Heterobimetallic complexes in organic synthesis

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Heterobimetallic Complexes in Organic Synthesis

by

David Thomas Rutherford
Bsc(Hons)

A Doctoral Thesis

Submitted in partial fulfilment of the requirements

for the award of

Doctor of Philosophy of Loughborough University

8th July 2001.

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Finally I would like to take this opportunity to dedicate this thesis to my parents Martin and Patricia Rutherford for their unwavering and total support in every thing I have done.
Abstract

Heterobimetallic cobaltmolybdenumcyclopentadienylalkynylpentacarbonyl complexes have been demonstrated to act as efficient substrates for the Pauson-Khand cycloaddition under appropriate conditions. The inherent chirality present in the heterobimetallic core has been shown to efficiently promote a stereoselective variant of the Pauson-Khand reaction. The unique mode of stereoinduction in contrast to existing methodology has enabled the first stereospecific Pauson-Khand reaction to be realised in the absence of an external source of chirality.

The scope of heterobimetallic alkyne complexes for more general asymmetric organic synthetic transformations has been briefly addressed. The heterobimetallic core has been shown to promote moderate to high levels of stereoselectivity in the addition of nucleophiles to remote centres of complexed propargylic aldehydes.

In light of the potential use of heterobimetallic complexes in organic synthesis a new robust and experimentally facile route for complex generation has been developed. Employing this route heterobimetallic complexes can be rapidly and routinely generated avoiding specialist techniques or apparatus.

Chapter 1: Provides a brief overview of the Pauson-Khand reaction and developments in this field.

Chapter 2: Highlights our work utilising heterobimetallic alkyne complexes as substrates in the Pauson-Khand reaction, their use in more general synthetic transformations and the development of a facile but robust route for their synthesis.

Chapter 3: Provides experimental data for our studies.
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2.2 Experimental Section.
1.0. Introduction.

1.0.1. Reaction discovery.

The Pauson-Khand reaction is in its simplest form a formal $[2+2+1]$ cycloaddition of an alkyne, an alkene and carbon monoxide mediated by a cobalt metal centre. The synthetically challenging cyclopentenone ring system is generated in regioselective manner and in favourable cases with a degree of stereoselectivity. Scheme(1).

![Scheme(1)](image)

The reaction was discovered in the early 1970’s by Pauson and Khand\cit{1} during their investigation, preparation and characterisation of various alkene and alkyne complexes derived from dicobaltoctacarbonyl.

1.0.2. Pauson-Khand Reaction Characteristics.

The Pauson-Khand reaction has several characteristic regiochemical and stereofacial features. The reaction is stereoselective with respect to the alkene, in that for bicyclic alkenes the newly formed ring junction is found to be exclusively cis exo fused. The reaction is regioselective with respect to an unsymmetrical alkyne in that the more sterically demanding substituent is found to be exclusively $\alpha$ to the newly formed carbonyl functionality. The reaction also displays regioselectivity with respect to the alkene to an extent, the larger alkene substituent being found $\alpha$ to the newly formed ketone functionality. Scheme(2).

![Scheme(2)](image)

1. Cis Exo ring fusion
2. Larger substituent on alkyne $\alpha$ to carbonyl.

Scheme(2)
Mechanistic studies of the Pauson-Khand reaction have been limited. Attempts to follow the reaction spectroscopically have been unsuccessful, the species being detected being the final product itself, which suggests that the rate determining step occurs relatively early in the reaction sequence preventing the formation of intermediates in significant concentrations. In only a few cases have any intermediates been isolated. In view of this lack of experimental data, postulated mechanisms are centred on steric considerations that may rationalise the stereofacial control and regiocontrol observed in the resultant cyclopentenoid products isolated initially by the Pauson group and then subsequent researchers. The generally accepted mechanism of the Pauson-Khand reaction is outlined in Scheme(3).

Scheme(3)
The first step of the reaction involves loss of a carbon monoxide ligand present in the alkyne dicobaltoctacarbonyl complex. This step is believed to be reversible and is thought to be the rate determining step. Upon dissociative loss of carbon monoxide, the alkene complexes to the coordinatively unsaturated metal. Once co-ordinated, the first carbon-carbon bond is formed generating a cobaltacycle. Carbon monoxide insertion into this metalacycle prior to a reductive elimination and decomplexation from the metallic residues yields the cyclopentenone product.

1.0.4. Stereochemical and Regiochemical Control.

The formation of the metalacycle (Step 3) is believed to be irreversible and sterically sensitive. Minimisation of steric interactions in this step is believed to account for the stereofacial and regiochemical control observed in the final cyclopentenone product. When a bicyclic alkene is employed the diastereofacial selectivity arises due to the preferential co-ordination of the less sterically demanding face of the alkene onto the co-ordinately unsaturated metal centre resulting in the observed cis exo ring fusion. If the complex contains an unsymmetrical alkyne component then the regioselectivity is believed to arise due to the alkene inserting into the less sterically demanding alkynyl carbon resulting in the larger substituent of the alkyne being found exclusively α to the carbonyl functionality in the cyclopentenoid product. The issue of alkene regiochemistry is not completely resolved. Bicyclic alkenes upon cycloaddition generate mixtures of regioisomers and simple alkenes often give rise to cyclopentenone products with very little or no regiocontrol. Krafft has suggested that steric effects play a controlling role prior to insertion by favouring specific configurational and conformational isomers of the alkene complex for the subsequent reaction.\textsuperscript{4} Scheme(4).
Dissociative loss of a carbon monoxide at a cobalt centre can lead to three possible configurational isomers. Of these three isomers the one most likely to lead to insertion contains the alkene complexed trans to the bond between cobalt and the substituted alkyne carbon avoiding any steric interaction with the latter. Of the two possible conformations the alkene can adopt if the R group on the alkene is sufficiently large, the conformation preferred is that in which the large group is anti to the cobalt-carbon bond. This results in a preference for the 5-substituted cyclopentenone.

1.0.5. Reaction conditions.

Pauson and Khand carried out the vast majority of the preliminary work in the area and rapidly developed a general synthetic procedure. By tradition, the Pauson-Khand reaction is carried out by moderately heating the dicobalt alkyne complex in a hydrocarbon solvent in the presence of a suitable alkene under an atmosphere of nitrogen or carbon monoxide to produce the desired
cyclopentenone in moderate yield ranging from 30-60%, depending on the alkyne bound in the cobalt complex and the alkene.

1.0.6. Reaction limitations.

Although the Pauson-Khand reaction involves multiple carbon carbon bond formations it is stoichiometric in terms of cobalt and is therefore commercially unacceptable. Application of the reaction was limited in that acceptable yields of the desired cyclopentenone were only achieved when strained olefins were used. The lack of regiocontrol obtained with unsymmetrical alkenes resulting in mixtures of cyclopentenone regioisomers also reduced the reaction's synthetic utility.

As may be expected from the proposed mechanism, which is based on steric considerations, the Pauson-Khand reaction was found to be sensitive to steric and electronic effects arising from the alkene or alkyne component. Virtually all alkynes have been found to act as substrates in the Pauson-Khand reaction. Simple terminal alkynes when complexed to the dicobalt metal core have been found to be most satisfactory. A limiting factor in the Pauson-Khand reaction became apparent soon after the discovery of the reaction. The choice of alkene was limited to highly reactive, strained alkenes. Steric hindrance around the alkene double bond has also been found to drastically reduce the efficiency of the reaction. This is believed to arise due to the reduction in the ability of the alkene to co-ordinate preferentially to the co-ordinatively unsaturated cobalt metal centre, the vacant site being competitively bound by other alkyne units resulting in undesirable side reactions such as alkyne trimerisation and other multi-component cycloadditions of the alkyne becoming the favoured reaction pathways.

The Pauson-Khand reaction does however tolerate a degree of functionality including ethers, alcohols, tertiary amines, sulfides, ketones, ketals, esters, tertiary amides and aromatic rings. Partial tolerance has been observed for alkyl and aryl halides, vinyl ethers and esters as well as less reactive alkenes and alkynes in the presence of more reactive unsaturation.

The Pauson-Khand reaction does not appear to be adversely affected by conjugation of either the alkyne or alkene component with other carbon carbon π bonds although reduced or abnormal reactivity has been reported for substrates containing allylic or propargylic functionality. In contrast is the behaviour of alkenes containing electron withdrawing substituents. When employed in the Pauson-Khand reaction instead of the desired
cyclopentenone, 1,3 dienes are formed, presumably resulting from the formal addition of a vinylic C-H across the triple bond. **Scheme(5).**

![Scheme(5)](image)

1.1. Reaction developments.
Since its discovery in 1973 the Pauson-Khand reaction has become an active area of research and the developments since the mid eighties have dramatically increased the synthetic potential. In its current form the Pauson-Khand reaction has become the widely accepted route to the challenging cyclopentenone ring system and its synthetic utility demonstrated in a number of natural product syntheses.\(^8\)

1.1.1. Intra-molecular Pauson-Khand reaction.
It became apparent early after the discovery of the Pauson-Khand reaction that the main limitation was imposed by the limited choice of alkene substrates. Cyclopentenone products were obtained in acceptable yield when highly strained bicyclic alkenes were employed. Less reactive acyclic alkenes did not readily undergo the desired cycloaddition. The lack of regiocontrol with respect to the alkene also resulted in the production of mixtures of regioisomers. The development of the intra-molecular Pauson-Khand reaction\(^9\) went some way to addressing these problems. Enynes and heteroatom containing enynes in which three or four atoms separate the double and triple bonds cyclise upon complexation with dicobaltoctacarbonyl to give bicyclic enones. The cycloaddition occurs readily under traditional thermal Pauson-Khand conditions. The development of this enyne methodology has addressed the issue of alkene regiochemistry and allowed access to a number of cyclopentenones in good to modest yields which were inaccessible with conventional bicyclic strained alkenes. **Scheme(6).**

6
1.1.2. Rate enhancement.

For more than a decade following the initial report of the Pauson-Khand cycloaddition, the standard reaction conditions were formation of the dicobalt cobalt alkyne complex followed by heating in the presence of a strained alkene in a hydrocarbon solvent. Under these reaction conditions cyclisation occurred at a relatively slow rate.

1.1.2.1 Dry state adsorption conditions.

The first reported rate enhancement in the Pauson-Khand reaction was reported by Smit in 1986. In the previous thirteen years forceful conditions were required in order to facilitate the Pauson-Khand cycloaddition. Smit reported a dramatic increase in the rate of the cycloaddition of a range of substituted dicobalt hexacarbonyl complexes of allyl propargyl ethers into their corresponding cyclopentenones when they were adsorbed onto silica. This methodology became known as dry state adsorption conditions (DSAC). DSAC conditions have been found to be especially suitable for enyne substrates. Scheme(7). Experimentally DSAC is simple to carry out. The complexed enyne is adsorbed onto chromatography grade silica. The reaction is warmed moderately upon which the characteristic deep red colour of the complex is superseded by the purple residues associated with decomposed residues. The organic product is then simply washed off the silica and purified if need be in the conventional manner.

The atmosphere in which the reaction is carried out in has been found to be critical, different products being isolated under atmospheres of oxygen and argon. In Scheme(7) the desired product was isolated when the reaction was carried out in the presence of oxygen. The role of the oxygen is not clear but may prevent the reduction of the ether linkage by cobalt hydride species. The rate enhancement is believed to arise due to the hydrophilic nature of the
surface of the silica. The complexed enyne is hydrogen bonded to the silica surface via the ether linkage and the hydrophobic arms are pushed together by the hydrophilic surface resulting in a favourable conformation for the cycloaddition.

\[
\text{Co}_2(\text{CO})_6 \quad \begin{array}{c}
\text{O} \\
\text{O} \\
\end{array} \quad \begin{array}{c}
\text{H} \quad \\
\text{H} \\
\end{array}
\]

Scheme(7)

1.1.2.2. \textit{N}-Oxides.
Despite the observed rate acceleration obtained when Pauson-Khand reactions were carried out under DSAC, reactions performed in solution still required to be heated at elevated temperatures for the desired cyclopentenone to be obtained. If the proposed mechanism of the Pauson-Khand reaction held, then addition of additives accelerating the rate determining step, the reversible dissociative loss of carbon monoxide, would be beneficial. As such, methods to promote or stabilise the resultant intermediate were sought.

The first such additive reported was \textit{N}-Methylmorpholine \textit{N}-Oxide (NMO). The potential of \textit{N}-oxides to dramatically increase the rate of the Pauson-Khand reaction was published in 1990.\textsuperscript{11} Schreiber used NMO to effect the cobalt mediated intramolecular cyclisation of enynes at room temperature with higher yield than obtained under thermal conditions. Scheme(8). It is generally accepted that the \textit{N}-oxide oxidises a carbon monoxide irreversibly generating a site for alkyne co-ordination. It is however uncertain as to whether or not the resultant tertiary amine generated on reduction of the \textit{N}-oxide or possibly by another molecule of \textit{N}-oxide stabilises the co-ordinatively unsaturated metal centre prior to the co-ordination of the alkene.
A number of other N-Oxides have been used to accelerate the Pauson-Khand reaction such as trimethylamine N-Oxide (TMNO)\textsuperscript{12}, but perhaps the most exciting development since the initial discovery is the use of chiral N-Oxides, which not only accelerate the reaction but also convey chiral information resulting in an enantioselective Pauson-Khand reaction.\textsuperscript{13}

### 1.1.2.3. Other additives.

In view of the success of N-Oxides as additives in the Pauson-Khand reaction other potential additives have been investigated. Sulfoxides\textsuperscript{14} have been found to be efficient accelerants for the Pauson-Khand reaction. The comparative merits of sulfoxides and N-Oxides were compared. The comparison indicated that similar yields were obtainable with either system although sulfoxide promotion required slightly elevated temperatures. The ability of sulfoxides to promote the Pauson-Khand reaction in contrast to N-Oxide was attributed to a co-ordination stabilisation of the co-ordinatively unsaturated cobalt site after dissociative loss of carbon monoxide rather than the irreversible oxidative generation of a co-ordinatively unsaturated site believed to be generated by the N-Oxide. Further attempts to exploit the rate enhancement due to the stabilisation of the co-ordinatively unsaturated cobalt have included the use of co-ordinating solvents. Acetonitrile was found to have no beneficial effects while Sugihara reported the use as solvent of primary amines containing secondary alkyl groups leads to a dramatic increase in reaction rates.\textsuperscript{15} Similar rate enhancements were observed when the solvent was changed to 1,2-dichloroethane with 3.5eq of cyclohexylamine used as an additive rather than a solvent albeit at higher temperatures. 

Scheme(9).

\[ \text{Scheme(8)} \]
The use of amines was however not without drawbacks. Cycloadditions occurred for only reactive alkenes, cycloaddition did not occur for simple alkenes. The formation of reductive cobalt residues also resulted in the cleavage of the carbon hetero atom bond at the α position of the complex in some cases.

Prompted by the work of Krafft, who reported that alkyne dicobalt hexacarbonyls having sulfides at a suitable position in the side chain gave the corresponding alkyne dicobaltpentacarbonyl sulfide by treatment with NMO, Sugihara screened aryl and alkyl sulfides as promoters for both inter- and intra-molecular Pauson-Khand reactions. It was found that 3.5eq of an aryl or alkyl sulfide resulted in a dramatic increase in rate and yield of the Pauson-Khand reaction. When aryl sulfides were screened, the most effective examples were found to be those which were not sterically demanding and contained electron donating substituents on the aromatic ring. In the case of dialkyl sulfides similar trends were observed, i.e. the steric requirements around the sulfur
and the electron density on it affected the Pauson-Khand reaction. In the case of alkyl methyl sulfides the most efficient promoters were those having a primary and secondary alkyl group. Scheme(10).

The alkyl methyl sulfides were also found to be efficient promoters of the inter-molecular Pauson-Khand reaction which to date had only been possible in a general manner with N-Oxides. The potential of sulfides to complement N-Oxide methodology was demonstrated by direct comparison. Scheme(11).

1.1.3 Krafft methodology.
The application of alkenes bearing a pendant atom, typically a sulfur or nitrogen capable of co-ordinating to an unsaturated cobalt centre prior to alkene insertion has been pioneered by Krafft.\textsuperscript{16} Krafft reported that alkenes with a pendant homoallylic co-ordinating centre when employed in the Pauson-Khand reaction were found to increase the rate of the cycloaddition and generate the desired cyclopentenone with substantially better yield and higher regiocontrol than obtained with previous intermolecular cycloadditions. Krafft attributed the observed increase in
the rate and yield of the intermolecular Pauson-Khand reaction to stabilisation of the co-
ordinatively unsaturated species in the reaction pathway. The increased regiochemical control
achieved was suggested to result from co-ordination of the pendant functionality to cobalt prior to
insertion, thereby fixing the conformation of the alkene to favour the 5-substituted product.

Scheme (12).

Krafft subsequently extended this methodology to 1, 6-enynes. The rate of the intramolecular
cycloaddition was found to be increased when a pendant sulfur, nitrogen or oxygen was
incorporated in the homopropargylic or bishomopropargylic position under thermal or N-oxide
promoted conditions. During Krafft's investigation with the sulfur substituted substrates with N-
oxides as promoters, analysis of the reaction mixture by thin layer chromatography revealed the
formation of a new complex which then appeared to be converted to the bicyclic cyclopentenone.
These complexes proved to be difficult to characterise, but in the case of the bishomopropargylic sulfide cobalt complex the intermediate was isolated and identified by NMR spectroscopy as the pentacarbonyl complex with the pendant sulfur co-ordinating to a cobalt centre and as such the first intermediate to be isolated in the Pauson-Khand reaction. Scheme(13).

1.1.4 Catalytic Pauson-Khand Reaction.

Since the discovery of the Pauson Khand reaction in 1973, research has been directed towards making the reaction catalytic. The main obstacle is believed to be the formation of the cluster complexes such as Co₅(CO)₁₀.¹⁸

The first truly catalytic inter-molecular cycloaddition involving a non strained alkene was reported by Rautenstrauch.¹⁹ Rautenstrauch reacted 1-heptyne with ethylene in the presence of 0.22mol% of Co₅(CO)₈ under high pressures of carbon monoxide (100bar) to generate 2-cyclopentenone in 47% yield. The turnover of the dicobalt was approximately 220.

1.1.4.1 Phosphorus additives.

The first report of a catalytic intra-molecular Pauson-Khand reaction was published by Jeong.²⁰ In an attempt to reduce the detrimental formation of cluster complexes, Jeong screened various phosphorous additives, hoping to stabilise the active cobalt intermediates. Under 1atm of carbon monoxide in various solvents it was observed that the catalytic turnover did not exceed four,
regardless of the additive added. The effect of external phosphite ligands did however become beneficial when the reactions were carried out under high pressures of carbon monoxide. A range of enynes was demonstrated to undergo catalytic cycloaddition, the yields ranging from 58-94%. The role of the triphenylphosphite in the catalytic processes is not understood with no intermediates being isolated. Scheme(15).

\[
\begin{align*}
\text{Scheme(15)} & \\
\text{5mol\% Co}_2\text{(CO)}_6 & \quad \text{20mol\% triphenylphosphite} \\
\text{3atm CO} & \quad \text{72hrs} \\
\text{DME} & \quad \text{p-Ts-N} \\
\end{align*}
\]

1.1.4.2 Modified cobalt sources.
Jeong, in contrast to his previous publication, reported that a modified source of cobalt, 1,5-cyclooctadiene(indenyl)cobalt complex, was found to catalyse both intra-molecular enyne cycloadditions and inter-molecular cycloaddition between strained alkenes and selected alkynes effectively without the addition of further additives. In order for efficient catalytic cycloaddition, a high pressure of carbon monoxide was required. Scheme(16).

\[
\begin{align*}
\text{Scheme(16)} & \\
\text{CH}_2\text{OH} & \quad \text{COD(indenyl)Cobalt 1mol\%} \\
\text{CO(15atm)} & \quad \text{DME, 100\^\circ C, 40hrs} \\
\end{align*}
\]

1.1.4.3 Photo and thermal initiation.
Livinghouse has been active in the area of catalytic Pauson-Khand chemistry. He initially reported high intensity light promoted a number of enynes to undergo catalytic cycloaddition in the presence of 5mol\% of very pure dicobaltoctacarbonyl. A 10^6 candle power light source photoinitiated the desired catalytic reaction with yields ranging from 67-95%. Livinghouse has also demonstrated that thermal conditions are sufficient to promote intra-molecular catalytic Pauson-Khand reactions. The catalytic process was found to proceed efficiently only within a
narrow thermal window of 60-70°C. As in the photoinitiated variant, dicobaltoctacarbonyl of very high purity was required in order to effect the reaction efficiently. Scheme(17).

Scheme(17)

The requisite for very pure dicobaltoctacarbonyl constituted an experimental disadvantage which was inherent to both procedures.

1.1.4.4 Cobalt surrogates.
Livinghouse later reported a novel experimental protocol which obviates the requirement for very high purity dicobaltoctacarbonyl.24 A range of dicobalthexacarbonyl alkyne complexes was shown to serve as convenient substitutes for the relatively labile dicobaltoctacarbonyl via reductive decomplexation with Et₃SiH. The presence of cyclohexylamine or thiophene was found to be advantageous, although not resulting in a rate acceleration, improved yields were noted when they were present. Scheme(18).

Scheme(18)

In a modification of Livinghouse’s work, Krafft used dicobalthexacarbonyl complexes of enynes as an efficient source of the catalyst precursor for a number of intramolecular Pauson-Khand
reactions. Krafft did not have to add Et₃SiH in order to generate the active catalyst, moderate heating was found to be sufficient to promote catalytic cycloaddition. The presence of cyclohexylamine was in certain cases found to be beneficial enabling higher yields of the desired cyclopentenones to be isolated. **Scheme(19).**

Krafft subsequently reported the use of dicobalthexacarbonyl alkyne complexes as a surrogate for the labile dicobalthexacarbonyl was not necessary. Krafft found that when the reaction was carried out in carefully base washed glassware, the catalytic reaction proceeded in most cases using 10 mol% of unpurified dicobaltoctacarbonyl.

**1.1.4.5 Supercritical fluids as reaction media.**

In an attempt to stop cluster formation and hence catalyst deactivation, Jeong has employed supercritical carbon monoxide as a reaction medium. The projected advantages of carrying out a catalytic Pauson-Khand reaction in supercritical fluids are increased reaction rates and selectivity arising from high solubility of reactant gases, rapid diffusion of solutes and weakening of the solvation forces around reacting species. Jeong’s preliminary results demonstrated that both inter- and intra-molecular Pauson-Khand reactions can be successfully carried out in supercritical carbon dioxide. **Scheme(20).**

16
Temperature and pressure of carbon monoxide was found to be critical, the catalytic process occurring at 90-95°C at a pressure of 110-120 atm in the presence of 2-5 mol% of dicobaltoctacarbonyl. Temperature was found to effect the rate of reaction and high pressures were required in order to prevent the precipitation of an unidentified white metallic precipitate.

Jeong has also carried out inter-molecular Pauson-Khand reactions in supercritical ethylene.\textsuperscript{28} Jeong demonstrated that supercritical ethylene could not only be used as a substrate but also as a solvent generating the desired cyclopentenones in moderate to good yield.

**1.1.4.6 Polymer supported catalytic Pauson-Khand cycloaddition.**

In a recent development Gibson\textsuperscript{29} has demonstrated that cobalt carbonyl complexes immobilised onto a polymer bound triphenylphosphine solid support are effective and practical catalysts of the Pauson-Khand reaction. Scheme(21).

Gibson reported that the immobilised cobalt complexes displayed increased air stability and as such were easier to handle than their dicobalthexacarbonyl analogues. Such characteristics combined with the projected advantages of performing the Pauson-Khand reaction on a solid support bode well for further developments in this area.
1.1.4.7 Dicobalt carbonyl phosphines.
Gibson subsequently reported that preformed dicobalt carbonyl phosphines and phosphites were capable of promoting the Pauson-Khand reaction in a catalytic fashion when not immobilised on a solid support. A range of dicobalt carbonyl phosphines and phosphites was screened, several of which provide an attractive practical alternative to catalyst systems currently available. Scheme(22).

\[
\begin{array}{c}
\text{TsN} \equiv \equiv \\
\text{(OC)}_3\text{Co-Co(OC)}_2\text{PPh}_3 \\
\xrightarrow{\text{5mol\%}} \\
70^\circ\text{C}, 24\text{h} \\
1.05 \text{atm CO} \\
\text{THF}
\end{array} \rightarrow \\
\text{TsN} \equiv \equiv \\
\text{84\%}
\]

\text{Scheme(22)}

1.1.4.8 Catalytic coupled Pauson-Khand Michael reaction with electron deficient alkenes.
The inability of alkenes bearing an electron withdrawing substituent to generate the desired cyclopentenone products is well known. Costa\textsuperscript{31} has however developed a catalytic dicobalt octacarbonyl mediated Pauson-Khand reaction in which alkenes bearing electron withdrawing substituents undergo cycloaddition with alkynes and carbon monoxide. Scheme(23).

\[
\begin{array}{c}
\equiv \\
\text{Co}_2\text{(CO)}_8 \text{20mol\%} \\
\text{CO, 40bar} \\
120^\circ\text{C, 32h} \\
methyl acrylate
\end{array} \rightarrow \\
\text{MeO}_2\text{C} \equiv \equiv \\
\text{MeO}_2\text{C} \\
44\%
\]

\text{Scheme(23)}

The catalytic process was a coupled process involving a Pauson-Khand and Michael type reaction. The formation of the cyclopentenone derivatives was found to be strongly dependent on the nature of the alkene and alkyne.

1.1.4.9 Other sources of cobalt.
Other sources of cobalt have been shown to promote the catalytic Pauson-Khand reaction. Chung envisioned that a catalytic Pauson-Khand system could be achieved if low valent cobalt could be
generated that could complex with dienes and alkynes or could produce cobalt carbonyls under an atmosphere of carbon monoxide. A number of cobalt salts were screened. The most efficient system was found to be Co(acac)$_n$ (n = 2,3) with sodium borohydride. Typically 5mol% of Co(acac)$_2$ and 10mol% of sodium borohydride under 40atm of carbon monoxide when heated to 80-100°C facilitated both the inter- and intra-molecular Pauson-Khand reactions in high yield. Scheme(24).

Jeong has also used Co$_6$(CO)$_{12}$ as a catalyst precursor in the inter and intramolecular Pauson-Khand reaction at 150°C under 10atm of carbon monoxide. Under high pressures of carbon monoxide, an equilibrium is established between Co$_6$(CO)$_{12}$ and Co$_2$(CO)$_8$, the equilibrium favours at high pressure the formation of Co$_2$(CO)$_8$ which is believed to be the active catalyst. Jeong found that the effect of pressure of carbon monoxide was found to be critical, higher pressures resulting in faster reaction rates. Scheme(25).

A sub-stoichiometric version of the Pauson-Khand reaction has been developed by Periasamy. An active cobalt complex resulted from CoBr$_2$ and Zn in toluene and tBuOH under an atmosphere of carbon monoxide. The potential of the system was illustrated using norbornene and cyclopentene, the yield for the catalytic process being lower for the less strained cyclopentene. Scheme(26).
1.1.5 Stereoselective Pauson-Khand reactions.

The ability to generate optically enriched cyclopentenones via an asymmetric Pauson-Khand reaction has been realised by a number of groups in four main areas. To date the most successful approaches have been based on the use of chiral auxiliaries, chiral metal complexes, chiral promoters and finally the use of chiral pool techniques.

1.1.5.1 Chiral complexes.

Chiral complexes have been used to effect asymmetric versions of the Pauson-Khand reaction. The use of chiral complexes relies on the transient desymmetrisation of the parent dicobalt alkynyl complex core of the dicobalthexacarbonyl fragment. Such desymmetrisation has been achieved by a number of groups by replacing a carbon monoxide in the parent complex generating diastereomeric complexes.

1.1.5.2 Glyphos based methodology.

Kerr used the optically active phosphine (R)-(+) Glyphos ligand in order to desymmetrize a variety of parent complexes.\textsuperscript{35} Subsequent separation of the diastereomeric complexes by preparative HPLC enabled the isolation of either diastereomerically pure complex. Reaction of either optically pure complex with norbornene under classical Pauson-Khand conditions yielded the desired cyclopentenone in modest yield, but with disappointingly low enantiomeric excess. Under milder conditions employing NMO as a promoter, the desired cyclopentenone was
obtained in excellent yield with excellent enantiomeric excess. Kerr attributed the decrease in selectivity under thermal conditions to result from the racemisation of the parent complex. Scheme(27).

\[
\begin{align*}
\text{HPLC separation of complexes} \\
\end{align*}
\]

\( \text{6 equiv. of anhydrous NMO added to a solution of the complex and alkene (6-8hrs)} \)

\( \text{1.1 equiv. of alkene} \)

\( \text{up to 76\%, >99\%e.e} \)

Scheme(27)

1.1.5.3 Achiral phosphorus based ligand in combination with chiral auxiliary.

Chung has adopted a similar approach. Instead of using a chiral phosphine ligand in order to desymmetrise the cobalt core Chung treated dicobalthexacarbonylpropargyl menthyl ether with phosphine or phosphite\(^6\). The diastereomeric complexes were readily separable by flash chromatography. Scheme(28).

\[
\begin{align*}
\text{Menthol} & \quad 1. \text{L} \\
& \quad 2. \text{separation by flash chromatography.} \\
\end{align*}
\]

\( \text{3a or 3a'} (L = \text{P(OMe)}_3) \)

\( \text{3a or 3a'} (L = \text{P(Ph)}_3) \)

Scheme (28)
The optically pure complexes in the presence of norbornene or norbornadiene under N-oxide conditions yielded the desired cyclopentenone in high yield with complete selectivity. Table(1). The rate of reaction was observed to increase in changing the solvent from dichloromethane to a 1:1 mixture of dichloromethane and tetrahydrofuran. Scheme(29).

![Scheme(29)]

**Scheme(29)**

Stereoselective Pauson-Khand reaction employing dicobaltpropargylmenthyletherpentacarbonyl phosphine or phosphite complexes. Table(1).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Alkene</th>
<th>Yield</th>
<th>Diastereomeric Excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>norbornene</td>
<td>98%(^b)</td>
<td>100% by H(^1) NMR</td>
</tr>
<tr>
<td>la</td>
<td>norbornadiene</td>
<td>90%(^b)</td>
<td>100% by C(^{13}) NMR</td>
</tr>
<tr>
<td>la'</td>
<td>norbornene</td>
<td>80%(^b)</td>
<td>100% by H(^1) NMR</td>
</tr>
<tr>
<td>la'</td>
<td>norbornadiene</td>
<td>40%(^a)</td>
<td>100% by C(^{13}) NMR</td>
</tr>
</tbody>
</table>

A CH\(_2\)Cl\(_2\) used as solvent. B 1:1 mixture of THF:CH\(_2\)Cl\(_2\) used as solvent.

**1.1.5.4 Bidentate chiral phosphorus based ligands.**

Both Kerr and Chung have employed monodentate phosphorus ligands in order to desymmetrise the prochiral metal core. As such, both groups require a chromatographic purification in order to separate the optically pure complexes formed in approximately equimolar amounts. Scheme(30).
Greene has tried to circumvent this problem by investigating the use of bidentate ligands.\textsuperscript{37} Greene synthesised a number of C\textsubscript{2} bidentate ligands with a phosphorus nitrogen phosphorus backbone. The corresponding cobalt complexes were readily formed in good yield (75-50\%). Scheme(31).

The ability of the complexes to act as substrates in the Pauson-Khand reaction was demonstrated by reaction with norbornene in toluene at 80°C, the desired cyclopentenones being isolated in 24-98\%. Scheme(32).

As a preliminary result, Greene reported that a chiral bidentate phosphorus ligand incorporating (+) α-methylbenzylamine in place of methylamine in the backbone afforded the desired cycloadduct in 54\% yield with a low but encouraging enantiomeric excess of 16\%. Scheme(33).
1.1.5.5 Chelating chiral auxiliaries bound to the alkynyl fragment of the complex.

An alternative approach to the asymmetric synthesis of cyclopentenones \textit{via} a Pauson-Khand reaction has been inspired by the work of Krafft. Krafft has investigated the effects of incorporating a tethered functionality within the complex capable of interacting with the metal centre along the reaction pathway. The presence of such pendant functionality has been found to increase the regiocontrol, rate and yield in the cycloaddition. Notably, the use of sulfur functionalised substrates has enabled the isolation of rare intermediates.\textsuperscript{24, 17a, 17b, 17c,38}

1.1.5.6 Chiral acetyleneoxyethers.

Inspired by the work of Krafft, Pericas designed a family of enantiomerically pure ligands based on (2R)-10-alkyl(thio)isoborneols as chiral auxiliaries. \textbf{Scheme(34)}. 

\[ E = (+)-\alpha \text{-methylbenzylamine}\]
The pendant sulfur present in the auxiliaries co-ordinates to and hence transfers chirality to the metal core during the course of the reaction.\textsuperscript{39} Scheme(35).
The ability of the pendant sulfur functionality of these ligands to co-ordinate to a cobalt centre was demonstrated upon complexation. Displacement of a carbon monoxide from the parent hexacarbonyl complex was achieved on moderately heating a solution of the (2R)-10-alkyl(thio)isobormeols in hexane under a stream of nitrogen in order to purge dissociated carbon monoxide. On cooling the pentacarbonyl chelated form of the complex was found to revert to the parent hexacarbonyl complex. NMR analysis of the equilibrium suggested that although two diastereomers could be formed by chelation of sulfur to either prochiral cobalt centre, only a single diastereomer was formed. Under thermal conditions Pericas found that it was not possible to achieve complete chelation. In order to generate the chelated complex NMO was used to irreversibly oxidise carbon monoxide ligands preventing the formation of the unchelated complex. Scheme(36).

![Scheme(36)](image)

The suitability of chelated pentacarbonyl complexes as substrates in the Pauson-Khand reaction was investigated. A variety of conditions was tried with a number of alkenes. Scheme(37).

![Scheme(37)](image)

The most successful conditions were found to be those in which the chelated pentacarbonyl was initially generated by the addition of NMO at room temperature. On complete formation of the chelated species the reaction mixture was cooled to $-20^\circ C$ and a strained alkene added. The system proved to be ineffective for unstrained alkenes. Table(2).
### Intermolecular Pauson-Khand Reactions Using Chelating Auxiliaries. Table(2).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Alkene</th>
<th>Cyclopentenone</th>
<th>Conditions</th>
<th>T (°C)</th>
<th>Yield%</th>
<th>d.e%</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Complex" /></td>
<td><img src="image2.png" alt="Alkene" /></td>
<td><img src="image3.png" alt="Cyclopentenone" /></td>
<td>A</td>
<td>r.t</td>
<td>65</td>
<td>40</td>
</tr>
<tr>
<td><img src="image4.png" alt="Complex" /></td>
<td><img src="image5.png" alt="Alkene" /></td>
<td><img src="image6.png" alt="Cyclopentenone" /></td>
<td>B</td>
<td>0</td>
<td>66</td>
<td>76</td>
</tr>
<tr>
<td><img src="image7.png" alt="Complex" /></td>
<td><img src="image8.png" alt="Alkene" /></td>
<td><img src="image9.png" alt="Cyclopentenone" /></td>
<td>B</td>
<td>-20</td>
<td>77</td>
<td>84</td>
</tr>
<tr>
<td><img src="image10.png" alt="Complex" /></td>
<td><img src="image11.png" alt="Alkene" /></td>
<td><img src="image12.png" alt="Cyclopentenone" /></td>
<td>C</td>
<td>50</td>
<td>69</td>
<td>20</td>
</tr>
<tr>
<td><img src="image13.png" alt="Complex" /></td>
<td><img src="image14.png" alt="Alkene" /></td>
<td><img src="image15.png" alt="Cyclopentenone" /></td>
<td>C</td>
<td>0</td>
<td>99</td>
<td>60</td>
</tr>
<tr>
<td><img src="image16.png" alt="Complex" /></td>
<td><img src="image17.png" alt="Alkene" /></td>
<td><img src="image18.png" alt="Cyclopentenone" /></td>
<td>A</td>
<td>r.t</td>
<td>95</td>
<td>20</td>
</tr>
<tr>
<td><img src="image19.png" alt="Complex" /></td>
<td><img src="image20.png" alt="Alkene" /></td>
<td><img src="image21.png" alt="Cyclopentenone" /></td>
<td>B</td>
<td>-20</td>
<td>82</td>
<td>92</td>
</tr>
<tr>
<td><img src="image22.png" alt="Complex" /></td>
<td><img src="image23.png" alt="Alkene" /></td>
<td><img src="image24.png" alt="Cyclopentenone" /></td>
<td>A</td>
<td>50</td>
<td>70</td>
<td>44</td>
</tr>
<tr>
<td><img src="image25.png" alt="Complex" /></td>
<td><img src="image26.png" alt="Alkene" /></td>
<td><img src="image27.png" alt="Cyclopentenone" /></td>
<td>B</td>
<td>-20</td>
<td>91</td>
<td>86</td>
</tr>
</tbody>
</table>

R = CH₂C(CH₃)₃

Conditions A: Thermal activation. B: 6eq of NMO at r.t., cool to indicated temperature then add olefin. C: Thermal activation at 50°C for 1hr, cooled to indicated temperature then add olefin.

1.1.5.7 Chiral acetylenethioethers.
Pericas had demonstrated that chiral acetyleneoxyethers with pendant functionality, efficiently transfer chirality to a cobalt centre of the metal core facilitating an asymmetric Pauson-Khand reaction. As such chiral acetylenethioether became potentially attractive. The replacement of oxygen with sulfur would enable easier preparation of the hexacarbonylcobalt complexes. Once formed these complexes may also be expected to be more stable than their analogues due to the
longer carbon sulfur bond reducing the strain in the ring formed on chelation of the sulfur pendant to a cobalt metal centre.

As for the chiral acetyleneoxyether, when the chiral acetylenethioether derived from (2R)-exo-10-(methylthio)-2-bornanethiol was complexed to dicobalthexacarbonyl, the chelated complex could be generated thermally or by addition of 6eq of NMO. Scheme(38).

The chelated complex was as expected considerably more stable than the oxyether analogue and was stable to chromatographic purification.

In order to assess the scope of the chiral acetylenethioethers in an asymmetric Pauson-Khand reaction the chelated complexes under the conditions optimised in the chiral acetyleneoxyether series were reacted with the strained alkenes norbornene and norbornadiene. Surprisingly only moderate yields and diastereomeric ratios where obtained.

Pericàs determined that the presence of an excess of NMO had a deleterious effect on diastereoselectivity. Removal of excess NMO after generation of the pentacarbonyl complex by filtration through Al₂O₃ prior to addition of norbornadiene enabled an enantiomeric ratio of 65-95% to be obtained after a 12hr period. Under these optimised conditions a diastereomeric ratio of 86% was recorded with norbornene albeit after a 120hr period. Less reactive alkenes were not investigated. Table(3).
Pauson-Khand Reactions of Dicobalt Pentacarbonyl of a Chiral Acetylene Thioether.

Table (3).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Alkene</th>
<th>Cyclopentenone</th>
<th>Conditions</th>
<th>Yield%</th>
<th>d.r.%</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Complex" /></td>
<td><img src="image" alt="Alkene" /></td>
<td><img src="image" alt="Cyclopentenone" /></td>
<td>A. 0°C, 552h</td>
<td>31</td>
<td>67 : 33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B. 0°C, 24h</td>
<td>64</td>
<td>68 : 32&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B. -20°C, 60h</td>
<td>67</td>
<td>52 : 48&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C. 0°C, 24h</td>
<td>52</td>
<td>92 : 8&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C. -20°C, 144h</td>
<td>53</td>
<td>93 : 7&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D. -10°C, 72h</td>
<td>65</td>
<td>95 : 5&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B. 0°C, 48h</td>
<td>66</td>
<td>37 : 63&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C. O°C, 48h</td>
<td>45</td>
<td>82 : 18&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D. -10°C, 120h</td>
<td>66</td>
<td>86 : 14&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Conditions A: Complex and olefin (10eq) in hexane under CO at specified temperature. B: formation of pentacarbonyl complex by addition of NMO (6eq) in dichloromethane then addition of olefin (10eq) at specified temperature. C: formation of pentacarbonyl complex by heating in hexane at 55°C prior to cooling and addition of olefin at specified temperature. D: formation of pentacarbonyl complex by NMO (3eq) in dichloromethane and then removal of the excess NMO by filtration through Al₂O₃ followed by addition of olefin (10eq) at specified temperature. <sup>1</sup>HPLC (Nucleosil C18, MeOH/H₂O 80:20). <sup>1</sup>By <sup>13</sup>C and <sup>1</sup>H NMR.

1.1.5.8 Non chelating chiral auxiliaries bound to the alkynyl fragment of the complex.

The importance of a chelating sulphur in the ability of the chiral acetylene-thioether system to induce an asymmetric Pauson-Khand reaction has been demonstrated by Pericas.<sup>41</sup> A variety of thioether ligands without a pendant sulphur functionalisation was generated derived from camphor thiols (1S-exo)2-Bornanethiol. Scheme (39).

![Scheme(39)](image)

When complexed to dicobaltoctacarbonyl, they were found to be effective substrates for intermolecular Pauson-Khand reaction but with generally low diastereomeric excesses. Scheme (40).
Intermolecular Pauson-Khand reaction of dicobalt R*-thioalkyne complexes

**Scheme (40).**

when $R' = H$

when $R' = -(CH_2)_4CH_3$

$R' = -(CH_2)_3CH_3$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Alkene</th>
<th>Cyclopentenone</th>
<th>Conditions $^a$</th>
<th>Yield%</th>
<th>d.r.%$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Complex 1" /></td>
<td><img src="image2" alt="Alkene 1" /></td>
<td><img src="image3" alt="Cyclopentenone 1" /></td>
<td>A, 50°C, 1h</td>
<td>56</td>
<td>1 : 1</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>B, -20°C, 1h</td>
<td>89</td>
<td>1 : 1</td>
</tr>
<tr>
<td><img src="image4" alt="Complex 2" /></td>
<td><img src="image5" alt="Alkene 2" /></td>
<td><img src="image6" alt="Cyclopentenone 2" /></td>
<td>A, 25°C, 3d</td>
<td>74</td>
<td>1 : 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B, -20°C, 1h</td>
<td>79</td>
<td>1 : 1</td>
</tr>
<tr>
<td><img src="image7" alt="Complex 3" /></td>
<td><img src="image8" alt="Alkene 3" /></td>
<td><img src="image9" alt="Cyclopentenone 3" /></td>
<td>A, 70°C, 48h</td>
<td>62</td>
<td>1 : 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B, -20°C, 3h</td>
<td>33</td>
<td>1 : 1</td>
</tr>
<tr>
<td><img src="image10" alt="Complex 4" /></td>
<td><img src="image11" alt="Alkene 4" /></td>
<td><img src="image12" alt="Cyclopentenone 4" /></td>
<td>A, 25°C, 24h</td>
<td>68</td>
<td>1 : 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B, -20°C, 16h</td>
<td>85</td>
<td>1 : 1</td>
</tr>
<tr>
<td><img src="image13" alt="Complex 5" /></td>
<td><img src="image14" alt="Alkene 5" /></td>
<td><img src="image15" alt="Cyclopentenone 5" /></td>
<td>A, 50°C, 1h</td>
<td>56</td>
<td>1 : 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B, -20°C, 1h</td>
<td>89</td>
<td>1 : 1</td>
</tr>
<tr>
<td><img src="image16" alt="Complex 6" /></td>
<td><img src="image17" alt="Alkene 6" /></td>
<td><img src="image18" alt="Cyclopentenone 6" /></td>
<td>A, 70°C, 48h</td>
<td>58</td>
<td>2.2 : 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B, -20°C, 28h</td>
<td>48</td>
<td>4.6 : 1</td>
</tr>
<tr>
<td><img src="image19" alt="Complex 7" /></td>
<td><img src="image20" alt="Alkene 7" /></td>
<td><img src="image21" alt="Cyclopentenone 7" /></td>
<td>A, 70°C, 3h</td>
<td>56</td>
<td>1 : 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B, -20°C, 25h</td>
<td>52</td>
<td>1 : 1</td>
</tr>
<tr>
<td><img src="image22" alt="Complex 8" /></td>
<td><img src="image23" alt="Alkene 8" /></td>
<td><img src="image24" alt="Cyclopentenone 8" /></td>
<td>A, 65°C, 22h</td>
<td>76</td>
<td>2.1 : 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B, -20°C, 48h</td>
<td>52</td>
<td>4.1 : 1</td>
</tr>
</tbody>
</table>

$^a$ Conditions A: dicobalthexacarbonyl complex in hexane at specified temperature. B: dicobalthexacarbonyl complex with 6eq of NMO in dichloromethane at specified temperature. $^b$By $^{13}$C NMR.
1.1.5.9 Chiral thioetherenynes with no pendant functionality.

Two chiral thioetherenynes were prepared. Complexation of these enynes proceeded smoothly on treatment with a slight excess of dicobaltoctacarbonyl. The complexes were found to undergo intramolecular cycloaddition under thermal conditions and on treatment with NMO. Scheme(41).

\[
\text{R}^*S=\text{C} \xrightarrow{1. \text{Co}_2(\text{CO})_6} \text{R}^*\text{S} \text{C}=\text{C} \xrightarrow{2. \text{hexane, heat} \text{ or } 10\text{eq NMO, DCM}} \text{R}^*\text{S} \text{C} \equiv \text{N}
\]

Scheme(41)

The yields of the cycloaddition were moderate 47-60%. Any stereoinduction arising from the chiral enynethioether was negligible. Table(5).

**Intramolecular Pauson-Khand reactions of thioetherenynes**

**Table(5).**

<table>
<thead>
<tr>
<th>Starting thioene</th>
<th>Conditions</th>
<th>Cyclopentenone</th>
<th>Yield%</th>
<th>d.r. %</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="" /></td>
<td>A, 65°C, 12h</td>
<td>55%</td>
<td>1.1 : 1</td>
<td></td>
</tr>
<tr>
<td><img src="image2" alt="" /></td>
<td>B, 0°C, 11h</td>
<td>50%</td>
<td>1.1 : 1</td>
<td></td>
</tr>
<tr>
<td><img src="image3" alt="" /></td>
<td>A, 65°C, 42h</td>
<td>60%</td>
<td>1.4 : 1</td>
<td></td>
</tr>
<tr>
<td><img src="image4" alt="" /></td>
<td>B, -20°C, 48h</td>
<td>47%</td>
<td>1.3 : 1</td>
<td></td>
</tr>
</tbody>
</table>

*Conditions A: dicobalthexacarbonyl complex in hexane at specified temperature. B: dicobalthexacarbonyl complex with 6eq of NMO in dichloromethane at specified temperature. *By $^{13}$C NMR.

1.1.5.10 N-Alkynol sultams.

From Pericàs detailed research in the area of alkoxy and thioether ligands as efficient promoters of an asymmetric Pauson-Khand reaction it would appear that the success of such ligands relied heavily on the presence of a pendant functionality which chelated a cobalt centre prior to its displacement by a co-ordinating alkene.

In a recent publication Pericàs however also reported that exceptionally high levels of regio and stereoselectivity can be easily achieved by pure steric control under standard reaction
conditions in the intermolecular Pauson-Khand reaction of N-(2-alkyne) derivatives of chiral oxazolidinones and sultams.\textsuperscript{42}

A series of 2-alkynol derivatives of the homochiral 2 oxazolidinones (a-c) and of (+) 10,2 camphorsultam was prepared and complexed with dicobaltoctacarbonyl. These complexes under traditional conditions or treatment with N-Oxide in the presence of norbornadiene generated the expected cycloadduct in 36-96% yield.

\[
\begin{align*}
\text{R} & = \text{Ph}(4), \text{Me}_3\text{Si}(5), \text{Me}(6) \\
\text{R} & = \text{Ph}(4), \text{Me}_3\text{Si}(5), \text{Me}(6) \\
\text{Me}_3\text{CCOCl}, \text{Et}_3\text{N} \\
\text{LiX}_c \text{ or } \text{HX}_d\text{LiCl} (5d) \\
\text{THF}, 0^\circ\text{C} \\
56-92\% \text{ yield.}
\end{align*}
\]

Scheme(42)

The reactions of the phenylpropionic(1a-d) and the (trimethylsilyl)propionic acid derivative(2a,d) were found to be completely regioselective. The 2-butynoic acid derivatives(3a-d) were found to be less regioselective.

From the experimental results it appeared that the stereoselectivity of the process was extremely sensitive to the structure of the chiral auxiliary, particularly the steric hindrance present at C\textsubscript{4} in the oxazolidinone ring. This was highlighted by the marked difference in stereoselectivity obtained with the benzoxazolidinone, phenyloxazolidinone and the camphor oxazolidinone. The highest levels of stereocontrol were however obtained with the
Phenylpropynol derivative of Oppolzer’s borane-10-2-sultam which resulted in almost exclusive selective reaction with six equivalents of NMO in the presence of norbornadiene in an open vessel yielded the desired cycloadduct in 93% yield with a diastereomeric ratio of >800:1. Scheme(42). Table(6).

3-Carbamoylcyclopentenones from the Pauson-Khand Reaction of N-Alkynoyl Derivatives of Oxazolidinones and Sultams with Norbornadiene. Table(6).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Starting alkyne</th>
<th>Reaction*</th>
<th>Product yield, d.r.**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>A. r.t., 24h</td>
<td>7a (97%, 1:1)</td>
</tr>
<tr>
<td>2</td>
<td>6a</td>
<td>A. r.t., 14h</td>
<td>9b (36%, 2:1)</td>
</tr>
<tr>
<td>3</td>
<td>4b</td>
<td>A. r.t., 21h</td>
<td>7b (96%, 5.2:1)</td>
</tr>
<tr>
<td>4</td>
<td>5b</td>
<td>B. 0°C to r.t., 14h</td>
<td>8b (88%, 3.6:1)</td>
</tr>
<tr>
<td>5</td>
<td>6b</td>
<td>A. r.t., 72h</td>
<td>9b (53%, 7.6:1)</td>
</tr>
<tr>
<td>6</td>
<td>5c</td>
<td>A. r.t., 21h</td>
<td>7c (97%, 14:1)</td>
</tr>
<tr>
<td>7</td>
<td>6c</td>
<td>A. r.t., 96h</td>
<td>9c (34%, 17.5:1)</td>
</tr>
<tr>
<td>8</td>
<td>5d</td>
<td>A. 45°C, 21h</td>
<td>7d (91%, 523:1)</td>
</tr>
<tr>
<td>9</td>
<td>4d</td>
<td>B. 0°C to r.t., 1h</td>
<td>7d (93%, &gt;800:1)</td>
</tr>
<tr>
<td>10</td>
<td>5d</td>
<td>B. 0°C to r.t., 18h</td>
<td>8d (78%, &gt;800:1)</td>
</tr>
<tr>
<td>11</td>
<td>6d</td>
<td>A. r.t., 12h</td>
<td>9d (55%, 318:1)</td>
</tr>
</tbody>
</table>

Reaction* (A) dicobalt enyne complex and olefin 10eq under nitrogen at specified temperature. (B) dicobalt enyne complex and olefin 10eq under nitrogen at specified temperature NMO activation.

1.1.5.11 Sulfoxide for asymmetric Pauson-Khand reaction

Pericas has also investigated the scope of alkynyl chiral sulfoxides as a promoters for an asymmetric Pauson-Khand process. In previous publications Pericas has demonstrated that chiral acetylene dicobalt complexes are able to induce high levels of stereoselectivity in the Pauson-Khand reaction. This has been achieved despite the remote nature of the stereogenic centre in the auxiliary being between four and five bonds away from the newly created stereogenic centre in the Pauson-Khand cycloadduct.

In an effort to reduce the distance between the two stereogenic centres Pericas investigated the use of enantiomerically pure alkynyl sulfoxides in which the stereogenic centre is bound directly to the acetylenic carbon.
A number of enantiomerically pure alkynyl sulfoxides containing a range of sterically and electronically different substituents were synthesised and subsequently complexed with dicobaltoctacarbonyl to yield the desired complexes.

The complexed alkynyl sulfoxides were found to be generally inactive as substrates in the Pauson-Khand reaction with a number of strained alkenes generating the desired cyclopentenones in low yield. The ability of the sulfoxide to act as a chiral auxiliary was also found to be low with negligible levels of stereoisinduction being observed in the cyclopentenone product. Scheme(43).

The inability of the sulfoxide to induce any stereoisinduction in the Pauson-Khand reaction was subsequently attributed to racemisation of the cobaltcarbonyl complex which was found to occur readily at room temperature.

1.1.5.12 tert-Butylsulfinyl group.
Although Pericàs has shown that alkynyl sulfoxides are inefficient auxiliaries for a stereoselective Pauson-Khand reaction, Carretero has shown that the sulfinyl group can be used as an efficient chiral auxiliary in intramolecular asymmetric Pauson-Khand reaction.\(^\text{44}\) Despite their electron withdrawing nature, a series of racemic trans-1-sulfinylhepten-6-yne dicobalt complexes underwent cycloaddition to yield the desired diastereomeric cyclopentenones in modest yield. Scheme(44).
The stereoselectivity of the reaction was found to be dependent on the substituent on the sulfur. The Pauson-Khand reaction of the tert-butyl-sulfoxide occurred with very high stereoselectivity affording crude mixture in which only one isomer could be detected by proton NMR spectroscopy under both thermal and N-Oxide conditions. Table(7).

<table>
<thead>
<tr>
<th>Enyne</th>
<th>Conditions (^\text{a})</th>
<th>Cyclopentenone</th>
<th>11 : 12 (^\text{c})</th>
<th>Yield (^\text{d})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{R} = \text{Me}_2\text{N}C_6\text{H}_4)</td>
<td>A</td>
<td>75 : 25</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>73 : 27</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>(\text{R} = \text{t-Bu})</td>
<td>A</td>
<td>71 : 29</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>&gt;98 &lt; 2</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

\(^\text{a}\)CH\(_3\)CN, 80°C, B\(3\)NMO.H\(_2\)O (6eq), CH\(_2\)Cl\(_2\), room temperature. \(^\text{b}\)By \(^1\)H NMR on crude reaction mixtures after filtration of cobalt by products. \(^\text{c}\)In pure adducts A and B.

In order to access the synthetic utility of this auxiliary, a number of of (S)\(\text{trans}\) tert-butylsulfinylated enynes were prepared by olefination of the corresponding alkynyl aldehyde with (R) diethyl tert-butylsulfinylmethylphosphonate. The \(\text{cis}\) and \(\text{trans}\) mixture was readily separable by flash chromatography. All of the dicobalt enynes bearing a terminal alkyne underwent cycloaddition with complete stereoselectivity. No reaction was observed with enynes bearing substituted alkynes. Scheme(45). Table(8).
Thermal Pauson-Khand reactions of (S) Trans Enynes Table(8).

<table>
<thead>
<tr>
<th>Enyne</th>
<th>n</th>
<th>T °C</th>
<th>Cyclopentenone</th>
<th>Yielda %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>80</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>60</td>
<td></td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>80</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>80</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>80</td>
<td></td>
<td>b</td>
</tr>
</tbody>
</table>

*In pure product after flash chromatography. bThe starting enyne was recovered unchanged.

Interestingly, unexpected results were obtained in the cobalt mediated reactions of the sulfinylated enynes of cis conformation. The tert-butyl sulfoxides (S)-cis –3 and (S)- cis--9 gave the same diastereomeric cyclopentenones with equal selectivity as the (S)- trans-3 and (S)- trans-9 enynes. Thus a 55:45 mixture of trans and cis olefin sulfoxide afforded only one isomer
enabling the Pauson-Khand reaction to be carried out directly after the olefination step. 

\[ \text{Scheme(46).} \]

\[
\begin{align*}
\text{cis-3} & \quad \text{t-Bu-SO} \\
\text{(S) cis-3} & \quad 1. \text{Co}_2(\text{CO})_6 \quad \text{CH}_3\text{CN, 80°C} \\
& \quad 41\% \\
\text{(S) trans/cis} & = 55:45
\end{align*}
\]

1.1.5.13 Chiral Promoters.

It has been known since the early 1990s that N-oxides were efficient promoters of the Pauson Khand reaction. Kerr extended this methodology by using a chiral N-Oxide to promote an asymmetric Pauson-Khand reaction.\(^4\) Kerr found that at low temperature low stereoselectivity could be achieved by treatment of dimethylpropargylalcohol with brucine N-Oxide. \textbf{Scheme(47).}

Table(9). Kerr rationalised these experimental results by proposing that the observed asymmetric control arose from a stereoselective decarbonylation of the prochiral starting hexacarbonyl complex. Alternatively or additionally Kerr suggested that the brucine generated may selectively stabilise one of the two possible co-ordinatively unsaturated cobalt sites of an intermediate in the Pauson-Khand reaction process resulting in an asymmetric cyclisation since the alkene reacts preferentially at this unsaturated site. \textbf{Scheme(48).}

\[ \text{Scheme(47).} \]
Asymmetric Pauson-Khand Cyclisations Using Brucine N-Oxide Table(9).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conditions</th>
<th>Yield</th>
<th>Enantiomeric ratio&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>r.t., 5min</td>
<td>91</td>
<td>0</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-10°C, 12hr</td>
<td>61</td>
<td>45:55</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;/MeOH</td>
<td>r.t., 2hr</td>
<td>80</td>
<td>46:54</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;/MeOH</td>
<td>-10°C, 16hr</td>
<td>78</td>
<td>42:58</td>
</tr>
<tr>
<td>THF</td>
<td>-17°C, 1.5hr</td>
<td>97</td>
<td>35:55</td>
</tr>
<tr>
<td>THF</td>
<td>-37°C, 6hr</td>
<td>88</td>
<td>32:68</td>
</tr>
<tr>
<td>THF</td>
<td>-55°C, 48hr</td>
<td>69&lt;sup&gt;b&lt;/sup&gt;</td>
<td>30:70</td>
</tr>
<tr>
<td>THF</td>
<td>-70°C, 5days</td>
<td>76&lt;sup&gt;b&lt;/sup&gt;</td>
<td>28:72</td>
</tr>
<tr>
<td>THF/CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-20°C, 48hr</td>
<td>78</td>
<td>32:68</td>
</tr>
</tbody>
</table>

<sup>a</sup>: Calculated using a CHIRACELL-OD-H chiral HPLC column and 2% EtOH/Heptane as mobile phase. <sup>b</sup>: yield based on recovered starting material.

1.1.5.14 Chiral Pool Techniques.

A large number of groups have exploited the stereoselective nature of the Pauson-Khand reaction to transfer chirality originating in component substrates to the final cyclised product. For example, Hoveyda has combined the stereoselective heteroatom assisted allylic alkylation of cyclic ethers with Grignard reagents and a Pauson-Khand reaction. The stereoselective alkylation of the cyclic ether was found to proceed in high yield and selectively to generate the enyne which when
complexed with dicobaltoctacarbonyl and in the presence of NMO underwent the desired intramolecular cycloaddition in good yield with complete diastereoselectivity. Scheme(49).

Hanaoka has also described a highly diastereoselective construction of optically active bicyclo[3.3.0]octenone derivatives via an intramolecular Pauson-Khand reaction. The requisite chiral enynes were derived with a variety of substituents from diethyl L-tartrate and L-Ascorbic acid. Scheme(50).
The nature of the R Groups and the reaction conditions were found to affect the yield and the stereoselectivity of the intramolecular Pauson-Khand reaction. From the experimental results, several trends become apparent. Under thermal cyclisation conditions groups at the terminus of the alkyne other than hydrogen yielded the desired bicyclo[3.3.0]octenone stereoselectively. When the reaction was promoted by chemical means (TMNO), cyclisation was inhibited when the substituent at the terminus of the alkyne was TMS substituted. The nature of the ether groups was also found to affect the stereoselectivity of the cycloaddition. Notably the presence of tert-butyldimethylsilyl moieties proved universally to give high selectivity.

Maro-Contelles demonstrated that the Pauson-Khand reaction of functionalised 1,6-enyne in carbohydrate templated was an efficient method for the rapid and highly stereo selective synthesis of annulated sugars. 3,4-di-O-Acetyl-L-arabinol was treated with propargyl alcohol under Ferrier conditions to yield a mixture of $\alpha$ and $\beta$ anomers which could be separated by chromatography. Complexation with dicobaltoctacarbonyl yielded the enantiomerically pure highly oxygenated tricycle. This tricycle possessed the stereochemistry suitable for conversion to the natural iridoid aglycones. Scheme(51).

\[
\begin{align*}
\text{OAc} & \quad \text{1.} \text{Co}_{2}(\text{CO})_{8} \\
\text{H} & \quad \text{2.} \text{NMO}
\end{align*}
\]

\begin{equation}
\text{CH}_2\text{Cl}_2 \\
40\%
\end{equation}

\textbf{Scheme}(51)

Schreiber has published the cobalt mediated total synthesis of (+)-epoxydictymene. Key steps in the total synthesis were cobalt mediated, the complexed core of a bound alkyne was used in two successive reactions, maximising metal economy. The initial cobalt mediated reaction involved a Lewis acid catalysed Nicholas cyclisation enabling the construction of a key cyclic intermediate. This intermediate was suitably functionalised for an intra-molecular Pauson-Khand reaction. The intact cobalt core successfully underwent cyclisation in good yield. \textbf{Scheme}(52).
1.1.6 Alternative metals effecting a Pauson-Khand type cycloaddition.

Although the Pauson-Khand cycloaddition is traditionally associated with cobalt carbonyl complexes a number of other carbonyl complexes are known to facilitate Pauson-Khand type cycloadditions. Iron\(^\text{50}\), nickel\(^\text{51}\), tungsten\(^\text{52}\), ruthenium\(^\text{53}\) and rhodium\(^\text{54}\) carbonyl complexes under appropriate conditions promote the desired cycloaddition generating cyclopentenoid products.

Of all the metal carbonyl systems known to promote Pauson-Khand type reactions perhaps the of bis(cyclopentadienyl)tetracarbonyldimolybdenum alkyne complex system is the most closely related to the original cobalt system. The molybdenum complex is isoelectronic with the bis-cobalt system and has a very similar geometry. Hanaoka\(^\text{55}\) reported that bis(cyclopentadienyl)tetracarbonyldimolybdenum alkyne complexes mediated the Pauson-Khand cycloaddition. Hanaoka noted that in contrast to the dicobalt system the cycloaddition in the molybdenum variant proceeded with some loss in regioselectivity, with both the 2-substituted and the 3-substituted cycloadducts being isolated. Scheme(53).
Jeong has demonstrated that a Pauson-Khand cycloaddition of alkynes, alkenes and carbon monoxide occurs in the presence of a stoichiometric amount of molybdenum hexacarbonyl utilising dimethylsulfoxide as a promoter.\textsuperscript{56} Scheme(54).

Metal complexes affecting the Pauson-Khand cycloaddition are not limited to metal carbynyls. [Ni(COD)\textsubscript{2}] has been found to promote cyclisation of enynes to iminocyclopentenes in the presence of isocyanides.\textsuperscript{57}

The closely related titanocene\textsuperscript{58} and zirconocene\textsuperscript{59} systems also provide effective routes to cyclopentenoid products. For both systems the active catalyst in the presence of a suitable enyne provides a template for reductive cyclisation to generate a metalocycle. In the titanocene system isocyanide incorporation into the metalocycle prior to reductive elimination of the metallic residue enables iminocyclopentenes to be isolated. Facile hydrolysis furnishes the cyclopentene in high yield. In the case of the zirconocene carbon monoxide can be incorporated into the metalocycle generating the cyclopentene directly. Developments in titanocene methodology have resulted in the development of an enantioselective catalytic Pauson-Khand type formation of bicyclic cyclopentenones from a variety of enyne substrates.\textsuperscript{60} Scheme(56).
1.1.7 New Substrates in the Pauson-Khand Reaction.

Early reports of Pauson-Khand cyclisations were limited with respect to substrate choice, and as such reduced the Pauson-Khand reactions synthetic potential. In an attempt to address the apparent lack of substrate variability attention has been focused on identifying substrates which under appropriate conditions would cyclise efficiently.

1.1.7.1 Electron deficient internal alkynes.

The inability to utilise substrates containing electron withdrawing substituents has limited the application of the Pauson-Khand reaction and as such has been an active area of research. Krafft determined that the cobalt carbonyl complexes of electron deficient internal alkynes undergo Pauson-Khand cycloaddition efficiently and regioselectively under classical thermal conditions and N-Oxide promoted reaction conditions at ambient temperatures.\(^6\) Scheme(57).

Interestingly, in the intermolecular Pauson-Khand reaction with electron deficient alkynes, a reversal in regioselectivity with respect to the alkyne was noted, the sterically demanding electron withdrawing group being found \(\beta\) to the newly formed carbonyl in the isolated cyclopentenone. Scheme(58).
Krafft suggested that this reversal in regioselectivity arose due to the polarisation of the alkyne, increasing the rate at which the carbon-carbon bond formation occurs at the electropositive alkynyl carbon \( \alpha \) to the electron withdrawing group. Such carbon-carbon bond formation at the \( \alpha \) carbon would be expected to decrease the electropositive character of the \( \alpha \) carbon whereas insertion and formation of the carbon-carbon at the \( \beta \) carbon should lead to an increase in the electropositive nature of the \( \alpha \) carbon. **Scheme(59).**

**Scheme(59)**

**1.1.7.2 Electron Deficient alkenes.**

The Pauson-Khand reaction with electron deficient alkenes has been realised by Cases.\(^2\) Cases has reported that the Pauson-Khand reaction of alkynes and electron deficient alkenes is promoted by 2-methylmorpholine oxide at 0-20°C and generated 5-functionalised cyclopent-2-enones in moderate to fair yield with high regioselectivity. **Scheme(60).**
The undesired Michael addition was minimised by reducing the amount of the acrylate, reaction with only two equivalents of the acrylate furnished the desired cyclopentenone in moderate yield. Scheme(61).

1.1.7.3 Vinyl esters as ethylene equivalents in the Pauson-Khand annulation reaction.

Kerr has extended the substrate scope of the Pauson-Khand reaction to include vinyl esters as ethylene equivalents in the Pauson-Khand annulation. Kerr suggested that the isolated cyclopentenones lacking the expected ester functionality were generated on reduction of the ester linkage after cycloaddition by a low oxidation state cobalt species, the hydrogen atom required to complete the reduction was suggested to originate from water present in the hydrated N-Oxide.
1.1.7.4 Aromatic Enynes.

The use of hept-1-en-6-yne, propargyl allyl ethers or amines in the intra-molecular Pauson-Khand reaction has become routinely accepted. Peréz-Castells has shown that substituted aromatic enynes are efficient substrates for an intramolecular Pauson-Khand reaction. The reaction was found to proceed in moderate to good yield for a range of substrates by slow addition of a solution of NMO. Interestingly, isomerisation of the double bond in the tricyclic cyclopentenone product was observed. Scheme(63).

Scheme(63).

1.1.7.5 Pauson-Khand reaction with allenic Compounds.

Cazès has demonstrated that the intramolecular cobalt mediated cycloaddition of alkynes and allenes is efficiently promoted by NMO at room temperature and leads to 4-acetylidenec-2-cyclopentenones. Cazes subsequently extended this methodology to include functionalised allenes to yield 4- and 5-alkylidenecyclopent-2-enones. Cazès found that for allenes bearing an electron donating substituent typically the 4-alkylidenecyclopent-2-enone is the predominant product. In order to account for the observed regioselectivity Cazès proposed that cycloaddition occurs via insertion of the central carbon atom of the allene into a cobalt centre generating a common \( \text{allyl} \) intermediate. Carbon monoxide insertion then takes place favouring insertion into the \( \pi \) bond of the allene that is least sterically hindered. Scheme(64).
CO insertion into less hindered allyl system.

\[
\text{Co(CO)\textsubscript{3} \rightarrow \text{Co(CO)}_{2}}
\]

CO insertion into more hindered allyl system.

\[
\text{Co(CO)\textsubscript{3} \rightarrow \text{Co(CO)}_{2}}
\]

Scheme(64)

However, if an electron withdrawing group such as an ester is present in the allene, then mixtures of 5-alkylidene cyclopent-2-enone and 4-alkylidene cyclopentenones are obtained. Scheme(65)

Cazes suggested that the 5-alkylidene cyclopent-2-enone was formed due to an increased tendency for the insertion of the more electron rich double bond of the allene into a cobalt centre generating the \(\alpha\) vinyl organocobalt intermediate rather than a \(\pi\) allyl intermediate.

1.1.7.6 Exocyclic Alkenes. The ability of exocyclic alkenes to participate in an intramolecular Pauson-Khand reaction was highlighted by Hoshino.\(^7\) Hoshino found that the intramolecular Pauson-Khand reaction of the various vinyl \(\text{exo}\) alkylidene-cyclohexanes and pentane yielded
angular tricyclic compounds bearing two continuous quaternary centres in moderate to high yield. Scheme(66).

\[
\text{Scheme(66)}
\]

Borodkin has demonstrated that exocyclic olefins may be employed in the Pauson Khand reaction. Cyclisation of the carbohydrate derived enyinic substrates with the double bond being an exo substituent of the sugar ring was found to proceed in moderate yield under thermal reaction conditions and as such enables access to densely functionalised [3.3.0]bicyclooctenone derivatives. \(^6\) Scheme(67)

\[
\text{Scheme(67)}
\]

Introduction Summary.

The Pauson-Khand reaction has seen increased use in the last thirty years since its discovery. The developments in methodology now allow all types of alkynes and alkenes to be employed. Significant steps have also been taken to make the reaction catalytic in metal and stereoselective in nature.

However despite these developments much work is still being done to further enhance the reaction. The remainder of this thesis outlines our work in the utilisation of heterobimetallic alkyne complexes as chiral control agents in the Pauson-Khand reaction and other stereoselective reactions.
2. Results and discussion.

2.0.1 Evaluation of current stereoselective methodology.

The development of stereoselective variants of the Pauson-Khand reaction has greatly increased the synthetic scope of the reaction allowing access to optically enriched cyclopentenones. A number of groups have developed complementary methodology which facilitates an asymmetric variant of the Pauson-Khand reaction by desymmetrisation of the prochiral core of the parent dicobaltacetylene hexacarbonyl complex. These methods of desymmetrisation in effect generate a complex in which the two metal centres of the complex are inequivalent. To date efforts towards desymmetrisation have been focused on utilising chiral auxiliaries or chiral promoters in order to differentiate the cobalt centres. Scheme(68).

\[
R_1 \neq R_2
\]

Scheme(68)

Perhaps the most elegant approach to an asymmetric Pauson-Khand reaction was adopted by Kerr with the application of a chiral promoter in the form of brucine N-Oxide. The mode of action of the brucine N-Oxide was initially believed to arise due to the ability of the chiral promoter to discriminate between two enantiotopic cobalt centres of a parent complex resulting in a selective decarbonylation.\(^{45}\) In a subsequent publication Kerr however illustrated that only substituted propargyl alcohol complexes with a specific substitution pattern at the propargylic position act as suitable substrates\(^{69}\) Scheme(69). Table(10).
Brucine N-Oxide mediated asymmetric Pauson-Khand reaction.

Table (10).

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Temp. (°C)</th>
<th>Reaction Time (h)</th>
<th>Yield (%)</th>
<th>Enantiomeric Ratio&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R&lt;sub&gt;OH&lt;/sub&gt;</td>
<td>-67</td>
<td>120</td>
<td>75</td>
<td>22:78</td>
</tr>
<tr>
<td>2</td>
<td>R&lt;sub&gt;OSiMe&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt;</td>
<td>-49</td>
<td>120</td>
<td>61</td>
<td>49:51</td>
</tr>
<tr>
<td>3</td>
<td>R&lt;sub&gt;OH&lt;/sub&gt;</td>
<td>-49</td>
<td>168</td>
<td>49</td>
<td>58:52</td>
</tr>
</tbody>
</table>

<sup>a</sup>Enantiomeric ratios were determined by chiral HPLC analysis and are presented as the 1<sup>st</sup> 2<sup>nd</sup> eluting enantiomers

The requisite for a substituted propargylic complex has cast doubt over the ability of the brucine N-Oxide to carry out a selective decarbonylation without interaction with the propargylic centre. Such interaction between the hydroxyl functionality and the brucine presumably in the form of hydrogen bonding may effectively align the N-Oxide in such an orientation that discrimination occurs between the two enantiotopic cobalt centres. The substitution at the propargylic centre may enforce asymmetric interactions of the N-Oxide by restricting conformational freedom of the ‘tethered’ oxidant or simply discriminate between the enantiotopic faces of the complex on steric grounds. Other groups have investigated the application of other chiral N-Oxides such as indolinino[3,4-b]quinoline N-Oxide and sparteine N-Oxide but they have proved ineffective. Such restrictions severely limit the synthetic application of Kerr's chiral promoter methodology in its current form.

An alternative approach adopted by a number of groups has been to desymmetrise the complex employing chiral auxiliaries. Complex desymmetrisation has been achieved by substitution of a carbon monoxide ligand present in the parent complex with a chiral ligand. Such an approach has been adopted by Kerr. Kerr replaced a carbon monoxide ligand with (R)-(+)-Glyphos, a chiral phosphine ligand in order to generate diastereomeric complexes. These diastereomERICally pure complexes under thermal Pauson-Khand conditions were found to racemise and therefore underwent the Pauson-Khand reaction with no stereoinduction. Under milder conditions promoted by N-Oxides high levels of stereoinduction were obtained. Although
this methodology appears not to be substrate specific, its practical application is somewhat limited as separation of the optically pure (R)-(+)Glyphos containing complexes could be achieved only by preparative HPLC. Scheme(70).

\[ \text{Ph..H} \quad \text{OC} \quad \text{r~po} \quad \text{10'-C} \quad \text{OC} \quad \text{I I CO} \quad \text{CO} \quad \text{TMANO. 2H2O, r.t.,} \quad \text{CH2Cl2, 30-60min.} \]

Scheme(70)

60:40

Separable by chiral HPLC only.

Chung, in a similar fashion to Kerr, has used a number of phosphorus ligands to desymmetrise a parent complex core.\(^6\) Chung’s approach differs from Kerr in that achiral phosphorus ligands were utilised substituting a carbon monoxide ligand in a parent prochiral dicobaltacyclopenyne hexacarbonyl complex bearing a menthol chiral auxiliary bound to the alkynyl fragment of the dicobalt complex. Chung reported, in contrast to Kerr, that the diastereomerically pure complexes were routinely available by flash chromatography. Chung’s methodology gave rise to excellent levels of stereoinduction. However, this variation suffers in that the chiral auxiliary is redundant after complex separation but is carried throughout the cycloaddition and is therefore found in the cyclopentenone product. Scheme(71).
Pericàs has also employed chiral auxiliaries bound to the alkynyl fragment in order to effect an asymmetric Pauson-Khand cycloaddition. Of particular note is the development of auxiliaries bearing a pendant functional group capable of co-ordinating to a cobalt centre during the reaction pathway.\textsuperscript{39,40} Under optimised conditions the pendant functionality effectively transfers chirality during the annulation. Pericàs’s variant suffers in a similar fashion to Chung’s in that the auxiliary which plays an active role throughout the cycloaddition is transferred to the cyclopentenone product. Pericàs’s chelation methodology suffers to a greater extent than Chung’s in that the auxiliary is not commercially available and must be synthesised and then complexed in order to form the required complex in a multistep sequence. Scheme(72).
2.1 The chiral nature of hybrid complexes.

To date, asymmetric Pauson-Khand cycloadditions have been realised by successful desymmetrisation of the core of a parent dicobalt complex. This principle of desymmetrisation could be extended to hybrid complexes containing two different metals instead of modification of a prochiral dicobalt core with an external source of chirality. The core of such a hybrid, in contrast to the prochiral core of a dicobaltacetylene complex, when bound to an unsymmetrically substituted alkynyl fragment would be chiral, the four corners of the metal alkyne core being differentiated. Scheme (73).

In view of the range of metal alkyne complexes which under appropriate conditions have been found to participate in the Pauson-Khand reaction\textsuperscript{50, 51, 52, 53, 54} it would seem surprising that to date research into the potential of mixed metal alkyne complexes as substrates in the Pauson-Khand
reaction has been overlooked. Although novel in application, the true potential of the mixed metal alkyne complexes in the Pauson-Khand reaction lies in the exploitation of the inherent chirality of the complexes themselves. Development of hybrid, inherently chiral mixed metal systems would therefore be an attractive and potentially powerful approach toward an asymmetric variant of the Pauson-Khand reaction relying on the inherent chirality of the complex core rather than chiral pool materials, chiral promoters or auxiliaries. By incorporating the chirality directly into the core of a hybrid complex the negative aspects of auxiliary based methodology experienced by Kerr, Chung and Pericas could be circumvented.

2.1.1. Development of cobalt molybdenum hybrid systems.

The preparation of hybrid cobalt molybdenum complexes is documented in inorganic literature. These hybrid complexes are prepared by displacement of a Co(CO)$_3$ fragment from the parent dicobaltalkynylhexacarbonyl complex by an isolobal [Mo(CO)$_3$Cp]$^-$ moiety.

Although there appeared to be no uniform approach in generating these hybrid cobalt molybdenum complexes, each group optimising their own conditions, the isolobal displacements may be loosely categorised according to the manner in which the [Mo(CO)$_3$Cp]$^-$ Na$^+$ moiety was generated. It became apparent that the main synthetic routes adopted for generating the [Mo(CO)$_3$Cp]$^-$ Na$^+$ moiety were treatment of molybdenumcyclopentadienyltricarbonyl dimer with a sodium mercury amalgam,$^{71}$ or alternatively by treatment of molybdenum hexacarbonyl with cyclopentadienyl anion.$^{72}$ Scheme (74).

![Scheme (74)](image_url)
2.1.2 Cyclopentadiene route.

In accordance with literature precedent the molybdenumcyclopentadienyltricarbonyl anion was generated by treatment of freshly cracked cyclopentadiene with sodium under an atmosphere of nitrogen in diglyme. To the resultant pink solution was added molybdenum hexacarbonyl as a solid and the reaction mixture refluxed for one hour. After one hour, the colour of the reaction mixture had changed from the characteristic pink colour of the cyclopentadienyl anion to orange corresponding to the formation of the molybdenumcyclopentadienyltricarbonyl anion. The reaction was cooled to room temperature prior to the addition of dicobaltphenylacetylenehexacarbonyl complex. Formation of the mixed metal complex did not occur. Scheme(75).

2.1.3 Dimerisation.

In order to determine whether the molybdenumcyclopentadienyltricarbonyl anion was being generated efficiently it was decided to dimerise the molybdenumcyclopentadienyltricarbonyl anion according to literature precedent instead of adding dicobaltphenylacetylenehexacarbonyl complex. Dimerisation was achieved on treatment of a reaction mixture containing the molybdenumcyclopentadienyltricarbonyl anion with a filtered solution of glacial acetic acid water and hydrated iron(II) sulfate. Addition of the filtered solution to the orange reaction mixture immediately resulted in a colour change to purple indicating the formation of molybdenumcyclopentadienyltricarbonyl dimer which was isolated in a moderate yield of 70% after filtration and extensive washing. (Method A). Scheme(76).
The moderate yield of molybdenumcyclopentadienyltricarbonyl dimer obtained suggested that at room temperature the desired isolobal displacement was not taking place.

2.1.4. Optimisation of displacement conditions.
In addition to the failure of molybdenumcyclopentadienyltricarbonyl anion to participate in an isolobal displacement of the cobalttricarbonyl fragment from the parent core experimental difficulties were experienced due to the diglyme solvent. Recovery of the thermally sensitive dicobalt alkyne complex starting material from the reaction mixture proved difficult due to the high boiling point of the solvent. In view of this it was envisioned that similar problems would be encountered on trying to isolate any hybrid complexes once formed. In light of these difficulties it was decided to change the reaction solvent from diglyme to tetrahydrofuran.

In order to assess the experimental consequences on changing the solvent from diglyme to tetrahydrofuran dimerisation of the molybdenumcyclopentadienyltricarbonyl anion was undertaken to gauge the effect on anion formation. Under identical conditions the yield of the molybdenumcyclopentadienyltricarbonyl dimer was found to be substantially lower than that obtained in diglyme. This reduction in yield may have arisen due to increased stabilisation of the molybdenumhexacarbonyl by the greater co-ordinating ability of tetrahydrofuran or alternatively anion formation was more favoured at the higher temperatures achieved in diglyme compared to those achieved in tetrahydrofuran.

In an attempt to increase the formation of molybdenumcyclopentadienyltricarbonyl anion, the reaction mixture containing molybdenumhexacarbonyl and the cyclopentadienyl anion was refluxed for an extended period. After being refluxed for 12 hours, on dimerisation of the reaction mixture the yield of molybdenumcyclopentadienyltricarbonyl dimer was typically in the region...
of 60%. Refluxing the reaction mixture for periods longer than 12 hours did not appear to have any substantial beneficial effect on dimer yield. (Method B). Scheme(77).

2.1.5 Isolobal displacements in tetrahydrofuran.
Modification of the isolobal displacement reaction conditions incorporating 12 hours of reflux in order to maximise the formation of molybdenumcyclopentadienyltricarbonyl anion proved initially disappointing. Addition of dicobalt(diphenylacetylenehexacarbonyl to the molybdenumcyclopentadienyltricarbonyl anion did not facilitate an isolobal displacement at room temperature. Scheme(78).

In order to facilitate the desired isolobal displacement the reaction mixture containing molybdenum cyclopentadienyltricarbonyldimer and the dicobaltdiphenylacetylenehexacarbonyl had to be refluxed. The reaction was followed by thin layer chromatography which indicated the consumption of the dicobaltdiphenylacetylenehexacarbonyl and the formation of a new more polar red complex as well as a variety of other coloured by-products. On reaction completion the tetrahydrofuran was removed under reduced pressure and the residue subjected to an aqueous workup. The new complex was then isolated by flash chromatography and characterised as the hybrid cobaltmolybdenumcyclopentadienyl(diphenylacetylenepentacarbonyl complex. Scheme(79).
The other highly coloured compounds, which we believed to be inorganic, either decomposed during the aqueous work up, or on chromatographic separation. Those by products that were isolated were paramagnetic in nature making spectroscopic analysis difficult.

2.1.6 Optimised Isolobal displacements in tetrahydrofuran.
Under the optimised conditions dicobalt(diphenyl, phenyl, butyl and dimethylacetylenehexacarbonyl were subjected to an isolobal displacement generating the hybrid mixed metal complexes in moderate yield ranging from 58-61%. (Method A).
Formation of hybrid cobaltmolybdenum cyclopentadienylalkynylpentacarbonyl complexes.

Table (11).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Complex 16" /></td>
<td>16</td>
</tr>
<tr>
<td><img src="image2" alt="Complex 17" /></td>
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<tr>
<td><img src="image3" alt="Complex 18" /></td>
<td>18</td>
</tr>
<tr>
<td><img src="image4" alt="Complex 19" /></td>
<td>19</td>
</tr>
</tbody>
</table>

To a solution of freshly prepared cyclopentadiene anion in tetrahydrofuran was added molybdenum hexacarbonyl. The reaction mixture was refluxed for 12 hrs and then subsequently allowed to cool to room temperature prior to the addition of the dicobaltacetylenehexacarbonyl complex. The reaction mixture was refluxed and monitored for the disappearance of the dicobaltacetylenehexacarbonyl complex. Upon disappearance of the dicobaltacetylenehexacarbonyl complex the reaction mixture was allowed to cool to room temperature and the tetrahydrofuran removed under reduced pressure. The residue was subjected to an aqueous workup and purified by column chromatography.

2.2 Reaction of the hybrid system with strained and unstrained alkenes under thermal Pauson-Khand conditions.

Upon isolation of the hybrid mixed metal complexes we were eager to investigate their suitability as substrates for the Pauson-Khand reaction. Cobaltmolybdenum cyclopentadienyl diphenylacetylenepentacarbonyl was subjected to classical thermal Pauson-Khand reaction conditions first reported by Pauson and Khand in 1973.1

The formal [2+2+1] cycloaddition occurred rapidly between the hybrid complex and norbornadiene or norbornene when refluxed in toluene generating the corresponding cyclopentenones with yields of 38 and 29% respectively. (Method A). Scheme (81).
Preliminary attempts to isolate the desired cyclopentenone with the mixed metal alkyne complex with less reactive alkenes proved unsuccessful. Under traditional Pauson-Khand thermal reaction conditions cycloaddition between cobaltmolybdenumcyclopentadienyldiphenylacetylene pentacarbonyl and camphene or 1-octene proved not to yield the desired cyclopentenone product. Scheme(82).

2.2.1 Initial comparisons of the *bis homo* cobalt and *bis homo* molybdenum systems with the hybrid *bis hetero* cobalt molybdenum system.

Preliminary results indicated as hoped that the hybrid alkyne complexes would act as substrates in a Pauson-Khand cycloaddition. The yields obtained with the hybrid system were similar to those obtained by other groups with the *bis homo* metallic cobalt system. They were however substantially lower than those reported by Hanaoka with the *bis homo* metallic molybdenum system.55
2.2.2 Optimisation of reaction conditions and determination of regioselectivity.

From literature precedent\textsuperscript{24} it was noted that in certain cases the reaction of the \textit{bis homo} metallic cobalt system at lower temperatures resulted in the formation of cyclopentenones with greater yield. In a similar fashion it was found that reaction of the hybrid \textit{bis hetero} metallic system with both norbornadiene and norbornene at a lower temperature of 60-75°C albeit over longer reaction period generated the desired cyclopentenone with increased yield. (Method B.) \textbf{Scheme(83)}.

\begin{align*}
16-19 & \\
\text{OC} & \text{M} & \text{CO} \\
\text{CO} & \text{C} & \text{CO} \\
\text{R}_1 & \text{R}_2 & \text{R}_1 \\
\text{R}_2 & \text{R}_2 \text{toluene reflux.} & \text{60-75°C} \\
\text{20-27} & \\
\text{R}_1 & \text{R}_1 = \text{Ph}, \text{R}_2 = \text{Ph} \\
\text{22, 23.} & \text{R}_1 = \text{Ph}, \text{R}_2 = \text{H} \\
\text{24, 25.} & \text{R}_1 = \text{Bu}, \text{R}_2 = \text{H} \\
\text{26, 27.} & \text{R}_1 = \text{Me}, \text{R}_2 = \text{Me}
\end{align*}
Cyclopentenone formation from hybrid cobaltmolybdenum complexes. Table (12).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Alkene</th>
<th>Cyclopentenone</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Complex 16" /></td>
<td><img src="image2" alt="Alkene 16" /></td>
<td><img src="image3" alt="Cyclopentenone 16" /></td>
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<td>26</td>
</tr>
<tr>
<td><img src="image22" alt="Complex 23" /></td>
<td><img src="image23" alt="Alkene 23" /></td>
<td><img src="image24" alt="Cyclopentenone 23" /></td>
<td>27</td>
</tr>
</tbody>
</table>

To a solution of the cobaltmolybdenumcyclopentadienylacetylenepentacarbonyl complex in toluene was added the alkene. The reaction mixture was heated at 60-75°C and monitored for the disappearance of the complex. Upon reaction completion the reaction was allowed to cool to room temperature and then subjected to an aqueous work up. The crude residue was purified employing column chromatography.
2.2.3 Regioselectivity of the hybrid cobalt molybdenum system.

Under these optimised conditions reaction of cobaltmolybdenumcyklopentadienylphenyl acetylene demonstrated that the regioselectivity of the reaction was the same as that observed in the \textit{bis homo} metallic cobalt system. Cyclopentenones were generated with the larger substituent being found exclusively on the newly formed carbonyl functionality. This exclusive regioselectivity was in contrast to the reduction in regioselectivity noted by Hanaoka with the \textit{bis homo} metallic molybdenum system in which the 4- and 5-substituted cyclopentenones were isolated.\textsuperscript{55}

2.3 Investigation of the inherent chirality of the hybrid core.

In order to investigate whether the inherent chirality of the hybrid metal alkynyl core would facilitate a stereoselective Pauson-Khand cycloaddition a means of generating optically pure hybrid complex material had to be developed. This was approached in a number of ways.

2.3.1 Chiral auxiliary approach.

An approach to obtaining optically pure hybrid complex material was to utilise a chiral auxiliary. The presence of a suitable chiral auxiliary incorporated into the hybrid system either bound to the alkynyl component or directly to the hybrid metal core it was hoped would allow separation of optical pure hybrid complex material prior to cycloaddition. \textit{Scheme(84)}.

\begin{equation*}
\text{chiral auxiliary bound to Alkynyl moiety} \quad \text{diastereomeric complexes} \quad \text{chromatographic separation} \quad \text{Scheme(84)}
\end{equation*}
2.3.2 Chiral Cyclopentadienyl auxiliary.
The utilisation of a chiral auxiliary bound to the hybrid core in a similar fashion to that of Kerr\textsuperscript{35} appeared attractive primarily for two reasons. The close proximity of the chiral auxiliary to the chiral core it was hoped would maximise chiral interactions increasing the possibility of achieving a chromatographic separation. The second predicted advantage was that if the auxiliary was incorporated in the metal core then during the subsequent cycloaddition the auxiliary would remain in the metallic residues and not be transferred to the organic cyclopentenone generated. In contrast to Kerr methodology in which the auxiliary replaced a carbon monoxide it was decided to utilise the cyclopentadiene which is bound to the molybdenum and as such is a characteristic of the hybrid system. Attention was directed towards generating a hybrid system containing a chiral cyclopentadiene.

2.3.3 Generation of menthylcyclopentadienyl auxiliary.
The chiral menthyl cyclopentadiene(28) was prepared in low yield (11\%) by treating menthol tosylate with cyclopentadienyl anion generated by treatment of freshly cracked cyclopentadiene with sodium hydride. Scheme(85).

![Scheme(85)](image)

2.3.4 Incorporation of chiral menthylcyclopentadienyl auxiliary into the hybrid core.
The menthyl cyclopentadiene was incorporated into the hybrid system using the previously optimised conditions. The menthyl cyclopentadienyl anion was generated in tetrahydrofuran on addition of sodium hydride. To the pink reaction mixture was added molybdenumhexacarbonyl and the reaction mixture refluxed for 12 hours. The reaction mixture was cooled to room temperature and dicobaltphenylacetylenehexacarbonyl was added as a solution in a minimal volume of tetrahydrofuran. The reaction was monitored for the consumption of the dicobalt phenylacetylenehexacarbonyl. Thin layer chromatography of the reaction mixture indicated that
consumption of the phenylacetylenehexacarbonyl occurred and the presence of a new complex. Attempts to isolate this complex however proved unsuccessful. Scheme(86).

Scheme(86)

2.3.5 Utilisation of chiral auxiliaries bound to the alkyne.
In light of the experienced difficulties employing a chiral cyclopentadienyl based auxiliary it was decided to pursue an auxiliary bound to the alkynyl fragment. Application of such an auxiliary although perhaps not as elegant as cyclopentadienyl methodology would be less restrictive as synthesis of cyclopentadienyl chiral auxiliaries and incorporation into the hybrid core could prove to be a lengthy exercise in comparison to the rapid incorporation of a variety of commercially available auxiliaries which could be incorporated into the hybrid employing Nicholas methodology. Application of Nicholas methodology would enable a library of bis homo metallic cobaltpropargylacetylene complexes bearing commercially available nitrogen, sulfur or oxygen based auxiliaries to be generated. These complexes could then be subjected to isolobal displacements in order to generate a library of hybrid complexes bearing a variety of auxiliaries. Scheme(87).

Scheme(87)
2.3.6 Utilisation of menthol as the chiral auxiliary.

Initial efforts were directed towards generating the hybrid dicobaltpropargylmenthyletherhexacarbonyl. Complexation of propargyl alcohol to dicobaltoctacarbonyl was achieved as expected in good yield (97%). Scheme(88).

The dicobaltpropargylmenthyletherhexacarbonyl complex was synthesised utilising Nicholas methodology. Treatment of a solution of dicobaltpropargylalcoholoctacarbonyl and menthol in dichloromethane with a catalytic quantity of hydrofluoroboric acid etherate in the presence of molecular sieves was found to effectively generate the desired complex. The dicobaltpropargyl menthyletherhexacarbonyl complex was isolated by quenching the reaction mixture with sodium hydrogen carbonate prior to filtration and removal of the solvent under reduced pressure. The crude residue was purified by flash chromatography to yield the desired complex (72%). Scheme(89).

With the dicobaltpargylmenthyletherhexacarbonyl complex in hand the complex was subjected to an isolobal displacement. Under the optimised conditions the hybrid cobaltmolybdenumcyclopentadienyl propargylmenthyletherpentacarbonyl complex was isolated in good yield (78%). (Method A). Scheme(90).
2.3.7 Incorporation of Auxiliaries into cobaltmolybdenum cyclopentadienylpropargyl alcoholhexacarbonyl complex.

Although generation of the dicobaltpropargylalcoholhexacarbonyl complex, incorporation of the auxiliary and subsequent isolobal displacement on the complex appeared a viable route to the hybrid complexes bearing propargylic auxiliaries, the approach was recognised as being time consuming primarily due to the 12hr reflux required to generate the molybdenumcyclopentadienyl anion during the isolobal displacement.

A faster approach would be to generate the hybrid propargyl complex and then employ Nicholas methodology to this substrate. Scheme(91).
The hybrid propargyl complex was prepared from the dicobaltpropargylalcoholacetlene hexacarbonyl utilising optimised isolobal displacement conditions to yield the desired complex after purification in moderate yield (67%). Scheme (92).

Incorporation of the menthol auxiliary into the complex was achieved in an analogous fashion to that of the dicobalt system, the desired complex after purification being isolated in good yield (78%). (Method B). Scheme (93).

2.4 Chromatographic separation of cobaltmolybdenumcyclopentadienylpropargylmenthyl etherpentacarbonyl complex.
With the hybrid cobaltmolybdenumcyclopentadienylpropargylmenthyletherpentacarbonyl complex, in hand effort was directed towards affecting a chromatographic separation of the diastereomeric complexes in order to obtain optically pure material. A variety of solvents was
employed with no success. After numerous combinations of solvents it was noted that a chromatographic separation occurred employing hexane:dichloromethane 5:1. Utilising the optimised solvent system, quantities of the first and second diastereoisomer were isolated. The stability of the second eluting diastereoisomer with respect to chromatography was lower than that of the first eluting diastereoisomer. The stability of the second diastereomer was found to be sensitive to the grade of silica employed in the separation. Merck kieselgel 60H proved to be the most effective stationary phase minimising the decomposition of the second eluting diastereomer.

2.5 Pauson-Khand reaction with optically pure hybrid complex material.
With the hybrid optically cobaltmolybdenumcyclopentadienylpropargylmenthyl etherpentacarbonyl complex in hand, we were in a position to evaluate the degree of stereoinduction that the chiral the core was able to exert during the Pauson-Khand annulation.

The optically pure complexes were subjected to the optimised Pauson-Khand reaction conditions in the presence of norbornadiene generating the desired cyclopentenones in moderate yield (61% and 67%). Spectroscopic analysis of the cyclopentenones showed that a single diastereomeric cyclopentenone was isolated from each cyclisation reaction. Thus each diastereomerically pure hybrid complex gave rise to distinct organic products with no sign of the other diastereomer in either case. Scheme(94).
2.5.1 Pauson-Khand reaction with dicobaltpropargylmenthyletherhexacarbonyl.

Although we believed that the observed stereoinduction observed in the cyclopentenone products originated from the core of the hybrid complex, the presence of the menthol chiral auxiliary utilised to separate the diastereomeric complexes could not be discounted. In order to eliminate this possibility, the control Pauson-Khand reaction with the dicobaltpropargylmenthyletherpenta carbonyl complex was undertaken. The expected cyclopentenone was isolated and spectroscopic analysis indicated that the menthol auxiliary had promoted negligible levels of stereoinduction. Scheme(95).
2.5.2 Explanation of stereoinduction.

The stereoinduction observed in the cyclopentenone products we believe to arise from the chiral nature of the hybrid core. In order to account for this stereocontrol we postulate that the cycloaddition was being templated around either the cobalt or molybdenum centre present in the hybrid complex, but not both. Such a template affect may arise due to electronic or steric differences between the two metal centres. In accordance with the postulated mechanism of the Pauson-Khand reaction, such preferential co-ordination of the alkene to either but not both centres followed by irreversible insertion into the metalocycle would fix the stereochemistry of the developing cyclopentenone skeleton. Subsequent carbon monoxide insertion and reductive elimination from the metallic residue would generate the experimentally obtained optically pure cyclopentenone product. Although these experimental results indicate that cycloaddition is templated around one of the two possible metal centres it is not possible to determine which metal the cyclisation is being templated on. The high levels of regiocontrol observed in the cyclopentenone product are characteristic of the dicobalt system and in contrast to the loss in regiocontrol noted by Hanaoka in the molybdenum system. Such observations may tentatively suggest that cycloaddition is being templated around the cobalt centre. Such an argument holds however if the metals react independently of each other and the hybrid nature of the core does not
alter the nature of the metal centres. **Scheme** (96).

![Scheme 96](image)

**2.5.3 Enantioselective Pauson-Khand reaction.** Although the ability of the hybrid core to induce a stereoselective Pauson-Khand reaction had been demonstrated, the menthol chiral auxiliary incorporated into the complex in order to enable separation of diastereomerically pure hybrid complex material was incorporated into the organic cyclopentenone and as such limited the applicability of the methodology.

To date, with the exception of Kerr’s chiral promotor methodology, which is severely limited with respect to the choice of substrate, all stereoselective Pauson-Khand reactions have employed a chiral auxiliary within the complexes.

In order to highlight the unique mode of stereoinduction achieved by the hybrid core, it was decided to remove the menthol auxiliary once its presence in the hybrid complex was no longer...
required, the auxiliary becomes redundant after chromatographic separation of the diastereomerically pure hybrid complexes and its removal was envisaged as being possible employing Nicholas methodology.

2.5.4 Generation of enantiomerically pure hybrid complexes.

In a similar fashion to their cobalt analogues the cobaltmolybdenum core of heterobimetallic alkyne complexes is capable of stabilising proparagylic cations. As such it was hoped that application of Nicholas methodology would enable the chiral auxiliary to be removed generating the enantiomerically pure salts. Although there was no literature precedent for employing Nicholas methodology to generate optically pure hetero bimetallic complexes we were confident that salt generation would not result in racemisation of the chiral core as the synthetic alteration being carried out was on a remote centre in the complex and not on the core. Complex racemisation could result only upon the alkynyl fragment of the complex decomplexing from the core and subsequently recomplexing in the opposite orientation.\textsuperscript{77} Scheme(97).

\begin{center}
\begin{tikzpicture}[scale=0.5]
  \node (a) at (0,0) {BF\textsubscript{4}^{-}};
  \node (b) at (2,0) {\begin{tikzpicture}[scale=0.5]
    \node (c) at (0,0) {Co};
    \node (d) at (1,0) {Co};
    \node (e) at (0.5,1) {Mo};
    \draw (c) -- (d);
    \draw (c) -- (e);
    \draw (d) -- (e);
    \node (f) at (0.5,1.5) {\text{OC}};
    \node (g) at (0.5,2.5) {\text{OC}};
    \node (h) at (1.5,1.5) {\text{OC}};
    \node (i) at (1.5,2.5) {\text{OC}};
    \node (j) at (2,1.5) {\text{CO}};
    \node (k) at (2,2.5) {\text{CO}};
  \end{tikzpicture}};
  \node (c) at (4,0) {\begin{tikzpicture}[scale=0.5]
    \node (l) at (0,0) {Co};
    \node (m) at (1,0) {Co};
    \node (n) at (0.5,1) {Mo};
    \draw (l) -- (m);
    \draw (l) -- (n);
    \draw (m) -- (n);
    \node (o) at (0.5,1.5) {\text{OC}};
    \node (p) at (0.5,2.5) {\text{OC}};
    \node (q) at (1.5,1.5) {\text{OC}};
    \node (r) at (1.5,2.5) {\text{OC}};
    \node (s) at (2,1.5) {\text{CO}};
    \node (t) at (2,2.5) {\text{CO}};
  \end{tikzpicture}};

  \draw [->] (b) -- (k);
  \draw [->] (k) -- (c);
  \node at (1,1) {\text{racemisation}};
  \node at (1,0.5) {\text{decomplexation}};
  \node at (1,0) {\text{recomplexation}};
  \node at (1,0) {\text{racemisation}};

  \draw [->] (j) -- (s);
  \draw [->] (s) -- (t);
  \node at (3,1) {\text{BF\textsubscript{4}^{-}}};
\end{tikzpicture}
\end{center}

Scheme(97)

Treatment of these enantiomerically pure salts with a range of achiral nucleophiles would result in the generation of a series of enantiomerically pure hybrid complexes. With these enantiomerically pure complexes in hand it was hoped that under Pauson-Khand reaction conditions the chiral core would enforce a stereoselective cycloaddition in the absence of an external source of chirality. Scheme(98).
2.5.5 Generation of enantiomerically pure hybrid tetrafluoroborate salts.

Treatment of either diastereomerically pure cobaltmolybdenumcyclopentadienylpropargyl menthyletherpentacarbonyl hybrid in ether with one equivalent of hydrofluoroboric acid resulted in the immediate precipitation of the tetrafluoroborate salt of the metal stabilised propargylic cation as an orange salt (64-78%). Scheme(99).
These enantiomerically pure salts were found to be bench stable and could be stored for extended periods without appreciable decomposition. The enantiomerically pure tetrafluoroborate salts were also found to be configurationally stable. Treatment of either enantiomerically pure tetrafluoroborate salt with menthol in the presence of sodium hydrogen carbonate yielded the original diastereomERICALLY pure cobaltmolybdenumcyclopentadienylpropargylmenthyl etherpentacarbonyl hybrid complex after purification in good yield (69%). (Method B). 

Scheme (100).
2.5.6 Generation of enantiomerically pure hybrid complexes.

With the enantiomerically pure and configurationally stable tetrafluoroborate salts in hand, a number of enantiomerically pure hybrid complexes were generated in good yield by reaction with oxygen, sulfur and nitrogen nucleophiles in acetone. Scheme(101).
Formation of enantiomerically pure hybrid complexes. Table(13)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Nucleophile</th>
<th>Complex</th>
<th>Yield%</th>
</tr>
</thead>
</table>
| \[
\left[ \text{BF}_4^+ \right]_{\text{cyclopentadienyl} \text{cobaltmolybdenumpropargylicpentacarbonyl tetrafluoro borate salt}}
\] | \[^1\text{PrOH}\] | ![Complex Diagram] | 74* |
| PhOH            | ![Complex Diagram] | 35a/b 60 |
| PrSH            | ![Complex Diagram] | 45* |
| benzatriazole   | ![Complex Diagram] | 71* |

To a solution of the cobaltmolybdenumcyclopentadienylpropargylicpentacarbonyl tetrafluoroborate salt in acetone in the presence of molecular sieves was added the nucleophile and N-Ethylidisopropylamine. The reaction mixture was stirred for approximately 30 minutes prior to the addition of excess sodium hydrogen carbonate and magnesium sulfate. The reaction mixture was filtered and the solvent removed under reduced pressure. The residue was purified employing column chromatography. *Carried out by A.J. Fletcher.

Effort was directed towards reducing the tetrafluoroborate salt in order to generate the methyl substituted complex. Initial efforts were focused on utilising sodium cyanoborohydride as a hydride source. Reaction of the racemic tetrafluoroborate salt with sodium cyanoborohydride resulted in decomposition of the salt under a variety of conditions with a mere trace of the desired methyl substituted complex being isolable. Attention was directed towards borane-methyl sulfide (BH₃SMe₂). It was hoped that the sulfur would co-ordinate to the tetrafluoroborate salt during the hydride transfer stabilising the complex and by doing so preventing complex decomposition. BH₃SMe₂ was found at reduced temperatures in dichloromethane to efficiently deliver a hydride to either enantiomerically pure tetrafluoroborate salt effectively generating the methyl substituted enantiomerically pure hybrid complex. **Scheme(102).**
2.5.7 Pauson-Khand cycloaddition with enantiomerically pure hybrid complexes.

These enantiomerically pure hybrid complexes were found to be effective substrates for the Pauson-Khand cycloaddition generating the desired cyclopentenones in moderate to good yield. Scheme (103).
Formation of cyclopentenones form enantiomerically pure hybrid. Table (13)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Alkene</th>
<th>Cyclopentenone</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Complex 1" /></td>
<td><img src="image2" alt="Alkene 1" /></td>
<td><img src="image3" alt="Cyclopentenone 1" /></td>
<td>75*</td>
</tr>
<tr>
<td><img src="image4" alt="Complex 2" /></td>
<td><img src="image5" alt="Alkene 2" /></td>
<td><img src="image6" alt="Cyclopentenone 2" /></td>
<td>45</td>
</tr>
<tr>
<td><img src="image7" alt="Complex 3" /></td>
<td><img src="image8" alt="Alkene 3" /></td>
<td><img src="image9" alt="Cyclopentenone 3" /></td>
<td>60*</td>
</tr>
<tr>
<td><img src="image10" alt="Complex 4" /></td>
<td><img src="image11" alt="Alkene 4" /></td>
<td><img src="image12" alt="Cyclopentenone 4" /></td>
<td>71*</td>
</tr>
<tr>
<td><img src="image13" alt="Complex 5" /></td>
<td><img src="image14" alt="Alkene 5" /></td>
<td><img src="image15" alt="Cyclopentenone 5" /></td>
<td>80</td>
</tr>
</tbody>
</table>

To a solution of the cobaltmolybdenumcyclopentadienylacetylenepentacarbonyl complex in toluene was added the norbornadiene. The reaction mixture was heated at 60-75°C and monitored for the disappearance of the complex. Upon reaction completion the reaction was allowed to cool to room temperature and then subjected to an aqueous work up. The crude residue was purified employing column chromatography. *Carried out by A.J. Fletcher.

2.5.8 Determination of the enantiomeric purity of the cyclopentenone products. Attempts to determine the enantiomeric purity of the cyclopentenones were directed, due to literature precedent, towards chiral HPLC. Unfortunately a suitable system to separate these particular substrates was not found. Similarly chiral shift reagents were found not to induce any shifts in the NMR spectrum of the cyclopentenones.
In order to determine the enantiomeric purity of the cyclopentenone products we were forced to consider derivatisation of the cyclopentenone. In accordance with literature precedent\textsuperscript{28} it was decided to generate the chiral ketals produced from reaction of the cyclopentenones with (+)-R,R-2,3-butanediol.

2.5.9 Derivatisation of the racemic cyclopentenone series.

In an effort to ascertain if the formation of the diastereomeric ketals would allow determination of the enantiomeric purity of the cyclopentenones, the racemic series was generated and derivatised with the chiral diol. \textit{Scheme}(104).

\[
\text{BF}_4^- \quad \text{and} \quad \text{BF}_4^+ \\
\text{Nucleophile} \quad \text{N-N-diisopropylamine} \\
\text{mol sieves} \quad \text{acetone} \\
\]

\[
35 \text{ Nuc} = \text{OAr 63\%} \\
36 \text{ Nuc} = \text{H 69\%} \\
37 \text{ Nuc} = \text{OAr 47\%} \\
38 \text{ Nuc} = \text{H 82\%} \\
39 \text{ Nuc} = \text{OAr 4\%} \\
40 \text{ Nuc} = \text{H 3\%} \\
\text{Scheme}(104)
Unexpectedly, the yield of the ketal was very low. We attribute this disappointing yield to unfavourable steric interactions between the bridgehead of the norbornadiene skeleton and the newly formed ketal. Scheme(105).

Scheme(105)

Despite the low isolated yield, spectroscopic analysis of each racemic ketal in the series illustrated different peaks for the diastereotopic methyl groups in addition to other peaks that could be identified in the racemic ketals.

2.6 Derivatisation of the chiral cyclopentenone series.

Protection of the enantiomerically pure cyclopentenones with (+)-R, R-2,3-butanediol generated as expected the diastereomeric ketals in poor yield. Spectroscopic analysis of the diastereotopic ketals generated from the enantiomerically pure hybrid complexes showed them to be diastereomerically pure with only one set of peaks being present in each case. Such diastereomeric purity could have arisen only from enantiomerically pure cyclopentenones. These spectroscopic data confirmed that the different enantiomers of the hybrid complexes produced under Pauson-Khand conditions enantiomers of the corresponding cyclopentenone regardless of the substituent attached to the propargylic centre in the hybrid complex. In addition, the cyclopentenones produced from the same enantiomerically pure tetrafluoroborate salt all had the same sign of optical rotation. The tetrafluoroborate salt of the less polar cobaltmolybdenumcyclopentadienylpropargylylmenthyletherpentacarbonyl complex gave rise to cyclopentenones with a positive optical rotation. The tetrafluoroborate salt of the more polar cobaltmolybdenumcyclopentadienylpropargylylmenthyletherpentacarbonyl complex gave rise to cyclopentenones with a negative optical rotation. Scheme(106).
2.6.1 Stereoselective Pauson-Khand reaction with alkene substrates with no facial restrictions.

The inherent chirality of the hybrid metal core has been shown to effectively enforce a stereospecific variant of the Pauson-Khand reaction. We have however in common with many other research groups active in this area employed an alkene which reacts preferentially on the exo face resulting in cis exo fused cyclopentenone products. By employing such an alkene we have effectively limited the number of conformations the alkene can adopt prior to co-ordination to a metallic centre and subsequent irreversible insertion into the metallacycle. Scheme(107).
To date only a single stereoselective variant of the Pauson-Khand reaction employing an alkene with no facial constraints and hence stereofacial bias has been reported. Pericas demonstrated that at reduced temperatures a dicobaltalkynyl complex bearing a chiral thioether promoted a stereoselective cyclisation on reaction with cyclopentene.\textsuperscript{41}

Scheme(108).

In light of the high levels of stereoinduction obtained with the hybrid complexes with norbornadiene it was decided to investigate the stereochemical nature of cycloaddition of the cobaltmolybdenumcyclopentadienylpropargylmenthyletherpentacarbonyl with an alkene which does not have facial constraints. In order to avoid the regiochemical issue that would arise if an unsymmetrical alkene was chosen as the test substrate the symmetrical cyclopentene was selected as a suitable alkene.

2.6.2 Pauson-Khand reaction of dicobaltpropargylmenthyletherhexacarbonyl with cyclopentene

Reaction of dicobaltpropargylmenthyletherhexacarbonyl with an excess of cyclopentene yielded the desired cyclopentenone once purified in modest yield (54%) under thermal Pauson-Khand conditions. Spectroscopic analysis of the resultant cyclopentenone as expected indicated that cycloaddition had occurred with only marginal facial preference resulting in an essentially racemic cyclopentenone product. Scheme(109).
In the case of the homometallic complex, the racemic mixture of the cyclopentenoid product may arise due to the initial co-ordination and subsequent insertion of the cyclopentene in a syn or anti manner with respect to the alkynyl fragment of the complex into the same metallic centre of the complex core. Alternatively insertion may occur in a syn or an anti conformation into the opposite metal centres present in the complex core. Scheme(110).

The generally accepted mechanism of the Pauson-Khand reaction is based on minimisation of steric interactions and as such it would be reasonable to suggest that insertion of the cyclopentene
into the metalocycle would be favoured in a *anti* fashion. The marginal selectivity observed in the cobalt system may be attributed to these subtle steric interactions. **Scheme(111).**

---

2.6.2 **Pauson-Khand reaction of diastereomerically pure cobaltmolybdenum cyclopentadienylpropargylmenthyletherpentacarbonyl hybrid complex with cyclopentene**

Cycloaddition of cyclopentene with the chiral cobalt-molybdenum hybrid system in contrast to the prochiral *bis* cobalt system generated optically enriched cyclopentenones. Reaction of diastereomerically pure cobaltmolybdenum cyclopentadienylpropargylmenthyletherpentacarbonyl hybrid complex under identical conditions employed in the *bis* cobalt cyclisation generated the cyclopentenone in low yield (27 and 29%). Spectroscopic analysis of the cyclopentenone product by proton NMR to determine the stereoinduction enforced by the chiral core was not possible with no clear signals evident in the spectrum. Examination of the carbon spectrum did however indicate that the cycloaddition had occurred with a degree of steroselectivity. The first and second eluting cobaltmolybdenum cyclopentadienylpropargylmenthylethers yielded the desired cyclopentenones with opposite diastereoselectivity with magnitudes of approximately 60%. Whilst the carbon NMR does not provide the diastereoselectivity without ambiguity it does suggest the chiral nature of the hybrid core is able to effect a stereoselective Pauson-Khand cycloaddition with alkene substrates without facial constraints. **Scheme(112).**
From our previous results with the cobalt-molybdenum hybrid system which suggested that cyclisation is preferentially templated around either cobalt or molybdenum but not both, then the modest levels of stereoinduction observed with the mixed metal system in comparison to those obtained with the cobalt system may be attributed to an increase in steric interactions generated between syn or anti incorporation of the cyclopentene into either the cobalt or molybdenum centre of the metalacycle. **Scheme (113)**
The origin of the increase in steric discrimination between anti and syn incorporation into the heterobimetallic complex is not clear.

2.7 Simplification of complex generation.

Whilst modification of literature procedures provided initially a convenient method of obtaining hybrid complexes in order to access the ability of the chiral core to induce a stereoselective variant of the Pauson-Khand reaction, the conditions were lengthy and involved.

Although reliable, an alternative to existing isolobal displacement methodology enabling the hybrid complexes to be generated in a rapid manner would increase the synthetic utility of employing such hybrid substrates in the Pauson-Khand reaction. When the conditions required in order to facilitate the isolobal displacement are examined then the main limiting factor in the protocol is the efficient generation of the molybdenumcyclopentadienyltricarbonyl anion.

2.7.1 Isolation of molybdenum cyclopentadienyltricarbonyl anion

In our desire to simplify the synthesis of the hybrid complexes, the isolation of the molybdenumcyclopentadienyltricarbonyl anion was investigated. If the anion could be isolated
and stored in an efficient manner without loss of activity then the hybrid complexes could be generated in a far faster manner.

Isolation of the molybdenumcyclopentadienyltricarbonyl anion proved to be possible. Addition of hexane to a solution of molybdenumcyclopentadienyltricarbonyl anion generated in a conventional manner resulted in the rapid precipitation of a fine white powder which was assumed to be molybdenumcyclopentadienyltricarbonyl anion. The anion was however found to be highly sensitive to air, rapidly darkening and undergoing a vigorous exothermic reaction on filtration. Scheme(114).

\[
\text{heat} \quad \begin{array}{c}
\text{NaH} \\
\text{THF}
\end{array} \xrightarrow{\text{reflux 12hrs}} \begin{array}{c}
\text{Mo(CO)}_6 \\
\text{hexane}
\end{array} \quad \begin{array}{c}
\text{OC}^{-}\text{Mo-CO} \\
\text{Na}^+
\end{array}
\]

Scheme(114)

2.7.2 Isolobal displacement with molybdenum cyclopentadienyltricarbonyl anion.
After storing the residue in a freezer under an inert atmosphere, we were surprised to find that under appropriate conditions the salt successfully facilitated an isolobal displacement. When added to a solution of dicobaltphenylacetylenehexacarbonyl in tetrahydrofuran and refluxed the desired hybrid complex was generated and subsequently isolated in low yield (28%). (Method B). Scheme(115).

\[
\begin{array}{c}
\text{OC}^{-}\text{Mo-CO} \\
\text{Na}^+
\end{array} \xrightarrow{\text{THF reflux}} \begin{array}{c}
\text{H} \\
\text{OC} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{Ph}
\end{array} \xrightarrow{28\%} \begin{array}{c}
\text{H} \\
\text{OC} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{Ph}
\end{array}
\]

Scheme(115)

Due to the highly sensitive nature of the molybdenumcyclopentadienyltricarbonyl anion despite being a potentially faster route for the generation of the hybrid complexes, isolation and utilisation of the molybdenumcyclopentadienyltricarbonyl anion would require specialist apparatus and techniques resulting in a decrease in the general utility of the method.

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2.7.3 Development of the molybdenumcyclopentadienyltricarbonyl dimer as a precursor for an isolobal displacement.

The generation of molybdenumcyclopentadienyltricarbonyl anion by reductive cleavage of the molybdenumcyclopentadienyltricarbonyl dimer with a sodium mercury amalgam is well known and has been utilised by several groups in order to generate the anion required in order to effect the desired isolobal displacement.71

The utilisation of the molybdenumcyclopentadienyltricarbonyl dimer as an anion precursor appeared attractive due to its ease of preparation in multigram quantities and its essentially bench stable nature enabling storage for extended periods.74

2.7.4 L-Selectride promoted molybdenumcyclopentadienyltricarbonyl anion formation.

It is somewhat surprising that Gladysz’s79 report that treatment of the molybdenumcyclopentadienyltricarbonyl dimer with a borohydride at room temperature results in the formation of the anion in a rapid manner has been overlooked as an efficient means for generating the desired anion. This method, to our knowledge, has not been used as a means of generating the anion in order to facilitate an isolobal displacement despite its obvious advantages compared to the amalgam method. Scheme(116).

In agreement with Gladysz, reaction of the molybdenumcyclopentadienyltricarbonyl dimer with L-selectride at room temperature resulted in the efficient formation of the molybdenumcyclopentadienyltricarbonyl anion with the associated colour change from red corresponding to the presence of the molybdenumcyclopentadienyltricarbonyl dimer to the translucent orange colour of the anion occurring rapidly. Once generated, at elevated temperatures the anion was found to effectively participate in the desired isolobal displacement. The reaction procedure was simplified further in that on reaction completion the reaction was
absorbed onto silica and chromatographed directly to yield the desired hybrid complex. (Method C). Scheme (117). Table (15).
Isolobal displacement employing Gladysz methodology. Table(15).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Complex 1" /></td>
<td>45 59</td>
</tr>
<tr>
<td><img src="image2" alt="Complex 2" /></td>
<td>46 78</td>
</tr>
<tr>
<td><img src="image3" alt="Complex 3" /></td>
<td>47 55</td>
</tr>
<tr>
<td><img src="image4" alt="Complex 4" /></td>
<td>16 89</td>
</tr>
<tr>
<td><img src="image5" alt="Complex 5" /></td>
<td>17 61</td>
</tr>
<tr>
<td><img src="image6" alt="Complex 6" /></td>
<td>18 61</td>
</tr>
<tr>
<td><img src="image7" alt="Complex 7" /></td>
<td>19 100</td>
</tr>
</tbody>
</table>

To a solution of dimolybdenumdicyclopentadienylhexacarbonyl in tetrahydrofuran was added L-selectride. The reaction mixture was stirred for 1h prior to the addition of the dicobaltalkynylhexacarbonyl complex. The reaction mixture was refluxed and monitored for the disappearance of starting material. Upon reaction completion the crude reaction mixture was adsorbed onto silica gel and chromatographed to yield the desired heterobimetallic complex.

The displacement of the cobalttricarbonyl moiety was achieved with a number of mono and disubstituted bishomometallic complexes. Some interesting trends became apparent. In the case of the disubstituted alkynyl dicobalt complexes the displacement proceeded in an exceptionally clean manner yielding the desired complexes with a dramatic increase in yield in comparison to that obtained under conventional condition for generating the molybdenumcyclopentadienyltricarbonyl anion. In contrast, the monosubstituted hydride complexes were isolated in the similar yields to those obtained under the conventional conditions. At present a rationale to explain these experimental observations is not known.
2.7.5 Advantages of L-selectride molybdenumcyclopentadienyltricarbonyl anion formation.

Generation of the molybdenumcyclopentadienyltricarbonyl anion by treatment of the molybdenumcyclopentadienyltricarbonyl dimer with L-selectride has several distinct advantages over existing methodology for molybdenumcyclopentadienyltricarbonyl anion formation.

The molybdenumcyclopentadienyltricarbonyl dimer which is the precursor for the anion can be generated in excellent yield and is bench stable enabling its storage for extended periods. L-Selectride is a commercially available reagent and is readily handled using standard techniques. Treatment of the dimer with the Selectride generates the desired anion in a rapid manner enabling access to a range of hybrid complexes without the use of specialist techniques or apparatus. This method has been found experimentally to be especially effective for the generation of disubstituted hybrid complexes.

2.8 Utilisation of hybrid complexes as chiral auxiliaries.

In order to extend the synthetic scope of these hybrid complexes outside Pauson-Khand methodology attention was directed towards harnessing their chiral nature for more general organic transformations.

During the Pauson-Khand reaction the chiral core interacts directly with the alkene resulting in high stereoinduction. Our attention was directed to investigating the ability of the chiral metal core to effect a stereoselective reaction at a remote centre. In such a sense, the role of the hybrid core would be that of a chiral auxiliary.

2.8.1 Creation of chiral centres at propargylic centres utilising hybrid complexes.

In order to investigate the ability of the hybrid core to behave as a chiral auxiliary the creation of chiral centres at the propargylic position became of interest. Methods for the preparation of stereocentres next to alkynes by stereoselective addition of nucleophiles to propargylic aldehydes include the use of titanium catalysts, boron reagents and metal catalysed ene reactions.

In order to test the ability of the chiral metal core to control the remote addition of a nucleophile to a propargylic carbonyl functionality leading to the diastereoselective synthesis of complexed propargylic alcohols, the requisite hybrid propargylaldehyde had to be prepared.
2.8.2 Generation of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl
Complexation of 2-butynal diethyl acetal with dicobaltoctacarbonyl occurred in high yield (93%) as expected to generate the protected alkynyldicobalt complex. This complex was found to participate in the expected isolobal displacement at elevated temperatures in the presence of the molybdenumcyclopentadienyltricarbonyl anion generated by the treatment of molybdenumcyclopentadienyltricarbonyl dimer with L-selectride. In situ deprotection of the hybrid complex during chromatographic purification yielded the desired hybrid aldehyde in good yield (69%). (Method B) Scheme(118).

\[ \text{Scheme(118)} \]

2.8.3 Stereoselective nucleophilic addition to cobaltmolybdenumcyclopentadienylbut-2-ynal
With the desired hybrid aldehyde in hand we were in a position to investigate the ability of the hybrid core to control the addition to the remote propargylic carbonyl functionality. A series of Grignard and organolithium reagents was chosen to test the difference in stereoselectivity. Scheme(119).

\[ \text{Scheme(119)} \]

Addition of organolithium and Grignard reagents to the propargylic aldehyde occurred rapidly in tetrahydrofuran at \(-78^\circ\text{C}\). The reactions were easily followed by thin layer chromatography, the propargylic alcohol being markedly less polar than the starting propargylic aldehyde.

The diastereomeric ratios of the hybrid propargylic alcohols were determined spectrocopically.
The experimental results indicated that the chiral core of the aldehyde was able to direct nucleophilic addition at the propargylic position with good to excellent levels of stereoinduction. The best results were obtained with \textit{butyl}magnesiumbromide generating the desired hybrid propargylic alcohol with a diastereomeric excess of 92%. The nucleophilic addition of a lithium acetylide was achieved with a degree of stereoinduction, the hybrid propargyl alcohol being isolated with a diastereomeric excess of 33%. This moderate level of stereoinduction was to be expected on consideration of the linear nature of the nucleophile. Table (16).
Stereoselective generation of cobaltmolybdenum propargylalcohols. Table(16).

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Complex</th>
<th>Diastereomeric excess%</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuLi</td>
<td><img src="image" alt="BuLi complex" /></td>
<td>49</td>
<td>62</td>
</tr>
<tr>
<td>MeMgBr</td>
<td><img src="image" alt="MeMgBr complex" /></td>
<td>50</td>
<td>72</td>
</tr>
<tr>
<td>MeLi</td>
<td><img src="image" alt="MeLi complex" /></td>
<td>50</td>
<td>62</td>
</tr>
<tr>
<td>PhMgBr</td>
<td><img src="image" alt="PhMgBr complex" /></td>
<td>51</td>
<td>72</td>
</tr>
<tr>
<td>PhLi</td>
<td><img src="image" alt="PhLi complex" /></td>
<td>51</td>
<td>75</td>
</tr>
<tr>
<td>iBuMgBr</td>
<td><img src="image" alt="iBuMgBr complex" /></td>
<td>52</td>
<td>92</td>
</tr>
<tr>
<td>MeCCMgCl</td>
<td><img src="image" alt="MeCCMgCl complex" /></td>
<td>53</td>
<td>33</td>
</tr>
</tbody>
</table>

To a solution of the cobaltmolybdenum cyclopentadienyl but-2-ynal pantacarbonyl in tetrahydrofuran at -78°C was added the organometallic reagent. The reaction mixture was monitored for the disappearance of starting material. Upon reaction completion the reaction mixture was quenched with ethanol and allowed to attain room temperature. The mixture was then filtered through a plug of silica and the solvent removed under reduced pressure to yield the desired complex.
2.8.4 Explanation of stereoselective nucleophilic addition.

In order to account for the ability of the hybrid core to behave as a chiral auxiliary for the addition of Grignard and organolithium nucleophiles to the remote propargylic aldehyde functionality we propose that two control elements may be operating.

If the aldehyde oxygen adopts an orientation in which it bisects the two metal centres of the hybrid core then the proximity of the prochiral faces to the two different metal centres effectively differentiates the prochiral faces. Reaction of a nucleophile with either face requires the nucleophile to pass the sterically and electronically inequivalent metal centres. These steric and electronic differences would be expected to lead to the preferential addition to one of the prochiral faces resulting in stereospecific nucleophilic addition.

The second control element we believe arises due to the steric bulk of the hybrid metal core effectively shielding the lower complexed face of the alkyne and aldehyde. The importance of such shielding effects would become more pronounced if the aldehyde adopts the conformation in which it is in the same plane as the alkynyl component. In this conformation, the oxygen of the aldehyde must face either the cobalt or molybdenum centres. In this conformation one of the prochiral faces is shielded by the steric bulk of the core with the opposite prochiral face being exposed to the nucleophile in each case. The prochiral face exposed is dependent on whether the aldehyde is orientated towards the cobalt or molybdenum centre. Scheme(120).

\[
\text{Scheme(120)}
\]
In such a conformation, addition of a Lewis acid may have been expected to increase the selectivity of the addition, the interaction between the aldehyde Lewis acid and a carbon monoxide ligand present on a metal centre effectively locking the aldehyde in the desired conformation. Scheme(121).

\[ \text{Scheme(121)} \]

2.8.5 Effect of external Lewis acid on stereoselective addition.

In an attempt to ascertain the effect on addition of a Lewis acid source boron trifluoride etherate was employed. An identical series of reactions was carried out in toluene and in the presence of boron trifluoride etherate. Table(17).
Stereoselective generation of cobaltmolybdenum propargylalcohols in the presence of an external Lewis acid. Table(17).

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Lewis acid</th>
<th>Complex</th>
<th>Diastereomeric excess%</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuLi</td>
<td>None</td>
<td><img src="image1.png" alt="Complex 1" /></td>
<td>49</td>
<td>69</td>
</tr>
<tr>
<td>BuLi</td>
<td>BF₃</td>
<td><img src="image2.png" alt="Complex 2" /></td>
<td>49</td>
<td>78</td>
</tr>
<tr>
<td>MeMgBr</td>
<td>None</td>
<td><img src="image3.png" alt="Complex 3" /></td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>MeMgBr</td>
<td>BF₃</td>
<td><img src="image4.png" alt="Complex 4" /></td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>PhMgBr</td>
<td>None</td>
<td><img src="image5.png" alt="Complex 5" /></td>
<td>51</td>
<td>41</td>
</tr>
<tr>
<td>PhMgBr</td>
<td>BF₃</td>
<td><img src="image6.png" alt="Complex 6" /></td>
<td>51</td>
<td>41</td>
</tr>
<tr>
<td>PhLi</td>
<td>None</td>
<td><img src="image7.png" alt="Complex 7" /></td>
<td>51</td>
<td>41</td>
</tr>
<tr>
<td>PhLi</td>
<td>BF₃</td>
<td><img src="image8.png" alt="Complex 8" /></td>
<td>51</td>
<td>41</td>
</tr>
</tbody>
</table>

To a solution of the cobaltmolybdenumcyclopentadienylbut-2ynalpentacarbonyl in toluene at –78°C was added the organometallic reagent. The reaction mixture was monitored for the disappearance of starting material. Upon reaction completion the reaction mixture was quenched with ethanol and allowed to attain room temperature. The mixture was then filtered through a plug of silica and the solvent removed under reduced pressure to yield the desired complex.
Experimental results indicated an increase in the stereoselectivity of the nucleophilic addition in a number of cases but the magnitude was not large enough to suggest that the preferred conformation of the aldehyde is that in which the aldehyde lies in the same plane as the alkynyl fragment of the complex. In addition, treatment of the cobaltmolybdenumcyclopentadienylbut-2-ylnalpentacarbonyl complex with either phenylmagnesium bromide or phenyllithium in the presence of boron trifluoride etherate resulted in the precipitation on workup of a unidentified orange micro crystalline solid.

2.9 Conclusion.
The use of heterobimetallic alkyne complexes as suitable substrates in the Pauson-Khand reaction has been realised. The cycloaddition proceeds under thermal conditions to yield cyclopentenones in a regioselective manner with generally higher or at least comparable yields as the conventional cobalt based system. Scheme(122).

![Scheme(122)](image)

The inherent chirality of the complexes has been exploited, optically pure heterobimetallic alkyne complexes have been demonstrated to undergo stereospecific cycloaddition furnishing optically pure cyclopentenoid products. The unique mode of stereoinduction observed we attribute to templating of cycloaddition around one but not both of the metal centres present in the core. The metal upon which cyclisation is templated has yet to be determined. Scheme(123).

![Scheme(123)](image)
Application of heterobimetallic complexes to more general organic synthetic applications has been briefly investigated. The heterobimetallic core has been found to promote moderate to high levels of stereocontrol on addition of nucleophiles to complexed propargylic aldehydes. The stereocontrol observed we believe may be explained in terms of steric considerations. Scheme(124).

In view of the development of heterobimetallic Pauson-Khand methodology and the potential application of these heterobimetallic complexes for more general organic transformations, complex accessibility has been addressed and simplified by employing Gladysz methodology in order to generate the requisite molybdenumcyclopentadienyltricarbonyl anion required for the isolobal displacement. Scheme(125).

2.10 Further work.
Heterobimetallic alkyne complexes in contrast to existing methodology have been demonstrated to effect stereospecific Pauson-Khand cycloadditions in a non substrate specific manner in contrast to chiral promotors and without the disadvantages incurred employing auxiliary based approaches.
As such, the development of this field provides an attractive alternative to previously established methodology. The potential of heterobimetallic complexes would however be greatly enhanced if a viable route to the stereoselective generation of mixed metal complexes could be achieved alleviating the requirement for a chromatographic separation to obtain optically pure material. Such a stereoselective isolobal displacement may be envisaged employing chiral cyclopentadienylanions. Although preliminary attempts to carry out an isolobal displacement with a molybdenum menthylcyclopentadiene anion proved unsuccessful further research in this area perhaps with more elaborate and hence sterically demanding anions would appear warranted.

Scheme(126).

To date we have found it necessary in order to achieve the desired isolobal displacement of the cobalttricarbonyl moiety to reflux the reaction mixture. Such forceful conditions may not enable the displacement to be carried out in a stereoselective manner. Our group has however recently determined that displacement does occur abeit at reduced rates at room temperature if the molybdenumcyclopentadienyln anion is generated employing Gladysz methodology. Such an approach would require dimerisation of the chiral molybdenium anion prior to its regeneration on treatment with a suitable borohydride source and reaction at room temperature with a suitable cobaltalkynyl complex. If chiral anions do effect the desired isolobal displacement at room temperature but with no selectivity then investigation on the effect of carrying out the isolobal
displacement at reduced temperatures employing these conditions should not be discounted. Scheme(127).

Effort in obtaining optically pure heterobimetallic alkyne complexes need not be confined to a quest for a stereoselective isolobal displacement. The heterobimetallic core has been shown to control addition of nucleophiles at remote centres of a complexed propargylic aldehyde. Such control in conjunction with a chiral reducing agent may enable the generation of potentially enriched propargylic alcohols via a kinetic resolution. Such a resolution would enable isolation of optically enriched cobaltmolybdenumcyclopentadienylpropargylalcoholpentacarbonyl from which via Nicholas methodology a large range of optically pure complexes could be obtained. Scheme(128).
An alternative but related approach would be to investigate the influence the chiral core may be able to exert a enzymatic kinetic resolution.

The application of heterobimetallic alkyne complexes as chiral auxiliaries has been briefly investigated and although moderate to high levels of stereocontrol are observed on nucleophilic addition to a complexed propargylic aldehyde, the predominant stereoisomer generated has yet to be confirmed. In order to do so crystallographic data of a generated substituted propargylic alcohol must be obtained. In light of the ability of the heterobimetallic core to control additions at metal centres then it may be of interest to investigate the influence of the core on enolate reactions. Preliminary results prove encouraging. Treatment of a complexed propargylic aldehyde with lithium hexamethyldisilane (LHMDS) and subsequent quench with benzylbromide yielded the desired complex in low yield. A second deprotonation again with LHMDS of this complex and quench with allyl bromide yielded the desired disubstituted complex again in low yield. Spectroscopic analysis of the complex indicated that the new chiral centre had been created with complete stereocontrol, only a single diastereomer being present in the carbon NMR spectrum.
In view of this result further investigation and optimisation of reaction conditions is necessary.

Experimental section.

General information.

Solvents and reagents

All solvents were dried, distilled and stored under anhydrous conditions when necessary.

- dichloromethane: distilled from phosphorous pentoxide,
- diethyl ether: distilled from sodium and benzophenone,
- ethyl acetate: distilled from calcium chloride,
- petroleum ether: (fraction boiling between 40°C and 60°C), distilled from calcium chloride,
- tetrahydrofuran: distilled from sodium and benzophenone.

Chemicals used in this work were obtained from Aldrich Chemical Co. Ltd, Lancaster Synthesis Ltd and Strem Chemical company Ltd. The chemicals were distilled or sublimed if required.
Chromatographic Procedures

Flash Chromatography was carried out using Merck Kieselgel 60 H silica. Pressure when required was applied at the column head using hand bellows. Samples were applied as saturated solutions in the appropriate solvent or pre-absorbed onto the minimum quantity of silica. Analytical thin layer Chromatography (TLC) was carried using aluminium backed plates coated with Merck Kieselgel 60 GF254. Plates were visualised under UV light (at 254 and/or 360nm) or by staining with either potassium permanganate or iodine.

Spectra

Infra red spectra were recorded in the range 4000-600cm\(^{-1}\) using a Nicolet 250 FT-IR Spectrometer with internal calibration. Solid samples were run as nujol mulls, and liquids as thin films.

\(^1\)H Nuclear magnetic resonance spectra were recorded using either a Bruker AC250, or DPX400 Spectrometer. Multiplicities were recorded as broad peaks (br), singlets (s), doublets (d), triplets (t), quartets (q), double doublets (dd) and multiplets (m) etc. \(^{13}\)C Nuclear magnetic resonance spectra were recorded using either a Bruker AC250 or DPX400 Spectrometer. All NMR samples were made up in deuterated solvents with all values quoted in \(\delta\) ppm relative to the internal standard tetramethylsilane. Coupling constants (\(J\) values) are reported in hertz (Hz). Diastereoisomer ratios were calculated from the integration of suitable peaks in the proton NMR or from the carbon NMR spectrum. For clarity numbering of spectral data refers to the structure as indicated rather than to UPAC nomenclature.

Other data

Elemental analyses were carried out on a Perkin Elmer 2400 CHN Elemental Analyser. Melting points were determined on a Leica Galen III Instrument. All yields are for isolated pure products. Optical rotations were measured on a polAAR 2001 polarimeter in chloroform.
Method A.

To a solution of sodium hydride (0.151g, 3.79mmol) in diglyme (50cm³) was added freshly cracked cyclopentadiene (0.90cm³, 10.61mmol). The reaction mixture was stirred for 30 minutes. To the resultant pale pink solution was added molybdenum hexacarbonyl (1.00g, 3.79mmol) and the reaction refluxed for 40 minutes. The resultant orange reaction mixture was allowed to cool to room temperature upon which ethanol (1.00cm³) and subsequently water (1.00cm³) was added to the reaction mixture to destroy any remaining sodium hydride and sodium cyclopentadiene. A filtered solution of iron sulfate (3.60g) glacial acetic acid (2.70cm³) and water (45cm³) was added to the reaction mixture resulting in an immediate precipitation of a purple microcrystalline solid. The reaction mixture was filtered under reduced pressure and the solid washed with water (50cm³), ethanol (5.0cm³) and then hexane (5.0cm³) prior to drying under reduced pressure for 12 hrs to yield the title complex as a red microcrystalline solid (0.650g, 70%).

H¹ NMR (400MHz, CDCl$_3$) 5.30(s, 10H).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 92.03(CH).

$m/z$ Submitted to ESPRC National Mass Spectrometry Service Centre Swansea. No molecular ion found.


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Method B.

To a solution of sodium hydride (0.151g, 3.79mmol) in tetrahydrofuran (50cm³) was added freshly cracked cyclopentadiene (0.90cm³, 10.61mmol). The reaction mixture was stirred for 30 minutes. To the resultant pale pink solution was added molybdenum hexacarbonyl (1.00g,
3.79 mmol) and the reaction refluxed for 12 hrs. The resultant orange reaction mixture was allowed to cool to room temperature upon which ethanol (1.0 cm³) and subsequently water (1.0 cm³) was added to the reaction mixture to destroy any remaining sodium hydride and sodiumcyclopentadiene. A filtered solution of iron sulfate (3.60 g) glacial acetic acid (2.70 cm³) and water (45 cm³) was added to the reaction mixture resulting in a immediate precipitation of a purple microcrystalline solid. The reaction mixture was filtered under reduced pressure and the solid washed with water (50 cm³), ethanol (5.0 cm³) and then hexane (5.0 cm³) prior to drying under reduced pressure for 12 hours to yield the title complex as a red microcrystalline solid (0.556 g, 60%).

For spectroscopic data see compound 11 Method A.

Dicobalt(diphenylacetylene)hexacarbonyl (12).

![Dicobalt(diphenylacetylene)hexacarbonyl](image)

To a solution of dicobaltoctacarbonyl (1.6 g, 4.68 mmol) in light petroleum was added diphenylacetylene (0.86 cm³, 4.68 mmol). The reaction was stirred for 12 hours. The reaction mixture was filtered through a plug of celite and the solvent removed under reduced pressure to yield the title complex as a dark red solid (100%, 2.17 g).

IR (Nujol) 2089, 2054, 2026, 2010 cm⁻¹.

$^1$H NMR (400 MHz, CDCl₃) 7.61-7.59 (4H, m, Ar), 7.37-7.33 (6H, m, Ar).

$^{13}$C NMR (100.62 MHz, CDCl₃) 199.24 (q, C₆), 138.32 (q, C₄), 129.24 (CH, C₃), 129.06 (CH, C₂), 127.89 (CH, C₁), 92.01 (q, C₅).

$m/z$ [NH$_3$Cl$^+$, Cl$^+$] , (M-CO)$^+$ calculated 435.9192, obtained 435.9188.

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Dicobaltphenylacetylenehexacarbonyl. (13).

To a solution of dicobaltoctacarbonyl (1.88g, 5.50mmol) in light petroleum was added phenylacetylene (0.60cm³, 5.50mmol). The reaction was stirred for 12 hours. The reaction mixture was filtered through a plug of celite and the solvent removed under reduced pressure to yield the title complex as a red oily solid (2.13g, 100%).

IR(neat) 2093, 2052, 2017cm⁻¹.

¹H NMR (400MHz, CDCl₃) 7.53-7.51(m, 2H, Ar), 7.34-7.29(m, 3H, Ar), 6.36(1H, s, H1).

¹³C NMR (100.62MHz, CDCl₃) 199.39(q, C7), 137.43(q, C3), 130.26(CH, C4), 128.87(CH, C5), 128.16(CH, C6), 90.17(q, C2), 72.59(CH, C1).

m/z [NH₄⁺Cl⁻]⁺ calculated 388.8906, obtained 388.8896.

Dicobalt 1-hexynehexacarbonyl. (14).

To a solution of dicobaltoctacarbonyl (2.39g, 6.99mmol) in light petroleum was added 1-hexyne (0.80cm³, 6.99mmol). The reaction was stirred for 12 hrs. The reaction mixture was filtered through a plug of celite and the solvent removed under reduced pressure to yield the title complex as a red oil (1.61g, 88%).

IR(neat) 2086, 2042, 2011cm⁻¹.

¹H NMR (400MHz, CDCl₃) 6.00(1H, t, J 4Hz, H6), 2.86(2H, td, J 8, 1.2Hz, H4), 1.65-1.57(2H, m, H3), 1.52-1.42(2H, m, H2), 0.96(3H, t, J 8Hz, H1).

¹³C NMR (100.62MHz, CDCl₃) 200.37(q, C7), 98.06(q, C5), 73.54(CH, C6), 34.42(CH₂, C4), 34.31(CH₂, C3), 22.78(CH₂, C2), 14.12(CH₃, C1).
To a solution of dicobaltoctacarbonyl (1.75g, 5.12mmol) in light petroleum was added 2-butyne (0.40 cm³, 5.12mmol). The reaction was stirred for 12 hours. The reaction mixture was filtered through a plug of celite and the solvent removed under reduced pressure to yield the title complex as a red oily solid (88%, 1.53g).

IR (neat) 2088, 2042, 2009 cm⁻¹.

¹H NMR (400MHz, CDCl₃) 2.63(6H, s, H1).

¹³C NMR (100.62MHz, CDCl₃) 200.20(q, C3), 94.13(q, C2), 19.77(CH₃•Cl).

m/z [FAB], calculated 339.8828, obtained 339.8835.

Dicobalt 2-butynehexacarbonyl. (15).

Cobaltmolybdenumcyclopentadienylidiphenylacetylenepentacarbonyl. (16).

Method A.
To a solution of sodium hydride (0.278g, 6.95mmol) in tetrahydrofuran (50cm³) was added freshly cracked cyclopentadiene (0.65cm³, 7.72mmol). The reaction mixture was stirred for 30 minutes. To the resultant pale pink solution was added molybdenum hexacarbonyl (1.02g, 3.86mmol) and the reaction refluxed for 12 hours. The resultant orange reaction mixture was allowed to cool to room temperature and diphenylacetylenedicobalthexacarbonyl (1.72g, 3.86mmol) was added as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed and monitored for the disappearance of starting material. Upon disappearance of
starting material, the solvent was removed under reduced pressure and the crude residue extracted between dichloromethane and water. The organic phases were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue adsorbed onto silica gel and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether (10:1) as the eluent to yield the title complex as a red solid (1.34g, 65%).

IR(neat) 2047, 1978, 1935 cm⁻¹.

¹H NMR (400MHz, CDCl₃) 7.12-7.14 (10H, m, Ar), 5.35 (5H, s, H6).

¹³C NMR (100.62MHz, CDCl₃) 225.04 (q, C7), 203.30 (q, C7), 141.92 (q, C4), 129.31 (CH, C3), 128.30 (CH, C2), 126.57 (CH, C1), 93.35 (q, C5), 91.40 (CH, C6).

m/z [FAB], requires 539.9312, obtained 539.9316.

C₂₄H₁₅O₅MoCo requires C 53.55, H 2.81, obtained C 53.79, H 3.04.

Cobaltmolybdenumcyclopentadienylphenylacetylenepentacarbonyl. (17).

Method A.

To a solution of sodium hydride (0.278g, 6.95mmol) in tetrahydrofuran (50cm³) was added freshly cracked cyclopentadiene (0.65 cm³, 7.72mmol). The reaction mixture was stirred for 30 minutes. To the resultant pale pink solution was added molybdenum hexacarbonyl (1.02g, 3.86mmol) and the reaction refluxed for 12 hours. The resultant orange reaction mixture was allowed to cool to room temperature and phenylacetylenedicobalthexacarbonyl (1.49g, 3.86mmol) was added as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed and monitored for the disappearance of starting material. Upon disappearance of starting material, the solvent was removed under reduced pressure and the crude residue extracted between dichloromethane and water. The organic phases were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue adsorbed onto silica gel and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether (10:1) as the eluent to yield the title complex as a red oily solid (1.03g, 58%).
IR(neat) 2049, 1977, 1939 cm⁻¹.

¹H NMR (250MHz, CDCl₃) 7.16-7.13(5H, m, Ar), 5.86(1H, s, H1), 5.37(5H, s, H7).

¹³C NMR (100.62MHz, CDCl₃) 226.11(q, C8), 225.90(q, C8), 203.58(q, C8), 142.46(q, Ar), 130.05(CH, Ar), 126.69(CH, Ar), 127.17(CH, Ar), 91.64(CH, C7), 87.68(q, C2), 74.69(CH, C1).

m/z [FAB], requires 463.8993, obtained 463.8990.

C₁₈H₁₁O₂MoCo requires C 46.78, H 2.40, obtained C 46.53, H 2.33.

Cobaltmolybdenumcyclopentadienyl 1-hexynepentacarbonyl (18).

Method A.

To a solution of sodium hydride (0.278g, 6.95mmol) in tetrahydrofuran (50cm³) was added freshly cracked cyclopentadiene (0.65cm³, 7.72mmol). The reaction mixture was stirred for 30 minutes. To the resultant pale pink solution was added molybdenum hexacarbonyl (1.02g, 3.86mmol) and the reaction refluxed for 12 hours. The resultant orange reaction mixture was allowed to cool to room temperature and 1-hexynedicobalthexacarbonyl (1.42g, 3.86mmol) was added as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed and monitored for the disappearance of starting material. Upon disappearance of starting material, the solvent was removed under reduced pressure and the crude residue extracted between dichloromethane and water. The organic phases were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue adsorbed onto silica gel and chromatographed employing light petroleum (bp 40-60°C) as the eluent to yield the title complex as a red oil (1.04g, 61%).

IR(neat) 2046, 1989, 1934cm⁻¹.

¹H NMR (400MHz, CDCl₃) 5.77(1H, s, H1), 5.38(5H, s, H7), 2.90-2.69(6H, m, H3, 4, 5), 0.92(3H, t, J 6.9Hz, H6).
\(^{13}\)C NMR (100.62MHz, CDCl\(_3\)) 227.10(q, C8), 226.15(q, C8), 203.70(q, C8), 90.99(q, C2), 90.78(CH, C7), 77.02(CH, C1), 35.44(CH\(_2\), C3), 34.19(CH\(_2\), C4), 22.60(CH\(_3\), C5), 13.85(CH\(_3\), C6).

\(m/z\) [FAB] requires 443.9309, obtained 443.9309.

Cobaltmolybdenumcyclopentadieny1 2-butynepentacarbonyl. (19).

Method A.

To a solution of sodium hydride (0.278g, 6.95mmol) in tetrahydrofuran(50cm\(^3\)) was added freshly cracked cyclopentadiene (0.65cm\(^3\), 7.72mmol). The reaction mixture was stirred for 30 minutes. To the resultant pale pink solution was added molybdenum hexacarbonyl (1.02g, 3.86mmol) and the reaction refluxed for 12 hours. The resultant orange reaction mixture was allowed to cool to room temperature and 2-butynebicobalthexacarbonyl (1.24g, 3.86mmol) was added as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed and monitored for the disappearance of starting material. Upon disappearance of starting material, the solvent was removed under reduced pressure and the crude residue extracted between dichloromethane and water. The organic phases where combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue adsorbed onto silica gel and chromatographed employing light petroleum (bp 40-60°C) as the eluent to yield the title complex as a red oily solid (1.05g, 66%).

IR(neat) 2042, 1966, 1928cm\(^{-1}\).

\(^1\)H NMR (250MHz, CDCl\(_3\)) 5.55(5H, s, H3), 2.56(6H, s, H1)

\(^{13}\)C NMR (100.62MHz, CDCl\(_3\)) 226.54(q, C4) 204.81(q, C4), 93.37(q, C2), 91.26(CH, C3), 21.05(CH\(_3\), C1).

\(m/z\) submitted to ESPRC National Mass Spectrometry Service Centre Swansea. No molecular ion found.
Method A.

To a solution of cobaltmolybdenumcyclopentadienyldiphenylacetylene (0.134g, 0.249mmol) in toluene (15cm³) was added norbomene (0.112g, 1.24mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petrolatum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound (0.022g, 29%).

IR(neat) 1695cm⁻¹.

¹H NMR (250MHz, CDCl₃) 7.30-7.17(10H, m), 3.21(1H, d, J 5.3), 2.61(1H, s), 2.51(1H, d, J 5.3Hz), 2.11(1H, s), 1.70-1.64(2H, m), 1.44-1.38(2H, m), 1.26-1.21(1H, m), 1.04-1.00(1H, m).

¹³C NMR (100.62MHz, CDCl₃) 209.00(q), 170.00(q), 143.25(q), 135.30(q), 132.40(q), 129.84(CH), 129.69(CH), 128.91(CH), 128.76(CH), 128.70(CH), 128.12(CH) 54.44(CH), 51.12(CH), 39.88(CH), 38.68(CH), 31.97(CH₂), 29.36(CH₂), 29.22(CH₃).

m/z [FAB], (M+ H)⁺ requires 301.1592, found 301.1588.


4, 5-diphenyltricyclo[5.2.1.0^2,6]deca-4,8-dien-3-one. (21)

Method A.

To a solution of cobaltmolybdenumcyclopentadienyldiphenylacetylene (0.150 g, 0.27 mmol) in toluene (15 cm^3) was added norbornadiene (0.15 cm^3, 1.39 mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound (0.031 g, 38%).

IR (neat) 1695 cm^-1.

^1H NMR (400 MHz, CDCl_3) 7.23-7.08 (10H, m), 6.23-6.19 (2H, m), 3.24 (1H, d, J 5.2 Hz), 3.02-3.02 (1H, m), 2.52-2.50 (2H, m), 1.36-1.33 (2H, m).

^13C NMR (100 MHz, CDCl_3) 207.55 (q), 170.29 (q), 144.16 (q), 138.77 (CH), 138.77 (CH), 135.41 (q), 132.50 (q), 130.03 (CH), 129.73 (CH), 128.90 (CH), 128.82 (CH), 128.78 (CH), 128.24 (CH), 53.22 (CH), 50.76 (CH), 44.60 (CH), 43.74 (CH), 42.29 (CH_2).

m/z [FAB], (M + H)^+ requires 299.1435, found 299.1435.

4, 5-diphenyltricyclo[5.2.1.02,6]dec-4-en-3-one. (20)

Method B.
To a solution of cobaltmolybdenumcyclopentadienylidiphenylacetylene (0.139g, 0.258mmol) in toluene (15cm³) was added norbornene (0.121g, 1.29mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound (0.030g, 39%).

For spectroscopic data see compound 20 Method A.

4-phenyltricyclo[5.2.1.02,6]dec-4-en-3-one. (22)

Method B.
To a solution of cobaltmolybdenumcyclopentadienylphenylacetylene (0.201g, 0.435mmol) in toluene (15cm³) was added norbornene (0.204g, 2.18mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude
residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (10:1) as the eluent to yield the title compound (0.063g, 69%).

IR(neat) 1698cm⁻¹.

¹H NMR (250MHz, CDCl₃) 7.72-7.67(2H, m), 7.60(1H, d, J  2.9Hz), 7.39-7.29(3H, m), 2.67-2.64(1H, m), 2.49-2.48(1H, m), 2.33(1H, d, J 5.2Hz), 2.25(1H, d, J 3.3) 1.70-1.55(2H, m), 1.40-1.26(2H, m), 1.14-0.95(1H, m), 0.99-0.92(2H, m).

¹³C NMR (250MHz, CDCl₃) 208.53(q), 159.76(CH), 145.98(q), 131.49(q), 128.22(CH), 128.19(CH), 126.92(CH), 54.82(CH), 47.58(CH), 39.33(CH), 38.30(CH), 31.13(CH₂), 29.04(CH₂), 28.28(CH₂).

m/z [EI], requires 224.1201, obtained 224.0720.

4-butyltricyclo[5.2.1.0²⁶]dec-4-en-3-one. (24).

Method B.

To a solution of cobaltmolybdenumcyclopentadienylhexyne (0.166g, 0.376mmol) in toluene (15cm³) was added norbornene (0.177g, 1.87mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (7:1) as the eluent to yield the title compound (0.037g, 52%).

IR(neat) 1678cm⁻¹.

¹H NMR (400MHz, CDCl₃) 7.10(1H, t, J 1.6Hz), 2.56(1H, s), 2.37(1H, d, J 3.6Hz), 2.18-2.09(4H, m), 1.70-1.52(2H, m), 1.49-1.42(2H, m), 1.37-1.26(4H, m), 1.00-0.88(5H, m, containing 0.91(3H, t, J 7.2Hz)

¹³C NMR (100.62MHz, CDCl₃) 211.43(q), 158.91(CH), 149.80(q), 54.20(CH), 48.48(CH), 39.31(CH), 38.39(CH), 31.33(CH₂), 30.01(CH₂), 29.40(CH₂), 28.78(CH₂), 24.73(CH₂), 22.82(CH₂), 14.16(CH₃)

m/z [EI], required 204.1514, obtained 204.1510.
Method B.

To a solution of cobaltmolybdenumcyclopentadienyl2-butyne (0.145g, 0.35mmol) in toluene (15cm³) was added norbornene (0.19cm³, 1.75mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound (0.403g, 72%).

IR(neat) 1649, 1646cm⁻¹.

¹H NMR (400MHz, CDCl₃) 2.27(1H, s), 2.18(1H, s), 2.07(1H, s), 1.96(1H, d, J 5.2Hz), 1.53(3H, s), 1.52-1.36(5H, m), 1.16-1.09(2H, m), 0.73(2H, s).

¹³C NMR (100.62MHz, CDCl₃) 210.78(q), 171.03(q), 139.38(q), 53.70(CH), 52.89(CH), 38.85(CH), 37.31(CH), 31.39(CH₂), 29.29(CH₂), 28.86(CH₂), 15.92(CH₃), 8.14(CH₃).

m/z [EI] requires 176.1201, obtained 176.1201.
4, 5-diphenyltricyclo[5.2.1.0^2,6]deca-4,8-dien-3-one. (21)

Method B.
To a solution of cobaltmolybdenumcyclopentadienyldiphenylacetylene (0.113g, 0.21mmol) in toluene (15cm\(^3\)) was added norbornadiene (0.11cm\(^3\), 1.05mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound (0.039g, 60%).

For spectroscopic data see compound 21 Method A.

4-phenyltricyclo[5.2.1.0^2,6]deca-4,8-dien-3-one. (23).

Method B.
To a solution of cobaltmolybdenumcyclopentadienyldiphenylacetylene (0.207g, 0.5mmol) in toluene (15cm\(^3\)) was added norbornadiene (0.27cm\(^3\), 2.5mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound (0.084g, 84%).
IR(neat) 1710 cm$^{-1}$.

$^1$H NMR (400MHz, CDCl$_3$) 7.70-7.65(3H, m), 7.73-7.24(3H, m), 6.32(1H, dd, $J$ 5, 3Hz), 6.23(1H, dd, $J$ 5, 3Hz), 3.00(1H, s), 2.82-2.80(1H, m), 2.76(1H, s), 2.44(1H, d, $J$ 5Hz), 1.41(1H, d, $J$ 10Hz), 1.32(1H, d, $J$ 9Hz).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 207.59(q), 159.80(CH), 147.14(q), 138.53(CH), 137.10(CH) 131.65(q), 128.44(CH), 128.37(CH), 127.01(CH), 53.55(CH), 47.14(CH) 44.11(CH), 43.35(CH), 41.37(CH$_2$).

$m/z$ [El] requires, 222.1044, obtained 222.1046.


4-butyltricyclo[5.2.1.0$^{2,6}$]deca-4,8-dien-3-one (25).

Method B.

To a solution of cobaltmolybdenumcyclpentadieny1-hexyne (0.245g, 0.554mmol) in toluene (15cm$^3$) was added norbornadiene (0.30cm$^3$, 2.77mmol), the reaction mixture was heated to 65$^\circ$C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60$^\circ$C)/diethyl ether (7:1) as the eluent to yield the title compound (0.100g, 97%).

IR(neat) 1699cm$^{-1}$.

$^1$H NMR (400MHz, CDCl$_3$) 7.07(1H, s), 6.19-6.10(2H, m), 2.80(1H, s), 2.60(1H, d, $J$ 16Hz), 2.19(2H, d, $J$ 4Hz), 2.08(2H, t, $J$ 7.6Hz), 1.41-1.11(6H, m), 0.83 (3H, t, $J$ 8Hz).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 210.19(q), 158.97(CH), 151.15(q), 138.72(CH), 137.35(CH), 52.86(CH), 47.95(CH), 43.94(CH), 43.32(CH), 41.49(CH$_2$), 30.28(CH$_2$), 25.01(CH$_2$), 22.83(CH$_2$), 14.17(CH$_3$).

$m/z$ [Cl], requires 202.1357, obtained 202.1357.
Method B.

To a solution of cobaltmolybdenumcyclopentadienyl2-butyne (0.150g, 0.36mmol) in toluene (15cm³) was added norbornadiene (0.20cm³, 1.8mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound as a colourless oil (0.056g, 90%).

IR(neat) 1695, 1646cm⁻¹.

¹H NMR (250MHz, CDCl₃) 6.24(1H, dd, J 5.5, 3.0Hz), 6.19(1H, dd, J 5.5, 1Hz), 2.89-2.88(1H, m), 2.74-2.73(1H, m), 2.56(1H, d, J 4.6Hz), 2.25(1H, d, J 5Hz), 2.00(3H, s), 1.67(3H, s), 1.35(1H, dm, J 9.3), 1.11(1H, d, J 9.2Hz).

¹³C NMR (100.62MHz, CDCl₃) 210(q), 171(q), 141(q), 138.18(CH), 137.83(CH), 52.52(CH), 52.35(CH), 43.59(CH), 42.34(CH), 41.67(CH₃), 15.86(CH₃), 8.23(CH₃).

m/z [EI], requires 174.1044, obtained 174.1046.
Menthylcyclopentadiene. (28).

To a solution of sodium hydride (3.08g, 77mmol) in tetrahydrofuran (50cm³) was added freshly cracked cyclopentadiene (6.55cm³, 77mmol). The reaction mixture was stirred for 30 minutes and then cooled to −5°C. To the resultant pale pink solution was added menthol tosylate (10.0g, 32mmol) as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was allowed to warm to room temperature and then slowly heated to reflux. After the reaction mixture was refluxed for one hour the reaction mixture was allowed to cool and 50cm³ of water added. The tetrahydrofuran was removed under reduced pressure and the aqueous phase extracted with diethylether, the organic fractions combined and dried with magnesium sulphate prior to the solvent being removed under reduced pressure. The crude residue was chromatographed employing light petroleum (bp 40-60°C) as the eluent to yield the title complex as a colourless oil (1.745g, 11%)

IR (neat) 3075, 2947, 2924, 2868, 2841 cm⁻¹.

¹H NMR (400MHz, CDCl₃) 6.53-6.05(3H, m), 3.07-2.89(3H, m), 2.25-0.81(18H, m).

m/z [EI], requires 204.1878, obtained 204.1883.


Dicobaltpropargylalcoholhexacarbonyl. (29).

To a solution of dicobaltoctacarbonyl (1.78g, 5.20mmol) in light petroleum was added propargyl alcohol (0.30cm³, 5.20mmol). The reaction was stirred for 12 hours. The reaction mixture was
filtered through a plug of celite and the solvent removed under reduced pressure to yield the title complex as a red solid (1.72g, 97%).

IR (neat) 2095, 2060, 2025, 2010 cm⁻¹.

¹H NMR (400MHz, CDCl₃) 6.01(1H, t, J 4Hz, H1), 4.74(1H, d, J 4Hz, H3a), 4.73(1H, d, J 4Hz, H3b), 1.85(t, 1H, J 4Hz, OH).

¹³C NMR (100.62MHz, CDCl₃) 199.75(q, C4), 95.50(CH, C1), 71.63(q, C2), 63.77(CH₂, C3)

m/z [FAB] requires 341.8621, obtained 341.8617.

**Dicobaltpropargylmenthyletherhexacarbonyl (30).**

\[
\begin{align*}
\text{H} & \quad \text{C} \\
\text{OC} & \quad \text{CO} \\
\text{OC} & \quad \text{CO} \\
\end{align*}
\]

To a solution of dicobaltpropargylalcoholhexacarbonyl (1g, 2.92mmol) and L-menthol (0.84g, 5.35mmol) in dichloromethane (50cm³) with molecular sieves was added a catalytic quantity of tetrafluoroboric acid. The reaction was stirred for 45 minutes and then quenched on the addition of sodium hydrogen carbonate and magnesium sulfate. The crude reaction mixture was filtered through a celite plug and the solvent removed under reduced pressure. The residue was then chromatographed on silica employing light petroleum as the eluent to yield the title complex as a red oil (1.00g, 72%).

IR (neat) 2094, 2027 cm⁻¹.

¹H NMR (250MHz, CDCl₃) 6.01(1H, s), 4.77(1H, dd, J 13, 0.9Hz), 4.48(1H, dd, J 13, 0.9Hz), 3.23(1H, td, J 10.4, 3.9Hz), 2.34-2.20(1H, md, J 2.6Hz), 2.12(1H, dm, J 10.6Hz), 1.67-1.58(3H, m), 1.51-1.15(2H, m), 1.08-0.82[(8H, m, containing 0.93(3H, d, J 6.5Hz), 0.88(3H, d, J 4.9Hz)], 0.78(3H, d, J 6.9Hz).

¹³C NMR (100.62MHz, CDCl₃) 200.59(q, C14), 94.08(q, C2), 80.08(CH, C1), 72.03(CH, C4), 69.23(CH₂, C3), 49.26(CH, C10), 41.27(CH₂, C8), 35.47(CH₂, C9), 32.55(CH, C6), 26.35(CH, C11), 24.17(CH₂, C5), 23.19(CH₃, C12), 21.78(CH₃, C13), 17.01(CH₃, C7).

m/z [NH₄⁺Cl⁻ Cl]⁻ (M- CO)⁻ requires 452.0080, obtained 452.0089.

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Method A.

To a solution of sodium hydride (0.278g, 6.95mmol) in tetrahydrofuran (50cm$^3$) was added freshly cracked cyclopentadiene (0.65cm$^3$, 7.72mmol). The reaction mixture was stirred for 30 minutes. To the resultant pale pink solution was added molybdenum hexacarbonyl (1.02g, 3.86mmol) and the reaction refluxed for 12 hours. The resultant orange reaction mixture was allowed to cool to room temperature cobaltmolybdenumcyclopentadienylpropargylmenthyletherpentacarbonyl (1.63g, 3.86mmol) was added as a solution in a minimal volume of tetrahydofuran. The reaction mixture was refluxed and monitored for the disappearance of starting material. Upon disappearance of starting material, the solvent was removed under reduced pressure and the crude residue extracted between dichloromethane and water. The organic phases were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue adsorbed onto silica gel and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether as the eluent to yield the title complex as a red oil (1.68g, 78%).

IR(neat) 2050, 1997, 1979, 1939cm$^{-1}$.

$^1$H NMR (250MHz, CDCl$_3$) 5.68(0.5H, s), 5.66(0.5H, s), 5.43(2.5H, s), 5.42(2.5H, s) 4.81(0.5H, d, J 12.3Hz), 4.70(0.5H, d, J 12Hz), 4.57(0.5H, d, J 12.0Hz), 4.45(0.5H, d, J 12.3Hz), 3.14(0.5H, td, J 15.0, 4.6Hz), 3.13(0.5H, td, J 10.4, 3.9Hz, 3.9Hz), 2.32-2.17(1H, m), 2.13-2.04(1H, m), 1.70-1.53(2H, m), 1.45-1.11(2H, m), 1.05-0.70[(12H, m, containing 0.92(3H, d, J 6.5Hz), 0.88(3H, t, J = 3.7Hz), 0.773(1.5H, d, J 6.9Hz), 0.771(1.5H, d, J 6.9Hz)].

$^{13}$C NMR (100.62MHz, CDCl$_3$) 225.99, 225.88(q), 225.78, 225.49(q), 90.80, 90.63(CH), 88.50, 88.25(q), 79.31(CH), 75.54, 75.04(CH), 71.93, 71.83(CH$_2$), 48.74, 48.69(CH), 40.82, 40.71(CH$_2$), 34.88, 34.85(CH$_2$), 31.90, 31.86(CH), 25.74, 25.66(CH), 23.52, 23.49(CH$_2$), 22.67(CH$_3$), 21.38, 21.29(CH$_3$), 16.45(CH$_3$).
Cobaltmolybdenumcyclopentadienylpropargylalcoholpentacarbonyl. (32).

To a solution of sodium hydride (0.526g, 13.15mmol) in tetrahydrofuran (75cm³) was added freshly cracked cyclopentadiene (1.54cm³, 17.54mmol). The reaction mixture was stirred for 30 minutes. To the resultant pale pink solution was added molybdenum hexacarbonyl (2.32g, 8.77mmol) and the reaction refluxed for 12 hours. The resultant orange reaction mixture was allowed to cool to room temperature and dicobaltpropargylalcoholhexacarbonyl (3.00g, 8.77mmol) was added as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed and monitored for the disappearance of starting material. Upon disappearance of starting material, the solvent was removed under reduced pressure and the crude residue extracted between dichloromethane and water. The organic phases were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue adsorbed onto silica gel and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether (2:1) as the eluent to yield the title complex as a red solid (2.48g, 67%).

IR(neat) 2049, 1976, 1983cm⁻¹.

¹H 250MHz 5.68(1H, s, H1), 5.45(5H, s, H4), 4.95-4.89(1H, m, H3a), 4.74-4.66(1H, m, H3b) ¹³C 100.16MHz 226.56(q, C5), 226.25(q, C5), 199.87(q, C5), 126.58(CH, C1), 95.55(q, C2), 71.63(CH₂, C3), 63.78(CH, C4).

m/z [FAB], requires 417.8785, obtained 417.8750.
Method B.

To a solution of cobaltmolybdenumcyclopentadienylpropargylalcoholpentacarbonyl (1.618g, 3.8mmol) and L-menthol (1.210g, 7.75mmol) in diethylether (100cm³) with molecular sieves was added a catalytic quantity of tetrafluoroboric acid. The reaction was stirred for 45 minutes and then quenched on the addition of sodium hydrogen carbonate and magnesium sulfate. The crude reaction mixture was filtered through a celite plug and the solvent removed under reduced pressure. The residue was then chromatographed on silica employing light petroleum (bp 40-60°C) as the eluent to yield the racemic title complex as a red oil (1.64g, 78%).

For spectroscopic data see compound 31 method A.

The diastereomeric complexes were separated employing column chromatography utilising hexane/dichloromethane (5:1).

31a Topspot cobaltmolybdenumcyclopentadienylpropargylmenthyletherpentacarbonyl complex.

\[ \begin{align*}
{^1}H \text{ NMR (400MHz, CDCl}_3) & 5.64(1H, s), 5.42(5H, s), 4.69(1H, d, J 12Hz), 4.56(1H, d, J 12Hz), \\
& 3.13(1H, td, J 10.4, 4Hz), 2.29-2.20(1H, m), 2.09(1H, dm, J 14Hz), 1.68-1.58(2H, m), 1.40- \\
& 1.29(1H, m), 1.25-1.21(1H, m), 1.03-0.73[(12H, m, containing 0.92(3H, d J 6.8Hz), 0.88(3H, d J \\ & 6.8Hz), 0.81(3H, d J 6.8Hz)].
\end{align*} \]

\[ \begin{align*}
{^13}C \text{ NMR (100.62MHz, CDCl}_3) & 226.07(q), 225.97(q), 203.89(q), 90.09(CH), 88.54(q), \\
& 79.43(CH), 75.14(CH), 71.94(CH), 48.86(CH), 49.93(CH), 34.99(CH), 31.96(CH), 25.78(CH), \\
& 23.65(CH), 22.77(CH), 21.39(CH), 16.58(CH).
\end{align*} \]

\[ [\alpha]_D = -167(c = 0.103 \text{ in chloroform}) \]
31b Bottomspot cobaltmolybdenumcyclopentadienylpropargylmenthyletherpentacarbonyl complex.

$^{1}H$ NMR (250MHz, CDCl$_3$) 5.68(1H, s), 5.42(5H, s), 4.79(1H, d, J 12.3Hz), 4.45(1H, d, J 12.3Hz), 3.13(1H, td, J 10.6, 4.2Hz), 2.27-2.17(1H, m), 2.09(1H, dm, J 13Hz), 1.67-0.76(16H, m, containing at 0.91(6H, app t, J 6.2Hz), 0.77(3H, d, J 6.9Hz]).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 226.01(q), 225.71(q), 204.19(q), 90.84(CH), 88.40(q), 79.52(CH), 75.76(CH), 72.13(CH$_2$), 48.91(CH), 40.93(CH$_2$), 35.07(CH$_2$), 32.12(CH), 25.97(CH), 23.72(CH$_3$), 22.86(CH$_3$), 21.59(CH$_3$), 16.67(CH$_3$).

C$_{28}$H$_{27}$CoMoO$_6$ requires C 49.83, H 4.91, obtained C 49.12, H 5.02.

$[\alpha]_D = +197$ (c = 0.092 in chloroform.)

4-((5-Methyl)cyclohexyl)oxy)methyltricyclo[5.2.1.0$^{2,6}$]deca-4, 8-dien-3-one. (33a).

To a solution of optically pure first eluting cobaltmolybdenumcyclopentadienylpropargylmenthyl ether (0.197g, 0.35mmol) in toluene (15cm$^3$) was added norbornadiene (0.19cm$^3$, 1.77mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/ethyl acetate (10:1) as the eluent to yield the title compound as a colourless oil (0.067g, 61%).

IR(neat) 1698, 1633cm$^{-1}$.

$^{1}H$ NMR (400MHz, CDCl$_3$) 7.43-7.42(1H, m), 6.29(1H, dd, J 5.6, 3.2Hz), 6.20(1H, dd, J 5.6, 2.8Hz), 4.32(1H, ddd, J 14, 1.6, 1.6Hz), 4.03-3.98(1H, m), 3.12(1H, d, J 14.4, 4Hz), 2.92(1H, s), 2.78-2.77(1H, m), 2.71(1H, s), 2.33(1H, ddd, J 4.8Hz, 1.2, 1.2Hz), 2.29-2.17(1H, md, J 2.8Hz), 2.13(1H, dm, J 12Hz), 1.67-1.58(3H, m), 1.43-1.19(4H, m), 1.01-0.82(8H, m, containing 0.91(6H, t, J 6.4Hz)), 0.77(3H, d, J 7.2Hz).
$^{13}$C NMR (100.62MHz, CDCl$_3$) 209.07(q), 159.66(CH), 148.33(CH), 138.90(CH), 137.47(CH),
80.48(CH), 62.81(CH$_2$), 53.54(CH), 48.60(CH), 48.60(CH), 43.97(CH), 43.36(CH), 41.71(CH$_2$),
40.68(CH$_2$), 34.93(CH$_2$), 31.88(CH), 26.21(CH), 22.69(CH$_3$), 22.69(CH$_3$), 21.27(CH$_2$),
16.77(CH$_3$).

$m/z$ requires 314.2245, obtained 314.2246.


4-({[5-Methyl)cyclohexyl]oxy}methyl)tricyclo[5.2.1.0$^{2,6}$]deca-4, 8-dien-3-one. (33b)

To a solution of optically pure second eluting cobaltmolybdenumcyclopentadienylpargylmenthylether (0.064g, 0.115mmol) in toluene (15cm$^3$) was added norbornadiene (0.062cm$^3$, 0.57cm$^3$), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/ethylacetate (5:1) as the eluent to yield the title compound as a colourless oil (0.036g, 67%).

$^1$H NMR (400MHz, CDCl$_3$) 7.44-7.43(1H, m), 6.29(1H, dd, $J$ 5.6, 3.2Hz), 6.20(1H, dd, $J$ 5.6, 3.2Hz), 4.93(1H, ddd, $J$ 14, 2.0, 2.0Hz), 4.01(1H, ddd, $J$ 14, 1.6, 1.6Hz), 3.12(1H, td, $J$ 14.8, 4Hz), 2.92(1H, s), 2.78-2.77(1H, m), 2.71(1H, s), 2.32(1H, dm, $J$ 5.2Hz), 2.24-2.16(1H, md, $J$ 2.8Hz), 2.15-2.09(1H, dm, $J$ 12Hz), 1.67-1.59(3H, m), 1.43-1.22(4H, m), 1.00-0.82[(8H, m, containing 0.91(6H, t, $J$ 7.2Hz)], 0.77(3H, d, $J$ 6.8Hz).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 209.01(q), 160.59(CH), 148.81(q), 138.87(CH), 137.47(CH),
80.24(CH), 62.40(CH$_2$), 53.48(CH), 48.57(CH), 48.52(CH), 43.95(CH), 43.34(CH), 41.69(CH$_2$),
40.71(CH$_2$), 34.93(CH$_2$), 31.91(CH), 26.18(CH), 23.86(CH$_2$), 22.68(CH$_3$), 21.29(CH$_2$),
16.74(CH$_3$).

To a solution of dicobaltpropargyldimethylether (0.142g, 0.29mmol) in toluene (15cm³) was added norbornadiene (0.15cm³, 1.479mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/ethylacetate (5:1) as the eluent to yield the title compound as a colourless oil (0.078mg, 85%).

$^1$H NMR (400MHz, CDCl₃) 7.36(1H, s), 6.22(1H, dd, J 5.2, 2.8), 6.13(1H, dd, J 5.6, 2.8Hz), 4.25(0.5H, ddd, J 14.0, 2.0, 2.0), 4.23(0.5H ddd, J 14.0, 2.0, 2.0), 3.97-3.90(1H, m), 3.04(1H, td, J 10.4, 4.0Hz), 2.85(1H, s), 2.70(1H, s), 2.64(1H, s), 2.25(1H, dd, J 4.8, 1.2Hz), 2.13(1H, md, J 2.8Hz), 2.07(1H, dm, J 9.6Hz), 1.64-1.52(3H, m), 1.34-1.07(4H, m), 0.93-0.68(11H, m, containing 0.84(6H, t, J 6.4Hz), 0.70(1.5H, d, J 7.2Hz), 0.69(1.5H, d, J 7.2Hz).

$^{13}$C NMR (100.62MHz, CDCl₃) 209.02, 208.96(q), 160.5, 160.20(CH), 148.85, 148.79(q), 138.88, 138.85(CH), 137.44(CH), 80.45, 80.20(CH), 62.79, 62.37(CH₂), 53.51, 53.45(CH), 48.58, 48.55(CH), 48.50(CH), 43.94, 43.93(CH), 43.33, 43.32(CH), 41.69, 41.67(CH₂), 40.69, 40.66(CH₃) 34.91(CH₂), 31.88, 31.86(CH), 26.19, 26.16(CH), 23.84(CH₃), 22.68(CH₃), 21.28, 21.26(CH₃), 16.76, 16.73(CH₃).
Cobaltmolybdenumcylopentadienylpropargylicpentacarbonylcationtetrafluoroborate salt (34a).

To a solution of the topspot cobaltmolybdenumcylopentadienylpropargylicpentacarbonylmenthylether pentacarbonyl (0.500g, 0.90mmol) in diethylether (20cm³) was added hydrofluoroboric acid (0.13cm³, 0.99mmol) which resulted in the immediate precipitation of a fine orange solid. The reaction mixture was stirred for a further 15 minutes. The reaction mixture was filtered and washed extensively with diethylether until the washings remained colourless. The orange solid was dried to yield the title complex as a fine orange powder (0.306g, 70%)

IR (DCM) cm⁻¹ 2100, 2060, 2005, 1975.

¹H NMR (400MHz, CDCl₃) 6.40(1H, s), 5.96(5H, s), 5.43(1H, s), 5.04(1H, s)

m/z [FAB], (M-BF₄⁻) calculated 400.8771, obtained 400.8761.

Top spot [α]₀ = -376(c = 0.138 in acetone.)


Cobaltmolybdenumcylopentadienylpropargylicpentacarbonylcationtetrafluoroborate salt (34b).

To a solution of the bottomspot cobaltmolybdenumcylopentadienylpropargylicpentacarbonylmenthylether pentacarbonyl complex (0.500g, 0.90mmol) in diethylether (20cm³) was added hydrofluoroboric acid (0.13cm³, 0.99mmol) which resulted in the immediate precipitation of a fine orange solid. The reaction mixture was stirred for a further 15 minutes. The reaction mixture was filtered and
washed extensively with diethylether until the washings remained colourless. The orange solid was dried to yield the title complex as a fine orange powder (0.319g, 73%)

Bottom spot $[\alpha]_D = +365$ (c = 0.126 in acetone.)

For remaining spectroscopic data see compound 34a

Cobaltmolybdenumcyclopentadienylproparagylmenthyletherpentacarbonyl. (31a).

Method B

To a solution of the cobalt molybdenum salt originating from the first eluting diastereomer (0.100g, 0.182mmol) in acetone (15cm$^3$) was added L-menthol (0.576g, 3.64mmol) and N-Ethylidiisopropylamine (0.04cm$^3$, 0.23mmol). The reaction mixture was stirred for one hour. Excess sodium hydrogen carbonate was added prior to filtration and the solvent being removed under reduced pressure. The residue was chromatographed using silica gel as absorbent and light petroleum (bp 40-60°C)/diethyl ether as eluent to yield the title complex (0.070g, 69%) as a red oil.

For spectroscopic data see compound 31a. Method A.
Cobaltmolybdenumcyclopentadienylproparagylmenthyletherpentacarbonyl. (31b).

Method B
To a solution of the cobalt molybdenum salt originating from the second eluting diastereomer (0.100g, 0.182mmol) in acetone (15cm$^3$) was added L-menthol (0.576g, 3.64mmol) and N-Ethyldiisopropylamine (0.04cm$^3$, 0.23mmol). The reaction mixture was stirred for one hour. Excess sodium hydrogen carbonate was added prior to filtration and the solvent being removed under reduced pressure. The residue was chromatographed using silica gel as absorbent and light petroleum (bp 40-60°C)/diethyl ether as eluent to yield the title complex (0.070g, 69%) as a red oil.

For spectroscopic data see compound 31b. Method A

Cobaltmolybdenumcyclopentadienyl-(prop-2-ynyloxy)benzene. (35a/b).

To a solution of the cobalt molybdenum salt (0.100g, 0.182mmol) in acetone (15cm$^3$) was added phenol (342mg, 3.64mmol) and N-Ethyldiisopropylamine (0.04cm$^3$, 0.23mmol). The reaction mixture was stirred for one hour. Excess sodium hydrogen carbonate was added prior to filtration and the solvent being removed under reduced pressure. The residue was chromatographed using silica gel as absorbent and light petroleum (bp 40-60°C)/diethyl ether (10:1) as eluent to yield the title complex (0.053g, 60%) as a red oily solid.

IR(neat) 2051, 1981, 1940, 1598, 1586cm$^{-1}$. 

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\textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}) 7.28-7.27(2H, m, Ar), 6.94-6.89(3H, m, Ar), 5.70(1H, s, H1), 5.42(5H, s, H8), 5.22(1H, d, J 12.4Hz, H3a), 5.10(1H, d, J 12.4Hz, H3b).

\textsuperscript{13}C NMR (100.62MHz, CDCl\textsubscript{3}) 225.30(q, C9), 225.04(q, C9), 158.86(q, C4) 129.89(CH, C5), 121.28(CH C6), 115.03(CH, C7), 90.74(CH, C8), 84.19(q, C2), 76.89(CH, C1), 71.98(CH\textsubscript{2}, C3).

\textit{m/z} [FAB] Requires 493.9103, obtained 493.9103.

Top spot [\(\alpha\)\textsubscript{D} = -380.9(c = 0.10 in chloroform.)

Bottom spot [\(\alpha\)\textsubscript{D} = +368.5(c = 0.14 in chloroform.)

**Cobaltmolybdenumcyclopentadienylpropynepentacarbonyl (36a/b).**

![Cobaltmolybdenumcyclopentadienylpropynepentacarbonyl](image)

To a solution of the cobalt molybdenum salt (0.200g, 0.365mmol) in dichloromethane (20cm\textsuperscript{3}) in the presence of molecular sieves at -40°C was added borane-methyl sulfide complex (1.0M solution in dichloromethane)(0.36mmol, 0.36cm\textsuperscript{3}), the reaction mixture was stirred for 12 hours. The reaction was quenched with ethanol at -40°C and allowed to attain room temperature prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (10:1) as the eluent to yield the title complex as a red oil (0.102g, 70%).

IR(neat) 2046, 1975, 1932, 1882cm\textsuperscript{-1}.

\textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}) 5.47(1H, s, H1), 5.31(5H, s, H4), 2.59(3H, s, H3).

\textsuperscript{13}C NMR (100.62MHz, CDCl\textsubscript{3}) 227.30(q, C5), 225.88(q, C5), 91.04(CH, C4), 90.37(q, C2), 73.61(CH, C1), 21.57(CH\textsubscript{3}, C3).

Top spot [\(\alpha\)\textsubscript{D} = 117.1(c = 0.140 in chloroform.)

Bottom spot [\(\alpha\)\textsubscript{D} = -125.9(c = 0.108 in chloroform.)
4-[(phenyloxy)methyl]tricyclo[5.2.1.0²,0]deca-4,8-dien-3-one. (37a/b).

To a solution of cobaltmolybdenumcyclopentadienylphenolacetylene (0.300 g, 0.6 mmol) in toluene (15 cm³) was added norbornadiene (1.29 cm³, 12 mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound (0.071 g, 48%).

IR (dcm) 2051, 1981, 1940, 1598, 1586 cm⁻¹.

Mp = 85-87°C.

¹H NMR (400 MHz, CDCl₃) 7.54-7.53 (1H, m, H3), 7.31-7.30 (2H, Ar), 6.99-6.89 (3H, m, Ar), 6.30 (1H, dd, J 5.6 Hz, 2.8 Hz, H7 or H6), 6.22 (1H, dd, J 5.6 Hz, 3.2 Hz, H7 or H6), 4.73 (2H, t, J 2 Hz, H11), 2.96 (1H, s, H8 or H5), 2.82-2.81 (1H, m, H4), 2.72 (1H, s, H8 or H5), 2.83 (1H, dt, J 5.2, 1.6 Hz, H10), 1.43-1.39 (1H, m, H9a), 1.25 (1H, d, J 9.2 Hz, H9b)

¹³C NMR (100.62 MHz, CDCl₃) 208.57 (q, C1), 161.38 (CH, C3), 158.63 (q, C2), 146.55 (q, C12), 138.90 (CH, C7 or C6), 137.50 (CH, C7 or C6), 129.91 (CH, C13), 121.54 (CH, C14), 114.98 (CH, C15), 62.28 (CH₂, C11), 53.53 (CH, C8 or C5), 48.76 (CH, C4), 44.44 (CH, C8 or C5), 44.06 (CH, C10), 41.70 (CH₂, C9).

m/z requires 252.1150, obtained 252.1148

Top spot [α]D = 60.3 (c = 1.48 in chloroform).
Bottom spot [α]D = -56.8 (c = 0.5 in chloroform.)
To a solution of cobaltmolybdenumcyclopentadienylpropynepentacarbonyl (0.270 g, 0.67 mmol) in toluene (15 cm³) was added norbornadiene (1.47 cm³, 13.43 mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (5:1) as the eluent to yield the title compound (0.086 mg, 80%).

IR (neat) 1697 cm⁻¹.

¹H NMR (400 MHz, CDCl₃) 7.12 (1H, d, J 1.2 Hz), 6.19 (1H, dd, J 5.6, 3.2 Hz), 6.12 (1H, dd, J 5.6, 2.8 Hz), 2.83 (1H, s), 2.63 (1H, s), 2.59 (1H, s), 2.19 (1H, dd, J 5.2, 1.2 Hz), 1.70-1.69 (3H, m), 1.31-1.28 (1H, m), 1.14-1.11 (1H, m).

¹³C NMR (100.62 MHz, CDCl₃) 210.49 (q), 159.96 (CH), 146.53 (q), 138.70 (CH), 137.36 (CH), 52.62 (CH), 47.98 (CH), 44.02 (CH), 43.29 (CH), 42.01 (CH₂), 10.71 (CH₃).

m/z Requires 160.0881, observed 160.0887.

Top spot [α]D = 144.9 (c = 0.73 in chloroform.)
Bottom spot [α]D = -138.8 (c = 1.15 in chloroform.)

To a solution of the cobaltmolybdenum cyclopentadienylpropargylicpentacarbonyl complex (0.650g, 1.17mmol) in diethylether (20cm³) was added hydrofluoroboric acid (0.143cm³, 1.17mmol) which resulted in the immediate precipitation of a fine orange solid. The reaction mixture was stirred for a further 15 minutes. The reaction mixture was filtered and washed extensively with diethylether until the washings remained colourless. The orange solid was dried to yield the title complex as a fine orange powder (0.444g, 78%)

For relevant spectroscopic data see compound 34a.

Cobaltmolybdenumcyclopentadienyll-(prop-2-ynyloxy)benzene. (35).

To a solution of the cobalt molybdenum salt (0.200g, 0.41mmol) in acetone (15cm³) was added phenol (0.771mg, 8.2mmol) and N-Ethylidiisopropylamine (0.91cm³, 0.52mmol). The reaction mixture was stirred for one hour. Excess sodium hydrogen carbonate was added prior to filtration and the solvent being removed under reduced pressure. The residue was chromatographed using silica gel as absorbent and light petroleum(bp 40-60°C)/diethyl ether (10:1) as eluent to yield the title complex (0.127g, 63%) as a red oily solid.

IR(neat) 2051, 1981, 1940, 1598, 1586cm⁻¹.

¹H NMR (400MHz, CDCl₃) 7.28-7.27(2H, m, Ar), 6.94-6.89(3H, m, Ar), 5.70(1H, s, H1), 5.42(5H, s, H8), 5.22(1H, d, J 12.4Hz, H3a), 5.10(1H, d, J 12.4Hz, H3b ).
$^{13}$C NMR (100.62MHz, CDCl$_3$) 225.30(q, C9), 225.04(q, C9), 158.86(q, C4) 129.89(CH, C5), 121.28(CH C6), 115.03(CH, C7), 90.74(CH, C8), 84.19(q, C2), 76.89(CH, C1), 71.98(CH$_2$, C3).

$m/z$ [FAB] Requires 493.9103, obtained 493.9103.

**Cobaltmolybdenumcyclopentadienylpropynepentacarbonyl.** (36).

![Diagram of cobaltmolybdenumcyclopentadienylpropynepentacarbonyl](image)

To the cobaltmolybdenumcyclopentadienylpentacarbonylsalt (0.150g, 0.31mmol) in dichloromethane (20cm$^3$) in the presence of molecular sieves at −40°C was added borane-methyl sulfide complex (1.0M solution in dichloromethane)(0.31mmol, 0.31cm$^3$), the reaction mixture was stirred for 12 hours. The reaction was quenched with ethanol at −40°C and allowed to attain room temperature prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (10:1) as the eluent to yield the title complex as a red oil. (0.085g, 69%).

IR(neat) 2046, 1975, 1932, 1882cm$^{-1}$.

$^1$HNMR (400MHz, CDCl$_3$) 5.47(1H, s, H1), 5.31(5H, s, H4), 2.59(3H, s, H3).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 227.30(q, C5), 225.88(q, C5), 91.04(CH, C4), 90.37(q, C2), 73.61(CH, C1), 21.57(CH$_2$, C3).

**4-[(phenyloxy)methyl]tricyclo[5.2.1.0$^{2,6}$]deca-4,8-dien-3-one.** (37).

![Diagram of 4-[(phenyloxy)methyl]tricyclo[5.2.1.0$^{2,6}$]deca-4,8-dien-3-one](image)

To a solution of cobaltmolybdenumcyclopentadienylphenolacetylenepentacarbonyl (0.210g, 0.43mmol) in toluene (15cm$^3$) was added norbornadiene (0.86cm$^3$, 8.6mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined
and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound (0.051g, 47%). IR(dcm) 2051, 1981, 1940, 1598, 1586 cm⁻¹.

Mp = 85-87°C.

1H NMR (400MHz, CDCl₃) 7.54-7.53(1H, m, H3), 7.31-7.30(2H, Ar), 6.99-6.89(3H, m, Ar), 6.30(1H, dd, J 5.6Hz, 2.8Hz, H7 or H6), 6.22(1H, dd, J 5.6Hz, 3.2Hz, H7 or H6), 4.73(2H, t, J 2Hz, H11), 2.96(1H, s, H8 or H5), 2.82-2.81(1H, m, H4), 2.72(1H, s, H8 or H5), 2.83(1H, dt, J 5.2, 1.6Hz, H10), 1.43-1.39(1H, m, H9a), 1.25(1H, d, J 9.2Hz, H9b)

13C NMR (100.62MHz, CDCl₃) 208.57(q, C1), 161.38(CH, C3), 158.63(q, C2), 146.55(q, C12), 138.90(CH, C7 or C6), 137.50(CH, C7 or C6), 129.91(CH, C13), 121.54(CH, C14), 114.98(CH, C15), 62.28(CH₂, C11), 53.53(CH, C8 or C5), 48.76(CH, C4), 44.44(CH, C8 or C5), 44.06(CH, C10), 41.70(CH₃, C9).

m/z requires 252.1150, obtained 252.1148

4-Methyltricyclo[5.2.1.0²,6]deca-4,8-dien-3-one. (38).

To a solution of cobaltmolybdenumcyclopentadienylpropynepentacarbonyl (0.310g, 0.77mmol) in toluene (15cm³) was added norbornadiene (1.66cm³, 15.4mmol), the reaction mixture was heated to 65°C and monitored for the disappearance of starting material. The reaction mixture was extracted between diethyl ether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (5:1) as the eluent to yield the title compound (101mg, 82%).

IR(neat) 1697 cm⁻¹.

1H NMR (400MHz, CDCl₃) 7.12(1H, d, J 1.2Hz), 6.19(1H, dd, J 5.6, 3.2Hz), 6.12(1H, dd, J 5.6, 2.8Hz), 2.83(1H, s), 2.63(1H, s), 2.59(1H, s), 2.19(1H, dd, J 5.2, 1.2Hz), 1.70-1.69(3H, m), 1.31-1.28(1H, m), 1.14-1.11(1H, m).
I\(^{13}\)C NMR (100.62MHz, CDCl\(_3\)) 210.49(q), 159.96(CH), 146.53(q), 138.70(CH), 137.36(CH), 52.62(CH), 47.98(CH), 44.02(CH), 43.29(CH), 42.01(CH\(_2\)), 10.71(CH\(_3\)).

Acc Mass Requires 160.0881, observed 160.0887.


4-[(phenyloxy)methyl]tricyclo[5.2.1.0\(^2,6\)]deca-4,8-dien-3-one 2R, 3R-(-)-2,3-butanediol ketal.

To a solution of the cyclopentenone (0.070g, 0.28mmol) in benzene was added a catalytic quantity of camphorsulfonic acid and a single drop of a Pasteur pipette of (2R,3R)-(-)-2,3-butanediol. The reaction was refluxed under Dean-Stark conditions for four days. The crude reaction mixture was adsorbed onto silica and chromatographed employing light petroleum(bp 40-60\(^\circ\)C)/diethyl ether (8:1) to yield the title compound as a clear colourless oil (0.004g, 4%).

IR 3058, 2970, 2872, 1087cm\(^{-1}\).

\(^1\)H NMR (400MHz, CDCl\(_3\)) 7.28-7.24(2H, m, Ar), 6.95-6.90(3H, m, Ar), 6.13-6.10(2H, m, H7, H6), 5.95-5.93(1H, m, H3), 4.67-4.58(2H, m, H11), 3.68-3.58(2H, m, H16, H17), [2.86(1H, s), 2.73(0.3H, br s), 2.66-2.61(0.7H, br m), 2.56(1H, s), 2.21(0.3H, d, J 6.4Hz), 2.07(0.7H, d, J 6.4Hz), H9, H4, H8, H5], 1.47-1.43(1H, m, H10a), [1.32-1.26(3H, d, J 5.2Hz), 1.27(3H, d, J 5.6Hz), H10b, H18, H19].

\(^13\)C NMR (100.62MHz, CDCl\(_3\)) 159.22(q, Cl), 143.27, 138.30(q, C12), 138.47, 138.30(CH, C7 or C6), 137.67, 137.56(CH, C7 or C6), 136.21, 136.19(CH, C3), 129.71(CH, C13), 121.00, 120.98(CH, C14), 116.40, 116.16(q, C2), 115.13, 115.11(CH, C15), 80.26, 79.88(CH, C16 or C17), 79.47, 78.01(CH, C16 or C17), 63.61, 63.48(CH\(_2\), C11), [53.95, 53.89(CH), 50.97, 50.82(CH), 44.11, 44.06(CH), 42.11(CH), C9, C4, C8, C5], 43.06, 42.85(CH\(_2\), C10), 17.58, 17.23(CH\(_3\), C18 or C19), 16.72, 16.29(CH\(_3\), C18 or C19).

m/z requires 342.1725, obtained 324.1731.
To a solution of the cyclopentenone (0.120g, 0.75mmol) in benzene (15cm³) was added a catalytic quantity of camphorsulfonic acid and a single drop via a Pasteur pipette of (2R,3R)-(−)-2,3-butanediol. The reaction was refluxed under Dean-Stark conditions for four days. The crude reaction mixture was adsorbed onto silica and chromatographed employing light petroleum (bp 40–60°C)/diethyl ether (7:1) to yield the title compound as a clear colourless oil (0.005g, 3%).

IR 3057, 2969, 2918, 1089cm⁻¹.

1H NMR (400MHz, CDCl₃) 6.04(2H, s, H6 and H7), 5.51(1H, br s, H3), 3.63-3.51(2H, m, H12 and H13), 2.74(0.65H, s), 2.62(0.35H, s), 2.47(2H, m), 2.05(0.35H, d, J 6.8Hz), 1.91(0.65H, d, J 6.8Hz), H10, H4, H8, H5), 1.60(3H, br d, J 1.2Hz, H11), [1.24-1.12(8H, m, containing 1.23(3H, d, J 5.6Hz), H9, H14, H15).

13C NMR (100.62MHz, CDCl₃) 142.81, 142.09(q, C1), 136.98, 136.77(CH, C7 or C6), 136.19, 136.06(CH, C7 or C6), 132.87, 132.60(CH, C3), 115.47, 115.28(q, C2), 78.83, 78.40(CH, C12 or C13), 76.43, 78.27(CH, C12 or C13), [51.79(CH), 49.20, 49.08(CH), 42.83, 42.76(CH), 42.21(CH), C10, C4, C8, C5) 41.61, 41.36(CH₂, C9), 16.329, 15.89(CH₃, C14 or C15), 15.34, 14.92(CH₃, C14 or C15), 10.29, 9.95(CH₃, C11).

m/z requires 232.1463, found 232.1458.
4-[(phenyloxy)methyl]tricyclo[5.2.1.0²⁶]deca-4,8-dien-3-one 2R, 3R-(-)-2,3-butanediol ketal.

From first eluting optically pure cobaltmolybdenumcyclopentadienylpropargyl menthyletherpentacarbonyl.

To a solution of the cyclopentenone (0.040g, 0.15mmol) in benzene was added a catalytic quantity of camphorsulfonic acid and a single drop via a Pasteur pipette of (2R,3R)-(-)-2,3-butanediol. The reaction was refluxed under Dean-Stark conditions for four days. The crude reaction mixture was adsorbed onto silica and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether (8:1) to yield the title compound as a clear colourless oil (0.002g, 4%).

$^1$H NMR (400MHz, CDCl$_3$) 7.29-7.24(2H, m), 6.95-6.91(3H, m), 6.13(1H, dd, $J$ 5.6, 2, H6 or H7), 6.12(1H, dd, $J$ 5.6, 2.8Hz, H6 or H7), 5.95-5.92(1H, m, H3), 4.61 (2H, s, H11), 3.72-3.65(1H, m, H16 or H17), 3.63-3.56(1H, m, H16 or H17), [2.73(1H, s), 2.68-2.63(1H, m), 2.56(1H, s), 2.21-2.19(1H, m), H9, H4, H8, H5], 1.47-1.45(1H, m, H10a), 1.33-1.26(7H, m, containing 1.30(3H, d, $J$ 6.0Hz), 1.26(3H, d, $J$ 6.0Hz), H10b, H18, H19).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 158.83(q, C1), 142.91(q, C12), 138.11(CH, C7 or C6), 137.20(CH, C7 or C6), 135.82(CH, C3), 129.36(CH, C13), 120.64(CH, C14), 116.04(q, C2), 114.75(CH, C15), 79.52(CH, C16 or C17), 79.11(CH, C16 or C17), 63.25(CH$_3$, C11), [53.53(CH), 50.47(CH), 43.70(CH), 42.70(CH$_3$), 41.75(CH), C9, C4, C8, C5, C10], 17.23(CH$_3$, C18, or C19), 16.37(CH$_3$, C18 or C19).

From second eluting optically pure cobaltmolybdenumcyclopentadienylpropargyl menthyletherpentacarbonyl (39b).

To a solution of the cyclopentenone (0.040g, 0.16mmol) in benzene was added a catalytic quantity of camphorsulfonic acid and a single drop via a Pasteur pipette of (2R,3R)-(-)-2,3-butanediol. The reaction was refluxed under Dean-Stark conditions for four days. The crude reaction mixture was adsorbed onto silica and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether (8:1) to yield the title compound as a clear colourless oil (0.003g, 6%).
From second eluting optically pure cobaltmolybdenum cyclopentadienylpropargyl menthyletherpentacarbonyl.

To a solution of the cyclopentenone (0.072 g, 0.45 mmol) in benzene was added a catalytic quantity of camphorsulfonic acid and a single drop via a Pasteur pipette of (2R,3R)-(-)-2,3-butanediol. The reaction was refluxed under Dean-Stark conditions for four days. The crude reaction mixture was adsorbed onto silica and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether (8:1) to yield the title compound as a clear colourless oil (0.005 g, 5%).

$^1$H NMR (400 MHz, CDCl$_3$) 6.13 (1H, dd, $J$ 5.6, 2.8 Hz, H6 or H7), 5.09 (1H, dd, $J$ 5.6 Hz, 2.8 Hz, H6 or H7), 3.70-3.54 (2H, m, H12 and H13), 2.10 (1H, d, $J$ 6.4 Hz, H14, H4, H8, H5), 1.67 (3H, t, $J$ 1.6 Hz, H11), 1.43-1.19 (8H, m, containing 1.31 (1H, d, $J$ 5.6 Hz), 1.26 (3H, d, $J$ 5.6 Hz), H14, H15, H9).

$^{13}$C NMR (100.62 MHz, CDCl$_3$) 143.77 (q, C1), 137.46 (CH, C7 or C6), 134.03 (CH, C3), 116.85 (q, C2), 79.77 (CH, C12 or C13), 79.64 (CH, C12 or C13), 53.12 (CH), 50.46 (CH), 44.13 (CH), 42.99 (CH2), 42.04 (CH), C10, C4, C8, C5, C9] 17.69 (CH3, C14 or C15), 16.73 (CH3, C14 or C15), 11.72 (CH3, C11).
From second eluting optically pure cobalt(molybdenum)cyclopentadieny1propargylmenthyletherpentacarbonyl. (40b).

To a solution of the cyclopentenone (0.090g, 0.56mmol) in benzene was added a catalytic quantity of camphorsulfonic acid and a single drop via a Pasteur pipette of (2R,3R)-(−)-2,3-butanediol. The reaction was refluxed under Dean-Stark conditions for four days. The crude reaction mixture was adsorbed onto silica and chromatographed employing light petroleum(bp 40-60°C)/diethyl ether (8:1) to yield the title compound as a clear colourless oil (0.002g, 2%).

$^1$H NMR (400MHz, CDCl$_3$) 6.11-6.09(2H, m, H6 and H7), 5.59(1H, s, H3), 3.70-3.56(2H, m, H12 and H13), [2.81(1H, s), 2.56-2.53(2H, m), 1.98(1H, dm, $J$ 6.4Hz), H10, H4, H8, H5], 1.68(3H, t, $J$ 2Hz, H11). 1.38-1.19[(8H, m, containing 1.31(3H, d, $J$ 5.6Hz), 1.27(3H, d, $J$ 6Hz), H14, H15, H9).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 143.41(q, C1), 138.18(CH, C7 or C6), 137.59(CH, C7 or C6), 134.31(CH, C3), 116.63(q, C2), 80.23(CH, C12 or C13), 77.81(CH, C12 or C13), [53.14(CH), 50.58(CH), 44.21(CH), 43.58(CH), C10, C4, C8, C5], 42.74(CH$_2$, C9), 17.31(CH$_3$, C14 or C15), 16.32(CH$_3$, C14 or C15), 11.37(CH$_3$, C11).

2-({S-methyl-2-(1-methylethyl)cyclohexyl]oxy}-methyl)-13a, 4, 5, 6, 6a-hexahydropentalen-1-one. (41).

To a of solution dicobaltpropargy1menthyletherhexacarbonyl (0.200mg, 0.36mmol) in toluene (15cm$^3$) was added cyclopentene (0.64cm$^3$). The reaction mixture was heated at 40°C and monitored for the disappearance of starting material. After 4 days the reaction mixture was allowed to cool and extracted between diethyl ether and water. The organic fractions were combined and dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was chromatographed on silica gel employing light petroleum (bp
40-60°C/diethyl ether (4:1) as the eluent to yield the title compound as a colourless oil (0.033g, 31%).

13C suggested a 7% d.e.

IR(neat) 1702, 1642 cm⁻¹.

1H NMR (400MHz, CDCl₃) 7.39(1H, s, H7), 4.33-4.27(1H, m, H9a), 4.03-3.97(1H, m, H9a), 3.28(1H, s, H6), 3.11(1H, td, J 10.4, 3.2Hz, H10), 2.76(1H, app dd, J 8.8Hz, 6Hz, H2), 2.26-2.17(1H, m, H16), 2.12(1H, dm, J 12Hz, H15e), 1.90(1H, app dd, J 12.8, 6.4Hz, H3e), 1.76-1.56(5H, m, H5ea, 4e, 11e, 14e), 1.40-1.30(1H, m, H12), 1.29-1.16(3H, m, H4a, 17, 3a), 0.97-0.96(1H, m, H14a), 0.905(3H, app t, J 6.4Hz, H18), 0.902(3H, app, t, J 6.4Hz, H19), 0.85-0.80(2H, m, H15a, 11a), 0.77(3H, br d, J 13.6Hz, H13).

13C NMR (100.62MHz, CDCl₃) 212.06, 212.01(q, Cl), 162.28, 161.97(CH, C7), 144.93, 144.88(q, C8), 80.34, 80.12(CH, C10), 62.86, 62.45(CH₂, C9), 51.08, 51.06(CH, C2), 48.58, 44.80(CH, C17), 44.85, 44.80(CH, C6), 40.71, 40.68(CH₂, C15), 34.92(CH₂, C11), 31.88, 31.85(CH, C12), 30.41(CH₂, C3), 29.83, 29.80(CH₂, C5), 26.17, 26.15(CH, C16), 24.04, 24.03(CH₂, C4), 23.85(CH₂, C14), 22.68(CH₃, C19), 21.27(CH₃, C18), 16.74(CH₃, C13).

m/z [EI], requires, 290.2245, obtained 290.2245.

2-((5-methyl-2-(1-methylethyl)cyclohexyl)oxy)-methyl-13a, 4, 5, 6, 6a-hexahydro pentalen-1-one. (41a).

From first eluting optically pure cobaltmolybdenumcyclopentadienylpropargyl menthyletherpentacarbonyl.

To a solution of the first eluting optically pure cobaltmolybdenumcyclopentadienylpropargyl menthyletherhexacarbonyl (0.198g, 0.357mmol) in toluene(15cm³) was added cyclopentene (2.00cm³, 22.69mmol). The reaction mixture was heated at 40°C and monitored for the disappearance of starting material. After 4 days the reaction mixture was allowed to cool and
extracted between diethyl ether and water. The organic fractions were combined and dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether (4:1) as the eluent to yield the title compound as a colourless oil (0.030g, 29%).

$^{13}$C suggested a d.e with a magnitude of approximately 60%

$^1$H NMR (400MHz, CDCl$_3$) 7.39(1H, d, $J$ 1.2Hz, H7), 4.33-4.27(1H, m, H9a), 4.03-3.89(1H, m, H9b), 3.31-3.23(1H, m, H6), 3.11(1H, td, $J$ 10.4, 4.0Hz, H10), 2.77(1H, td, $J$ 5.6Hz, 5.6Hz, H2) 2.27-2.17(1H, m, H16), 2.12(1H, dm, $J$ 12Hz, H15e), 1.90(1H, dt, $J$ 6.4Hz, 6.4Hz, H3e), 1.75-1.55(5H, m, H5ea, 4e, 11e 14e), 1.41-1.31(1H, m, H12), 1.29-1.15(3H, m, H4a, 17, 3a), 1.00-0.96(1H, m, H14a), 0.91(6H, app t, $J$ 6.4Hz, H19, 18), 0.87-0.81(2H, m, H15a, 11a), 0.77(3H, d, $J$ 6.8Hz, H13).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 211.77, 211.72(q, C1), 161.95, 161.64(CH, C7), 144.59, 144.53(q, C8), 80.05, 79.79(CH, C10), 62.53, 61.12(CH$_2$, C9), 50.74, 50.67(CH, C2), 48.24, 48.19(CH, C17), 44.50, 44.46(CH, C6), 40.33, 40.02(CH$_2$, C15), 34.34, 34.45(CH$_2$, C11), 31.51(CH, C12), 30.34, 30.07(CH$_2$, C3), 29.71-29.64(CH$_2$, C5), 25.82, 25.68(CH, C16), 23.68, 23.49(CH$_3$, C4), 22.33(CH$_2$, C14), 20.91(CH$_3$, C19), 16.39, 16.22(CH$_3$, C18), 14.12(CH$_3$, C13).

$[\alpha]_D$ = -56.0(c = 1.09 in chloroform.)

2-({(5-methyl-2-(1-methylethyl)cyclohexyl)oxy}-methyl)-13a, 4, 5, 6, 6a-hexahydropentalen-1-one. (41b).

From second eluting optically pure cobaltmolybdenumcyclopentadienylpropargylmenthyletherpentacarbonyl.

To a solution of the second eluting optically pure cobaltmolybdenumcyclopentadienylpropargylmenthyletherpentacarbonyl (0.160g, 0.29mmol) in toluene (15cm$^3$) was added cyclopentene (2.45cm$^3$, 27.87mmol). The reaction mixture was heated at 40°C and monitored for
the disappearance of starting material. After 4 days the reaction mixture was allowed to cool and 
extracted between diethyl ether and water. The organic fractions were combined and dried over 
magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue 
was chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethyl ether(4:1) as 
the eluent to yield the title compound as a colourless oil (0.023g, 27%).

$^{13}$C suggested a d.e with a magnitude of approximately 60%

$^1$H NMR (400MHz, CDCl$_3$) 7.39(1H, s, H7), 4.33-4.27(1H, m, H9a), 4.03-3.90(1H, m, H9b),
3.28-3.32(1H, m, H6), 3.11(1H, td, J 10.4, 4Hz, H10), 2.77(1H, app dd, J 9.6Hz, 5.6Hz, H2),
2.27-2.16(1H, m, H16), 2.12(1H, dm, J 12Hz, H15e), 1.91(1H, app dd, J 12.4, 6.0Hz, H3e), 1.76-
1.58(5H, m, H5ea, 4e, 11e, 14e), 1.40-1.29(1H, m, H12), 1.28-1.17(3H, m, H4a, 17, 3a),
0.98(1H, br dd, J 12.8, 3.2Hz, H14a), 0.91(6H, app t, J 6.4Hz, H17, 18), 0.87-0.80(2H, m, H15a,
11a), 0.77(0.75H, d, J 6.8Hz, approx , H13), 0.76(2.25H, d, J 6.8Hz, H13).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 212.13, 212.07(q, C1), 162.31, 162.00(CH, C7), 144.95,
144.89(q, C8), 80.41, 80.15(CH, C10), 62.88, 62.48(CH$_2$, C9), 51.10, 51.04(CH, C2), 48.60,
48.56(CH, C17), 44.87, 44.82(CH, C6), 40.72, 40.69(CH$_3$, C15), 34.93, 34.82(CH$_3$, C11), 31.90,
31.87(CH, C12), 30.42(CH$_2$, C3), 29.84, 29.81(CH$_3$, C5), 26.17, 26.04(CH, C16), 24.06(CH$_2$,
C4), 23.86(CH$_2$, C14), 22.68(CH$_3$, C19), 21.28(CH$_3$, C18), 16.75(CH$_3$, C13).

$\alpha_\text{D} = -9.8$ (c = 2.14 in chloroform.)

Cobaltmolybdenumcyclopentadienylphenylacetylenepentacarbonyl. (17).

Method B
To a solution of the molybdenumcyclopentadienyltricarbonyl anion (-0.250g, 0.93mmol) in 
terahydrofuran was added phenylacetylene (0.388g, 1.86mmol), the reaction was refluxed and 
monitored for Fromation of the desired complex. When thin layer chromatography suggested that 
the reaction would proceed no further the solvent was removed under reduced pressure and the 
crude residue extracted between dichloromethane and water. The organic phases were combined
and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue adsorbed onto silica gel and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether (10:1) as the eluent to yield the title complex as a red oily solid (0.120g, 28%).

For spectroscopic data see compound 17. Method A.

Dicobalt but-2-ynalhexacarbonyl. (42).

To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynalpentacarbonyl (1.00g, 2.33mmol) in dichloromethane was added a catalytic quantity of pTSA and water (0.5cm³). The reaction was stirred vigorously for 3 hours. The reaction mixture was quenched by addition of excess sodium hydrogen carbonate and dried by addition of magnesium sulfate. The crude reaction mixture was filtered through a plug of celite and the solvent removed under reduced pressure to yield the title complex as a red oil (0.778g, 98%).

IR(neat) 2100, 2058, 2054, 1699cm⁻¹.

¹H NMR (250MHz, CDCl₃) 10.30(1H, s, H4), 2.74(3H, s, H1).

¹³C NMR (250MHz, CDCl₃) 197.95(q, C5), 190.69(CH, C4), 94.92(q, C3), 87.53(q, C2), 20.57(CH₃, C1).

m/z [FAB], calculated 353.8921, obtained 353.8921.
Dicobalt 4-octynehexacarbonyl (43).

\[
\begin{align*}
\text{OC} & \quad \text{C} \quad \text{C} \\
\text{CO} & \quad \text{CO} \quad \text{CO} \\
\end{align*}
\]

To a solution of dicobaltoctacarbonyl (5g, 4.38mmol) in light petroleum was added 4-octyne (0.64 cm\(^3\), 4.38mmol). The reaction was stirred for 12 hours. The reaction mixture was filtered through a plug of celite and the solvent removed under reduced pressure to yield the title complex as a red oil (1.63g, 94%).

IR (neat) 2086, 2042, 2011 cm\(^{-1}\).

\(^1\)H NMR (400MHz, CDCl\(_3\)) 2.83-2.79(4H, m, H3), 1.71-1.62(4H, m, H2), 1.07(6H, t, J 7.6Hz, H1).

\(^{13}\)C NMR (100.62MHz, CDCl\(_3\)) 200.39(q, C5), 99.62(q, C4), 36.32(CH\(_2\), C3), 25.01(CH\(_3\), C2), 14.22(CH\(_3\), C1).

\(m/z\) Submitted to ESPRC National Mass Spectrometry Service Centre Swansea. No molecular ion found.

Dicobalthex-3-yn-2-onehexacarbonyl (44).

\[
\begin{align*}
\text{OC} & \quad \text{C} \quad \text{C} \\
\text{CO} & \quad \text{CO} \quad \text{CO} \\
\end{align*}
\]

To a solution of dicobaltoctacarbonyl (1.78g, 5.21mmol) in light petroleum was added acetylene (0.56cm\(^3\), 5.21mmol). The reaction was stirred for 12 hours. The reaction mixture was filtered through a plug of celite and the solvent removed under reduced pressure to yield the title complex as a dark red solid (2.04g, 66%).

\(^1\)H NMR (250MHz, CDCl\(_3\)) 2.88(4H, q, J 7.4Hz, H2), 2.44(3H, s, H6), 1.30(3H, t, J 7.4Hz, H6)
Cobaltmolybdenumcyclopentadienylbut-2-ynalpentacarbonyl. (45).

To a solution of the dimolybdenumdicyclopentadienylhexacarbonyl (1.43g, 2.92mmol) in tetrahydrofuran (100cm³) was added L-selectride, (1M soln. tetrahydrofuran) (7.30cm³, 7.30mmol). The reaction mixture was stirred for 1 hour. To the resultant orange solution was added dicobalt 2-butyn-1-al diethyl acetal hexacarbonyl (2.50g, 5.84mmol) as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed for 1 hour. Upon reaction completion the reaction mixture was adsorbed on to silica gel and chromatographed using light petroleum(bp 40-60°C)/diethyl ether (2:1) as eluent to yield the title complex as a red solid (1.47g 59%).

IR(neat) 2057, 1996, 1946, 1648cm⁻¹.

¹H 400MHz 10.11(1H, s, H4), 5.43(5H, s, H5), 2.78(3H, s, H1).

¹³C 100.16MHz 224.22(q, C6), 222.70(q, C6), 193.99(CH, C4), 99.97(q, C3), 90.94(CH, C5), 82.65(q, C2), 21.46(CH₃, C1)

m/z [FAB], requires 429.8788, obtained 429.8788.

C₁₄H₉CoMoO₅ requires C 39.28, H 2.12, obtained C 38.76, H 2.12.

Cobaltmolybdenumcyclopentadienyl4-octynepentacarbonyl. (46).

To a solution of the dimolybdenumdicyclopentadienylhexacarbonyl (0.617g, 1.26mmol) in tetrahydrofuran (100cm³) was added L-selectride, (1M soln. tetrahydrofuran) (3.15cm³, 3.5mmol). The reaction mixture was stirred for 1 hour. To the resultant orange solution was added dicobalt 4-octynehexacarbonyl (1.00g, 2.52mmol) as a solution in a minimal volume of
tetrahydrofuran. The reaction mixture was refluxed for 1 hour. Upon reaction completion the reaction mixture was adsorbed on to silica gel and chromatographed using light petroleum (bp 40-60°C) as eluent to yield the title complex as a red solid (0.833g, 78%).

$^1$H NMR (400MHz, CDCl$_3$) 5.32(5H, s, H5), 2.86-2.77(4H, m, H3), 1.63-1.53(m, 4H, H2), 1.02(6H, t, $J = 7.2$Hz, H1).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 226.95(q, C6), 97.85(q, C4), 91.09(CH, C5), 38.84(CH$_2$, C3), 25.21(CH$_2$, C2), 14.86(CH$_3$, C1).

C$_{18}$H$_{19}$CoMoO$_5$ requires C 45.98, H 4.07, obtained C 45.65, H 4.07.

Cobaltmolybdenumcyclopentadienylhex-3-yn-2-onepentacarbonyl. (47)

To a solution of the dimolybdenumdicyclopentadienylhexacarbonyl (0.319g, 0.65mmol) in tetrahydrofuran (100cm$^3$) was added L-selectride, 1M soln. Tetrahydrofuran (1.64cm$^3$, 1.64mmol). The reaction mixture was stirred for 1 hour. To the resultant orange solution was added dicobalthex-3-yn-2-one hexacarbonyl (0.50g, 0.130mmol) as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed for 1 hour. Upon reaction completion the reaction mixture was adsorbed on to silica gel and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether (2:1) as eluent to yield the title complex as a red solid (0.330g, 55%).

IR(neat) 2054, 1987, 1939cm$^{-1}$.

$^1$H 400MHz 5.53(5H, s, H7), 3.13-2.88(2H, m, H2), 2.31(3H, s, H6), 1.29(3H, t, $J = 7.2$Hz, H1)

$^{13}$C 100.16MHz 224.82(q,C8), 224.06(q, C8), 204.83(q, C5), 105.18(q, C4), 91.28(CH, C7), 83.00(q, C3), 30.68(CH$_3$, C6), 29.03(CH$_2$, C2), 16.39(CH$_3$, C1).

$m/z$ [ES], (M+H) requires 458.9176, obtained 458.9174.
Cobaltmolybdenumcyclopentadienyldiphenylacetylenepentacarbonyl. (16).

Method C.

To a solution of the dimolybdenumdicyclopentadienylhexacarbonyl (1.00g, 2.0mmol) in tetrahydrofuran (100cm³) was added L-selectride, (1M soln. tetrahydrofuran) (5.0cm³, 5.0mmol). The reaction mixture was stirred for 1 hour. To the resultant orange solution was added dicobaltcyclopentadienylhexacarbonyl (1.97g, 4.00mmol) as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed for 1 hour. Upon reaction completion the reaction mixture was adsorbed on to silica gel and chromatographed employing light petroleum (bp 40-60°C)/diethyl ether (10:1) as eluent to yield the title complex as a red solid (1.944g, 89%). For spectroscopic data see compound 16. Method A.

Cobaltmolybdenumcyclopentadienylphenylacetylene (17).

Method C.

To a solution of the dimolybdenumdicyclopentadienylhexacarbonyl (1.00g, 2mmol) in tetrahydrofuran (100cm³) was added L-selectride, (1M soln. tetrahydrofuran) (5.0cm³, 5mmol). The reaction mixture was stirred for 1 hour. To the resultant orange solution was added dicobaltphenylacetylenehexacarbonyl (1.35g, 4.00mmol) as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed for 1 hour. Upon reaction completion the reaction mixture was adsorbed on to silica gel and chromatographed using light petroleum (bp 40-60°C)/diethyl ether (10:1) as eluent to yield the title complex as a red solid (1.132g, 61%).
Cobaltmolybdenumcyclopentadienyl1-hexynepentacarbonyl. (18)

Method C.
To a solution of the dimolybdenumdicyclopentadienylhexacarbonyl (0.232g, 0.475mmol) in tetrahydrofuran (100cm³) was added L-selectride, (1M soln. tetrahydrofuran) (1.18cm³, 1.18mmol). The reaction mixture was stirred for 1 hour. To the resultant orange solution was added dicobalthexynehexacarbonyl (0.349g, 0.95mmol) as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed for 1 hour. Upon reaction completion the reaction mixture was adsorbed on to silica gel and chromatographed employing light petroleum (bp 40-60°C) as eluent to yield the title complex as a red solid (0.243g, 58%).

For spectroscopic data see compound 17. Method A.

Cobaltmolybdenumcyclopentadienylbutynehexacarbonyl. (19).

Method C.
To a solution of the dimolybdenumdicyclopentadienylhexacarbonyl (1.00g, 2mmol) in tetrahydrofuran (100cm³) was added L-selectride, (1M soln. tetrahydrofuran) (5cm³, 5mmol). The reaction mixture was stirred for 1 hour. To the resultant orange solution was added dicobalt 2-butynehexacarbonyl (1.36g, 4.00mmol) as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed for 1 hour. Upon reaction completion the reaction mixture was...
adsorbed on to silica gel and chromatographed employing hexane as eluent to yield the title complex as a red solid (1.655g, 100%).

For spectroscopic data see compound 19. Method A.

**Dicobalt 2-butyn-1-al diethyl acetal hexacarbonyl (48)**

![Diagram](image)

To a solution of dicobaltoctacarbonyl (5.0g, 14.61mmol) in light petroleum was added 2-butyn-1-al diethyl acetal (2.30cm³, 14.61mmol). The reaction was stirred for 12 hours. The reaction mixture was filtered through a plug of celite and the solvent removed under reduced pressure to yield the title complex as a dark red oil (5.82g, 93%).

IR 2092, 2050, 2019cm⁻¹.

**H NMR (400MHz, CDCl₃)** 5.42(1H, s, H₄), 3.75-3.69(2H, m, H₅), 3.63-3.56(2H, m, H₅), 2.61(3H, s, H₁), 1.18(6H, t, J 7.2Hz, H₆).

**¹³C NMR (100.62MHz, CDCl₃)** 200.06(q, C₇), 102.44(CH, C₄), 92.27(q, C₃), 92.11(q, C₂), 63.36(CH₂, C₅), 21.01(CH₃, C₁), 15.38(CH₃, C₆).

m/z [FAB], calculated 427.9353, obtained 427.9357.

**Cobaltmolybdenumcyclopentadienylbut-2-ynalpentacarbonyl (45).**

![Diagram](image)

Method B

To a solution of the dimolybdenumdicyclopentadienylhexacarbonyl (1.43g, 2.92mmol) in tetrahydrofuran (100cm³) was added L-selectride, (1M soln. tetrahydrofuran) (7.30cm³, 7.30mmol). The reaction mixture was stirred for 1 hour. To the resultant orange solution was
added dicobalt 2-butyn-1-al diethyl acetal hexacarbonyl (2.50g, 5.84mmol) as a solution in a minimal volume of tetrahydrofuran. The reaction mixture was refluxed for 1 hour. Upon reaction completion the reaction mixture was adsorbed on to silica gel and chromatographed using light petroleum (bp 40-60°C)/diethyl ether (2:1) as eluent to yield the title complex as a red solid (1.72g, 69%).

For spectroscopic data see compound 45, Method A.

Cobaltmolybdenumcyclopentadienyl oct-2-yne-4-ol pentacarbonyl. (49).

From n-butyllithium in tetrahydrofuran.
To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in tetrahydrofuran (15cm³) at -78°C was added n-butyllithium, 1.6M soln. hexanes (0.19cm³, 1.88mmol), the reaction mixture was stirred for 30 minutes at -78°C and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.053g 93%). Proton NMR indicated a 62% d.e.

Major diastereomer
IR(neat) 2044, 1974, 1930cm⁻¹
¹H NMR (250MHz, CDCl₃) 5.43(5H, s, H9), 4.53-4.46(1H, m, H4), 2.70(3H, s, H1), 1.66-1.20(7H, m, H11, H5, H6, H7), 0.92(3H, t, J 6.9Hz, H8).
¹³C NMR (100.62MHz, CDCl₃) 225.46(q, C10), 223.52(q, C10), 96.63(q, C3), 92.28(q, C2), 89.18(CH, C9), 74.73(CH, C4), 38.67(CH₂, C5), 27.67(CH₂, C6), 21.60(CH₂, C7), 19.58(CH₃, C1), 12.98(CH₃, C8).
m/z [FAB] requires 443.9309, obtained 443.9309.
Minor diastereomer

$^1$H NMR (250MHz, CDCl$_3$) 5.47(5H, s, H9), 4.81-4.75(1H, m, H4), 2.72(3H, s, H1), 1.66-1.20(7H, m, H11, H5, H6, H7), 0.91(3H, t, $J$ 6.9Hz, H8).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 224.52(q, C10), 223.85(q, C10), 97.50(q, C3), 93.15(q, C2), 89.05(CHO, C9), 74.31(CH, C4), 37.58(CH$_2$, C5), 27.48(CH$_2$, C6), 21.56(CH$_2$, C7), 19.42(CH$_3$, C1), 12.98(CH$_3$, C8).

Cobaltmolybdenumcyclopentadienyl pent-3-yne-2-ol pentacarbonyl (50)

\[
\begin{array}{c}
\text{Me} \\
\text{M} \\
\text{OH} \\
\text{O} \\
\text{Me}
\end{array}
\]

From methylmagnesiumbromide in tetrahydrofuran

To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in tetrahydrofuran (15cm$^3$) at $-78^\circ$C was added methylmagnesiumbromide, (3.0M, diethyl ether)(0.1cm$^3$, 0.3mmol), the reaction mixture was stirred for 30 minutes at $-78^\circ$C and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.050g, 94%). Proton NMR indicated a 72% d.e.

Major diastereomer

IR(neat) 2044, 1973, 1929cm$^{-1}$.

$^1$H NMR (250MHz, CDCl$_3$) 5.43(5H, s, H6), 4.76-4.72(1H, m, H4), 2.69(3H, s, H1), 1.51(1H, d, $J$ 5.5Hz, H7), 1.41(3H, d, $J$ 6.4Hz, H5).

$^{13}$C NMR (100.62MHz, CDCl$_3$) 225.31(q, C7), 223.38(q, C7), 96.62(q, C3), 93.53(q, C2), 89.10(CHO, C6), 70.82(CH, C4), 24.50(CH$_3$, C5), 19.22(CH$_3$, C1).

$m/z$ Submitted to ESPRC National Mass Spectrometry Service Centre Swansea. No molecular ion found.
Minor diastereomer

H\textsuperscript{1} NMR (250MHz, CDCl\textsubscript{3}) 5.47(5H, s, H6), 5.02-5.00(1H, m, H4), 2.69(3H, s, H1), 1.65(1H, br s, H7), 1.28(3H, d, J 6.3Hz, H5).

C\textsuperscript{13} NMR (100.62MHz, CDCl\textsubscript{3}) 224.47(q, C7), 223.75(q, C7), 97.41(q, C3), 94.10(q, C2), 89.02(CH, C6), 70.50(CH, C4), 23.24(CH\textsuperscript{3}, C5), 19.05(CH\textsubscript{3}, C1).

Cobaltmolybdenum cyclopentadienyl pent-3-yne-2-ol pentacarbonyl. (50)

From methyllithium in tetrahydrofuran

To a solution of cobaltmolybdenum cyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in tetrahydrofuran (15cm\textsuperscript{3}) at −78°C was added methyllithium, (1.5M)(0.20cm\textsuperscript{3}, 0.3mmol), the reaction mixture was stirred for 30 minutes at −78°C and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.050g, 95%). Proton NMR indicated a 62% d.e.

For spectroscopic data see 50 from methylmagnesiumbromide in tetrahydrofuran

Cobaltmolybdenum cyclopentadienyl 1-phenylbut-2-ynyl pentacarbonyl. (51)

From phenylmagnesiumbromide in tetrahydrofuran.

To a solution of cobaltmolybdenum cyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in tetrahydrofuran (15cm\textsuperscript{3}) at −78°C was added phenylmagnesiumbromide, (1.0M in tetrahydorufuran)(0.30 cm\textsuperscript{3}, 0.3mmol), the reaction mixture was stirred for 30 minutes at −78°C.
and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.059g, 98%). Proton NMR indicated a 72% d.e.

Major diastereomer.

IR(neat) 2044, 1974, 1929 cm⁻¹.

¹H NMR (250MHz, CDCl₃) 7.32-7.16(5H, m, Ar), 5.67(1H, d, J 3.5Hz, H4), 5.38(5H, s, H9), 2.59(3H, s, H1), 2.09(1H, d, J 3.2Hz, H11).

¹³C NMR (100.62MHz, CDCl₃) 226.29(q, C10), 224.70(q, C10), 143.75(q, C5), 128.54(CH, C6), 128.05(CH, C7), 126.09(CH, C8), 98.95(q, C3), 93.47(q, C2), 90.39(CH, C9), 78.70(CH, C4), 21.16(CH₃, C1).

m/z Submitted to ESPRC National Mass Spectrometry Service Centre Swansea. No molecular ion found.

Minor diastereomer

¹H NMR (250MHz, CDCl₃) 7.62-7.16(5H, m, Ar), 5.93(1H, d, J 3.0Hz, H4), 5.37(5H, s, H9), 2.65(3H, s, H1), 2.09(1H, d, J 3.2Hz, H11).

¹³C NMR (100.62MHz, CDCl₃) 226.88(q, C10), 224.08(q, C10), 144.93(q, C5), 128.65(CH, C6), 128.18(CH, C7), 126.09(CH, C8), 98.95(q, C3), 93.47(q, C2), 90.53(CH, C9), 78.70(CH, C4), 21.16(CH₃, C1).

Cobaltmolybdenumcyclopentadienyl 1-phenylbut-2-ynyl-1-ol pentacarbonyl(51)

From phenyllithium in tetrahydrofuran

To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in tetrahydrofuran (15cm³) at −78°C was added phenyllithium, (1.8M, cyclohexane, diethylether 70 to 30)(0.17cm³, 0.3mmol), the reaction mixture was stirred for 30 minutes at −78°C and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature.
temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.059g, 98%). Proton NMR indicated a 75% d.e. For spectroscopic data see compound 51 from phenylmagnesiumbromide in tetrahydrofuran.

Cobaltmolybdenumcyclopentadienyl 6-methylhept-2-yne-4-ol pentacarbonyl (52).

\[
\begin{align*}
\text{Cobaltmolybdenumcyclopentadienyl 6-methylhept-2-yne-4-ol pentacarbonyl (52).}
\end{align*}
\]

To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in tetrahydrofuran (15cm³) at -78°C was added butyllithium (1.1M, diethyl ether) (0.27cm³, 0.3mmol), the reaction mixture was stirred for 30 minutes at -78°C and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.055g, 95%).

NMR indicated a 92% d.e.

Major diastereomer

IR(neat) 2059, 2044, 1985cm⁻¹.

¹H NMR (250MHz, CDCl₃) 5.43(5H, m, H9), 4.62-4.55(1H, m, H4), 2.69(3H, s, H1), 1.98-1.82(1H, m, H6), 1.59-1.21(3H, m, H5, H11), 0.98(3H, d, J 3.0Hz, H7), 0.95(3H, d, J 2.8Hz, H8).

¹³C NMR (100.62MHz, CDCl₃) 225.44(q, C10), 223.54(q, C10), 96.57(q, C3), 93.48(q, C2), 89.33(CH, C9), 72.76(CH, C4), 48.24(CH₂, C5), 24.16(CH₃, C1), 22.70(CH₃, C6), 20.92(CH₃, C7), 20.66(CH, C8).

m/z [FAB] requires 443.9309, obtained 443.9309.

Minor diastereomer
\textsuperscript{1}H NMR (250MHz, CDCl\textsubscript{3}) 5.47(5H, s, H9), 4.62-4.55(1H, m, H4), 2.72(3H, s, H1), 1.98-1.82(1H, m, H6), 1.58-1.21(3H, m, H5, H11), 0.98(3H, d, J 3.0Hz, H7), 0.95(3H, d, J 3.0Hz, H8).

\textsuperscript{13}C NMR (100.62MHz, CDCl\textsubscript{3}) 224.53(q, C10), 223.84(q, C10), 96.57(q, C3), 93.48(q, C2), 89.19(CH, C9), 72.39(CH, C4), 47.06(CH\textsubscript{2}, C5), 23.91(CH, CH), 22.54(CH\textsubscript{3}, C1), 20.92(CH\textsubscript{3}, C7), 19.35(CH, C8).

Cobaltmolybdenumcyclopentadienyl hepta-2, 5-diyne-4-ol pentacarbonyl (53).

To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in tetrahydrofuran (15cm\textsuperscript{3}) at \(-78^\circ\text{C}\) was added 1-propynylmagnesium bromide, (0.5M, tetrahydrofuran)(0.6 cm, 0.3mmol), the reaction mixture was stirred for 30 minutes at \(-78^\circ\text{C}\) and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.036g, 64\%). Carbon NMR indicated a 33\% d.e.

Major diastereomer

IR(neat) 2046, 1967, 1931cm\textsuperscript{-1}.

\textsuperscript{1}H NMR (250MHz, CDCl\textsubscript{3}) 5.45(5H, s, H8), 5.20(1H, br, H4), 2.70(3H, s, H1), 2.00-1.93(1H, br m, H10), 1.83(3H, s, H7).

\textsuperscript{13}C NMR (100.62MHz, CDCl\textsubscript{3}) 226.37(q, C9), 224.36(q, C9), 98.53(q, C3), 91.98(q, C2) 90.53(CH, C8), 82.78(q, C5), 80.26(q, C6), 66.90(CH, C4), 20.39(CH\textsubscript{3}, C1), 3.75(CH\textsubscript{3}, C7).

m/z Submitted to ESPRC National Mass Spectrometry Service Centre Swansea. No molecular ion found.
Minor diastereomer

$^{1}$H NMR (250MHz, CDCl$_3$) 5.48(5H, s, H8), 5.22(1H, br, s, H4), 2.70(3H, s, H1), 2.00-1.93(1H, br m, H10), 1.83(3H, s, H7).
$^{13}$C NMR (100.62MHz, CDCl$_3$) 224.19(q, C9), 98.96(q, C3), 91.45(q, C2), 90.48(CH, C8), 82.51(q, C5), 79.56(q, C6), 66.99(CH, C4), 20.47(CH$_3$, C1), 3.79(CH$_3$, C7).

Cobaltmolybdenumcyclopentadienyl oct-2-yne-4-ol pentacarbonyl. (49)

From n-butyllithium in toluene.

To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in toluene (15cm$^3$) at -78°C was added n-butyllithium, (1.6M soln. Hexanes) (0.19cm$^3$, 0.3mmol), the reaction mixture was stirred for 30 minutes at -78°C and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.046g 78%). Proton NMR indicated a 69% d.e.

For spectroscopic data see compound 49 from n-butyllithium in tetrahydrofuran
Cobaltmolybdenumcyclopentadienyl oct-2-yne-4-ol pentacarbonyl. (49).

\[ \text{From n-butyllithium, boron trifluoride etherate in toluene} \]

To a solution of cobaltmolybdenumcyclopentadienylbut-2-yenal pentacarbonyl (0.050g, 0.12mmol) in toluene (15cm\(^3\)) at \(-78^\circ\text{C}\) was added boron trifluoride etherate(\(\text{cm}^3\) 0.12mmol), the reaction mixture was stirred for 15 minutes prior to the addition of \(n\)-butyllithium, (1.6M soln. Hexanes) (0.19cm\(^3\), 0.3mmol), the reaction mixture was stirred for 30 minutes at \(-78^\circ\text{C}\) and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.046g, 80%). Proton NMR indicated a 78% d.e.

For spectroscopic data see compound 49 from \(n\)-butyllithium in tetrahydrofuran.

Cobaltmolybdenumcyclopentadienyl pent-3-yne-2-ol pentacarbonyl. (50)

\[ \text{From methylmagnesiumbromide in toluene.} \]

To a solution of cobaltmolybdenumcyclopentadienylbut-2-yenal pentacarbonyl (0.050g, 0.12mmol) in toluene (15cm\(^3\)) at \(-78^\circ\text{C}\) was added methylmagnesiumbromide, (3.0M, diethylether)(0.1cm\(^3\), 0.3mmol), the reaction mixture was stirred for 30 minutes at \(-78^\circ\text{C}\) and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.041g, 77%). Proton NMR indicated a 50% d.e.

For spectroscopic data see compound 50 from methylmagnesiumbromide in tetrahydrofuran.
Cobaltmolybdenumcyclopentadienyl pent-3-yne-2-ol pentacarbonyl (50)

From methylmagnesiumbromide, boron trifluoride etherate in toluene.

To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in toluene (15cm³) at -78°C was added boron trifluoride etherate (cm³ 0.12mmol), the reaction mixture was stirred for 15 minutes prior to the addition of methylmagnesiumbromide, (3.0M, diethylether)(0.3cm³, 0.3mmol), the reaction mixture was stirred for 30 minutes at -78°C and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.042g, 79%). Proton NMR indicated a 60% d.e.

For spectroscopic data see compound 50 from methylmagnesiumbromide in tetrahydrofuran.

Cobaltmolybdenumcyclopentadienyl 1-phenylbut-2-ynyl-1-ol pentacarbonyl (51).

From phenylmagnesiumbromide in toluene.

To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in toluene (15cm³) at -78°C was added phenylmagnesiumbromide, (1.0M in tetrahydrofuran)(0.30 cm³, 0.3mmol), the reaction mixture was stirred for 30 minutes at -78°C and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.059g, 80%). Proton NMR indicated a 50% d.e.

For spectroscopic data see compound 51 from phenylmagnesiumbromide in tetrahydrofuran.
Cobaltmolybdenumcyclopentadienyl 1-phenylbut-2-yn-1-ol pentacarbonyl. (51).

From phenyllithium in toluene.

To a solution of cobaltmolybdenumcyclopentadienylbut-2-ynal pentacarbonyl (0.050g, 0.12mmol) in toluene (15cm³) at −78°C was added phenyllithium, (1.8M, cyclohexane, ether 70 to 30)(0.17cm³, 0.3mmol), the reaction mixture was stirred for 30 minutes at −78°C and then quenched with ethanol. The reaction mixture was allowed to warm to room temperature and filtered through a plug of silica. The solvent was removed under reduced pressure to yield the title complex as a red oil (0.047g, 78%). Proton NMR indicated a 41% d.e.

For spectroscopic data see compound 51 from phenylmagnesiumbromide in tetrahydrofuran.

Cobaltmolybdenumcyclopentadienylnon-1-en-6-yn-5-onepentacarbonyl. (54).

To a solution of Cobaltmolybdenumcyclopentadienylhex-3-yn-2-onepentacarbonyl (0.200g, 0.43mmol), in tetrahydrofuran (15cm³), at −78°C was added lithiumbis(trimethylsilyl)amide (ca 1.06M soln. in THF) (0.24cm³, 0.26mmol) the reaction mixture was stirred at −78°C for 5minutes after which the colour of the reaction mixture had changed from a light red to dark red. Allylbromide (0.18cm³, 2.2mmol) was subsequently added and the reaction mixture allowed to attain room temperature slowly and stirred for a further 4hours. The reaction mixture was extracted between diethylether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude
residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethylether (5:1) as the eluent to yield the title complex as a red oil (0.042g, 39%)

\[ \text{H NMR (250MHz, CDCl}_3 \text{)} 5.91-5.75(1H, m), 5.37(5H, s), 5.09-4.97(2H, m), 3.14-2.88(2H, m), 2.69-2.59(2H, m), 2.46-2.35(2H, m), 1.29(3H, t J 7Hz) \]

**Cobaltmolybdenumcyclopentadienylnon-1-en-6-yn-5-one. (55).**

To a solution of Cobaltmolybdenumcyclopentadienylnon-1-en-6-yn-5-onepentacarbonyl (0.042g, 0.08mmol), in tetrahydrofuran (15cm³), at -78°C was added lithiumbis(trimethylsilyl)amide (ca 1.06M soln. in THF) (0.083cm³, 0.088mmol) the reaction mixture was stirred at -78°C for 5 minutes after which the colour of the reaction mixture had changed from a light orange to dark red. Benzylbromide (0.10cm³, 0.85mmol) was subsequently added and the reaction mixture allowed to attain room temperature slowly and stirred for a further 4 hours. The reaction mixture was extracted between diethylether and water, the organic fractions combined and subsequently dried over magnesium sulfate prior to the solvent being removed under reduced pressure. The crude residue was then chromatographed on silica gel employing light petroleum (bp 40-60°C)/diethylether (5:1) as the eluent to yield the title complex as a red oil (008g, 18%)

IR 2053, 1997, 1938cm⁻¹.

\[ \text{H NMR (250MHz, CDCl}_3 \text{)} 7.28-7.12(5H, Ar), 6.75-6.86(1H, m), 5.14-5.13(1H, m), 5.10-5.09(1H, m), 4.94(5H, s), 3.08-3.01(2H, m), 3.10-2.97(1H, m), 2.87-2.69(1H, m), 2.48-2.41(1H, m), 1.56(2H, br s), 1.28(3H, t J 3.6Hz) \]

\[ \text{C NMR (100.62MHz, CDCl}_3 \text{)} 225.14(q), 224.02(q), 207.25(q), 140.92(q), 135.57(CH), 129.96(CH), 128.80(CH), 126.74(CH), 118.08(CH₂), 91.14(CH), 54.00(CH), 37.25(CH₃), 37.08(CH₂), 29.12(CH₂), 16.21(CH₃), \text{Alkyne quaternaries not present in carbon spectrum.} \]
Reference Section.


Heterobimetallic Alkyne Complexes in Organic Synthesis: An Asymmetric Variant of the Pauson-Khand Reaction

David T. Rutherford and Steven D. R. Christie*
Department of Chemistry, University of Loughborough, Loughborough, LE11 3TU, UK

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Abstract: The use of heterobimetallic alkyne complexes for the synthesis of cyclopentenones is described. The inherent chirality of the complexes has been used to effect high levels of stereocontrol in transformations giving optically enriched organic end products. © 1998 Elsevier Science Ltd. All rights reserved.

The Pauson-Khand reaction is perhaps one of the most widely used organometallic mediated reactions for the synthesis of cyclopentenones.1 A number of variations have been reported over the years that modify and enhance the original procedure.2 In addition, other transition metal systems have been shown to mediate similar cyclisation reactions.3 In this paper, we show that heterobimetallic alkyne complexes can be used to facilitate cyclopentenone formation (Scheme 1). The mixed metal complexes are formed from the reaction of a dicobalt hexacarbonyl alkyne complex with the cyclopentadienylmolybdenum tricarbonyl anion.4 The desired complexes are isolated in good yield, are stable to chromatography on silica gel, and can be stored for extended periods. Although complexes of this type have been known for some time, surprisingly they have not been utilised in reactions to form organic products.

\[ \text{H} \quad \text{C} - \text{C} \quad \text{M} \quad \text{M} \quad \text{R}^1 \]

\[ \rightarrow \]

\[ \text{O} \quad \text{R}^1 \]

Scheme 1

We have found that the desired complexes are easily formed by modification of the literature routes.4 Molybdenum hexacarbonyl was added to a solution of sodium cyclopentadienyl anion in THF. The mixture was refluxed overnight, then a solution of the bis-cobalt alkyne complex in THF added and the mixture heated for further two hours. Standard aqueous work-up provided the mixed metal complex in good yield after purification by silica gel chromatography (Scheme 2). The complexes are red crystalline solids or liquids and can be easily handled in air for extended periods.

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Scheme 2

Norbornene adduct 3a-d
Norbornadiene adduct 4a-d

Reaction of the complexes with alkenes was achieved by simply heating in toluene. Norbornene and norbornadiene were used initially since these are known to be active substrates in the Pauson-Khand reaction. Heating a mixture of the mixed metal alkyne complex with an excess of the alkene gave a clean reaction providing the desired organic products. The yields of cyclopentenone are moderate to excellent, as shown in Table 1, and compare favourably with those obtained from the corresponding bis-cobalt alkyne complexes under analogous reaction conditions. Thus, the new mixed metal system has shown promising activity and is a new variant on the Pauson-Khand reaction.

Of more interest is the inherent chirality of the mixed metal alkyne complexes. When unsymmetrical alkynes are employed, the four corners of the metal-alkyne core are differentiated, and the complex is rendered chiral. We reasoned that the electronic differences between the metals might induce chirality in a subsequent cyclisation reaction. The mixed metal complexes of propargyl menthyl ether (7a and 7a') were synthesised as indicated in Scheme 3. The diastereoisomers were separated by chromatography to yield the resolved complexes, and the purity of the products was assessed by $^1$H and $^{13}$C NMR spectroscopy. The chemical shift and coupling of the
propargylic protons was substantially different in the two complexes, allowing simple determination of the diastereoisomeric excess.

Once isolated, separate reaction of the individual, diastereomERICALLY pure complexes with norbornadiene gave the expected cyclopentenones (8a or 8a') in good yield (Scheme 4). $^1$C NMR spectroscopy showed that different diastereoisomERIC cyclopentenones were isolated from each cyclisation reaction. Thus the diastereomERICALLY pure metal alkynE complexes each gave rise to a distinct organic product, with no sign of the other diastereoisomer in either case. We attribute this to the chirality present in the metal-alkyne core.

Control experiments with the corresponding bis-cobalt alkynE complex (6) showed only a slight diastereomERIC excess in the cyclopentenone product, presumably arising from the presence of the menthyl group. We therefore assume that in the new mixed metal mediated cyclisation, reaction occurs preferentially around only one of the two possible metal sites. Cyclisation around, for example, the molybdenum, would lead to one diastereomERIC cyclopentenone being formed, while cyclisation around the cobalt would give the other
diastereoisomer. The difference in reactivity of the two metals has induced reaction to occur at one site preferentially, and produced a highly diastereoselective reaction. Thus we have differentiated the metal sites and produced an effective chiral induction in the cyclopentenone forming reaction.1 This tuning of reactivity of metals in metal-alkyne complexes has been noted previously,2 by complexion of a phosphine ligand. In our case, however, the mixed metal complexes are thermally more stable than the phosphine substituted complexes, which were prone to racemisation at the higher temperatures required for the classical Pauson-Khand reaction.3 We have thus produced a viable alternative to the established means of inducing chirality in the Pauson-Khand reaction.

Conclusion: We have illustrated a new variant of the Pauson-Khand. The complexes are easily synthesised and the cyclisation reactions simply carried out by heating. Further experiments with promoters such as N-oxides will be reported in due course. In addition, this new technique has great potential as an asymmetric version of the PKR. Work to determine the root of the stereoselection is in progress.

Acknowledgements: The authors wish to thank Alexandra Gillet for some preliminary work and the EPSRC for funding (Quota award to DTR). SDRC wishes to thank Loughborough University, Pfizer Central Research and The Nuffield Foundation for funding. This paper is dedicated to the late Gavin Forsyth, who was the inspiration for this work.

An Enantiospecific Pauson-Khand Reaction

Anthony J. Fletcher, David T. Rutherford, Steven D. R. Christie*  
Department of Chemistry, University of Loughborough, Loughborough, LE 11 3TU, UK  
E-mail: s.d.christie@lboro.ac.uk

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Abstract: The use of optically pure heterobimetallic alkyne complexes for the synthesis of enantiopure cyclopentenones is described. The inherent chirality of the complexes has been used to effect high levels of stereocontrol in transformations giving optically enriched organic end products.

Key words: alkyne complexes, stereoselective synthesis, organometallic reagents

The Pauson-Khand reaction (PKR) was first reported in the early 1970's,1 and since then has become one of the most popular metal-mediated reactions for the formation of cyclopentenoid systems. In recent years, emphasis has moved to developing catalytic and stereoselective methods for the reaction. Significant progress has been made by Livinghouse,2 Krafft3 and Gibson4 with respect to catalytic systems, whereas Kerr,5 Pericas6 and Chung7 have produced highly stereoselective reactions. In the latter examples, stereocontrol is normally induced by rendering the two cobalt atoms electronically dissimilar. In this vein, we recently reported a new variant of the Pauson-Khand reaction using heterobimetallic alkyne complexes.8 We found that by replacing one of the cobalt centres in the metal alkyne core with an isoelectronic molybdenum fragment, we could facilitate cyclopentenone formation in a similar manner to the traditional Pauson-Khand reaction (Scheme 1). Furthermore, by using a menthol chiral auxiliary, we could separate the diastereoisomeric complexes and form diastereoisomerically pure cyclopentenones.9 We believe that the stereocontrol in this reaction arises from the chirality of the metal-alkyne core, where one configuration gives one cyclopentenone.

In order to extend the utility of this reaction, and to further test the efficacy of the chiral metal-alkyne core as a stereocenter, we wanted to remove the chiral auxiliary and form enantiomerically pure complexes. With the exception of Kerr's chiral N-oxide Pauson-Khand reaction,10 all other stereoselective PKRs to date have employed some sort of chiral auxiliary within the complex itself. Here, we would have a truly enantioselective reaction since the only source of chirality is the metal alkyne core. After separation of the diastereoisomeric complexes, removal of the menthol auxiliary was achieved with hydrofluoroboric acid. The tetrafluoroborate salt of the metal stabilised propargylic cation, 3, precipitates from the ether solution as an orange solid.9 This was filtered and washed with ether to remove the menthol and the salt dried to remove the solvent. Remarkably, the enantiomerically pure propargylic salts are essentially air stable, and can be stored for extended periods without any appreciable decomposition or racemisation.10

To test what sort of nucleophiles would react with this stabilised propargylic cation, we chose oxygen, nitrogen and sulfur based reagents. The salt was taken up in dry acetone and reacted with a number of nucleophiles. Thus, reaction with isopropanol, phenol, thioisopropanol and benzotriazole provided the expected complexes, 4, in moderate to good yield. In addition, reaction with borane dimethyl sulfide complex in DCM effectively delivered a hydride to provide the methyl substituted complex. Thus, we are able to add hydrogen based nucleophiles, as well as oxygen, nitrogen and sulfur. With the optically pure complexes in hand, these were then subjected to the cyclopentenone forming conditions, and the organic products, 5, isolated in good yield.

Scheme 1

Scheme 2

**Scheme 1**

**Scheme 2**

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Cyclopentenones of this type have been resolved by chiral HPLC previously, however, we could not find a suitable system to separate these particular compounds. Similarly, chiral shift reagents did not induce any shift in the NMR spectra. Finally, we attempted to make derivatives of the cyclopentenones that we could use to determine the enantiomeric excess. We settled on the chiral ketals produced from (+)-(R,R)-2,3-butandiol as these have been used to determine optical purity of ketones previously.

We took the racemic compounds and measured the $^1$H and $^{13}$C NMR spectra of their ketals in order to determine if the chemical shifts of the diastereoisomers would be significantly different. As expected, we could identify different peaks for the diastereotopic methyl groups and certain other peaks of the two ketals in the racemic mixture. Protection of the cyclopentenones produced from each of the enantiomerically pure alkylene complexes showed that each individual cyclopentenone was enantiomerically pure, with only one set of peaks present in each case. In addition, different enantiomers of the metal-alkyne complex produced different enantiomers of the corresponding cyclopentenone, regardless of the substituent attached to the propargylic position. Thus, the propargylic salt from the less polar metal-alkyne menthol complex gave rise to cyclopentenones with a positive optical rotation. We believe that this is the first enantiospecific variant of the Pauson-Khand reaction which has been illustrated over a range of substrates.

In order to account for the stereocontrol, we believe that the cyclisation is templated around only one of the two possible metal sites. This may result as a consequence of the steric and/or electronic differences of the two metals. As shown below, loss of carbon monoxide and complexation of the norbornadiene proceeds around, for example, the cobalt atom in each of the enantiomerically pure complexes. The carbon-carbon bond forming reactions take place, including carbon monoxide insertion, to give the cyclopentenone product complexed to the metallic residue. Loss of the metal fragment produces the optically pure organic products. This simple representation does not take into account which carbon monoxide (basal or apical) is being replaced, but does give an indication of the origin and extremely high level of the stereoselection. A similar mechanism can be drawn for cyclisation around molybdenum, however, in each case the reaction must proceed around the same metal.

We have illustrated an enantiospecific variant of the Pauson-Khand reaction. We believe that the factor controlling the stereoselection is the chirality present in the metal-alkyne core. Further work to elucidate the mechanism and reasons for the selectivity is in progress.

Acknowledgement
The authors wish to thank the EPSRC for funding (Quota award to DTR and project studentship to AJF), SDRC wishes to thank Loughborough University, Pfizer Central Research and The Nuffield Foundation for additional support.
References and Notes


(10) The optically enriched salts are identical to those prepared previously by Grusselle (see below for procedure). The stabilised salts could be stored on the bench under air, and no decomposition was noted after several weeks. Reaction with menthol to reform the complex (1) showed only the original diastereoisomer to be formed.

(11) Representative Experimental Procedure: Preparation of stabilised salt 2:
To a solution of the optically pure cibul molybdenum enantiomeric complex 1 (760 mg, 1.37 mmol) in diethyl ether (30 mL) was added dropwise tetrabromoboric acid 54 wt.% sol. (0.11 mL, 1.51 mmol), this resulted in the precipitation of the stabilised salt 2 which could be stored on the bench under air, and no decomposition was noted after several weeks. Reaction with menthol to reform the complex (1) showed only the original diastereoisomer to be formed.


(13) Selected Data for ketals from cyclopentenone SB:
IR (DCM)/cm⁻¹ 2970, 2872, 1599, 1496/087.
Found: M⁺, 252.11486. Requires 252.11503.

Ketal from 2nd enantiomer of SB:
IR (DCM)/cm⁻¹ 2970, 2872, 1599, 1496/087.
Found: M⁺, 252.11378. Requires 252.11275.

Pauson-Khand reaction:
To a solution of the mixed metal complex 4B (300 mg, 0.6 mmol) in toluene was added norbornadiene (1.29 mL, 12 mmol). The mixture was heated at 70 °C and monitored for the disappearance of starting material. The crude material was filtered through Celite and the filtrate concentrated under reduced pressure. The filtrate was chromatographed using silica gel as absorbent and light petroleum (bp 40-60 °C) as eluent to yield the cyclopentenone SB (71 mg, 48%) as a white solid.

1H NMR (400 MHz, CDCl₃), 7.54-7.53 (1H, m), 7.30-7.27 (2H, m), 6.97-6.90 (3H, m), 6.30 (1H, d, J = 5.7, 9.8 Hz), 6.22 (1H, d, J = 6.5, 8.3 Hz), 4.71 (2H, t, J = 2.0 Hz), 2.95 (1H, d), 2.82-2.81 (1H, m), 2.71 (1H, s), 2.37 (1H, d, J = 5.2, 16.0 Hz), 1.43-1.39 (1H, m), 1.27-1.29 (1H, m).

13C NMR (100 MHz, CDCl₃), 208.57, 161.38, 158.63, 146.63, 138.50, 137.5, 129.91, 121.54, 114.98, 62.28, 53.33, 48.76, 44.44, 44.06, 41.70.

Ketal from 1st enantiomer of SB:
IR (DCM)/cm⁻¹ 2970, 2872, 1599, 1496/087.
Found: M⁺, 252.11378. Requires 252.11275.

Ketal from 1st enantiomer of SB:
IR (DCM)/cm⁻¹ 2970, 2872, 1599, 1496/087.
Found: M⁺, 252.11378. Requires 252.11275.

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Formation of Propargylic Stereocentres using Desymmetrised Alkyne Complexes

Anthony J. Fletcher, Ross Fryalt, David T. Rutherford, Mark R. J. Elsegood, Steven D. R. Christie*

Department of Chemistry, Loughborough University, Loughborough, LE11 3TU, UK
E-mail: s.d.christie@lboro.ac.uk
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Abstract: Addition of Grignard reagents to alkynyl aldehyde complexed bimetallic system proceeds with good to excellent stereocontrol.

Key words: asymmetric synthesis, chiral auxiliaries, transition metals, stereoselectivity, nucleophilic additions

The creation of chiral centres at propargylic (prop-1-ynyl) positions has received some interest in the past few years. Methods for the preparation of stereocentres next to alkynes include the addition of nucleophiles to propargylic aldehydes using titanium catalysis and boron reagents and a metal catalysed ene reaction. The other main methods have been the hydride reduction of propargylic ketones with chiral borohydrides, in particular the CBS oxazaborolidine catalyst system and by transfer hydrogenation. The importance of this chemistry is perhaps best illustrated when the newly formed stereocentre is used in the preparation of complex natural products, such as macrolactin, isocarbacyclin derivatives, methyl nonactate and scopaducic acid.

Our interest in metal alkyne chemistry prompted us to find a new method for the generation of propargylic stereocentres. Of relevance to this are the extensive studies by Nicholas and Hanaoka on the addition of enols and enolates to complexed propargylic aldehydes. The metal group facilitates high diastereocontrol in the reaction, and can be readily removed to leave the organic fragment with the newly created chiral centres. In addition, Nicholas has shown that phosphine substituted cobalt alkyne complexes can be used to form enantio-enriched propargylic stereocentres since the complex itself is rendered chiral by the introduction of the phosphine ligand. Access to products of this type has been achieved, again by Nicholas, by adding the PPh₃ ligand to the propargylic alcohol complexes. However, the diastereoselectivity was highly dependant on the size of the substituents. Remarkably, there have been, to the best of our knowledge, no reports of addition of Grignard or organolithium reagents to the same types of complexes.

Starting with 2-butyn-1-ol diethyl acetal (Scheme 1), complexation to cobalt was achieved simply by stirring with Co₂(CO)₈ in DCM. Treatment of the acetal with a catalytic amount of p-toluene sulfonic acid gave the aldehyde. This was then reacted with triphenyl phosphine to produce the desired complex 1a. Complex 1b was prepared in an analogous manner from propynal.

With the desired aldehyde in hand, we reacted this with a series of nucleophiles. All the reactions outlined in Scheme 2 proceeded quickly at low temperature (−78 °C) in THF to give the corresponding alcohols. The diastereomeric excess was measured directly in most cases since the complexes were easily separable by chromatography. With inseparable complexes, the diastereomeric excess was estimated from the ¹H NMR spectra. The results show that excellent diastereoisomeric excesses are achieved with all the nucleophiles we studied.

In order to account for the stereocontrol, we obtained X-ray crystal structures of the starting metal alkyne complex and one of the products. The aldehyde, 1a, is shown in Figure 1. The complex adopts the typical configuration of the metal-metal bond being perpendicular to the alkyn bond. Of more interest is the orientation of the aldehyde group where the oxygen is syn to the two cobalt atoms.
Table 1 Addition of Grignard Reagents to Complex 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>RMgX</th>
<th>de (%)</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Me</td>
<td>MeMgBr</td>
<td>90</td>
<td>92</td>
</tr>
<tr>
<td>b</td>
<td>Me</td>
<td>EtMgBr</td>
<td>76</td>
<td>93</td>
</tr>
<tr>
<td>c</td>
<td>Me</td>
<td>PhMgCl</td>
<td>&gt;95</td>
<td>95</td>
</tr>
<tr>
<td>d</td>
<td>Me</td>
<td>i-BuMgBr</td>
<td>&gt;95</td>
<td>74</td>
</tr>
<tr>
<td>e</td>
<td>H</td>
<td>PhMgCl</td>
<td>&gt;95</td>
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</tr>
<tr>
<td>f</td>
<td>H</td>
<td>MeMgBr</td>
<td>88</td>
<td>89</td>
</tr>
</tbody>
</table>

Reactions carried out in THF at -78 °C. A representative experimental is given below. All complexes in this table gave satisfactory spectroscopic and analytical data.

Thus one face of the aldehyde is almost completely blocked by the bulky triphenyl phosphine ligand. X-ray analysis of the product 2c, Figure 2, shows the phenyl group, derived from PhMgCl, syn to the Co(CO)₂ vertex, away from the Co(CO)₂PPh₃ group. Although the X-ray structures do not necessarily reflect the reactive conformation in solution, this conformation of the aldehyde does allow the Grignard reagent to approach anti to the bulky PPh₃ ligand.

Figure 1 X-ray structure of 1a

Figure 2 X-ray structure of 2c

An alternative mechanism may involve initial attack on a carbon monoxide ligand, followed by migration to the aldehyde to produce the product. Whilst we have no direct evidence for this, we have noticed there is a difference in reactivity between Grignard reagents and organolithiums. The Grignard reagents used, as shown in Table 1, produced the products cleanly and in high yield. However, when the corresponding organolithium reagents were employed, none of the desired product was isolated, the reaction mixture mostly decomposing on work-up.

We were also interested in the corresponding heterobimetallic alkyne complexes, where one of the Co(CO)₃ vertices is replaced by CpMo(CO)₃. We have used this type of complex to effect stereospecific Pauson-Khand reactions recently, but we were intrigued to see whether the scope of these complexes could be extended. In order to make the desired mixed metal complex 3, we wanted to test a new method to achieve the isolobal displacement of cobalt for molybdenum. Gladysz has shown that metal carbonyl anions can be generated by the addition of a borohydride source to the metal carbonyl dimer, [CpMo(CO)₃]₂. We used this technique to generate the molybdenum anion, and applied it to the isolobal displacement reaction. To the best of our knowledge, this is the first time these complexes have been generated in this manner and this procedure represents a much simpler and more effective method of synthesis of heterobimetallic alkyne complexes of this type. Reaction of complex 3 with a series of Grignard or organolithium reagents was then performed (Table 2).

Scheme 3

Table 2 Addition of Nucleophiles Reagents to Complex 3

<table>
<thead>
<tr>
<th>Entry</th>
<th>Nucleophile</th>
<th>de (%)</th>
<th>yield (%)</th>
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</thead>
<tbody>
<tr>
<td>a</td>
<td>n-BuLi</td>
<td>62</td>
<td>93</td>
</tr>
<tr>
<td>b</td>
<td>MeMgBr</td>
<td>72</td>
<td>94</td>
</tr>
<tr>
<td>c</td>
<td>PhLi</td>
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<td>98</td>
</tr>
<tr>
<td>d</td>
<td>MeLi</td>
<td>62</td>
<td>95</td>
</tr>
<tr>
<td>e</td>
<td>PhMgBr</td>
<td>72</td>
<td>98</td>
</tr>
<tr>
<td>f</td>
<td>i-BuMgBr</td>
<td>92</td>
<td>95</td>
</tr>
<tr>
<td>g</td>
<td>MeCCMeBr</td>
<td>33</td>
<td>64</td>
</tr>
</tbody>
</table>

Reactions carried out in THF at -78 °C. A representative experimental is given below. All complexes in this table gave satisfactory spectroscopic and analytical data.
Again, stereocontrol was good to excellent. X-ray structure of the starting aldehyde complex, 3, shows it has a similar orientation to that in the \( \text{Co} \)-cobalt system.

![X-ray structure of 3](image)

However, we have as yet been unable to obtain suitable crystals of the products for X-ray analysis, so cannot determine the relative configuration in 4. By analogy with the \( \text{bis} \)-cobalt system, we expect that the steric bulk of the cyclopentadienyl ring is directing the incoming nucleophile to attack from the opposite side, away from the metal centre. The relative sizes of the two blocking groups (PPh\(_3\) vs Cp) may account for the drop in stereocontrol us-

Preparation of 2c
Addition of PhMgCl to \( \text{Co/Co}(\text{PPh}_3) \) aldehyde complex 1a
To a solution of aldehyde 1a (0.5 g, 0.85 mmol) in dry THF (40 mL) at \(-78^\circ\text{C}\) was added phenylmagnesium chloride (1.7 mL of a 2 M solution in THF, 3.40 mmol). The resulting reaction mixture was left to stir at \(-78^\circ\text{C}\) for 1 h. After this time, the reaction was quenched with ethanol (5 mL). The reaction mixture was then allowed to warm to r.t. The reaction mixture was filtered through a pad of celite and silica to remove any metal residues and then concentrated in vacuo to give the product 2c as red crystals (0.537 g, 95%).

1H NMR (250 MHz, CDCl\(_3\)): \( \delta = 7.74-6.82 \) (20 H, m), 4.98 (1 H, d, \( J = 5.2 \) Hz), 2.15 (1 H, d, \( J = 5.2 \) Hz), 1.87 (3 H, s) ppm.

13C NMR (62.9 MHz, CDCl\(_3\)): \( \delta = 204.9 \) (CO), 201.6 (CO), 144.5 (Ar), 135.0 (Ar, \( J_{\text{C},\text{P}} = 4.1 \) Hz), 133.5 (Ar, \( J_{\text{C},\text{P}} = 11 \) Hz), 130.9 (Ar, \( J_{\text{C},\text{P}} = 3 \) Hz), 128.3 (Ar), 127.6 (Ar), 125.5 (Ar), 97.8 (alkynyl), 88.8 (alkynyl), 72.4 (CHOH), 20.4 (Me) ppm.

3P NMR (100.1 MHz, CDCl\(_3\)): \( \delta = 53.27 \) ppm.

**m/z** (FAB): Found (M\(^+\) - 2 CO) 610.01540; \( \text{C}_{18}\text{H}_{19}\text{CoMoO}_4 \) requires 610.01540.

\( \text{C}_{18}\text{H}_{19}\text{CoMoO}_4 \): Found 59.47\% C, 3.85\% H, requires 59.48\% C, 3.78\% H.

Addition of \( \alpha \)-BuLi to Co/Mo aldehyde complex 3
To a solution of aldehyde 3 (50 mg, 0.12 mmol) in THF (15 mL) at \(-78^\circ\text{C}\) was added \( \alpha \)-butyllithium (1 mL of a 1.6 M solution in hexane, 1.6 mmol) the reaction mixture was stirred for 30 min at \(-78^\circ\text{C}\) and then quenched with ethanol (5 mL). The reaction mixture was allowed to warm to r.t. and filtered through a pad of celite and silica. The solvent was removed in vacuo to yield the product 4a as a red oil (53 mg, 93%). The diastereoisomers could be separated by silica gel chromatography using ether–petrol (3:1). Dark red bands were isolated to give the major diastereoisomer (43 mg) and the minor diastereoisomer (10 mg).

Major diastereoisomer:

1H NMR (250 MHz, CDCl\(_3\)): \( \delta = 5.43 \) (5 H, s), 4.53–4.46 (1 H, m), 2.70 (3 H, s), 1.66–1.20 (7 H, m), 0.95–0.82 (3 H, m) ppm.

13C NMR (100.16 MHz, CDCl\(_3\)): \( \delta = 225.4 \) (CO), 223.8 (CO), 96.6 (alkynyl), 93.1 (alkynyl), 59.2 (Cp), 74.7 (CHOH), 38.7 (CH\(_2\)), 27.7 (CH\(_2\)), 21.6 (CH\(_3\)), 19.6 (CH\(_3\)), 13.0 (CH\(_3\)) ppm.

**m/z** (FAB): Found (M\(^+\) - 2 CO) 431.96683, \( \text{C}_{18}\text{H}_{19}\text{CoMoO}_4 \) requires 431.96690.

**v\(_{\text{max}}\) (neat)**: 2044, 1974, 1930 cm\(^{-1}\).

Minor diastereoisomer:

1H NMR (250 MHz, CDCl\(_3\)): \( \delta = 5.47 \) (5 H, s), 4.81–4.75 (1 H, m), 2.72 (3 H, s), 1.66–1.20 (7 H, m), 0.95–0.82 (3 H, m) ppm.

13C NMR (100.16 MHz, CDCl\(_3\)): \( \delta = 224.5 \) (CO), 223.9 (CO), 97.5 (alkynyl), 94.0 (alkynyl), 89.0 (Cp), 74.3 (CHOH), 37.6 (CH\(_2\)), 27.5 (CH\(_2\)), 21.6 (CH\(_3\)), 19.4 (CH\(_3\)), 13.0 (CH\(_3\)) ppm.

**m/z** (FAB): Found (M\(^+\) - 2 CO) 431.96628, \( \text{C}_{18}\text{H}_{19}\text{CoMoO}_4 \) requires 431.96690.

**v\(_{\text{max}}\) (neat)**: 2040, 1972, 1927 cm\(^{-1}\).

Acknowledgment

We would like to thank the EPSRC for project scholarships (AJF and RF) and a Quota Award (DTR). We would also like to thank Pfizer for additional funding. AJF, RF and SDRC would like to thank Mugal E. Shahi for continued inspiration during the course of this work. We would also like to thank the referees for their constructive comments.

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References

Homologation of allylic alcohols. An approach to cyclic and acyclic polyoxygenated compounds

Ryan J. Davoille, David T. Rutherford and Steven D. R. Christie*
Department of Chemistry, University of Loughborough, Loughborough, LE11 3TU, UK

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The combination of the Sharpless asymmetric epoxidation reaction with a sulfur ylide mediated synthesis of allylic alcohols from epoxides provides a powerful iterative process for the production of polyoxygenated compounds. The alkene installed in the sulfur ylide reaction has also been used in a number of ring closing metathesis reactions to produce highly oxygenated cyclic compounds. © 2000 Elsevier Science Ltd. All rights reserved.

The synthesis of highly oxygenated organic molecules continues to be an area of interest for synthetic chemists. The stereo- and regio-controlled placement of oxygen represents a particular challenge. Recent examples of iterative placement of oxygen have been shown by Hanessian, Lipshutz, McDonald, Sweeney and Rainer. Of particular relevance to the chemistry described herein is the use of silylated epoxides to produce 1,2-diols in an iterative fashion employed by Wicha. We wished to combine two reactions in order to produce a new protocol for directed oxygen placement on a growing alkyl chain. The Sharpless asymmetric epoxidation (SAE) is a well known reaction and has been widely used in organic synthesis for a number of years. It provides reliable, and importantly, predictable levels of enantiomeric excess in the epoxidation of allylic alcohols. Mioskowski has reported the conversion of epoxides to allylic alcohols using a sulfur ylide. The ylide reacts regioselectively at the less hindered end of the epoxide, transferring a methylene group with concomitant loss of dimethyl sulfide. We envisaged that these two reactions could be used in tandem: one produces epoxides from allylic alcohols, the other allylic alcohols from epoxides. The result is then a simple protocol for homologation of allylic alcohols. In addition, we also hoped to use the alkene installed in the sulfur ylide reaction to provide an entry to a number of substrates suitable for ring closing metathesis reactions. This would extend the scope of the protocol to cyclic as well as acyclic targets.

* Corresponding author. E-mail: s.d.christie@lboro.ac.uk (S. D. R. Christie)

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In order to test this proposal, we started with racemic glycidol (Scheme 1). Protection of the primary alcohol as its TBDMS ether (1) was followed by the first of the sulfur ylide reactions. As reported by Mioskowski, treatment of trimethylsulfonium iodide with n-butyllithium produced the requisite dimethylsulfonium methylidene. Reaction of three equivalents of this with the epoxide gave the allylic alcohol (2) in 66% yield. In these early experiments, we used an alternative epoxidation methodology to the Sharpless protocol. Thus, treatment with MCPBA gave the epoxide (3) in 61% yield in a diastereoisomeric ratio of ca. 1:1. In order to test the substrate directing effect of the hydroxy group already in place, we then used VO(acac)\(_2\)/BuOOH. This produced the same product, but with an increased diastereomeric ratio of ca. 4:1. The epoxy alcohol product was now ready to be subjected to a second cycle of the iterative procedure. At this juncture, we were concerned that the acidic proton of the free hydroxy group may quench the sulfur ylide, and possibly also facilitate a Payne rearrangement of the epoxide from the resultant alkoxide. To prevent this possibility, we decided to protect the alcohol. This protection would also allow for an orthogonal protection strategy on each hydroxyl as the chain grows. Thus, if we were to produce a polyol with this methodology, selective deprotection of the individual alcohols would allow manipulation of selected sites as they were unmasked. At this stage, we chose MEM as a suitable group. A subsequent sulfur ylide reaction produced the allylic diol (5) in good yield. Having established that the protocol was viable, we then sought to achieve the sequence in a stereocontrolled manner.

![Scheme 1](image)

Starting with benzyl protected racemic glycidol (6) (Scheme 2), a sulfur ylide reaction gave the allylic alcohol (7), as expected, which was then subjected to a Sharpless kinetic resolution epoxidation. Using standard conditions, one enantiomer of the alcohol was transformed into its epoxide (8), while the other was untouched. The enantiomeric excess of the desired product was found to be 96% by HPLC.
free alcohol was again protected as its MEM ether (9) before opening the epoxide with the sulfur ylide to give the allylic alcohol (10) in 83% yield.

Scheme 2. (a) Me$_3$Si, BuLi, THF, -25°C; (b) Ti(OiPr)$_4$, (+)-diisopropyl tartrate, 'BuOOH; (c) MEMCl, Hunig's base; (d) TiCl$_4$, 0°C, DCM; (e) 2,2-dimethoxypropane; (f) ozone, DCM

Removal of the MEM ether protection and conversion of the diol (11) into its dimethyl acetal was carried out before ozonolysis transformed the alkene into the expected carbonyl functionality (13). The yield for the ozonolysis was a moderate 43%, but it allowed us to confirm the stereochemistry of the product since this short scheme comprises a synthesis of a protected tetrose. In this short synthetic scheme, we have used Sharpless epoxidation chemistry and the sulfur ylide reaction to build up the molecule in an iterative fashion by homologation of the allyl alcohol functionality. The only other reactions employed in this scheme are protections and deprotections, and the final ozonolysis. It should be noted that this procedure could easily be extended to other longer polyol chains by repeating the iterative cycle an appropriate number of times.

In order to diversify this procedure, and to test the scope of the protocol, we wished to investigate the potential for transformations into other types of skeleton. Since the sulfur ylide reaction introduces a terminal alkene group, we envisaged using a ring closing metathesis to cyclise the chain into oxacycles of varying sizes. In this respect, we took the allylic alcohol (7) (Scheme 3) and allylated the hydroxyl group. This diene (14) was then cleanly metathesised with Grubb's catalyst to produce the dihydrofuran (15) in an excellent 91% yield.

To make a dihydropyran, we extended the chain, as shown in Scheme 4. Allylation of the alcohol (16) was achieved at low temperature in order to avoid a Payne rearrangement. The second sulfur ylide reaction proceeded as expected to produce the diene (18). Exposing this to Grubb's catalyst gave the dihydropyran (19) in good yield upon stirring at room temperature.

We have also looked at the possibility of attempting the sulfur ylide reaction on a bis epoxide, since this would allow the homologation to proceed in two directions at once (Scheme 5). Epoxidation of 1,5-hexadiene with MCPBA proceeded smoothly to give the expected product (21) in good yield. Reaction with excess sulfur ylide gave the diol (22) in an unoptimised 35% yield, however, each reaction is
therefore occurring in at least 60% yield. With two terminal alkenes having been placed in the chain, we
subjected the diol to a metathesis reaction. Stirring the diene in dichloromethane with Grubb’s catalyst
resulted in quantitative conversion to a mixture of the syn and anti isomers of cyclohexene-1,4-diol (23)
which were isolated in 71% yield. We were particularly pleased with this result, as it has been reported
that Grubb’s catalyst is sensitive to allylic substitution. Here we have two allylic alcohols, and have
successfully cyclised the diene without requiring protection of the hydroxyl groups.

Conclusion: We have illustrated a new procedure for homologation of allylic alcohols. The scheme
uses two simple reactions to produce a convenient route to densely functionalised organic molecules. We
have demonstrated how this can be used to furnish straight chain polyols. In addition, we have utilised
the terminal alkene that is installed by the sulfur ylide reaction, and used this in a metathesis approach to
oxygenated dihydrofuran, dihydropyran and cyclohexene diol compounds. Application of this protocol
to natural product synthesis is underway, and will be reported in due course.

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References

   For stereoselective dihydroxylation of allylic alcohols, see: Cha, J. K.; Christ, W. J.; Kishi, Y. Tetrahedron 1984, 40, 2247.
9. Preparation of 1-(phenylmethyl)oxy]but-3-en-2-ol. To a solution of dimethylsulfonium iodide (7.46 g, 36.58 mmol) in tetrahydrofuran (150 ml) at -25°C was added n-butyllithium (14.14 ml, 35.35 mmol). The reaction mixture was stirred for 30 minutes prior to the addition of benzyglycidol (2 g, 12.19 mmol) and then allowed to warm to 0°C over approximately 30 minutes. The reaction mixture was then stirred for a further 4 h, cooled to 0°C quenched with water and extracted with diethylether. The organic extracts were combined and dried with magnesium sulfate prior to the solvent being removed under reduced pressure. The crude material was then purified by silica gel chromatography (eluent petrol:diethylether 4:1) to yield 1.41 g (65%) of the title compound as a colourless oil. IR (neat film) 3426, 2860, 1645, 1453, 1104 cm⁻¹. ¹H NMR (250 MHz, CDCl₃) δ 7.23–7.27 (m, 5H, Ar), 5.80 (dd, 1H, J=17, 10, ·CH=CH₂), 5.32 (dt, 1H, J=17, 1, ·CH=CH₂), 5.15 (dt, 1H, J=10, 1, ·CH=CH₂), 4.52 (s, 2H, ArCH₂), 4.34–4.30 (m, 1H, ·CHOH), 3.48 (dd, 1H, J=9, 3, ·OCH₂), 1.71 (s, 3H, J=3, ·OCH₂). ¹³C NMR (250 MHz, CDCl₃) δ 138.00, 137.00, 136.71, 128.40, 127.75, 116.27, 74.03, 73.29, 71.40. HRMS (EI) calcd for C₁₁H₁₄O₁ 178.09938, found 178.09920.


11. Chiralcel OD column, eluent hexane:isopropanol 97:3, flow rate 0.75 ml/min, retention time 44.38 min.


