N), 1670, 1664, 1654, 1648 (C=O, P=O); \( \delta H \) (400 MHz; CDCl\(_3\)); 3.88, 3.85 (2 x 3H, s, H4), 2.28 (3H, s, H1); \( \delta C \) (100.6 MHz; CDCl\(_3\)); 109.3, 190.2 (2 x q, C2, C3), 54.0, 53.9 (2 x CH\(_3\), C4), 27.4 (CH\(_3\), C1)

2-Ethynylocyclopropane-1,1-dicarboxylic acid dimethyl ester (263)(\(^{150}\))

Dimethyl-1-diazo-2-oxopropylphosphonate (3.087 g, 16.08 mmol) was added to a solution of 2-formylcyclopropane-1,1-dicarboxylic acid dimethyl ester (1.500 g, 8.04 mmol) in dry methanol (35 mL) under a nitrogen atmosphere. K\(_2\)CO\(_3\) (2.222 g, 16.08 mmol) was then added and the mixture stirred at ambient temperature for 16 h. The product was then partitioned between diethyl ether (30 mL) and saturated NaHCO\(_3\) (2 x 20 mL), dried over MgSO\(_4\) then concentrated in vacuo to afford a pale yellow oil. The crude product was then purified via flash silica chromatography (5 : 1 petroleum ether : diethyl ether) to yield the title compound as a colourless oil (0.279 g, 19 %); C\(_9\)H\(_{10}\)O\(_4\), HRMS [EI] required 182.0579, found 182.0576; \( \nu_{\text{max}} \) (thin film)/cm\(^{-1} \) 2957 (CH), 2124 (C=O), 1736 (CO\(_2\)Me), 1438, 1281, 1132 (selected fingerprint); \( \delta H \) (400 MHz; CDCl\(_3\)) 3.74, 3.80 (2 x 3 H, s, H7), 2.46 (1H, ddd, \( J \) 2.2, 7.4, 9.4 Hz, H1), 1.96 (1H, d, \( J \) 2.2 Hz, H3), 1.85 (1H, dd, \( J \) 4.6, 7.4 Hz, 1 x H4), 1.58 (1H, dd, \( J \) 4.6, 9.4 Hz, 1 x H4); \( \delta C \) (100.6 MHz; CDCl\(_3\)) 169.3, 167.1 (q, C6), 80.0 (q, C2), 69.1 (CH, C1), 53.5, 53.3 (2 x CH\(_3\), C7), 36.2 (q, C5), 24.2 (CH, C3), 22.3 (CH\(_2\), C4); \( m/z \) 185 (M\(^+\), 7 %), 150 (15 %), 85 (45 %), 50 (40 %), 43 (100 %)

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2-(2,2-Dibromo-1-methyl-vinyl)-cyclopropane-1,1-dicarboxylic acid dimethyl ester

(264)

Carbon tetrabromide (3.552 g, 10.73 mmol) in Dry DCM (30 mL) was added dropwise to a solution of triphenylphosphine (5.628 g, 21.46 mmol), in dry DCM (50 mL) at 0 °C over a 5 min period. The colourless solution became a golden yellow colour. After 30 min 2-acetyl-cyclopropane-1,1-dicarboxylic acid dimethyl ester (1.00 g, 5.36 mmol) in dry DCM (10 mL) was added dropwise over a 10 min period at 0 °C. The solution darkened upon addition. After a further 1.5 h hexane (200 mL) was added in order to precipitate the triphenylphosphine oxide side product. The product was then filtered through a pad of celite and concentrated in vacuo to give the title compound (1.646 g, 89 %) as a colourless oil; C$_9$H$_{10}$Br$_2$O$_4$, HRMS [EI], required 339.8945, found 339.8942; $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 3003, 2952, 2845 (CH), 1734 (CO$_2$Me), 1436, 1331, 1214, 1130 (selected fingerprint); $\delta$H (400 MHz; CDCl$_3$) 6.06 (1H, d, $J$ 9.2 Hz, H6), 3.78 (3H, s, H1), 3.76 (3H, s, H1), 2.76 (1H, dq, $J$ 9.2 Hz, $J$ 1.5 Hz, H5), 1.68-1.77 (2H, m, H4); $\delta$C (100.6 MHz; CDCl$_3$) 167.5, 168.8 (2 x q, C2), 133.2 (CH, C6), 92.3 (q, C7), 52.76, 52.78 (2 x CH$_3$, C1), 34.8 (q, C3), 31.6 (CH, C5), 20.8 (CH$_2$, C4); $m/z$ 340 (M$^+$, 7 %), 231 (58 %), 229 (75 %), 59 (100 %).
Ethynyl magnesium bromide (6.00 mL, 3.00 mmol) (0.5 M soln in THF), was added dropwise to a solution of 2-formyl-malonic acid diethyl ester (0.300 g, 1.49 mmol) in dry THF (20 mL) at –78 °C. The solution was left to stir for 1.5 h while warming to ambient temperature. The reaction mixture was quenched with ammonium chloride then partitioned between diethyl ether (50 mL) and water (3 x 20 mL), dried over MgSO4, and concentrated in vacuo. Purification via flash silica chromatography (3 : 1, diethyl ether : petroleum ether) gave the title compound as a colourless oil (0.215 g, 63 %); νmax (thin film)/cm⁻¹ 3480 (OH), 3278 (HCC), 2981, 2938, (CH), 1729 (CO₂Me), 1370, 1264, 1156 (selected fingerprint); δH (400 MHz; CDCl₃) 4.51-4.48 (1H, m, H₆), 4.24-4.16 (4H, m, H₂), 3.68 (1H, t, J 7.2 Hz, H₄), 2.52 (1H, d, J 2.0 Hz, H₉), 2.45 (1H, d, J 5.9 Hz, H₇), 2.37-2.33 (2H, m, H₅), 1.28 (6H, t, J 7.1 Hz, H₁); δC (100.6 MHz; CDCl₃) 169.3, 169.2 (2 x q, C₃), 83.5 (q, C₈), 73.8 (CH, C₉), 61.73, 61.68 (2 x CH₂, C₂), 60.1 (CH, C₆), 48.4 (CH, C₄), 36.0 (CH₂, C₅), 13.9 (CH₃, Cl).

No mass ion found

Dicobalt hexacarbonyl-2-(1-Hydroxy-prop-2-vnyl)-malonic acid diethyl ester (267)
2-(1-Hydroxy-prop-2-ynyl)-malonic acid diethyl ester (0.165 g, 0.72 mmol) was added to a solution of dicobalt octacarbonyl (0.246 g, 0.72 mmol) in DCM (20 mL) under an atmosphere of nitrogen. After 3 h the dark purple solution was filtered through a plug of celite and silica to yield the title compound as a dark red viscous oil (0.371 g, quant) $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 3507 (OH), 2983, 2940 (CH), 2097, 2056, 2026 (M-CO), 1784, 1734 (CO$_2$Et), 1157 (selected fingerprint).

Although the IR spectra of the above compound expressed all of the expected functionality, and the product was clean by TLC, several attempts to gain clean NMR spectra failed. However, the addition of either Lewis or protic acids gave rise to the product below.

**Dicobalt hexacarbonyl-3-(ethoxycarbonyl)tetrahydrofuran-2-on-5-yl)-ethyne (268)**

Dicobalt hexacarbonyl-2-(1-Hydroxy-prop-2-ynyl)-malonic acid diethyl ester (0.370 g, 0.72 mmol) was dissolved in DCM (10 mL). The solution was cooled to 0 °C then tetrafluoroboric acid (0.20 mL, 1.44 mmol) added. The solution was then left to stir for 10 min before Hünigs base (0.25 mL, 1.44 mmol) was added. The solution was then allowed to warm to ambient temperature, dried with MgSO$_4$, then filtered through a pad of celite and silica then concentrated in vacuo. Purification via flash silica chromatography (3 : 1, diethyl ether : petroleum ether) gave the title compound (1 : 1 mix of inseparable diastereoisomers) as a red oil (1.370 g, 40 %); C$_{15}$H$_9$Co$_2$O$_{10}$, HRMS [FAB] (M$^+$-2CO), required 410.8961, found 410.8966; $\nu_{\text{max}}$ (thin film)/cm$^{-1}$ 2985, 2940 (CH), 2099, 2057, 2027 (M-CO), 1783, 1734 (CO), 1257, 1158 (selected fingerprint); $\delta$H (400 MHz; CDCl$_3$)
6.08, 6.07 (1H, d, J 0.8Hz, H1), 5.74 (1H, dt, J 6.8, 0.8Hz, H3), 5.54 (1H, ddd, J 8.9, 6.6, 0.8Hz, H3), 4.29 (2H, m, H8), 3.82-3.69 (1H, m, H5), 3.14-3.03 (1H, m, 1 x H4), 2.99-2.88 (1H, m, 1 x H4), 2.61-2.47 (1H, m, 1 x H4), 2.29-2.17 (1H, m, 1 x H4), 1.23 (3H, m, H9); δC (100.6 MHz; CDCl3) 199.7, 199.6 (q, M-CO), 170.2 (q, C6), 167.4, 167.2 (q, C7), 90.8, 90.4 (q, C2), 79.8, 78.8 (CH, C3), 72.1, 72.0 (CH, C1), 62.5, 62.3 (CH2, C8), 47.6, 47.0 (CH, C5), 34.6, 34.5 (CH2, C4), 14.0, 13.9 (CH3, C9); m/z 411 (M^+-2CO, 48 %), 383 (63 %), 355 (625 %), 327 (35 %), 299 (64 %).

**Dicobalt hexacarbonyl-2-methylbut-1-ynyl (269)**

2-Methyl-3-butyne-2-ol (1.294 g, 14.62 mmol) was added to a solution of dicobalt octacarbonyl (5.00 g, 14.62 mmol) in DCM (80 mL) under an atmosphere of nitrogen. After 2 h p-toluenesulfonic acid (1 spatula full) was added then the solution left to stir for 16 h. The solution was then filtered through a plug of celite and silica before purification via flash silica chromatography (9 : 1 petroleum ether: diethyl ether) to yield the title compound (3.996 g, 78 %) as a dark purple solid; mp 36-37 °C; C11H6Co2O6, HRMS [FAB](M^+) required 351.8828, found 351.8834; νmax (thin film)/cm⁻¹ 2092, 2054, 2020 (M-CO), 1653, 1559 (selected fingerprint); δH (400 MHz; CDCl3) 6.19 (1H, s, H1), 5.40 (1H, q, J 0.8 Hz, 1 x H5), 5.27 (1H, t, J 1.5 Hz, 1 x H5), 2.08 (3H, m, H4); δC (100.6 MHz; CDCl3) 199.7 (q, M-CO), 141.1 (q, C3), 117.7 (CH2, C5), 93.2 (q, C2), 73.4 (CH, C1), 24.0 (CH3, C4); m/z 352 (M^+, 27 %), 324 (64 %), 296 (41 %), 268 (30 %), 240 (73 %), 212 (33 %).

**Dicobalt hexacarbonyl 2,2-dimethyl-3-butyne-2-ol**, was also isolated (0.755 g, 14 %) as a dark red oil; C11H8Co2O7, HRMS [FAB](M^+) required 369.8934, found 369.8928; νmax (thin film)/cm⁻¹ 3454 (OH), 2981, 2933 (CH), 2094, 2049, 2028 (M-CO), 1514, 1361, 1160 (selected fingerprint; δH (400 MHz; CDCl3) 6.02 (1H, s, HCC), 1.57 (6H, s, 221
C(CH₃)₂); δC (100.6 MHz; CDCl₃) 199.7 (q, M-CO), 106.0 (q, CCHO), 72.7 (CH, HCC), 71.6 (q, CC(CH₃)₂OH), 33.2 (CH₃, C(CH₃)₂); m/z 370 (M⁺, 12 %), 353 (27 %), 342 (74 %), 314 (80 %), 286 (100 %), 258 (32 %).

**Dicobalt hexacarbonyl-4-methyl-pent-3-en-1-yne (270)**

![Structural formula](image)

4-Methyl-pent-1-yne-3-ol (0.860 g, 8.77 mmol) was added to a solution of dicobalt octacarbonyl (3.000 g, 8.77 mmol) in DCM (100 mL) under an atmosphere of nitrogen. After 2 h p-toluenesulfonic acid (1 spatula full) was added then the solution left to stir for 16 h. The solution was then filtered through a plug of celite and silica before purification via flash silica chromatography (100 % petroleum ether) to yield the title compound (2.79 g, 87 %) as a black oil; νₘₐₓ (thin film)/cm⁻¹ 2971, 2911 (CH, 2089, 2046, 2015 (M-CO), 1625, 1443, 1376 (selected fingerprint); δH (400 MHz; CDCl₃) 6.25 (1H, s, H1), 6.16 (1H, Br s, H3), 1.86 (3H, s, H5/6), 1.84 (3H, s, H5/6); δC (100.6 MHz; CDCl₃) 199.7 (q, M-CO), 140.3 (q, C4), 121.0 (CH, C3), 84.9 (q, C2), 73.2 (CH, C1), 25.7 (CH₃, C5), 20.3 (CH₃, C6).

**Dicobalt hexacarbonyl-1-pentyne-3-ol (204)**

![Structural formula](image)

1-Pentyne-3-ol (0.500 g, 5.94 mmol) was added to a solution of dicobalt octacarbonyl (2.030 g, 5.94 mmol) in DCM (50 mL) under an atmosphere of nitrogen. After 4 h the dark
purple solution was filtered through a plug of celite and silica then concentrated in vacuo to yield the title compound (2.199 g, 100%) as a dark red oil; \( \nu_{\text{max}} \) (thin film)/cm\(^{-1}\) 3447 (OH), 2970, 2937 (CH), 2094, 2050, 2018 (M-CO), 1457, 1100, 1047 (selected fingerprint); \( \delta \)H (250 MHz; CDCl\(_3\)) 6.06 (1H, s, H1), 4.63 (1H, dd, \( J \) 6.8 Hz, \( J \) 5.2 Hz, H3), 1.86 (1H, d, \( J \) 5.2 Hz, H6), 1.59-1.79 (2H, m, H4), 1.10 (3H, t, \( J \) 7.2 Hz); \( \delta \)C (100.6 MHz; CDCl\(_3\)) 199.5 (q, M-CO), 99.8 (q, C2), 74.0 (CH, C3), 71.6 (CH, C1), 33.0 (CH\(_2\), C4), 10.6 (CH\(_3\), C5).

**Dicobalt hexacarbonyl-pent-3-en-1-yne (E and Z isomers) (271)**

\[ \text{(OC)}_3\text{Co} \rightleftharpoons \text{Co(OC)}_3 \]

\( p \)-Toluenesulfonic acid (1 spatula) was added to a solution of dicobalt hexacarbonyl-1-pentyne-3-ol (1.934 g, 5.23 mmol) and 4Å sieves in DCM (100 mL), then left to stir for 16 h. The solution was then dried over MgSO\(_4\), filtered through a plug of celite and silica before purification via flash silica chromatography (100 % petroleum ether) to yield the title compound as inseparable E/Z isomers (1:1 ratio), (1.065 g, 58%) as a black oil; \( \nu_{\text{max}} \) (thin film)/cm\(^{-1}\) 2915 (CH), 2091, 2048, 2016 (M-CO), 1437, 942, 725 (selected fingerprint); \( \delta \)H (400 MHz; CDCl\(_3\)) 6.41-6.50 (1H, m, H3), 6.17, 6.26 (1H, s, H1), 6.09-6.14 (0.5 H, m, H4), 5.86-5.90 (0.5 H, m, H4), 1.79-1.84 (3H, m, H5); \( \delta \)C (100.6 MHz; CDCl\(_3\)) 199.5 (q, M-CO), 133.5, 130.2 (CH, C3), 126.5, 126.0 (CH, C4), 89.9 (q, C2), 73.3, 73.2 (CH, C1), 18.4, 15.3 (CH\(_3\), C5).

This complex was noticeably unstable on silica.
Dicobalt hexacarbonyl 1-ethynyl-1-cyclohexanol

1-Ethynyl-1-cyclohexanol (1.816 g, 14.62 mmol) was added to a solution of dicobalt octacarbonyl (5.00 g, 14.62 mmol) in DCM (80 mL) under an atmosphere of nitrogen. After 4 h the solution was filtered through a plug of celite and silica before purification via flash silica chromatography (6 : 1 petroleum ether: diethyl ether) to yield the title compound (5.464 g, 91 %) as a dark red oil; C_{14}H_{12}CoO_{7}, HRMS [FAB] \text{[M}^\dagger\text{-CO]} \text{required 381.9298, found 381.9297; } \nu_{\text{max}} \text{(thin film)/cm}^{-1} 3470 \text{ (OH), 2935, 2857 (CH), 2092, 2040, 2018 (M-CO), 1448, 1151, 1051, 961 (selected fingerprint); } \delta \text{H (250 MHz; CDCl}_3\text{) 6.06 (1H, s, H1), 1.53-1.83 (11H, m, H4-H9); } m/z \text{ 382 (M}^+\text{-CO, 46 %), 354 (74 %), 326 (100 %), 298 (27 %), 270 (19 %).}

Dicobalt hexacarbonyl 1-ethynyl-cyclohexene (272)^{113,197}

p-Toluenesulfonic acid (1 spatula) was added to a solution of dicobalt hexacarbonyl-1-ethynyl-1-cyclohexanol (3.502 g, 8.54 mmol) and 4Å sieves in DCM (150 mL) then left to stir for 16 h. The solution was then dried over MgSO_{4}, filtered through a plug of celite and silica before purification via flash silica chromatography (100 % petroleum ether) to yield the title compound (3.254 g, 97 %) as a dark red oil; C_{14}H_{10}CoO_{6}, HRMS [FAB] \text{[M}^\dagger\text{]} \text{required 391.9141, found 391.9138; } \nu_{\text{max}} \text{(thin film)/cm}^{-1} 2933, 2859 \text{ (CH), 2090, 2047, 2015 (M-CO), 1447, 1134 (selected fingerprint); } \delta \text{H (400 MHz; CDCl}_3\text{) 6.21-6.24 (1H, m,}
Manganese(III) acetate (2.689 g, 11.58 mmol), was added to a flame dried flask under an atmosphere of nitrogen. The flask was purged with nitrogen for 10 min, then acetic acid (25 mL) added and the solution purged for a further 15 min, then heated to 40 °C for 40 min. A solution of dicobalt hexacarbonyl-2-methylbut-1-ynyl (1.019 g, 2.89 mmol), and acetyl acetone (2.37 mL, 23.12 mmol) in acetic acid (10 mL) was then added and the solution stirred at 40 °C for 1 h while following by tlc. The reaction was quenched with H2O (10 mL), then the organic fraction extracted into diethyl ether (3 x 10 mL). This was neutralised with saturated aqueous NaHCO3, washed with H2O, dried over MgSO4, filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (15 : 1 petroleum ether : diethyl ether), to give the title compound as a red solid (0.751 g, 58 %). mp 63-64 °C (lit 61-62 °C); C16H12Co2O8, required: C 42.69 %, H 2.68 %, found: C 42.99 %, H 2.80 %; HRMS [FAB](M⁺), required 449.9196, found 449.9187; v_max (thin film)/cm⁻¹ 2978, 2928, 2863 (CH), 2095, 2023 (M-CH), 1674, 1622, 1601, 1378, 1248, 929 (selected fingerprint); δH (400 MHz; CDCl₃) 6.09 (1H, s, H1), 3.17 (1H, dd, J 14.5 Hz, J 1.6 Hz, 1 x H4), 2.87 (1H, dd, J 14.5 Hz, J 1.6 Hz, 1 x H4), 2.22 (3H, t, J 1.6 Hz, H9), 2.17 (3H, s, H10), 1.71 (3H, s, H8); δC (100.6 MHz; CDCl₃) 199.2 (q, M-CO), 194.2 (q, C7), 166.2 (q, C6), 111.5 (q, C5), 99.6 (q, C2), 87.9 (q, C3), 71.8 (CH, C1), 225
46.2 (CH₂, C4), 30.9 (CH₃, C9), 29.4 (CH₃, C10), 14.9 (CH₃, C8); m/z 450 (M⁺, 29 %), 422 (11 %), 394 (62 %), 366 (100 %), 338 (71 %), 310 (35 %), 282 (52 %).

**Dicobalt hexacarbonyl-5-ethynyl-2,5-dimethyl-4,5-dihydro-furan-3-carboxylic acid ethyl ester (274)**

\[
\begin{align*}
\text{H} & \quad \text{1} \\
\text{2} & \quad \text{3} \\
\text{4} & \quad \text{5} \\
\text{6} & \quad \text{O} \\
\text{7} & \quad \text{8} \\
\text{9} & \quad \text{10} \\
\text{11} & \quad (\text{OC})_3\text{Co} - \text{Co(OC)}_3
\end{align*}
\]

Manganese (III) acetate (5.275 g, 22.73 mmol) was added to a flame dried flask under an atmosphere of nitrogen. The flask was purged with nitrogen for 10 min, then acetic acid (50 mL) added and the solution purged for a further 15 min, then heated to 40 °C for 40 min. A solution of dicobalt hexacarbonyl-2-methylbut-1-enyne (2.001 g, 5.68 mmol), and ethylacetylacetate (5.78 mL, 45.45 mmol) in acetic acid (20 mL) was then added and the solution stirred at 40 °C for 1 h while following by TLC. The reaction was then quenched with H₂O (50 mL), then the organic fraction extracted into diethyl ether (3 x 15 mL). This was neutralised with saturated aqueous NaHCO₃, washed with H₂O, dried over MgSO₄, filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (18 : 1 petroleum ether : diethyl ether), to give the title compound as a red solid, (1.547 g, 57 %); mp 71 °C; C₁₇H₁₄C₀₂O₉, required: C 42.54 %, H 2.95 %, found: C 42.50 %, H 2.98 %; HRMS [FAB](M⁺), required, 479.9302, found, 479.9304; ν_{max} (thin film)/cm⁻¹ 2981 (CH), 2095, 2053, 2023 (M-CO), 1697, 1649 (CO), 1445, 1381, 1246, 1056 (selected fingerprint); δH (400 MHz; CDCl₃) 6.06 (1H, s, H1), 4.15 (2H, q, J 7.0 Hz, H8), 3.10 (1H, dd, J 14.7 Hz, J 1.5 Hz, H4), 2.87 (1H, dd, J 14.7 Hz, J 1.5 Hz, H4), 2.19 (3H, t, J 1.5 Hz, H10), 1.70 (3H, s, H11), 1.24 (3H, t, J 7.0 Hz, H9); δC (100.6 MHz; CDCl₃) 199.3 (q, M-CO), 166.4, 165.8 (2 x q, C6/C7), 101.3 (q, C5), 100.6 (q, C2), 88.4 (q, C3), 71.8 (CH, C1), 59.5 (CH₂, C8), 45.5 (CH₂, C4), 30.8 (CH₃, C11), 14.4, 14.0 (2 x CH₃, C9/C10); m/z 480 (M⁺, 13 %), 424 (36 %), 396 (100 %), 368 (87 %), 340 (28 %).
Dicobalt hexacarbonyl-5-ethynyl-2,4-dimethyl-4,5-dihydro-furan-3-carboxylic acid ethyl ester (275)

Manganese (III) acetate (1.09 g, 4.72 mmol) was added to a flame dried flask under an atmosphere of nitrogen. The flask was purged with nitrogen for 10 min, then acetic acid (10 mL) added and the solution purged for a further 15 min, then heated to 40 °C for 40 min. A solution of dicobalt hexacarbonyl-pent-3-en-1-yne (0.4154 g, 1.18 mmol), and ethylacetylacetate (0.97 mL, 9.44 mmol) in acetic acid (5 mL) was then added and the solution stirred at 40 °C for 2 h while following by TLC. The reaction was then quenched with H2O (10 mL), then the organic fraction extracted into diethyl ether (3 x 5 mL). This was neutralised with saturated aqueous NaHCO3, washed with H2O, dried over MgSO4, filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (20 : 1 petroleum ether : diethyl ether), to give the title compound as a red oil (2 x diastereoisomers 4 : 1 ratio) (0.078 g, 15 %) along with starting material (0.020 g, 5 %); C17H14Co2O9, HRMS [FAB](M+ -2CO), required 423.9404, found 423.9409; v max (thin film)/cm⁻¹ 2890, 2929, 2870 (CH), 2095, 2055, 2023 (M-CO), 1706, 1696, 1647 CO₂Et, 1381, 1216, 1076 (selected fingerprint); m/z 424 (M+ -2CO, 7 %), 396 (23 %), 368 (30 %), 340 (13 %).

NMR Data:

Major isomer (tentatively assigned as syn isomer)
δH (400 MHz; CDCl3)  6.11 (1H, s, H1), 5.20 (1H, d, J 4.4 Hz, H3), 4.17 (2H, q, J 6.9 Hz, H8), 2.98 (1H, dq, J 6.8 Hz, J 4.4 Hz, H4), 2.24 (3H, s, H11), 1.29 (3H, d, J 6.8 Hz, H10), 1.66 (3H, t, J 6.9 Hz, H9); δC (100.6 MHz; CDCl3) 199.8 (M-CO), 167.1, 165.7 (2 x q,
Minor isomer (tentatively assigned as anti isomer)

δH (400 MHz; CDCl₃) 6.12 (1H, s, H1), 5.69 (1H, d, J 8.4 Hz, H3), 4.18 (2H, q, J 6.9 Hz, H8), 3.49 (1H, dq, J 6.8 Hz, J 8.4 Hz, H4), 2.19 (3H, s, H11), 1.29 (3H, d, J 6.8 Hz, H10), 1.66 (3H, t, J 6.9 Hz, H9); δC (100.6 MHz; CDCl₃) 199.8 (M-CO), 167.1, 165.7 (2 x q, C6/C7), 107.5 (q, C5), 87.0 (CH, C3), 71.8 (CH, C1), 59.4 (CH₂, C8), 40.7 (CH₃, C10), 22.3 (CH₃, C11), 14.27 (CH₃, C9) (C2 not seen)

Dicobalt hexacarbonyl-7a-ethynyl-2-methyl-3a,4,5,6,7,7a-hexahydro-benzofuran-3-carboxylic acid ethyl ester (276)

Manganese (III) acetate (5.941 g, 25.60 mmol) was added to a flame dried flask under an atmosphere of nitrogen. The flask was purged with nitrogen for 10 min, then acetic acid (60 mL) added and the solution purged for a further 15 min, then heated to 40 °C for 40 min. A solution of dicobalt hexacarbonyl-1-ethynyl cyclohexene (1.752 g, 4.27 mmol), and ethylacetylacetate (5.26 mL, 51.3 mmol) in acetic acid (20 mL) was then added and the solution stirred at 40 °C for 2.5 h while following by tlc. The reaction was then quenched with H₂O (50 mL), then the organic fraction extracted into diethyl ether (3 x 15 mL). This was neutralised with saturated aqueous NaHCO₃, washed with H₂O, dried over MgSO₄, filtered through celite and silica then concentrated in vacuo. The crude product was purified via flash column chromatography (100 % petroleum ether), to give the title compound as a
Dicobalt hexacarbonyl-3-acetyl-5-ethynyl-5-methyl-tetrahydro-furan-2,3-dicarboxylic acid diethyl ester (278)

Boron trifluoride diethyl etherate (0.18 mL, 1.47 mmol) was added dropwise to a solution of dicobalt hexacarbonyl-5-ethynyl-2,5-dimethyl-4,5-dihydro-furan-3-carboxylic acid ethyl ester (0.177 g, 0.37 mmol) and ethyl glyoxylate (0.15 mL, 0.73 mmol) in dry DCM (6 mL) at ambient temperature under an atmosphere of nitrogen. This solution was stirred for 20 min, quenched with saturated aqueous NaHCO₃ (5 mL), then extracted into DCM (3 x 5 mL). The product was dried over MgSO₄, concentrated in vacuo then purified via flash column chromatography (4 : 1 petroleum ether : diethyl ether), to give the title compound as a red oil (4 diastereoisomers (0.151 g, 71 %, 1 : 2 : 4 : 2 d.r). The product diastereoisomers were then separated by a second column (7 : 1 petroleum ether : diethyl ether) in order to obtain analysis. (complete separation was not possible so identification of
each isomer could not be obtained, however it was possible to separate out the diastereoisomers into pairs for easier analysis; C_{21}H_{19}Co_{2}O_{12}, HRMS [FAB](M^+ - 3CO), required 496.9630, found 496.9691; ν_{max} (thin film)/cm^{-1} 2984, 2936 (CH), 2094, 2054, 2022 (M-CO), 1734, 1718 (CO), 1374, 1252, 1225, (selected fingerprint); m/z 497 (M^+ - 3CO, 20 %), 469 (100 %), 441 (16 %), 413 (59 %).

NMR Data:

2 First eluting isomers
δH (400 MHz; CDCl_{3}) 6.03, 6.09 (1H, s, H1), 5.29, 5.33 (1H, s, H6), 4.30-4.34 (1H, q, J 7.0 Hz, H8/H13), 4.12-4.21 (3H, m, H8 and H13), 2.80-2.92 (2H, m, H4), 2.24, 2.37 (3H, s, H11), 1.52, 1.56 (3H, s, H15), 1.28-1.36 (6H, m, H9 and H14); δC (100.6 MHz; CDCl_{3}) 200.0, 201.2 (q, C10), 199.5 (q, M-CO), 169.1, 169.4, 169.8, 170.3 (q, C7 and C12), 85.0, 85.6 (q, C2), 80.4, 81.4 (CH, C6), 73.0, 73.5 (CH, C1), 71.0, 71.5 (q, C3), 65.9 (q, C5), 61.43, 61.44, 62.4, 62.9 (CH_{2}, C8 and C13), 47.0, 47.4 (CH_{2}, C4), 29.2, 29.7 (CH_{3}, C15), 27.1, 27.9 (CH_{3}, C11), 13.8, 13.9, 13.95, 14.0 (CH_{3}, C9/C14).

2 Later eluting isomers (major isomer first)
δH (400 MHz; CDCl_{3}) 5.99 (1H, s, H1), 4.95 (1H, s, H6), 4.17-4.28 (4H, m, H8 and H13), 2.99 (1H, d, J 13.4 Hz, H4), 2.38 (1H, d, J 13.4 Hz, H4), 2.32 (3H, s, H11), 1.76 (3H, brs, H15), 1.18-1.35 (6H, m, H9 and H14); δC (100.6 MHz; CDCl_{3}) 200.9 (q, C10), 199.2 (q, C16), 168.6, 168.8 (q, C7 and C12), 84.6 (q, C2), 80.6 (CH, C6), 72.9 (CH, C1), 70.6 (q, C3), 65.9 (q, C5), 61.5, 62.5 (CH_{2}, C8/C13), 48.4 (CH_{2}, C4), 30.0 (CH_{3}, C15), 27.86 (CH_{3}, C11), 13.8, 14.1 (CH_{3}, C9/C14).

δH (400 MHz; CDCl_{3}) 5.88 (1H, s, H1), 4.13 (1H, s, H6), 4.17-4.28 (4H, m, H8 and H13), 2.92 (1H, d, J 13.6 Hz, H4), 2.69 (1H, d, J 13.6 Hz, H4), 2.27 (3H, s, H11), 1.79 (3H, brs, H15), 1.18-1.35 (6H, m, H9 and H14); δC (100.6 MHz; CDCl_{3}) 201.2 (q, C10), 199.2 (q, C16), 169.1, 170.4 (q, C7 and C12), 84.9 (q, C2), 80.8 (CH, C6), 72.7 (CH, C1), 70.7 (q, C3), 65.9 (q, C5), 61.6, 62.6 (CH_{2}, C8/C13), 47.0 (CH_{2}, C4), 29.9 (CH_{3}, C15), 27.90 (CH_{3}, C11), 13.9, 14.0 (CH_{3}, C9/C14).
Boron trifluoride diethyl etherate (0.10 mL, 0.84 mmol) was added dropwise to a solution of dicobalt hexacarbonyl-5-ethynyl-2,5-dimethyl-4,5-dihydro-furan-3-carboxylic acid ethyl ester (77) (0.104 g, 0.21 mmol) and acetaldehyde (0.023 mL, 0.42 mmol) in dry DCM (6 mL) at ambient temperature under an atmosphere of nitrogen. This solution was stirred for 1 h, quenched with saturated aqueous NaHCO₃ (5 mL), then extracted into DCM (3 x 5 mL). The product was dried over MgSO₄, concentrated in vacuo then purified via flash column chromatography (8 : 1 petroleum ether : diethyl ether), to give the title compound as a red oil (4 inseparable diastereoisomers 4 : 1 : 8 : 4) (0.058 g, 51 %); C_{17}H_{18}Co₂O₁₀, HRMS [FAB] (M⁺-2CO), required 467.9666, found 467.9669; ν_{max} (thin film)/cm⁻¹ 2982, 2936, (CH), 2093, 2052, 2022 (M-CO), 1742, 1713 (CO), 1443, 1237, 1088 (selected fingerprint); m/z 468 (M⁺-2CO, 38 %), 440 (34 %), 412 (100 %), 384 (43 %).

**NMR Data:**

**Major isomer**

δH (400 MHz; CDCl₃) 5.96 (1H, s, H1), 4.70 (1H, q, J 6.3 Hz, H6), 4.23-4.29 (2H, m, H11), 3.04 (1H, d, J 13.4 Hz, 1 x H4), 2.13 (1H, d, J 13.4 Hz, 1 x H4), 2.16 (3H, s, H9), 1.80 (3H, brs, H13), 1.28-1.43 (3H, m, H12), 1.21 (3H, d, J 6.3 Hz, H7); δC (100.6 MHz; CDCl₃) 201.9 (q, C8), 199.4 (q, M-CO), 170.0 (q, C10), 82.2 (q, C2), 76.0 (CH, C6), 73.0 (CH, C1), 69.7 (q, C3), 61.7 (CH₂, C11), 47.6 (CH₂, C4), 37.4 (q, C5), 32.0 (CH₃, C13), 27.8 (CH₃, C9), 15.8 (CH₃, C7), 13.8 (CH₃, C12).
Other isomers
δH (400 MHz; CDCl₃) 6.07, 6.10, 5.94 (1H, s, H1), 4.91, 4.69, 4.66 (1H, q, J 6.3 Hz, H6), 4.23-4.29 (2H, m, H11), 2.99, 2.92 (1H, d, J 13.4 Hz, 1 x H4), 2.37 (1H, d, J 13.4, 1 x Hz, H4), 2.24, 2.23 (3H, s, H9), 1.78 (3H, brs, H13), 1.28-1.43 (3H, m, H12), 1.22 (3H, d, J 6.3 Hz, H7); δC (100.6 MHz; CDCl₃) 202.3 (q, C8), 199.4 (q, M-CO), 171.7, 169.6 (q, C10), 82.3 (q, C2), 75.8 (CH, C6), 72.9 (CH, C1), 70.3 (q, C3), 61.6 (CH₂, C11), 47.4, 47.1 (CH₂, C4), 37.4 (q, C5), 29.3, 29.8, 28.8 (CH₃, C13), 27.3, 27.5 (CH₃, C9), 15.0, 15.4 (CH₃, C7), 13.7, 13.8, (CH₃, C12).

Due to the complexity of the spectra and overlapping signals only the major diastereoisomer could be conclusively characterised.

Dicobalt hexacarbonyl-5-ethynyl-5-(2-hydroxy-2-phenyl-ethyl)-2-methyl-4,5-dihydro-furan-3-carboxylic acid ethyl ester (280)

Boron trifluoride diethyl etherate (0.13 mL, 1.04 mmol) was added dropwise to a solution of dicobalt hexacarbonyl-5-ethynyl-2,5-dimethyl-4,5-dihydro-furan-3-carboxylic acid ethyl ester (77) (0.125 g, 0.26 mmol) and benzaldehyde (0.053 mL, 0.52 mmol) in dry DCM (4 mL) then heated to 45 °C under an atmosphere of nitrogen. This solution was stirred for 30 min while following by TLC, quenched with saturated aqueous NaHCO₃ (5 mL), then extracted into DCM (3 x 5 mL). The product was dried over MgSO₄, concentrated in vacuo then purified via flash column chromatography (3 : 1 petroleum ether : diethyl ether), to give the title compound as a red oil (2 diastereoisomers), (0.070 g, 46 %, 2.5 : 1 d.r). ν_max (thin film)/cm⁻¹ 3441 (OH), 3086, 3029, 2987, 2930 (CH), 2094, 2053, 2024 (M-CO), 1693, 1635 (CO), 1372, 1258, 1046 (selected fingerprint). No mass ion found.
NMR Data

First eluting isomer (minor)
δH (400 MHz; CDCl₃) 7.17-7.34 (5H, m, H14, H15, H16), 6.01 (1H, s, H1), 4.98 (1H, ddd, J 4.0 Hz, J 4.0 Hz, J 4.4 Hz, H12), 4.10 (2H, q, J 7.1 Hz, H9), 3.84 (1H, d, J 4.4 Hz, H17), 3.17 (1H, dd, J 13.9 Hz, J 4.0 Hz, H11), 3.10 (1H, d, J 15.5 Hz, H4), 2.86 (1H, dd, J 13.9 Hz, J 4.0 Hz, H11), 2.80 (1H, d, J 15.5 Hz, H4), 1.54 (3H, s, H7), 1.19 (3H, t, J 7.1 Hz, H10); δC (109.6 MHz; CDCl₃) 199.9 (q, M-CO), 166.5 (q, C8), 166.4 (q, C6), 143.5 (q, C13), 128.3 (2 x CH, C14), 127.4 (CH, C16), 125.6 (2 x CH, C15), 103.1 (q, C5), 89.2 (q, C3), 89.0 (q, C2), 72.4 (CH, C12), 72.0 (CH, C1), 60.0 (CH₂, C9), 45.3 (CH₂, C4), 37.6 (CH₂, C11), 30.5 (CH₃, C7), 14.4 (CH₃, C10).

Later eluting isomer (major)
δH (400 MHz; CDCl₃) 7.20-7.40 (5H, m, H14, H5, H16), 6.07 (1H, s, H1), 4.98 (1H, m, H12), 4.15-4.21 (3H, m, H9 and H17), 3.42-3.54 (1H, m, H11), 3.09 (1H, d, J 14.8 Hz, H4), 2.91 (1H, d, J 14.8 Hz, H4), 2.61-2.69 (1H, m, H11), 1.68 (3H, s, H7), 1.27 (3H, t, J 7.1 Hz, H10; δC (100.6 MHz; CDCl₃) 199.0 (q, C18), 166.4 (q, C8), 166.2 (q, C6), 143.8 (q, C13), 128.7 (CH, C14), 127.3 (CH, C16), 125.7 (CH, C15), 103.3 (q, C5), 89.1 (q, C3), 89.0 (q, C2), 72.0 (CH, C12), 71.7 (CH, C1), 59.9 (CH₂, C9), 45.1 (CH₂, C4), 37.7 (CH₂, C11), 30.3 (CH₃, C7), 14.1 (CH₃, C10).

Dicobalt hexacarbonyl-5-[2-(4-nitro-phenyl)-2-hydroxy-ethyl]-5-ethynyl-2-methyl-4,5-dihydro-furan-3-carboxylic acid ethyl ester (281)
Boron trifluoride diethyl etherate (0.11 mL, 0.88 mmol), was added dropwise to a solution of dicobalt hexacarbonyl-5-ethynyl-2,5-dimethyl-4,5-dihydro-furan-3-carboxylic acid ethyl ester (77) (0.104 g, 0.22 mmol) and 4-nitro-benzaldehyde (0.067 g, 0.44 mmol) in dry DCM (6 mL) then heated to 45°C under an atmosphere of nitrogen. This solution was left to stir for 1.5 h while following by tlc, quenched with saturated aqueous NaHCO₃ (5 mL), then extracted into DCM (3 X 5 mL). The product was dried over MgSO₄, concentrated in vacuo then purified via flash column chromatography (3 : 1 petroleum ether : diethyl ether), to give the title compound as a red oil (2 diastereoisomers), (0.045 g, 33 %, 2.5 : 1 d.r).

HRMS [FAB](M⁺+H) C₂₄H₁₉C₀₂N₂O₁₂, required 631.9649, found 631.9643; vₚₑₑₙₓ (thin film)/cm⁻¹ 3442 (OH), 2979 (CH), 2094, 2052, 2024 (m-CO), 1696, 1635 (CO), 1521, 1345 (NO₂), 1246, 1045, (selected fingerprint); m/z 632 (M+H, 8 %), 576 (8 %), 547 (29 %), 492 (38 %), 491 (60 %), 464 (19 %), 463 (55 %),

NMR Data

First eluting isomer (minor)
δH (400 MHz; CDCl₃) 8.17 (2H, d, J 8.8 Hz, H15), 7.56 (2H, d, J 8.8 Hz, H14), 6.05 (1H, s, H1), 5.15 (1H, m, H12), 4.14-4.22 (3H, m, H9 and H17), 3.31 (1H, dd, J 13.6 Hz, J 4.1 Hz, H11), 3.06 (1H, d, J 14.4 Hz, H4), 2.85 (1H, dd, J 13.6 Hz, J 4.1 Hz, H11), 3.06 (1H, d, J 14.4 Hz, H4), 1.52 (3H, s, H7), 1.26 (3H, t, J 7.1 Hz, H10); δC (100.6 MHz; CDCl₃) 199.2 (q, C18), 167.0 (q, C8), 165.7 (q, C6), 150.9 (q, C16), 147.2 (q, C13), 126.5 (CH, C14), 123.5 (CH, C15), 103.8 (q, C5), 89.7 (q, C3), 88.9 (q, C2), 71.8 (CH, C1), 71.6 (CH, C12), 60.4 (CH₂, C9), 45.0 (CH₂, C4), 37.6 (CH₂, C11), 30.5 (CH₃, C7), 14.3 (CH₃, C10).

Later eluting diastereoisomer (major)
δH (400 MHz; CDCl₃) 8.20 (2H, d, J 8.8 Hz, H15), 7.58 (2H, d, J 8.8 Hz, H14), 6.09 (1H, s, H1), 5.09 (1H, m, H12), 4.15-4.21 (2H, m, H9), 4.08 (1H, d, J 5.6 Hz, H17), 3.38 (1H, dd, J 14.4 Hz, J 9.6 Hz, H11), 3.10 (1H, d, J 14.8 Hz, H4), 2.92 (1H, d, J 14.8 Hz, H4), 2.65 (1H, d, J 14.4 Hz, H11), 1.69 (3H, s, H7), 1.26 (3H, t, J 7.1 Hz, H10); δC (100.6 MHz; CDCl₃) 199.2 (q, M-CO), 166.9 (q, C8), 165.6 (q, C6), 151.4 (q, C16), 147.3 (q, C13), 126.4 (CH, C14), 123.7 (CH, C15), 104.0 (q, C5), 89.9 (q, C3), 88.9 (q, C2), 71.9 (CH,
C1), 71.6 (CH, C12), 60.4 (CH2, C9), 45.1 (CH2, C4), 37.7 (CH2, C11), 30.6 (CH3, C7),
14.3 (CH3, C10).
4. References


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81. V. Derda, S. Laschat, I. Dix, P.G. Jones, Organometallics, 1999, 18, 3859.
86. K.D. Roth, Synlett., 1993, 125, 529.
199. E. Allert, PhD, First year report, Loughborough University, **2005**.
5.0 Appendix
SDRC5 pictures
Table 1. Crystal data and structure refinement for sdrc5.

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Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for sdrc5. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

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Table 4. Hydrogen coordinates and isotropic displacement parameters (Å²) for sdrc5.

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Table 5. Torsion angles [°] for sdrc5.

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