INVESTIGATIONS INTO METAL-OXO REAGENTS IN ORGANIC SYNTHESES AND TOWARDS THE SYNTHESES OF (-)-DYSIBETAINE USING THE AZA-[2,3]-WITTIG REARRANGEMENT-CYCLISATION

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Abstract

Part 1 of this thesis describes the continued development of a new method for the synthesis of olefins from sulfur reagents and carbonyl compounds. The proposed catalytic olefination investigated the reaction of sulfur ylides or sulfines with carbonyl compounds to produce the corresponding alkene, catalysed by a transition metal oxo complex. A variety of literature trioxo rhenium and molybdenum di-oxo and oxo-imido complexes were reacted with dimethylsulfoxonium methylide and generally led to degradation. The reaction of diphenylsulfonium benzylide with the rhenium and molybdenum oxo complexes gave no reaction or led to degradation. Diphenylsulfine was also reacted with the metal-oxo complexes and produced benzophenone and degradation of the metal oxo complex.

Part 2 of this thesis describes the investigation into the novel complex $MoO(N^tBu)(2,6\text{-}R_2C_6H_3O)_2py$ [where R = ^{i}Pr (**72a**) or Me (**72b**)], which was developed in the Anderson group, as an epoxidation catalyst. The initial epoxidation conditions were optimised for *trans*-stilbene. The optimised conditions were used to epoxidise a variety of alkenes. The catalyst **72** is effective at epoxidation of electron rich alkenes, will selectively epoxidise allylic alcohols and does not epoxidise electron deficient alkenes. The rate of epoxidation of *cis*-stilbene using catalyst **72a** and **72b** were compared and showed that **72b** had a faster rate of epoxidation than **72a**. The rate of reaction for catalyst **72b** was also compared with $MoO_2(2,6\text{-}Me_2C_6H_3O)_2py_2$ **98** for the

epoxidation of *cis*-stilbene and found to be similar, indicating that the catalytically active species may be common to both.

Part 3 of this thesis describes an investigation into the synthesis of (-)-dysibetaine using the aza-[2,3]-Wittig rearrangement-cyclisation protocol. The initial retrosynthesis led to a *β*-lactone enolate **57** in the aza-[2,3]-Wittig rearrangement cyclisation. However the desired cyclised product **58** was not obtained and instead ring opening of the *β*-lactone to the acrylic acid **80** was observed. A revised route used a phenyldimethylsilyl amino acid **106** as a masked hydroxyl group to mimic a serine amino acid that would not undergo *β*-elimination. The aza-[2,3]-Wittig precursor **109** was prepared and subjected to the standard aza-[2,3]-Wittig rearrangement-cyclisation protocol and the desired cyclised product **110** was obtained in 43% yield. This product contained the correct dysibetaine skeleton and would require functional group transformations to complete the synthesis.

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Finally special thanks to my Mum and Dad for all the support over the last three and half years, without them this thesis would never have been completed and therefore it is to them that I dedicate this thesis.

Abbreviations

δ	Chemical Shift
aq	Aqueous
Boc	*tert*-Butoxycarbonyl
br	broad
Bu	Butyl
18-C-6 / 18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
calcd	calculated
cat	Catalytic
Cp	cyclopentadienyl
CSA	Camphorsulfonic acid
d	doublet
DBU	1,8-Diazobicyclo[5.4.0]undec-7-ene
DCC	1,3-Dicyclohexylcarbodiimide
DCM	Dichloromethane
DEAD	Diethyl azodicarboxylate
DMAP	4,4-dimethylaminopyridine
DMPU	*N,N'*-Dimethyltetrahydropyrimidinone
dr	Diastereomeric ratio
E	Electrophile
EDG	Electron donating group
ee	Enantiomeric excess
er	Enantiomeric ratio
ES^+	Electrospray
EWG	Electron withdrawing group

HMPA	Hexamethylphosphorictriamide
hplc	High-performance liquid chromatography
HWE	Horner-Wadsworth-Emmons
i	Iso
KHMDS	Potassium hexamethyldisilazide
L	Ligand
LDA	Lithium di-*iso*-propylamide
m	Meta
m	Multiplet
MoOPH	oxoperoxymolybdenum(pyridine)(hexamethyl phosphoramide)
MS	Mass spectrometry
MTO	Methyltrioxorhenium
n	Straight chain
Nu	Nucleophile
o	Ortho
p	Para
PIFA	Phenyliodine (III) bis(trifluoroacetate)
ppm	Parts per million
Pr	Propyl
Py	Pyridine
q	Quartet
rt	Room temperature
s	Singlet
t	Tertiary

t	Triplet
TBAF	Tetra-n-butylammonium fluoride
TBDMS	*tert*-Butyldimethylsilyl
TBHP	*tert*-Butylhydroperoxide
TBS	*tert*-Butyldimethylsilyl
Tf	Triflate
TFA	Trifluoroacetic acid
TIPS	Triisopropylsilyl
TMS	Trimethylsilyl
Ts	Tosylate
VT	Variable temperature

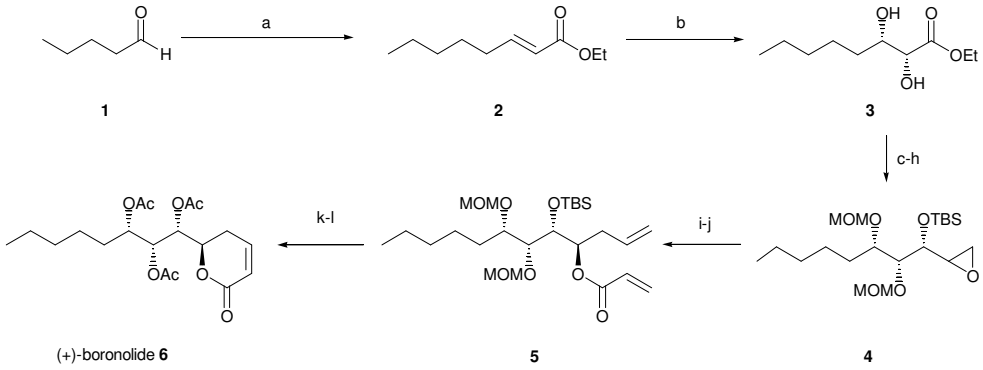
Contents

Part 1: Towards a Catalytic Carbonyl Olefination reaction using Metal-oxo complexes and Sulfur reagents

Chapter 1: Introduction

1.1 Alkene synthesis and use

Alkenes are used world wide in industrial processes to create a wide variety of products such as polymers, fuels, drugs and natural products, and therefore their synthesis is very important. Alkenes can be used to introduce functional groups or may be a desired component in the final product. The synthesis of (+)-boronolide **6** was published recently[1] and showed the diversity of reactions which can be carried out on alkenes. These include epoxidation and ring closing metathesis (RCM) and in addition it demonstrates a well-known method of introducing alkenes from carbonyl compounds *via* the Horner-Wadsworth-Emmons (HWE) reaction.



Reagents and conditions: (a) $(EtO)_2P(O)CH_2CO_2Et$, LiBr, Et_3N, THF, rt, overnight, 89%; (b) $(DHQ)_2PHAL$, K_2CO_3, $K_3Fe(CN)_6$, $MeSO_2NH_2$, *t*-BuOH/H_2O (1:1), 0.1 M OsO_4 (0.4 mol%), 0 °C, 24 h, 96%; (c) MOMCl, DIPEA, CH_2Cl_2, 0 °C to rt, overnight, 91%; (d) DIBAL-H, CH_2Cl_2, 0 °C to rt, 2 h 89% (e) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C to -60 °C, 95%. (f) CH_2=CHMgBr, $MgBr_2.Et_2O$, THF or CH_2Cl_2, -78 °C, 6 h, 90% (g) TBSOTf, 2,6-lutidine, CH_2Cl_2, 0 °C, 30 min, 98%; (h) *m*-CPBA, Na_2HPO_4, CH_2Cl_2, overnight, 91%; (i) CH_2=CHMgBr, CuI, THF, -30 °C, 86%; (j) $ClCOCH=CH_2$, Et_3N, cat. DMAP, CH_2Cl_2, 0 °C to rt, 91%; (k) 2 mol% $(PCy_3)_2Ru(Cl)_2$=CHPh, CH_2Cl_2, reflux, 8 h, 89%; (l) $BF_3.SMe_2$, -30 °C, then aq HF, CH_3CN, rt, then Ac_2O, Et_3N, cat DMAP, CH_2Cl_2, rt, (50% overall).

Scheme 1. The synthesis of (+)-Boronolide **6**[1]

Generally the synthesis of most alkenes can be classified as homolytic or heterolytic bond formation (Figure 1). The following section will discuss mainly the formation of alkenes *via* heterolytic formation.

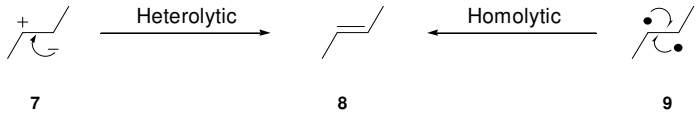


Figure 1. The formation of alkenes *via* homolytic or heterolytic bond formation

There are many different ways to produce alkenes, and the simplest way is an elimination reaction with acid or base (Figure 2). The problems which are encountered with these acid/base conditions are: 1) the lack of compatibility with other functional groups in the compound and 2) the low regioselectivity.

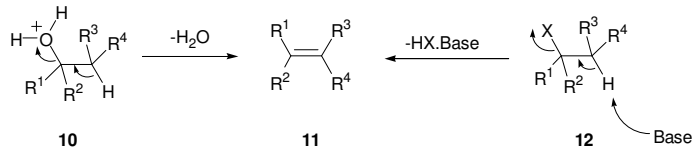


Figure 2. The formation of alkenes using acid/base conditions

This has led to the development of alternative methods to introduce alkenes into compounds, and some of the most common techniques are shown in Figure 3.[23] In addition to these standard transformations, there have also been a variety of modifications, and this has led to a diverse range of methods to introduce this functional group.

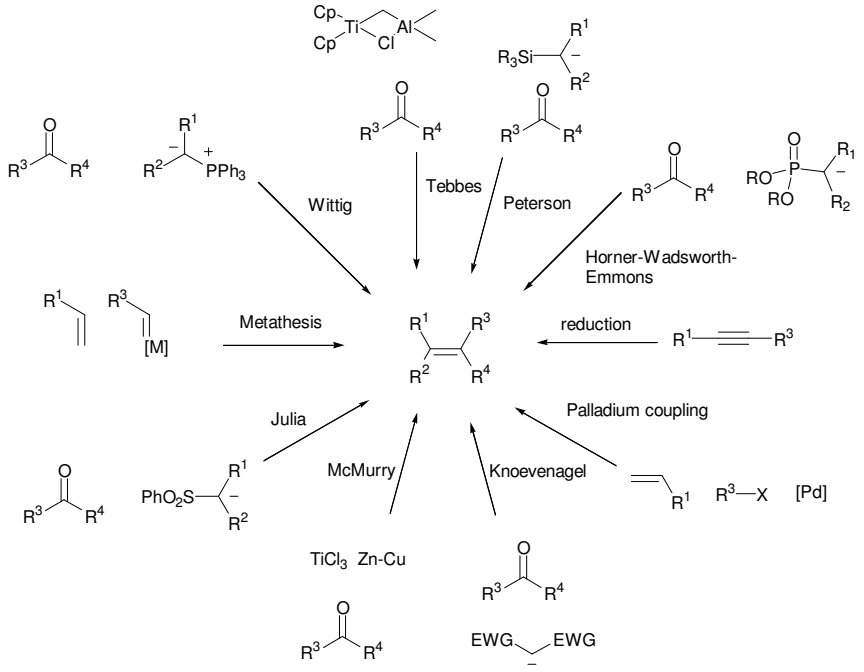
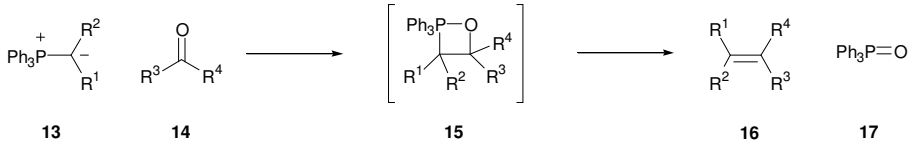


Figure 3. Various methods for the synthesis of alkenes

The Wittig Reaction

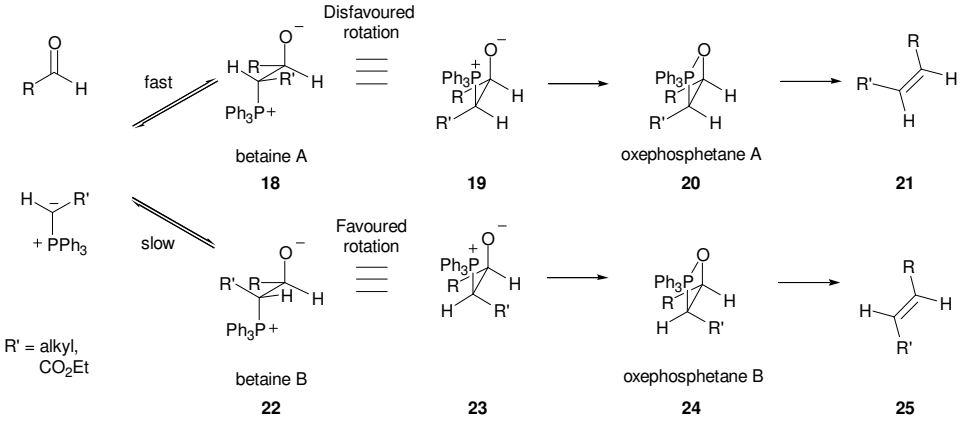
In 1953 Wittig discovered that phosphonium ylides **13** react with carbonyl compounds **14** to give alkenes **16** (Scheme 2).[4] This discovery led to Wittig winning the Nobel Prize for chemistry in 1979.[5] The Wittig reaction is still regularly used to produce alkenes and is widely used in industry.



Scheme 2. The Wittig reaction

The Wittig reaction is particularly useful and practical as the geometry of the double bond can usually be predicted. An unstabilised ylide (where R'= alkyl)

is high in energy as the negative charge can not be delocalised. The reaction of an unstabilised ylide with a carbonyl leads to the formation of betaine A **18** rather than betaine B **22** (Scheme 3 & Figure 4) as the rate of formation is faster (i.e. kinetic control). The rotation to form **19** leading to the oxephosphetane A **20** is disfavoured due to steric hindrance, however as the reaction is irreversible, due to the unstabilised ylide the major product obtained is often the Z-alkene **21**.



Scheme 3. The stereochemistry of the Wittig reaction for stabilised ylides

A stabilised ylide, where the carbanion is adjacent to an electron withdrawing group such as an ester (where R'=CO_2Et), is lower in energy due to delocalisation of the negative charge. The ylide may still form Betaine A **18** (Scheme 3), however the reaction is now reversible because it may return to the stabilised ylide and the carbonyl compound in preference to bond rotation to form oxephosphetane A **20**. The thermodynamically more favourable reaction to form **24** can then occur. Betaine B **22** can more easily access conformation **23** to produce the *E*-alkene **25**. The bond rotation from **22** to **23** is lower in energy than the rotation from **18** to **19** as shown in Figure 4.

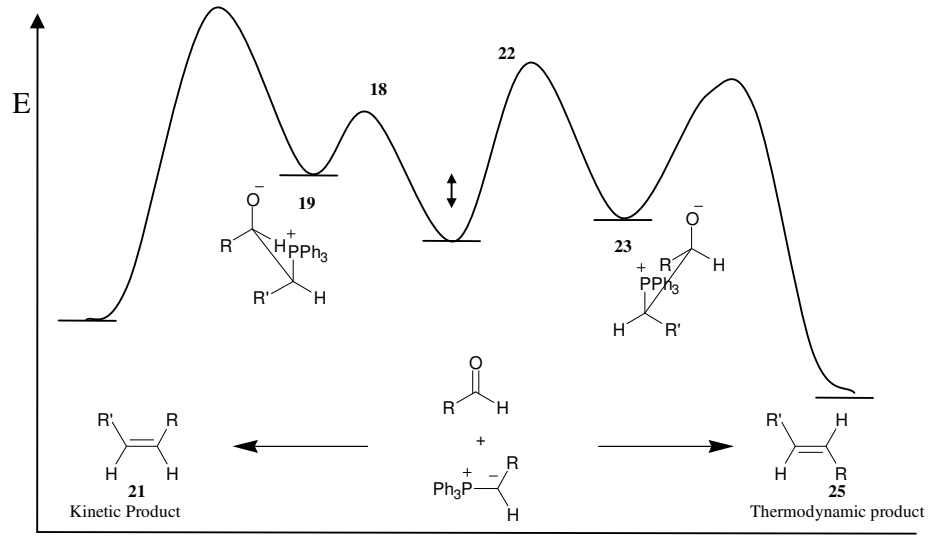


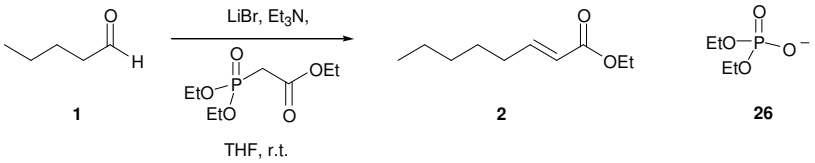
Figure 4. The energy profiles of the Wittig reaction

The main disadvantages with the Wittig reaction are that the reaction requires purification of the product from the triphenylphosphonium oxide by-product and the necessity to use stoichiometric quantities of the phosphonium ylide. In addition low selectivity is obtained when allylic and benzylic ylides are used due to the ability of these groups to stabilise charge. Low reactivity can also occur with enones and sterically hindered ketones. The reaction is also restricted to aldehydes and ketones.

The Horner-Wadsworth-Emmons reaction

The Horner-Wadsworth-Emmons (HWE) reaction is a modification of the Wittig reaction where a phosphonate anion is used instead of a phosphonium ylide.[6,7] The main advantage of the reaction is that a phosphonate anion is more reactive due to oxo and alkoxy groups donating charge onto the phosphorus atom, which in turn allows more negative charge on the carbon atom. If the

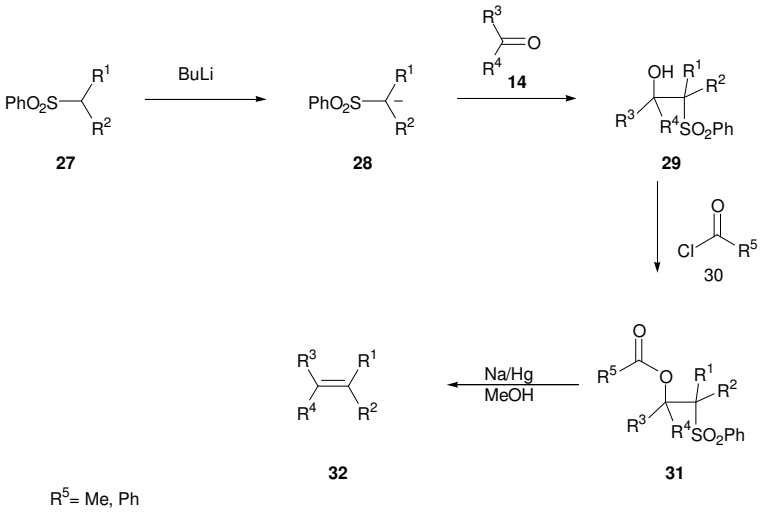
phosphonate anion is attached to an electron withdrawing group, then it will regularly react with ketones which would not undergo Wittig reactions. The same problem exists for HWE as it does for the Wittig reaction in that the reaction is stoichiometric. An advantage of using a phosphonate anion is that the dialkoxyphosphonate salt by-product **26** obtained is water soluble, unlike triphenylphosphonium oxide (Scheme 4).



Scheme 4. The Horner-Wadsworth-Emmons reaction in the synthesis of (+)-Boronolide[1]

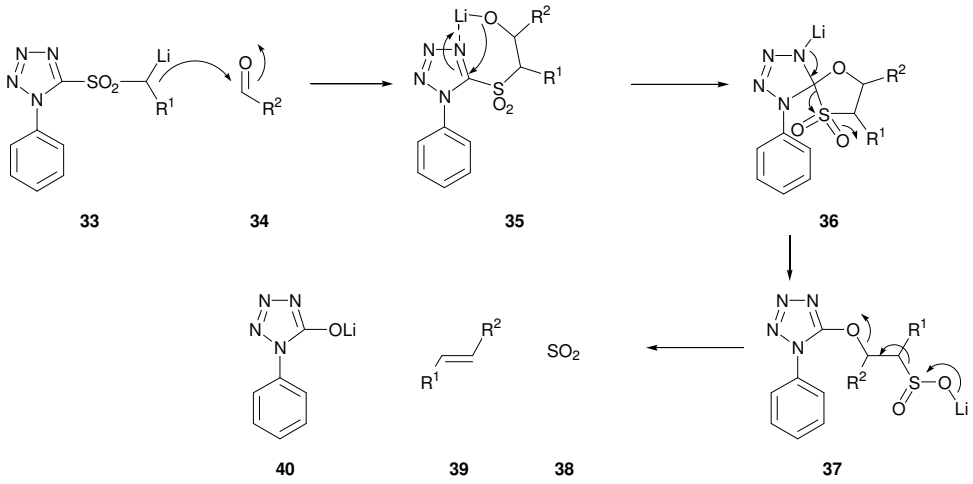
The Julia Reaction

The Julia reaction is a multi-step reaction to form an alkene **32** *via* 1) deprotonation of sulfones **27** by strong base, 2) reaction with a carbonyl **14** 3) conversion of the resultant alcohol **29** to a good leaving group **31**, 4) homolytic cleavage of sulfone **31** leading to an alkene **32** (Scheme 5).[8] The reaction is completely regioselective. The main disadvantage with the Julia reaction is the multi-step procedure, as generally the hydroxy group needs to be converted to a good leaving group and the product reduced to produce the alkene. In addition to this the synthesis of tri- and tetra- substituted alkenes proceed in low yield. However the stereochemistry of the β-hydroxysulfone **29**, does not dictate the geometry of the final alkene, and therefore the Julia reaction has become important in organic synthesis as it often produces the *E*-alkene in high stereoselectivity.



Scheme 5. The Julia reaction

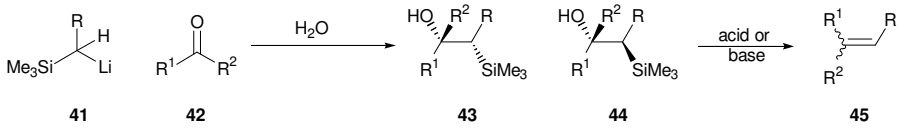
The modified Julia olefination is also known as the one-pot Julia olefination.[9] It replaces the phenylsulfone group **27** with a heteroarylsulfone. Kocienski used 1-phenyl-1*H*-tetrazol-5-yl sulfone **33** and found that a high *trans*-selectivity was obtained if there was no strong influence from electronic or steric factors. The mechanism is proposed as shown below (Scheme 6), and the major advantage compared to the traditional Julia olefination is the reaction is now a one-step process.



Scheme 6. The mechanism of the modified Julia reaction

The Peterson Reaction

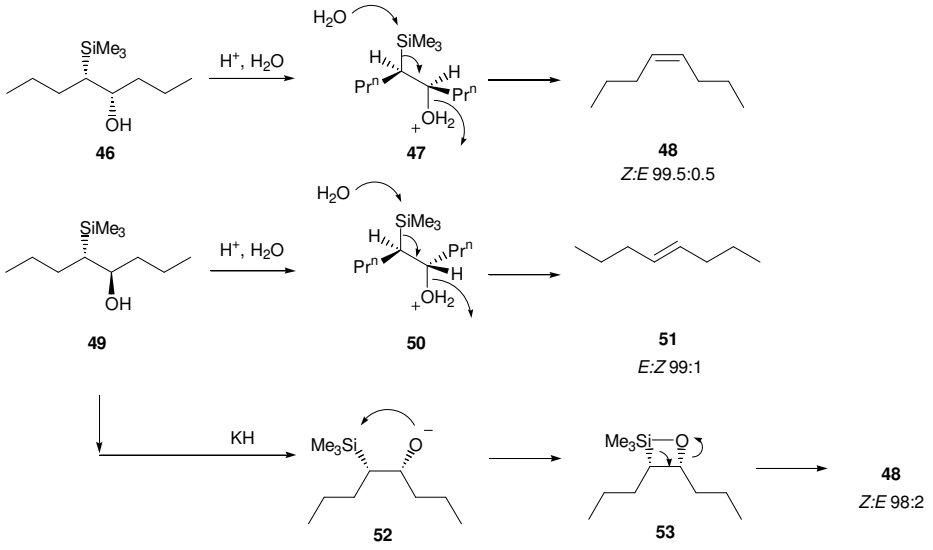
The Peterson reaction proceeds *via* a stereospecific elimination of silanol (**43** & **44**) to form an alkene (Scheme 7).[10] The reaction occurs by nucleophilic attack of an α-trialkylsilyl carbanion **41** on a carbonyl **42** to produce the β-hydroxy silanes **43** and **44**. The problem encountered with the Peterson reaction is the uncontrolled formation of the β-hydroxy silane which produces two diastereoisomers, **43** and **44** (Scheme 7).



41 **42** **43** **44** **45**

Scheme 7. The Peterson alkenylation reaction

The mechanism for the elimination reaction can occur under acidic or basic conditions (Scheme 8).[11] Under acidic conditions the elimination occurs *via* an *anti*-periplanar transition state, therefore depending on which diastereomer is used the *E*-alkene **51** or Z-alkene **48** can be isolated as the major product.

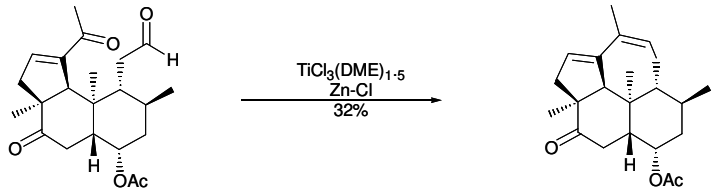


Scheme 8. Elimination in the Peterson reaction

In basic conditions the hydroxyl group is deprotonated, and the oxygen anion formed attacks the silyl group intramolecularly **52**. The transition state is *syn*-periplanar as the oxygen and silicon atom must be on the same side to form the new strong Si-O bond. This drives the reaction forward to produce the *E*-alkene **48**. The major problem with this reaction is making diastereoisomerically pure β-hydroxy silane to produce the desired alkene.

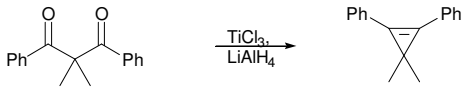
The McMurry Reaction

The McMurry reaction involves the use of a low valent titanium reagent to produce alkenes from aldehydes and ketones.[12] It is particularly useful in forming strained alkenes such as **55** & **57** as shown below (Scheme 9 and Scheme 10). [13,14] The reaction is a two-step process in which a 1,2-diol is formed from the coupled carbonyls which then deoxygenates to give the alkene. The evidence for the diols being formed is that under specific conditions they can be isolated.



54 **55**

Scheme 9. The McMurry reaction applied in the synthesis of kempene-2



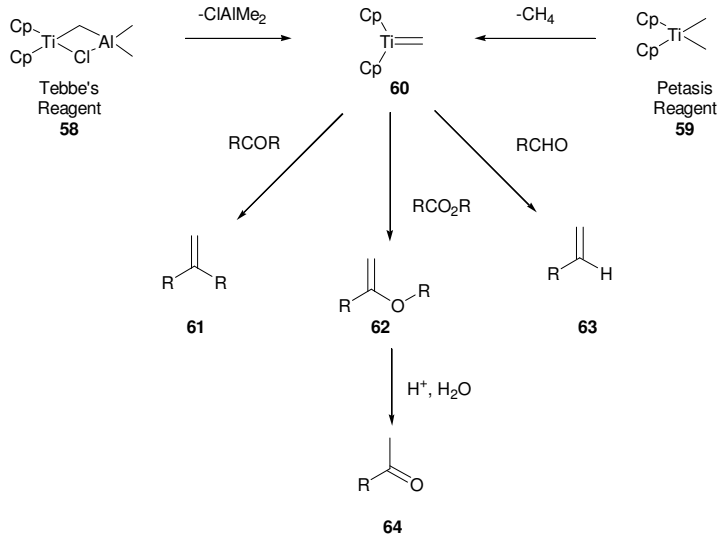
56 **57** 46%

Scheme 10. The McMurry reaction used to form a strained cyclopropene ring[13]

1.2 Transition Metal-Alkylidene chemistry and Olefin Metathesis

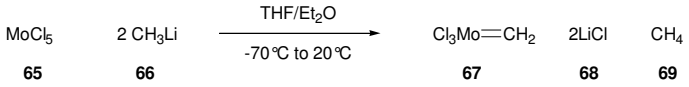
Metal-Catalysed Carbonyl Olefination Reaction

There are many ways to convert aldehydes or ketones to alkenes, however there are very few ways in which to convert a carboxylic ester C=O bond to an alkene. Tebbe's **58** and Petasis **59** reagent are therefore very useful in this respect (Scheme 11).[15,16] In addition to reacting with aldehydes and ketones they also react with carboxylic esters, lactones, amides and carbonates to from the corresponding methylene derivatives.[17] It is believed that both reagents form the same intermediate **60**. An advantage of the Tebbe reagent over the Wittig reaction is that it does not enolise ketones, and therefore optically active ketones can be methylenated without racemisation.

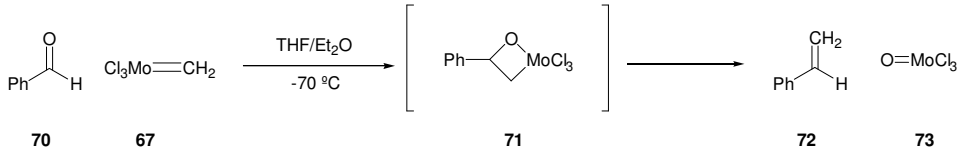


Scheme 11. Reactions carried out using Tebbe's and Petasis Reagent

The molybdenum complex $Cl_3Mo{=}CH_2$ **67** is known as a mild methylenating reagent.[18] The methylenating reagent can be prepared by reacting $MoCl_5$ **65** with methyl lithium **66** (Scheme 12). It reacts with aldehydes and ketones in good yields to produce terminal alkenes (Scheme 13). The reaction is not catalytic and produces the molybdenum-oxo complex **73** in a stoichiometric quantity as by-product.

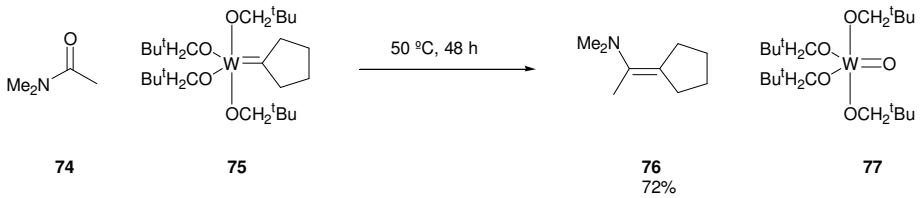


Scheme 12. Preparation of $Cl_3Mo{=}CH_2$



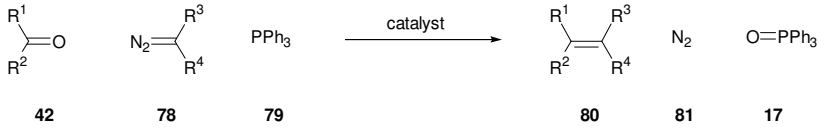
Scheme 13. Terminal alkene synthesis with $Cl_3Mo{=}CH_2$

Tungsten alkylidene complexes, such as **75**, can also act as powerful Wittig reagents.[19] The tungsten complex **75** can be prepared *via* metathesis reaction with methylenecyclopentane.[20] These types of tungsten complex can react with a variety of carbonyl compounds to form di-, tri- or tetra- substituted alkenes. The reactivity rates for these tungsten alkylidene complexes are: aldehyde > ketone > formate > ester > amide and good yields are obtained in all cases (Scheme 14).



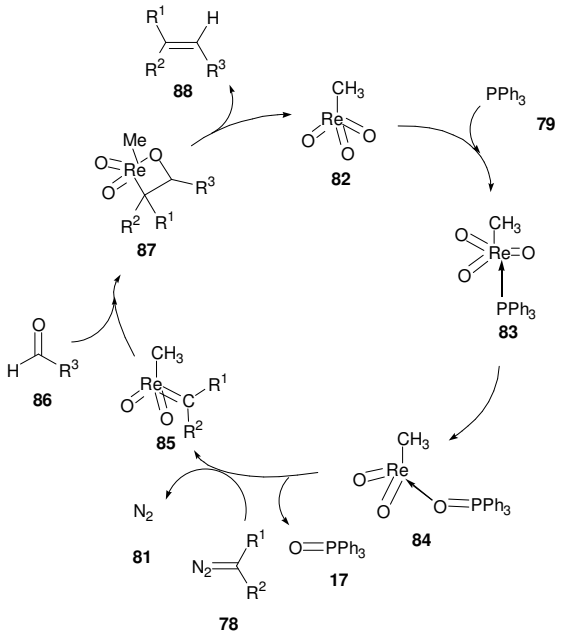
Scheme 14. Tungsten alkylidene reacting with an amide

Another method for producing alkenes is the olefination of carbonyl compounds with stable diazoalkanes using a metal catalyst and stoichiometric triphenylphosphine (Scheme 15). These have been developed for a variety of different metals including rhenium,[21] ruthenium,[22] rhodium,[23] iron,[24] cobalt[25] and molybdenum.[26] Although this reaction can be performed with many transition metals, they have significant differences in their mode of action. Unlike the Wittig reaction, this reaction does not require a base to produce the phosphorus ylide. The diazoalkanes **78** employed are stable and generally contain electron-withdrawing groups, but a stoichiometric quantity of $Ph_3P{=}O$ **17** is still generated.



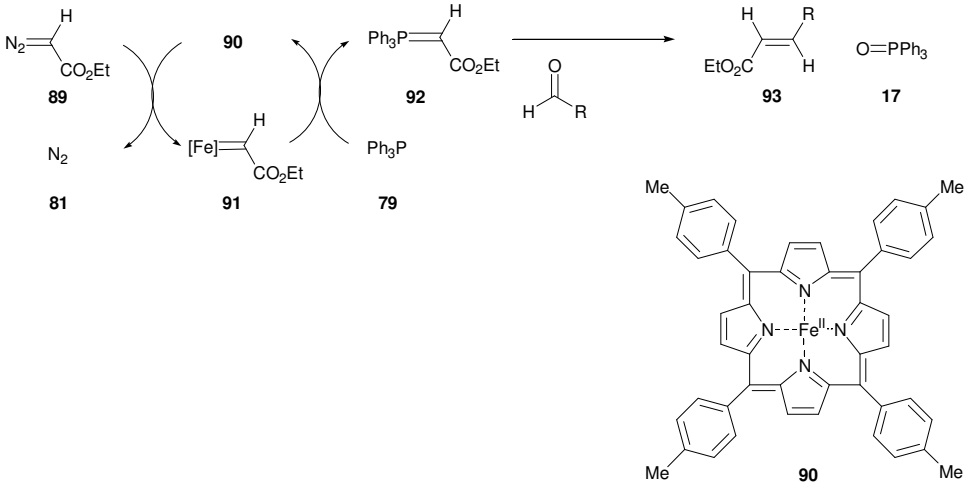
Scheme 15. General olefination reaction using diazoalkanes

Herrmann proposed that the reaction which uses methyltrioxorhenium **82** as a catalyst is believed to react *via* a rhenium alkylidene complex **85** to produce the alkene **88** (Scheme 16).[21] The reaction again requires triphenylphosphine **79** to remove the strong metal-oxo bond to allow the metal alkylidene **85** to reform from the diazoalkane **78**.



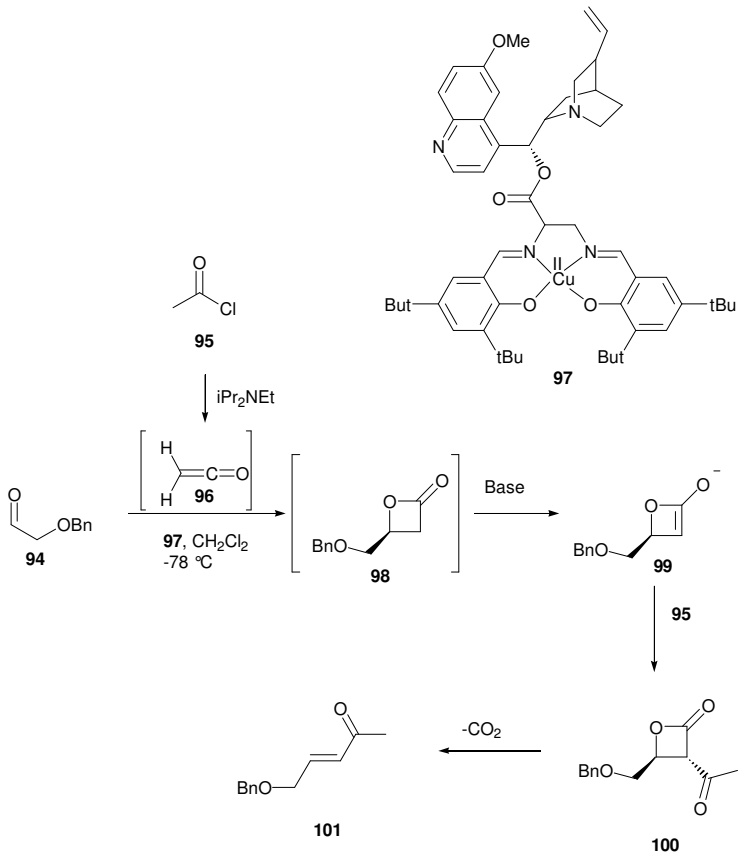
Scheme 16. Rhenium catalysed carbonyl olefination reaction

However, in the iron catalysed reaction the proposed mechanism suggests that the complex **91** is used to form directly the phosphorus ylide **92,** which then reacts with the carbonyl compound to produce the alkene **93** (Scheme 17).[24] At the moment, these reactions still produce stoichiometric triphenylphosphine oxide **17** as a by-product, however this may be avoided in the future by using other oxophilic co-reactants such as silyl compounds.



Scheme 17. Iron catalysed carbonyl olefination reaction

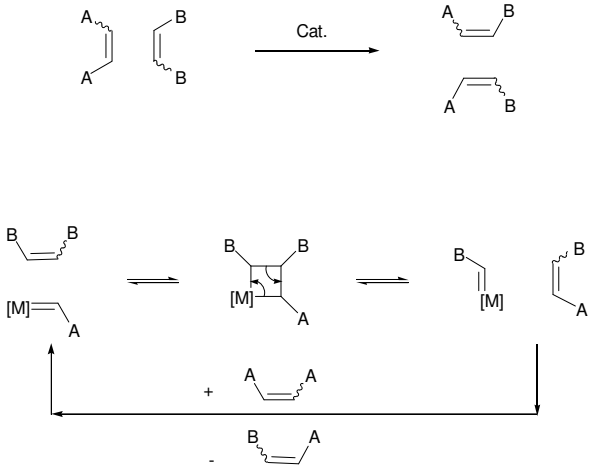
Recently, a copper (II) complex with a salen-quinine mixed ligand **97** was used to produce a catalytic aldehyde olefination reaction using *in-situ* generated ketene **96** (Scheme 18).[27] The reaction was carried out at -78 °C and warmed to -20 °C; after 42 h the *E*-alkene was obtained. The reaction is suggested to proceed *via* a β-lactone intermediate which decarboxylates to form the alkene, but at -20 °C the copper catalyst is most likely participating. The cobalt derivative using this ligand produces the β-lactone and not the alkene suggesting the metal used is important. In addition Mulzer has shown that β-lactones can be vacuum distilled at -78 °C without loss of carbon dioxide and hence this also suggests metal participation in the decarboxylation.[28]



Scheme 18. Catalytic aldehyde olefination reaction

Alkene Metathesis

Alkene metathesis involves the exchange of carbon atoms between a pair of double bonds using a metal alkylidene catalyst. The intermediate formed is a metallocyclobutane which can undergo a retro-cyclisation (Scheme 19).[29] The traditional catalysts such as $MoO_3/CoO/Al_2O_3$ and Re_2O_7/Al_2O_3 required high temperatures.[30] The control and selectivity with these catalysts were limited.



Scheme 19. The general reaction and mechanism for alkene metathesis

An increase in metathesis use in organic synthesis occurred once structurally defined catalysts were synthesised, which reacted at lower temperatures. The Schrock olefin metathesis catalyst **102** was highly active but air and moisture sensitive (Figure 5).[31] The first generation catalysts by Grubbs **103** and Hoveyda **104** were relatively air and moisture stable,[32,33] however second generation catalysts (**105** & **106**) were developed which are even more robust. [34,35] In addition the catalyst **105** often showed a similar functional group tolerance as complex **103** but with the reactivity of the Schrock catalyst **102**.[31] Metathesis can be used for polymerisation (acyclic diene metathesis), ring closing and ring opening metathesis. The reaction has also been used in the

synthesis of natural products to close large ring systems as shown in scheme 20 for the synthesis of manzamine A **112**.[36]

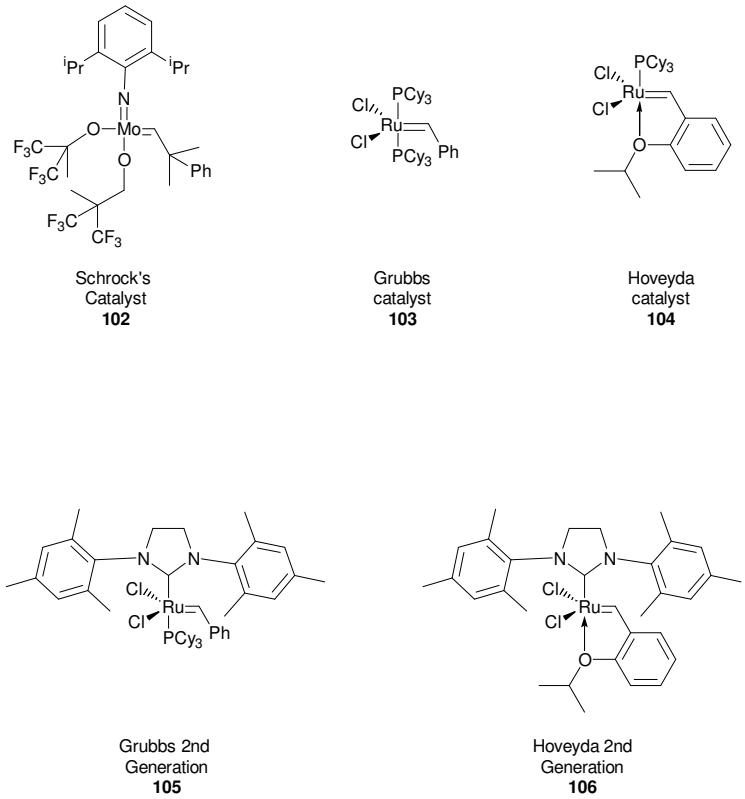
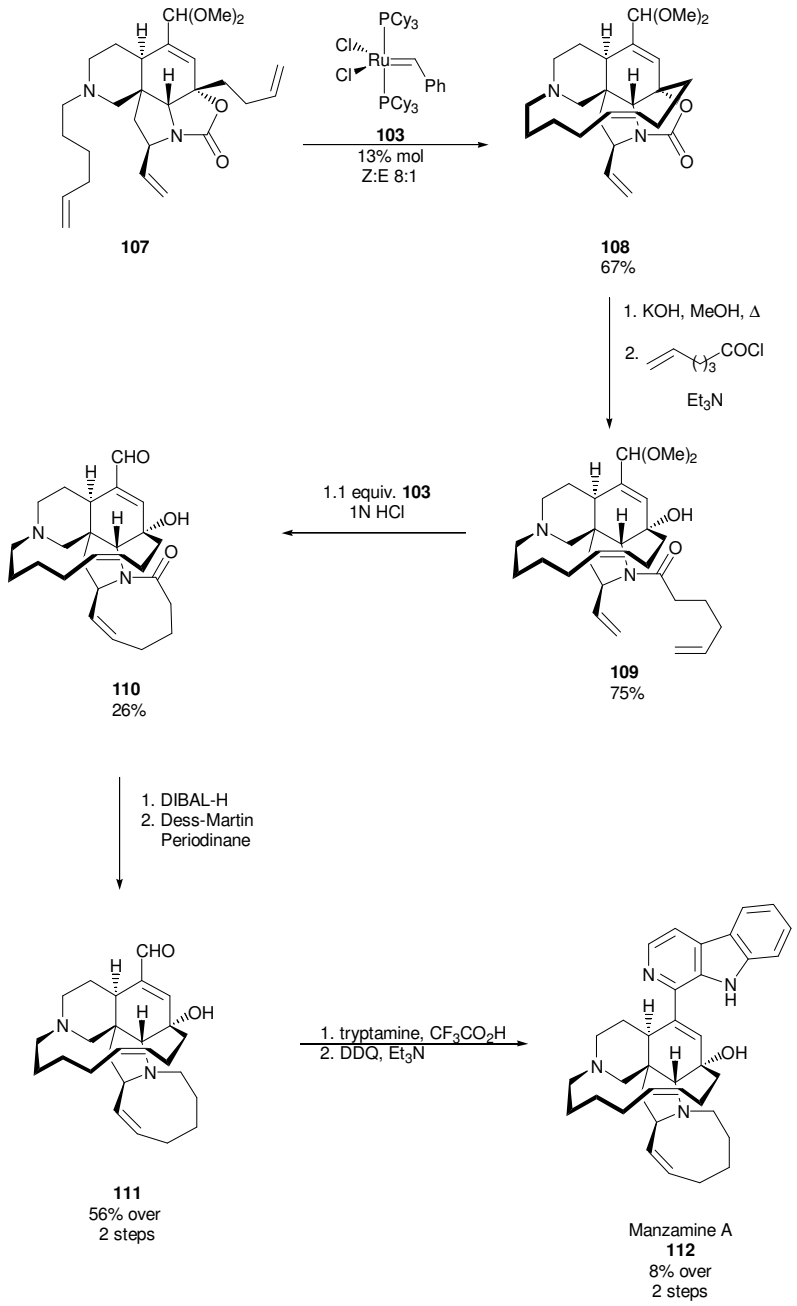


Figure 5. A variety of olefin metathesis catalysts



Scheme 20. The synthesis of manzamine A[36] using alkene metathesis

1.3 Transition Metal Alkylidene Carbonyl Olefination

Previous Work

Research in previous years in our group had focussed on producing a catalytic carbonyl olefination reaction using ketenes with transition metal-oxo complexes. The hypothetical mechanism is shown below (Figure 6).[37,38] It was envisaged that the catalytic cycle could proceed *via* a metallo-β-lactone **115** intermediate to generate carbon dioxide **116** and the metal alkylidene **117**. The second half of the hypothetical catalytic cycle is the reaction of a ketone or aldehyde with a metal alkylidene **117** to produce the desired alkene, and has previously been discussed in Chapter 1.2. The perceived problem encountered with this cycle was believed to be the strong metal-oxo bond **113** as it would be difficult to break the metal-oxo bond to form the metallo-cycle **115**.

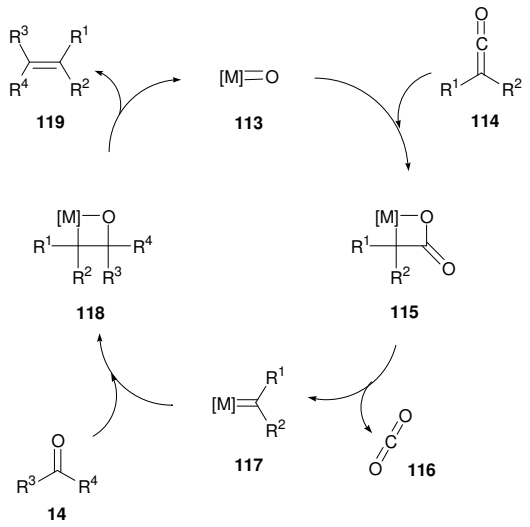
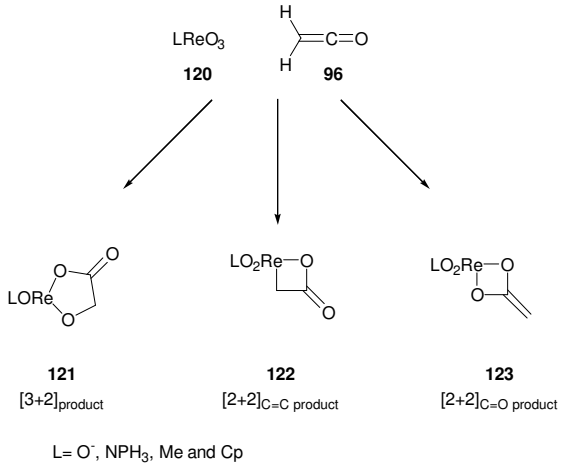


Figure 6. Proposed hypothetical catalytic cycle using ketenes

In 2001 Deubel published a theoretical paper on the [2+2] versus [3+2] addition of metal oxides across a ketene.[39] This had a variety of reaction pathways such as peri- ([2+2] versus [3+2]), stereo- (*cis* or *trans* isomers of [2+2] transition state or product) and chemoselectivity (addition across C=C or C=O). The paper focussed mainly on the rhenium trioxide complexes and their reaction with ketenes (Scheme 21) but also looked at osmium tetroxide.



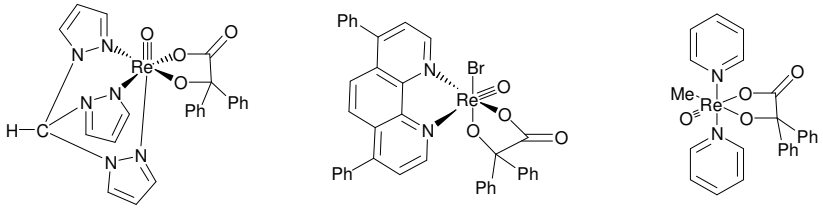
Scheme 21. Possible reaction pathways

The conclusions from this paper were:

1. the periselectivity was dependent on the metal centre i.e. OsO_4 is highly electrophilic at the oxo groups and scarcely electrophilic at metal. Therefore OsO_4 preferred the [3+2] pathway. In $LReO_3$ the oxo groups are nucleophilic and favour [2+2] cycloadditions to a ketene.
2. the chemoselectivity of the [2+2] addition of $LReO_3$ was dependent on the ligand. For example the O^- and NPh_3 ligands were calculated to have the lowest activation energy when reacted with the C=O of the ketene to produce the metallocycle **123**. When L is Me or Cp, the lowest activation energy calculated for the cycloaddition was to C=C of

the ketene to form **122**. However the difference in activation energy for the two [2+2] cycloadditions is very small.

In our group a variety of metal-oxo complexes were investigated with diphenylketene and these included cyclopentadienyl and scorpionate ligands.[37,38] Although the theoretical calculations by Deubel suggested that the rhenium-oxo complexes such as $MeReO_3$ and $CpReO_3$ should react with a ketene to give the product of a $[2+2]_{C=C}$ metallo-β-lactone, the observed results with a variety of rhenium oxo-complexes was the undesired [3+2] cyclised product (Figure 7). Although these novel complexes were interesting, they were not the correct geometry for the hypothetical catalytic cycle.

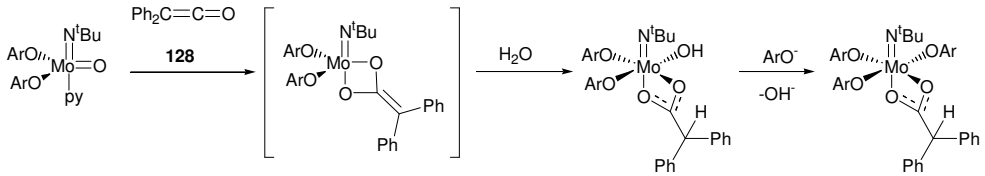


124 **125** **126**

Figure 7. [3+2] complexes

The mixed oxo, imido complexes $MoO(N^tBu)(2,6\text{-}^iPr_2C_6H_3O)_2py$ **127a** and $MoO(N^tBu)(2,6\text{-}Me_2C_6H_3O)_2py$ **127b** were synthesised in our group, and they were also tested with isotopically labelled diphenylketene.[40,41] The reaction with diphenylketene was analysed by ^{13}C NMR and IR.[40] The J_{CC} values for the NMR showed the major product contained a sp^2-sp^3 hybridisation for the two labelled carbons. This hybridisation was consistent with a metallo-β-lactone. The IR also suggested the loss of the metal-oxo ligand and the presence of a carbonyl compound (ν_{max} = 1589 cm^{-1}) which would also suggest a metallo-β-lactone. The isolation of a metallo-β-lactone was

unsuccessful. Small crystals precipitated from the reaction mixture and they were suitable for X-ray crystallography; however they were found to be the carboxylate compounds **130** & **131** (Scheme 22) that could be formed from the hydrolysis and ligand exchange of the ketene acetal. The data for the complexes **130** & **131** would also exhibit similar spectral data as the metallo-β-lactone, and therefore the major product could not confidently be identified. Complex **127** was also reported to epoxidise *cis*-cyclooctene.

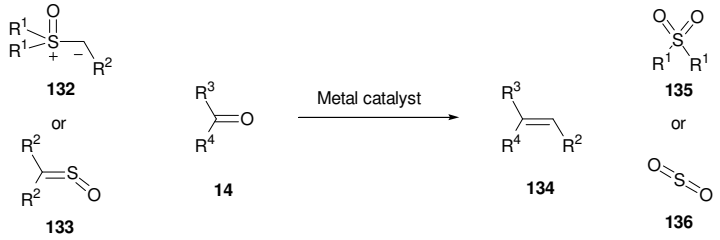


127a Ar = 2,6-$^{i}Pr_2C_6H_3O$ **129** **130** **131**
127b Ar = 2,6-$Me_2C_6H_3O$

Scheme 22. Proposed mechanism for formation of the carboxylates

Proposed Research

The previous research had shown some interesting results, but had yet to conclusively produce a metallo-β-lactone by a [2+2] cycloaddition between a metal-oxo complex and a ketene. Therefore a second hypothetical reaction using sulfur reagents such as sulfur ylides **132** or sulfines **133** to produce an alkene **134** and a sulfone **135** or sulfur dioxide **136** was devised (Scheme 23).



132 **133** **14** **134** **135** **136**

Scheme 23. Overall desired reaction

The hypothetical catalytic cycle for a sulfoxonium ylide is shown below (Figure 8). The first step of the envisaged catalytic cycle using a sulfur ylide **132** would require the formation of metallo-cycle **137,** either *via* a two-step zwitterionic intermediate or a $[2_\pi+2_\pi]$ cycloaddition. The metallo-cycle could then undergo a retro $[2_\pi+2_\pi]$ cycloaddition to give the sulfone **135** and the desired alkylidene **117**. The second half of the catalytic cycle involved the metal alkylidene **117** reacting with a carbonyl compound **138** to produce the desired alkene **140** and regeneration of the metal-oxo complex **113**.

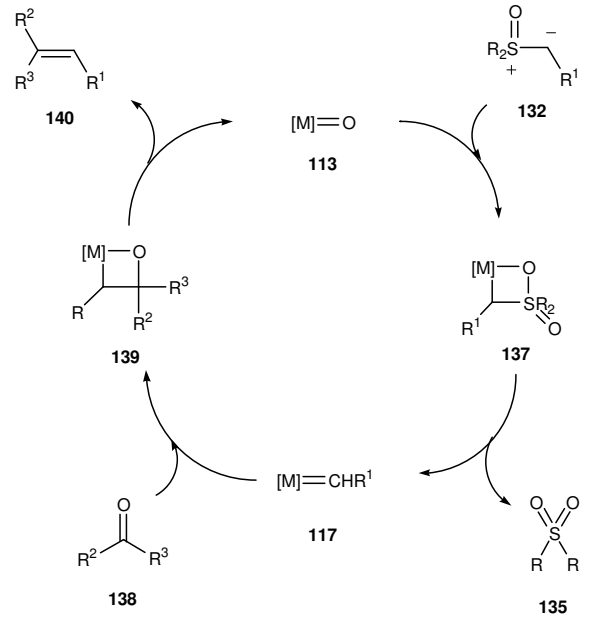


Figure 8. Proposed hypothetical catalytic reaction using sulfoxonium ylide

A sulfine **133** is a sulfur equivalent of a ketene, and it was hoped that the metal-oxo complex **113** may react *via* a $[2_\pi+2_\pi]$ cycloaddition across the C=S bond to form a metallo-cycle **141** (Figure 9). It could then undergo a retro $[2_\pi+2_\pi]$ cycloaddition to produce sulfur dioxide **136** and the metal-alkylidene **117**. Again the metal-alkylidene **117** would then be required to react with a carbonyl compound **14** to produce the alkene **119** and regenerate the metal-oxo complex **113**. The reaction of a metal alkylidene with a carbonyl compound is

known as a carbonyl olefination reaction, and this has been demonstrated successfully in the literature (Chapter 1.2). As the carbonyl olefination reaction is already known, our research investigated the first half of the catalytic cycle, the reaction of a metal-oxo complex with a sulfur reagent.

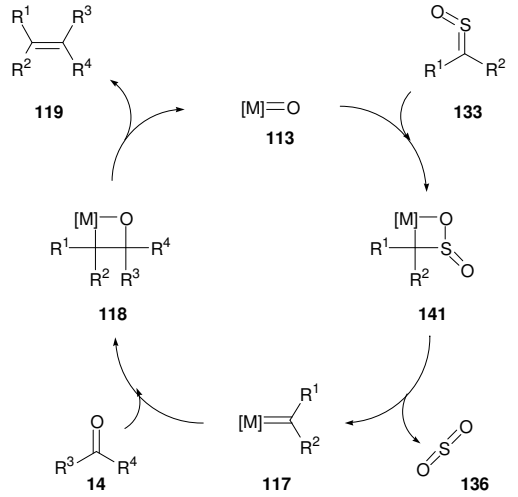
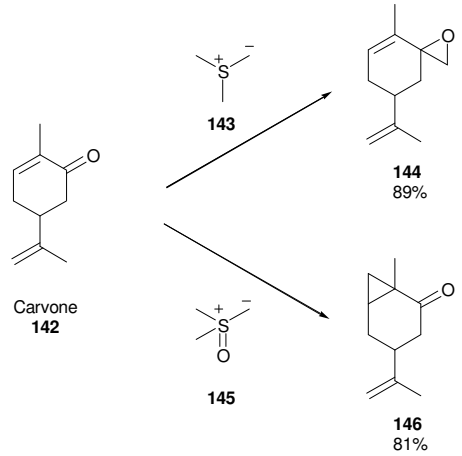


Figure 9. Proposed hypothetical catalytic cycle using sulfines

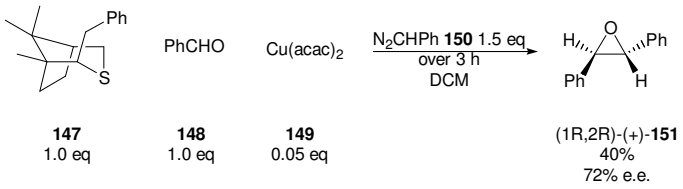
Sulfur Ylides

An ylide is a molecule with a positively charged atom from group 15 or 16 in the periodic table connected to a carbon atom containing a negative charge. The most widely used is probably the phosphonium ylide used in the Wittig reaction. In addition sulfur ylides have also been useful in organic synthesis. In the early sixties Corey reported the use of dimethylsulfonium methylide **143** and dimethylsulfoxonium methylide **145** as methylene transfer reagents for carbonyl compounds to form the corresponding epoxide.[42,43] However the reaction with enones produced different products depending on the sulfur ylide (Scheme 24). Dimethylsulfonium methylide **143** reacted as usual with the

carbonyl, however the dimethylsulfoxonium methylide **145** reacted in a Michael addition to form the cyclopropyl ketone. The reactions were both high yielding with 89% obtained for the epoxidation of carvone **144** and 81% for the cyclopropanation of carvone **146**.

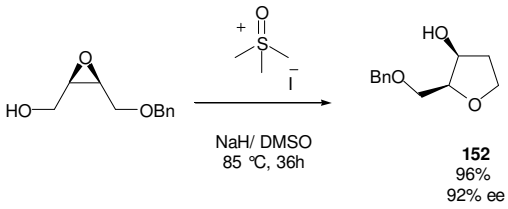


Scheme 24. Reaction of dimethylsulfonium methylide and dimethylsulfoxonium methylide



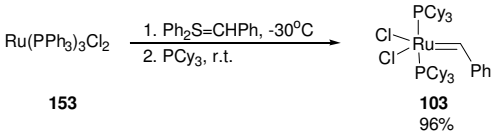
Scheme 25. Modern methods of sulfonium ylides in organic synthesis

Over the years these reactions have been further investigated and have led to the development of asymmetric ylide reactions including epoxidation, cyclopropanation, aziridination, olefination and rearrangements.[44] Asymmetric sulfur ylides can now be synthesised using a Cu catalyst **149** with a diazoalkane **150** and a chiral sulfide **147** (Scheme 25) to produce asymmetric products **151**.[45] More recently the dimethylsulfoxonium methylide has been used to make diastereomerically and enantiomerically pure 2,3-disubstituted tetrahydrofurans **152** (Scheme 26) by an initial Payne rearrangement followed by nucleophilic addition and elimination of dimethyl sulfoxide.[46]



Scheme 26. Synthesis of 2,3-disubstituted tetrahydrofurans

A recently reported paper by Milstein[47] uses a sulfonium ylide to generate metal carbenes and in particular to synthesise the Grubbs catalyst **103** (Scheme 27). This was generated in 96% isolated yield under mild conditions. It was interesting as in our desired catalytic cycle we wished to produce a metal-carbene complex using a sulfur ylide.



Scheme 27. Synthesis of Grubbs catalyst using diphenylsulfonium benzylide

Sulfines

In 1923 the preparation of chlorosulfoxide-camphor was published and it is believed to be the first example of a sulfine.[48] Although it was published in 1923, it would take approximately sixty years for the structure to be confirmed by X-ray analysis.[49] The name, sulfine (also known as thiocarbonyl *S*-oxide), comes from the structural relationship to sulfenes, which are thiocarbonyl *S,S*-dioxides (Figure 10).[50]

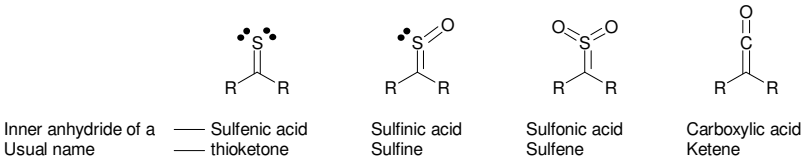
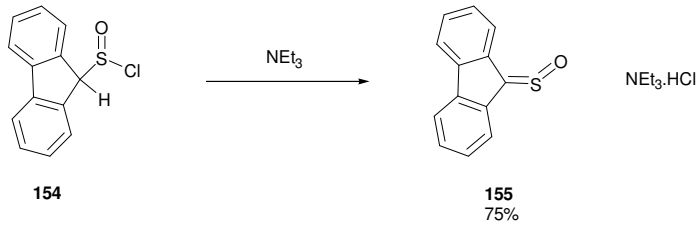


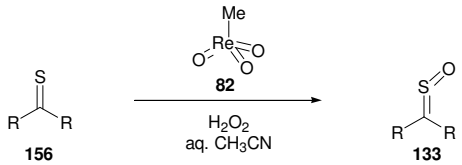
Figure 10. Structural relationship of thiocarbonyls, sulfines, sulfenes and ketenes.

Initially sulfines were synthesised by the elimination of hydrogen chloride from sulfonyl chlorides. An early example is the reaction of the unstable 9-fluorenone chloride **154** with triethylamine in ether that produced the thiofluorenone *S*-oxide **155** and the NEt_3.HCl salt (Scheme 28).[50]



Scheme 28. The synthesis of thiofluorenone *S*-oxide

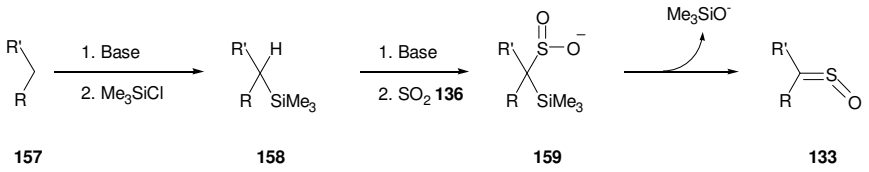
The sulfines could also be prepared by the oxidation of the thiocarbonyl compound **156**, and initially used monoperoxyphthalic acid.[51] Now *m*CPBA is more commonly used. In 1999 it was reported that sulfines could be prepared catalytically using methyltrioxorhenium **82** as the catalyst with hydrogen peroxide and the desired thioketone **156** (Scheme 29).[52] This produced the sulfine **133** in greater than 90% yield within 5 minutes at room temperature.



Scheme 29. Catalytic synthesis of sulfines

The modified Peterson reaction can also be used to produce sulfines **133**. It involves the reaction of an α-silyl carbanion with sulfur dioxide **136**, and this

method could be used if the thiocarbonyl compound is not accessible (Scheme 30).[49]



Scheme 30. The modified Peterson reaction to produce sulfines

Often the sulfines are trapped using a Diels-Alder reaction with a non-activated diene such as butadiene compounds to form the six-membered ring.[49] In addition, vinyl sulfines have also been investigated as the diene.[53]

Transition Metal Complexes

The choice of metal investigated was crucial, as the catalyst would require an electrophilic metal centre with a nucleophilic oxo ligand in order to produce the desired metallo-cycle **137** to allow formation of the metal alkylidene **117** (Figure 11). If the metal centre was nucleophilic then the undesired metallo-cycle **160** may be obtained which would not produce the desired metal alkylidene **117**. This allowed us to focus our investigations on molybdenum[54] and rhenium[37,39] complexes, as these metal oxo-complexes have been shown to contain nucleophilic oxo groups. The synthesis of a variety of complexes was known in the literature. In addition, the results obtained by Middleditch using diphenylketene would be compared with results obtained with sulfur ylides and sulfines.[37]

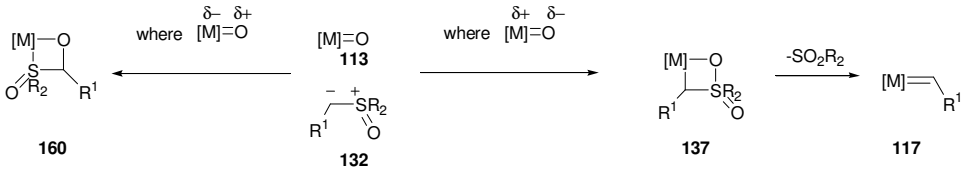


Figure 11. Possible reactions with metal oxo complexes

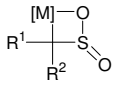


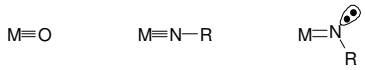
Figure 12. Proposed metallocycle with sulfine

A possible theory to reduce the activation energy of the hypothetical pathway to form the metallocycles **137** (Figure 11) and **141** (Figure 12) could be to invoke the spectator ligand effect. Rappe and Goddard first suggested the spectator ligand effect using theoretical calculations.[55] They investigated the metal mono-oxo species **161** and dioxo species **164** to observe the bond character. It was discovered that for mono-oxo species **161** (Scheme 31) the Mo-O bond had triple bond character. It implied the oxo ligand in the complex had one σ and two π bonds. The molybdenum has 6 valence electrons that can bond with ionic ligands. Four of these electrons are used to form the four partially ionic σ Mo-Cl bonds, and two are used to bond with the oxo ligand, one σ and one π bond. The lone pair on the oxygen can overlap with an empty d orbital of the metal and produce the triple bond i.e. two electrons from the metal and four from the oxygen.

Scheme 31. Reaction of metal-oxo complexes with alkenes

The dioxo molybdenum species **164** was compared to the mono-oxo species **161** in the reaction with an alkene **162** (Scheme 31).[55a] The reaction of **161** was calculated to be endothermic requiring ΔG_{300}= + 49 kcal mol^{-1}. When the reaction of **164** was calculated it was found to be exothermic with ΔG_{300}= -21 kcal mol^{-1}. This was explained by the spectator oxo effect.

The dioxo molybdenum complex **164** has 6 valence electrons from the metal, and these are used to form two partially ionic σ Mo-Cl bonds and for the dioxo ligands two covalent σ bonds and two π bonds. Triple bond character cannot occur in either O ligand as the d-orbital required for a triple bond overlap is already occupied by the Mo=O π bond of the other O ligand. In the reaction of the alkene one of the Mo=O π bonds is lost, thus releasing a d-orbital for Mo=O π overlap with the other O ligand. This overlap can begin to take place in the developing transition state and can make the reaction more thermodynamically and kinetically feasible. The mono-oxo species **161** does not have this stabilisation from the spectator ligand effect, and in this particular case the reaction is endothermic or unfavoured.



165 **166** **167**

Figure 12. The isoelectronic structure of imido ligands

The spectator ligand effect is not limited to only oxo ligands **165**, it can also occur with imido ligands **166** and **167** as they are isoelectronic (Figure 15). The imido group can also bond *via* two π bonds and one σ bond to the metal centre.[55a] Often the imido group bond order can be predicted. If the angle of M-N-R is approximately 180° it indicates a triple bond character. The bent imido ligand **167** is generally obtained when there are insufficient metal d-orbitals to produce a triple bond. The bond length can also confirm this as the triple bond is shorter than a double bond. The stabilisation effect of a spectator imido group is not as strong as an oxo group which could be an advantage in the breaking of the 4-membered metallocycle to produce an oxo or alkylidene ligand. An example which uses an imido ligand in catalysis is the Schrock olefin metathesis complex **102** (Figure 13) In a mixed oxo, imido complex of osmium,[56] the bond lengths for the Os-N were compared to the Os-O bond and they were found to be shorter (Figure 14). It was explained by the lower electronegativity of nitrogen and allows the imido ligand to be a greater π donor. Therefore the organoimido ligand has a higher bond order than the oxo ligand and in conclusion would reduce the bond strength of the metal-oxo ligand. The complex $MoO(N^tBu)(OAr)_2py$ **127** is also an example of the spectator ligand effect.

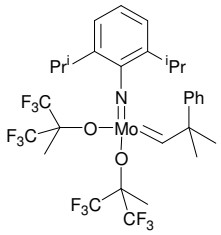


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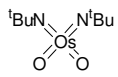
Figure 13. Schrock olefin metathesis complex



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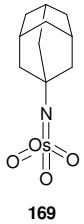


169

Figure 14. Mixed oxo-imido complexes of osmium

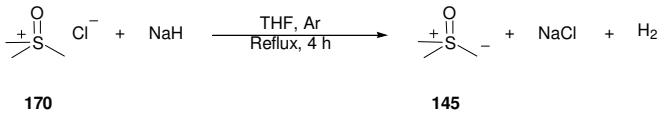
These concepts were considered when deciding which complexes to investigate. Therefore a variety of metal oxo complexes with more than one spectator ligand present, i.e. either a second oxo or imido ligand were investigated.

Chapter 2: Results & Discussion

2.1 *Synthesis of sulfur ylides*

Sulfonium ylides have been used in organic synthesis for over forty years to produce epoxides (Chapter 1.3). In this research the sulfonium ylides that were investigated were the dimethylsulfoxonium methylide and diphenylsulfonium benzylide.

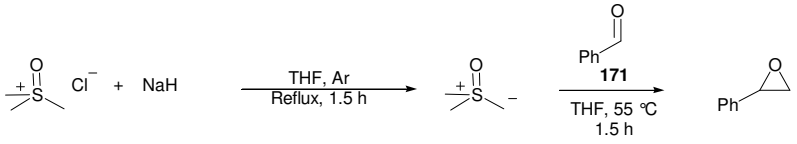
The dimethylsulfoxonium methylide **145** could be synthesised by deprotonating the trimethylsulfoxonium chloride salt **170** with sodium hydride in refluxing THF (Scheme 32).[43] The ylide **145** was investigated due to its stability as it could be stored in the freezer in a THF solution for several months without significant decomposition. The concentration of the ylide could be determined by titration with 0.1M hydrochloric acid.



170 **145**

Scheme 32

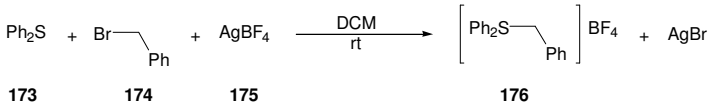
To confirm the formation of the dimethylsulfoxonium methylide, a portion of freshly prepared **145** was reacted with benzaldehyde **171** to form styrene oxide **172** (Scheme 33). The yield was low (20%, lit.[43] 56%) but proved the ylide had been formed to some extent.



170 **145** **172**
20%

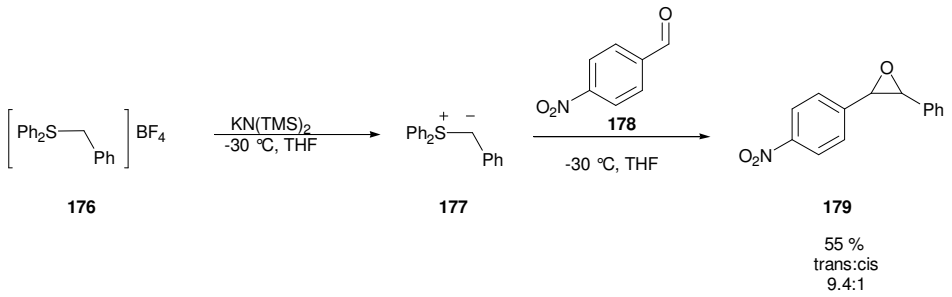
Scheme 33

Diphenylsulfonium benzylide **177** was also of interest to us as it had been used to synthesise the Grubbs catalyst **103** (Scheme 27, pg 27).[47] The diphenylsulfonium benzyl tetrafluoroborate salt **176** was synthesised (Scheme 34) and the ylide **177** was generated *in situ* when required as it was unstable (Scheme 35). The salt **176** was prepared from diphenylsulfide **173**, benzyl bromide **174** and silver tetrafluoroborate **175** (55%, lit.[47] 92%).



Scheme 34

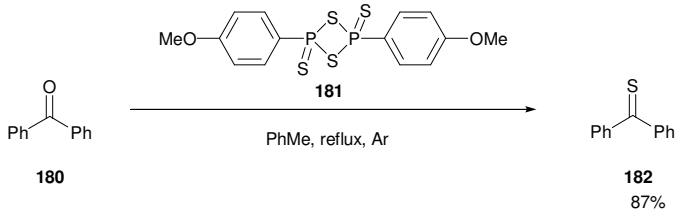
Again the formation of the ylide **177** was confirmed by the reaction with an aldehyde **178** to produce the epoxide **179** (55%, lit.[57] 72%) (Scheme 35).



Scheme 35

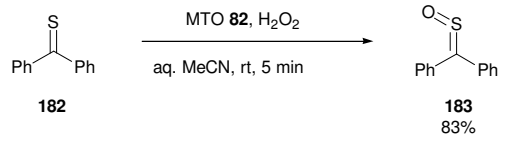
2.2 *Synthesis of Diphenylsulfine*

In the proposed research, the sulfur reagent diphenylsulfine **183** was desired to compare the results obtained by Middleditch with diphenylketene.[37] Therefore we investigated the synthesis of diphenylsulfine **183**, and decided to synthesise the compound *via* thiobenzophenone **182** that would be prepared from benzophenone **180** (Scheme 36).



Scheme 36

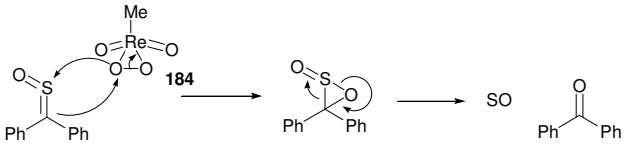
The reaction of benzophenone **180** with Lawesson's reagent **181** was reported to produce the desired thiobenzophenone **182** (Scheme 36).[58] The problem encountered with this reaction was the purification from the by-product produced from the Lawesson's reagent **181** as 4 equivalents of the reagent were required. Initially attempts to purify the thiobenzophenone **182** involved column chromatography. However it was observed that the blue semi-solid for thiobenzophenone **182** degraded to a pale off-white solid after purification by column chromatography. This was established as benzophenone **180** and believed to have formed by photo-oxidation in air.[59] Consequently the reaction was carried out under Schlenk conditions in argon and purified *via* vacuum distillation. This produced the desired thiobenzophenone **182** (87%, lit.[58] 98%).[60] The thiobenzophenone **182** was analysed by ^{1}H NMR, ^{13}C NMR and IR and found to be approximately 98% pure by ^{1}H NMR.



Scheme 37

The diphenylsulfine **183** was prepared by reacting thiobenzophenone **182** with catalytic methyltrioxorhenium **82** and hydrogen peroxide (Scheme 37).[52] The reaction was fast requiring only 5 minutes. Although there was no benzophenone **180** present in the thiobenzophenone **182**, the oxidation to the sulfine **183** was also generating benzophenone **180** in varying concentrations

(10-60%). This was believed to be occurring due to excess hydrogen peroxide being added and causing over oxidation of the sulfine **183** (Scheme 38). Therefore the concentration of hydrogen peroxide was calculated *via* titration with potassium permanganate. This reduced the concentration of benzophenone **180** present in the diphenylsulfine **183** to 4%. Diphenylsulfine **183** was isolated as a yellow oil (83%, lit.[52] 90%).



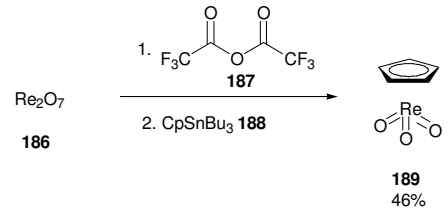
183 **185** **180**

Scheme 38

2.3 *Reactions of rhenium complexes with sulfur ylides*

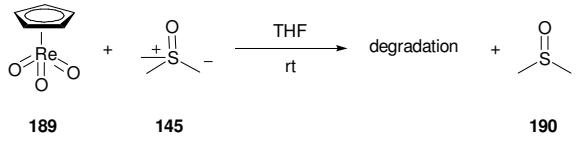
The reaction of a variety of rhenium complexes with diphenylketene had previously been investigated (Chapter 1.3).[37] Therefore we wished to compare the results obtained with diphenylketene with the results obtained from the ylides **145** & **177**.

The complex $CpReO_3$ **189** was prepared according to the literature method[61] and involved the reaction of Re(VII) oxide **186** with trifluoroacetic anhydride **187** followed by $CpSnBu_3$ **188** (Scheme 39). The yellow solid obtained was analysed by ^1H NMR, ^{13}C NMR and IR and corresponded with the data for this complex **189** (46%, lit.[61] 80%). The complex **189** was determined to be approximately 90% pure by ^1H NMR.



Scheme 39

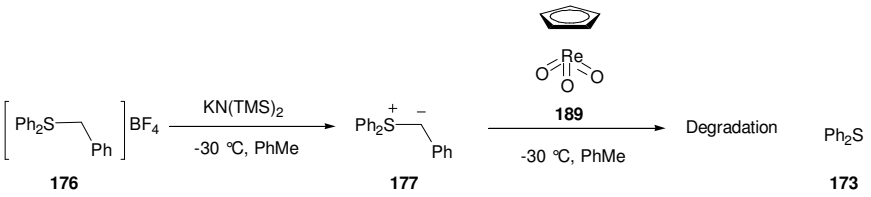
The $CpReO_3$ **189** complex was reacted with a titrated solution of the dimethylsulfoxonium methylide **145** (Scheme 40). On addition of the ylide **145** to the orange solution of **189** in THF the reaction immediately changed colour from orange to dark brown. The reaction was stirred for 4½ h at rt. The solvent was removed under vacuum to obtain a black residue that was analysed by ^1H NMR, ^{13}C NMR and IR. In the ^1H NMR there were no hydrogens that corresponded to a cyclopentadienyl ring. The presence of DMSO **190** was detected by ^1H and ^{13}C NMR. The IR of the residue did not match the complex $CpReO_3$ **189** as these stretches are found at 882 and 849 cm^{-1}. However strong stretches at 903 and 896 cm^{-1} were observed and this is in the correct region for Re-oxo bonds. From these results we concluded that the $CpReO_3$ **189** complex had degraded somehow when the dimethylsulfoxonium methylide **145** was added, but what to and by what mechanism was not clear.



Scheme 40

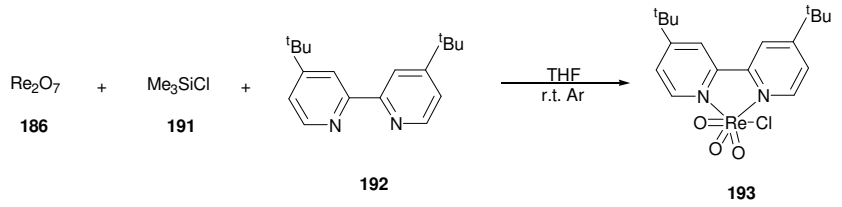
The reaction of $CpReO_3$ **189** was also investigated with the diphenylsulfonium benzylide **177**. The ylide **177** was generated by reacting the salt **176** with $KN(TMS)_2$ at -30 °C in toluene and immediately transferred *via* canula to a Schlenk containing the $CpReO_3$ **189** in toluene cooled to -30 °C (Scheme 41). The method was obtained from the Milstein paper which used this method to

generate the Grubbs catalyst.[47] Initially no colour change was observed on addition of the ylide **177**, however on warming to room temperature the yellow suspension changed colour to a black solution. The solvent was removed under vacuum and the black residue was analysed by ^{1}H NMR, ^{13}C NMR and IR. The ^{1}H NMR showed a trace amount of $CpReO_3$ **189** as the Cp H's were observed at 6.95 ppm. The main compound appeared to be diphenylsulfide **173**. There also appeared to be alkyl peaks between 1.5 ppm and 0.2 ppm. The ^{13}C NMR only showed the presence of diphenylsulfide **173**. Again the IR did not correspond to $CpReO_3$ **189** but did show very broad strong stretches at 905 cm^{-1} which suggested that a Re-oxo bond was still present. Our conclusion from these results was that the $CpReO_3$ **189** complex had again degraded and thus was unlikely to produce our desired catalytic cycle under these conditions.



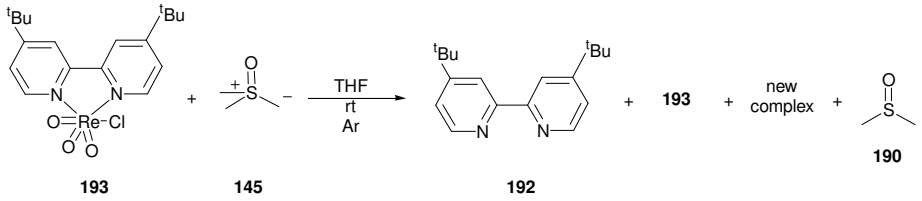
Scheme 41

The pale yellow complex (4,4'-di-*t*-butyl-2,2'-bipyridyl)ReO_3Cl **193** was synthesised from rhenium (VII) oxide **186**, chlorotrimethylsilane **191** and 4,4'-di-*tert*-butyl-2,2'-bipyridyl **192** in 95% yield (lit.[62] 90%) (Scheme 42). It was analysed by ^{1}H NMR, ^{13}C NMR and IR and corresponded with the data for this complex. The complex **193** was dried under high vacuum however it still contained THF by ^{1}H & ^{13}C NMR.

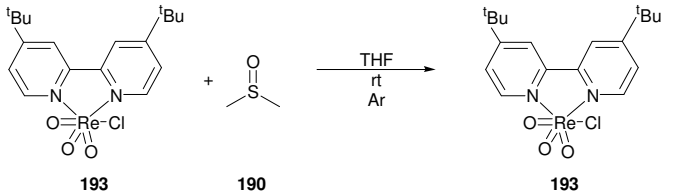


Scheme 42

The complex **193** was reacted with a solution of the dimethylsulfoxonium methylide **145** and it was observed that the complex **193** and the free ligand 4,4'-di-*tert*-butyl-2,2'-bipyridyl **192** was obtained (Scheme 43). The reaction also appeared to produce a new complex as the ^{1}H NMR showed peaks which were not the complex **193** or the free ligand 4,4'-di-*tert*-butyl-2,2'-bipyridyl **192**. However attempts to isolate the complex were unsuccessful and instead the free ligand **192** and DMSO **190** were obtained. In order to investigate whether the formation of the new complex or the decomposition to the free ligand **192** was due to the presence of DMSO **190** we performed a control reaction (Scheme 44). The complex **193** was dissolved in dry THF and 4 equivalents of dry DMSO **190** was added to the Schlenk. The reaction was stirred at room temperature for 5 days were upon the solvent was removed under vacuum to obtain an off-white residue. The ^{1}H NMR showed only the complex **193** and DMSO **190** present. This proved that decomposition of the complex **193** and the new complex observed was not due to the presence of DMSO **190**.



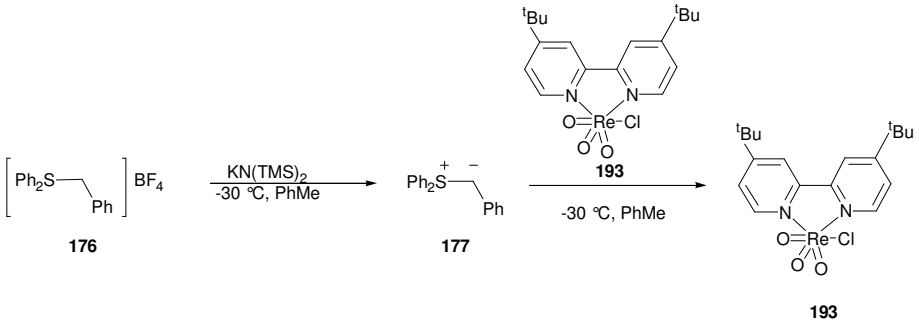
Scheme 43



Scheme 44

The presence of the DMSO **190** was investigated and several ^{1}H NMR experiments suggested the DMSO **190** was present in the THF solution of the ylide **145**.

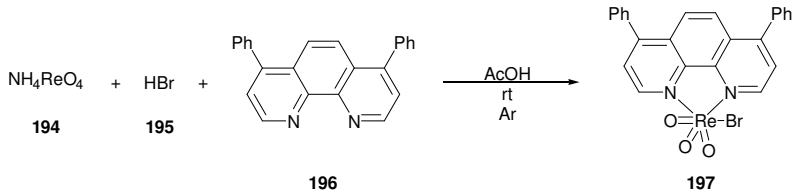
The diphenylsulfonium benzylide **177** (Scheme 45) was added to a suspension of complex **193** in toluene cooled to -30 °C and stirred at -30 °C for 2 h before being warmed to 0 °C. The solvent was removed under vacuum and the reaction was analysed by ^{1}H NMR and IR. The data obtained from the reaction only showed the complex **193** present. It suggested that no reaction had occurred with diphenylsulfonium benzylide **177** with toluene as a solvent.



Scheme 45

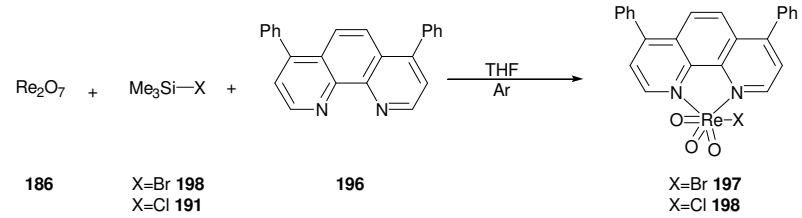
The complex (4,7-diphenyl-1,10-phen)ReO_3Br **197** had previously been synthesised in the Anderson group using NH_4ReO_4 **194**, HBr **195** in acetic acid and 4,7-diphenyl-1,10-phenanthroline **196** (Scheme 46).[63] However the complex was difficult to purify following this method and therefore was synthesised by reacting rhenium (VII) oxide **186** with bromotrimethylsilane

198 and 4,7-diphenyl-1,10-phenanthroline **196** (Scheme 47) in an analogous method as the preparation of **193** (Scheme 42).



Scheme 46

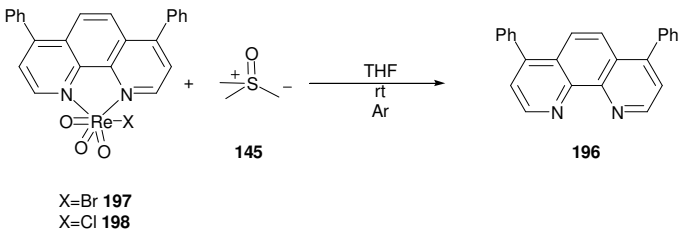
This latter preparation of **197** was simpler as the by-product from the reaction would be trimethylsilyl ether which could be removed under vacuum. The method also increased the yield from 44%[63] to 90%. The solid obtained was analysed by ^{1}H NMR, ^{13}C NMR and IR and corresponded with the data from literature.[63] The complex was approximately 90% pure by ^{1}H NMR with THF as the impurity. This method also allowed us to synthesise the novel chloride derivative of this complex (**198**, 76%). The pale cream solid was analysed by ^{1}H NMR, ^{13}C NMR, IR and CHN.



Scheme 47

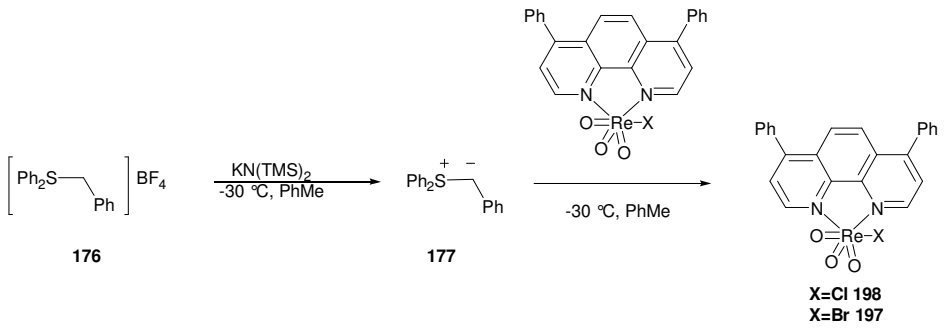
Dimethylsulfoxonium methylide **145** solution was added to a yellow suspension of (4,7-diphenyl-1,10-phen)ReO_3Br **197** and the suspension immediately changed colour to dark red (Scheme 48). The reaction was stirred at room temperature for 3½ h, where upon the solvent was removed under vacuum to obtain a dark red residue. The residue was analysed by ^{1}H NMR and ^{13}C NMR and showed the main compound to be the free ligand 4,7-diphenyl-1,10-phenanthroline **196**. In addition, a small quantity of the complex **197** was

observed by ^{1}H NMR. Attempts to grow crystals from the residue only gave the free ligand **196**. The same result was obtained when the chloride derivative **198** was reacted with dimethylsulfoxonium methylide **145**.



Scheme 48

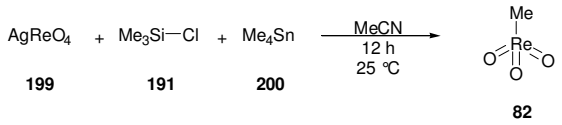
Diphenylsulfonium benzylide **177** was reacted with **197** and **198** (Scheme 49). No colour change was observed during the reaction. For the reaction with (4,7-diphenyl-1,10-phen)ReO_3Cl **198** the solvent was removed under vacuum to obtain a cream residue. This was analysed by ^{1}H NMR, ^{13}C NMR and IR. The data obtained for the residue was determined to be the unchanged complex **198**. The reaction with (4,7-diphenyl-1,10-phen)ReO_3Br **197** and diphenylsulfonium benzylide **177** produced the same result as the chlorine derivative **198**, in that no reaction was observed.



Scheme 49

The complex methyltrioxorhenium **82** can be synthesised in several ways and we decided to use silver perrhenate **199** with chlorotrimethylsilane **191** and tetramethyltin **200** (Scheme 50).[64] The clear crystals were obtained by

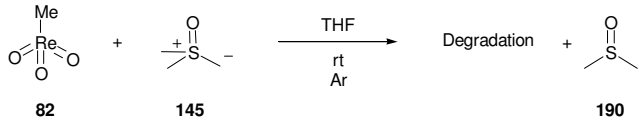
sublimation from a purple residue (63%, lit.[64] 76%). The clear crystals were analysed by ^{1}H NMR, ^{13}C NMR and IR and the data corresponded to the complex **82**. The ^{1}H NMR of MTO **82** showed the compound was 99% pure.



Scheme 50

A clear solution of dimethylsulfoxonium methylide **145** was added to a clear solution of methyltrioxorhenium **82** in THF (Scheme 51). An immediate colour change was observed to dark red. The reaction was stirred for 2½ h at room temperature prior to solvent being removed under vacuum. The brown residue obtained was analysed by ^{1}H NMR, ^{13}C NMR and IR. The ^{1}H NMR showed no methyltrioxorhenium **82** remained after the reaction. It also showed a singlet at 2.57 ppm which could be the CH_3-Re. However the chemical shift was significantly different compared to the complex **82** δ Me 1.21 ppm. In previous reactions involving dimethylsulfoxonium methylide **145** and metal oxo complexes, the compound DMSO **190** was observed and this was also the case for **82**, as it was observed in the ^{1}H NMR. The ^{13}C NMR showed a peak at δ 40.6 and δ 29.6. The peak at δ 40.6 was assigned as DMSO **190**. The signal δ 29.6 was therefore assigned as the CH_3-Re. Again this chemical shift was significantly different to MTO **82** in which the carbon is found at δ 17.8. The IR of the residue showed a strong stretch at 903 cm^{-1} which suggested a rhenium-oxo bond was still present. However the IR stretches for Re-O bond in MTO **82** were distinctly different at 966, 958 and 948 cm^{-1}. In the reaction with $CpReO_3$ **189** and dimethylsulfoxonium methylide **145** (Scheme 40) a strong stretch was also observed at 903 cm^{-1}. It suggested the Re-oxo group had

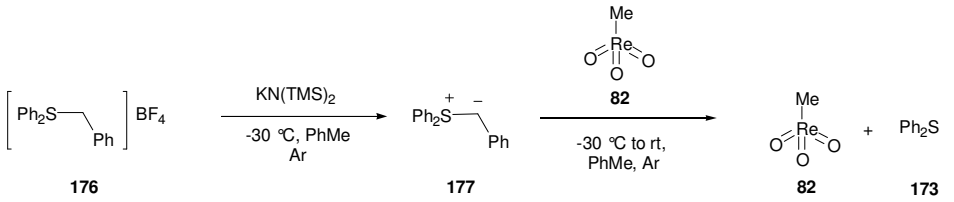
formed a similar structure in both reactions and also suggested the complex was no longer $MeReO_3$ **82**.



82 **145** **190**

Scheme 51

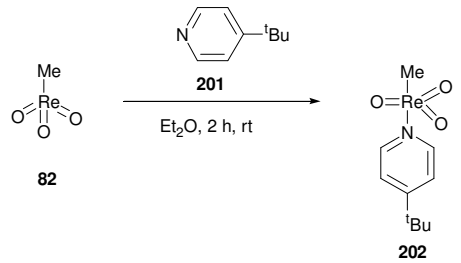
The methyltrioxorhenium complex **82** was also reacted with diphenylsulfonium benzylide **177**. No colour change was observed on addition of the ylide **177** to the clear solution of MTO **82** at -30 °C, however a colour change was observed from clear to orange/brown on warming to room temperature. The solvent was removed under vacuum to obtain a brown residue. The ^{1}H NMR, ^{13}C NMR and IR showed MTO **82** still present in the reaction. In addition, diphenylsulfide **173** was also observed in the ^{1}H NMR and ^{13}C NMR.



176 **177** **82** **173**

Scheme 52

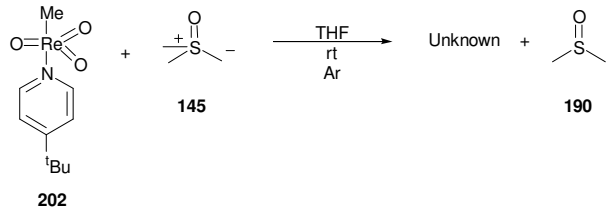
We also decided to test the complex $MeReO_3$(4-*t*-butylpyridine) **202** which was synthesised from MTO **82** and 4-*tert*-butylpyridine **201** (82%, lit.[65] 52%). The complex **202** was analysed by ^{1}H NMR, ^{13}C NMR and IR and corresponded to data for the complex **202** (Scheme 53).



82 **202**

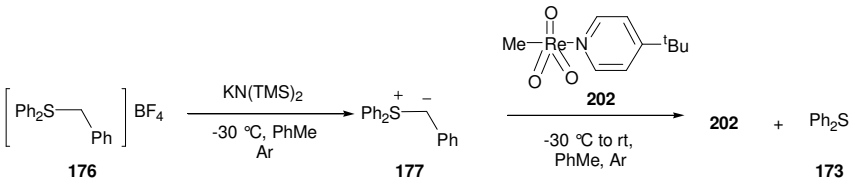
Scheme 53

The reaction of dimethylsulfoxonium methylide **145** with **202** was carried out at room temperature in THF (Scheme 54). The reaction immediately changed colour on addition of the ylide **145** from a pale yellow solution to red/brown solution. The reaction was stirred for 2½ h before solvent was removed under vacuum to obtain a brown residue. A ^{1}H NMR, ^{13}C NMR and IR were recorded for the residue. The ^{1}H NMR signals for the 4-*tert*-butylpyridine did not match the complex **202** or the free ligand **201**. The *o*-H had been moved downfield by 0.2 ppm compared to the complex **202**. The singlet which had been observed in the MTO **82** reaction at δ 2.57 was also detected in this reaction and we believe it is the CH_3-Re. The ^{13}C NMR was very similar to the complex **202**. A peak at δ 29.5 was also present and it is the same peak observed in the MTO reaction with the ylide **145** (Scheme 51). Again DMSO **190** was observed in the ^{1}H NMR and ^{13}C NMR when the methylide **145** was reacted with the complex **202**. The IR only showed the complex MeReO$_3$(4-*t*-butylpyridine) **202**. We were therefore unable to determine the product in this reaction.



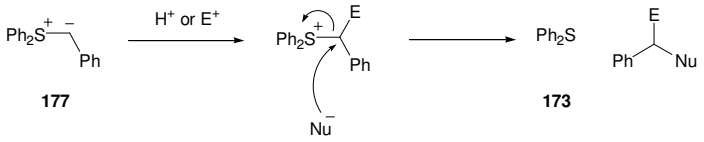
Scheme 54

A solution of diphenylsulfonium benzylide **177** in toluene at -30 °C was added to a pale yellow solution of MeReO$_3$(4-*t*-butylpyridine) **202** in toluene at -30 °C (Scheme 55). The reaction was warmed to room temperature and solvent was removed under vacuum to obtain a yellow/brown residue. The residue was analysed by ^{1}H NMR, ^{13}C NMR and IR. The data obtained showed the MeReO$_3$(4-*t*-butylpyridine) **202** complex and diphenylsulfide **173**.



Scheme 55

The results thus far had been disappointing. We had been unable to isolate any new complexes. Often the reaction with these ylides led to degradation of the complex or no reaction and the complex was unchanged. The diphenylsulfonium benzylide was unstable at room temperature. This may explain why no obvious reaction appeared to occur until the reactions were warmed to room temperature. The diphenylsulfide **173** may be occurring due to decomposition of the ylide **177** (Scheme 56). The reaction with sulfur ylides appeared to be distinctly different compared to the ketene as no new complexes were isolated. Therefore our research turned towards the investigation of molybdenum complexes with these ylides.



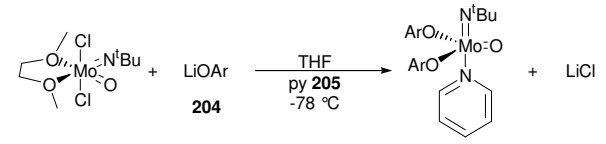
Scheme 56

2.4 *Reactions of molybdenum complexes with sulfur ylides*

Many of the rhenium complexes investigated had been co-ordinately saturated 18-electron complexes. Therefore we wished to investigate several co-ordinately unsaturated complexes to allow coordination of the ylide to metal

centre and subsequent reaction. We had previously prepared the 16-electron complexes $MoO(N^tBu)(OAr)_2py$ **127** (OAr = 2,6-$^i Pr_2C_6H_3O$, 2,6-$Me_2C_6H_3O$),[41] which were based on oxo-analogues of the Schrock family of olefin metathesis catalysts. These had been shown by our group to react with diphenylketene (Chapter 1.3). In addition, the $MoO_2(2,6\text{-}Me_2C_6H_3O)_2py_2$ **208** complex was also synthesised and investigated as a potential catalyst for the catalytic carbonyl olefination reaction.

The complexes $MoO(N^tBu)(2,6\text{-}^i Pr_2C_6H_3O)_2py$ **127a** and $MoO(N^tBu)(2,6\text{-}Me_2C_6H_3O)_2py$ **127b** were prepared by the same method used previously in the group (Scheme 57). The complex $MoO(N^tBu)Cl_2dme$ **203** was reacted with the appropriate lithium aryloxide salt **204** in the presence of pyridine **205** in THF at -78 °C. The complex $MoO(N^tBu)(2,6\text{-}^i Pr_2C_6H_3O)_2py$ **127a** was obtained in a 31% yield (lit[41] 49%) and $MoO(N^tBu)(2,6\text{-}Me_2C_6H_3O)_2py$ **127b** was obtained in 39% (lit[41] 48%). Both complexes were analysed by ^1H NMR, ^{13}C NMR and IR and they matched the reported data for these complexes. The ^1H NMR appeared to show greater than 95% purity.



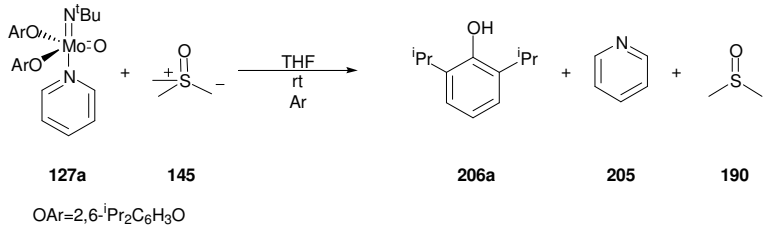
203 **204** **127**

LiOAr= Li(2,6-$^i Pr_2C_6H_3O$) **204a** OAr= (2,6-$^i Pr_2C_6H_3O$) **127a**
LiOAr= Li(2,6-$Me_2C_6H_3O$) **204b** OAr= (2,6-$Me_2C_6H_3O$) **127b**

Scheme 57

A yellow solution of $MoO(N^tBu)(2,6\text{-}^i Pr_2C_6H_3O)_2py$ **127a** in THF was reacted with dimethylsulfoxonium methylide **145** at room temperature (Scheme 58). The clear yellow solution changed to a cloudy yellow solution when the ylide **145** was added. The reaction was stirred at room temperature for 3 h at which

point the solvent was removed under vacuum to obtain an orange residue. The ^{1}H NMR of the residue revealed a mixture of products which included 2,6-diisopropylphenol **206a**, DMSO **190** and pyridine **205**, which was confirmed by ^{13}C NMR. The IR no longer contained the Mo-oxo stretch at 901 cm^{-1} and a new strong broad signal appeared at 818 cm^{-1}. From these results it would appear that the complex **127a** had degraded in the presence of the ylide.

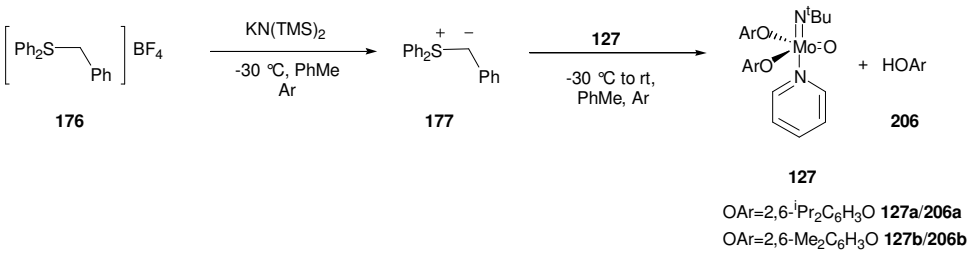


127a **145** **206a** **205** **190**

OAr=2,6-$^{i}Pr_2C_6H_3O$

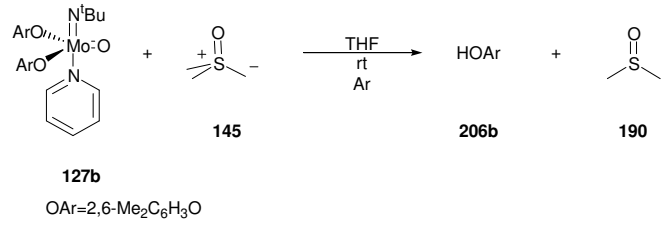
Scheme 58

Diphenylsulfonium benzylide **177** was added to the MoO(N^{t}Bu)(2,6-$^{i}Pr_2C_6H_3O)_2$py **127a** complex in toluene at -30 °C (Scheme 59). The reaction was slowly warmed to room temperature and the solvent was removed to obtain a yellow residue. The ^{1}H NMR showed the main compound in the reaction to be the unchanged complex MoO(N^{t}Bu)(2,6-$^{i}Pr_2C_6H_3O)_2$py **127a**. However some degradation occurred as 2,6-diisopropylphenol **206a** was observed. The identities of the two compounds were confirmed by ^{13}C NMR. The IR confirmed the complex **127a** was present in the crude reaction mixture by the stretches at 1603, 1193, 899 and 855 cm^{-1}. It appeared that rather than forming a new complex the reaction of **127a** with either sulfur ylide caused degradation or no reaction.



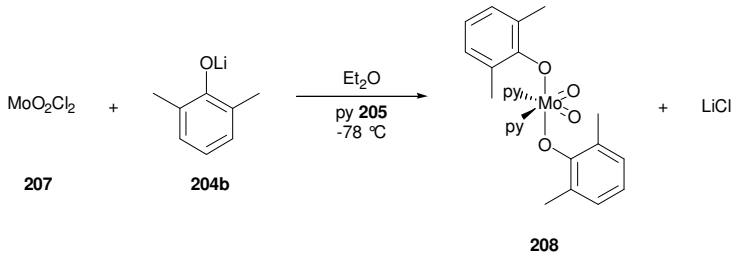
Scheme 59

The reaction of $MoO(N^tBu)(2,6\text{-}Me_2C_6H_3O)_2py$ **127b** with diphenylsulfonium benzylide **177** was carried out and the same result was observed (Scheme 59). The main compound in the crude reaction mixture by ^1H NMR, ^{13}C NMR was the unchanged complex **127b** and a small amount of the 2,6-dimethylphenol **206b**. Again the IR confirmed the presence of the complex $MoO(N^tBu)(2,6\text{-}Me_2C_6H_3O)_2py$ **127b**. The reaction of the $MoO(N^tBu)(2,6\text{-}Me_2C_6H_3O)_2py$ **127b** with the dimethylsulfoxonium methylide **145** led to degradation to the 2,6-dimethylphenol **206b** (Scheme 60), very similar results compared to **127a**.



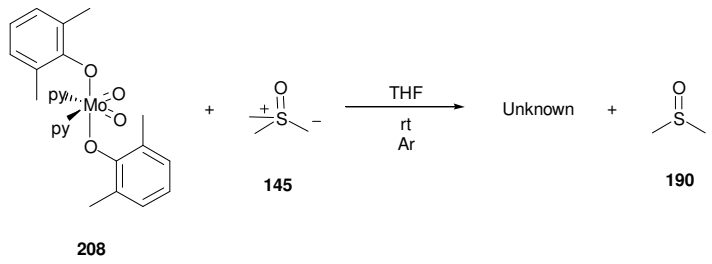
Scheme 60

The complex $MoO_2(2,6\text{-}Me_2C_6H_3O)_2py_2$ **208** was synthesised from molybdenum dioxo dichloride **207** with $Li(2,6\text{-}Me_2C_6H_3O)$ **204b** and pyridine **205** in diethyl ether at -78 °C (Scheme 61). The reaction produced orange crystals (28%, lit[66] 37%) which were spectroscopically identical to the literature. The complex **208** was also greater than 95% pure by ^1H NMR.



Scheme 61

Complex **208** was reacted with a solution of dimethylsulfoxonium methylide **145** (Scheme 62). A pale orange precipitate formed when the ylide **145** was added. The reaction was stirred at room temperature for 1½ h before the solvent was removed. The crude reaction mixture was analysed by ^{1}H NMR and ^{13}C NMR which showed no pyridine ligands present. The signals present belonged to a 2,6-$Me_2C_6H_3O$ group but were not the phenol **206b** or the complex **208**. The IR had similar signals to the complex **208**, however this did not necessarily imply a new complex. The observed signals could have been due to the co-ordinately unsaturated MoO_2(2,6-$Me_2C_6H_3O)_2$ without the pyridines present. This was our main problem analysing this complex. The lability of the pyridine ligands meant they could be removed under vacuum during work up.

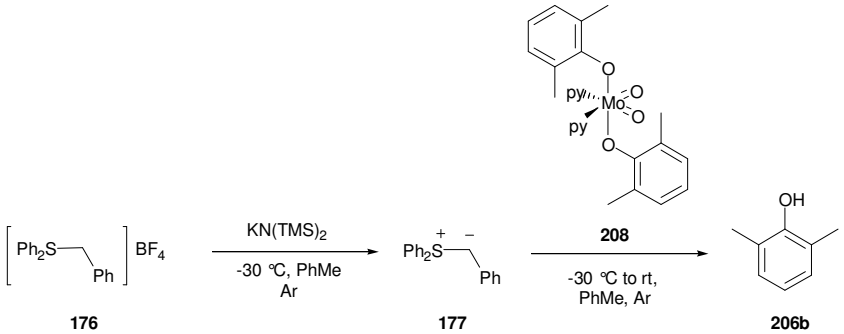


Scheme 62

The reaction was repeated and again the solvent was removed under vacuum. The residue obtained was dissolved in Et_2O, and an excess of pyridine (35 equiv) was added in an attempt to obtain crystals. However no crystals formed and the solvent was removed from the reaction. The analysis of this residue

showed phenol **206b** present which suggested that the complex **208** had been destroyed.

The complex **208** was also reacted with the diphenylsulfonium benzylide **177** (Scheme 63), however the same problems were encountered as with the reaction of dimethylsulfoxonium methylide **145**. The reaction was again carried out at -30 °C for the addition to complex **208** in toluene. The reaction was stirred at -30 °C for 1½ h before being warmed to room temperature. The reaction changed colour from red/orange to black on warming to room temperature. The solvent was removed under vacuum. Again, due to the lability of the pyridine ligands, the residue was dissolved in Et_2O, and excess pyridine **205** (35 equiv) was added in an attempt to obtain crystals. Unfortunately no crystals were obtained. The analysis of this reaction showed decomposition as the phenol **206b** was obtained. The IR was compared to the starting material. It showed a strong peak at 799 cm^{-1}. This was very different compared to the starting material complex with Mo-oxo stretches observed at 934, 903, & 869 cm^{-1}.



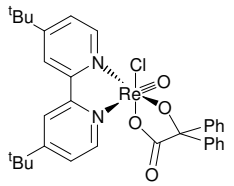
176 177 206b

Scheme 63

Therefore we concluded that the reaction of these ylides with molybdenum complexes did not look a viable option to produce the desired catalytic cycle.

2.5 *Reaction of metal-oxo complexes with diphenylsulfine*

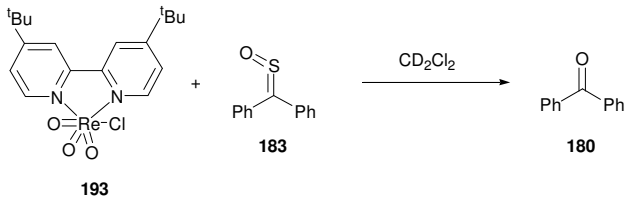
The rhenium trioxo (**189** & **193**) and molybdenum oxo imido complexes **127** were investigated as they had previously reacted with diphenylketene. The reactions were carried out under Schlenk conditions and the reactions were monitored by ^{1}H NMR and ^{13}C NMR. The (4,4'-di-*t*-butyl-2,2'-bipyridyl)ReO_3Cl **193** complex had been shown to react in a [3+2] reaction with diphenylketene (Figure 15) to give a green powder which was isolated after 18 h at room temperature.[37] Therefore we were interested in the reaction of **193** with diphenylsulfine **183**.



209

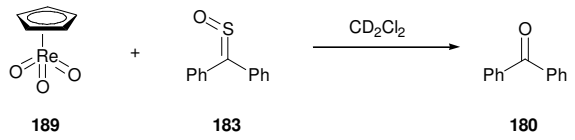
Figure 15

The complex (4,4'-di-*t*-butyl-2,2'-bipyridyl)ReO_3Cl **193** was added to a solution of diphenylsulfine **183** in deuterated DCM and the reaction was monitored for one week (Scheme 64). Initially the ^{1}H NMR and ^{13}C NMR showed very little evidence of a reaction occurring. The reaction was heated to 40 °C and monitored for 5 days. It was observed that the diphenylsulfine **183** concentration decreased and the concentration of benzophenone **180** increased from 11% to 34%.



Scheme 64

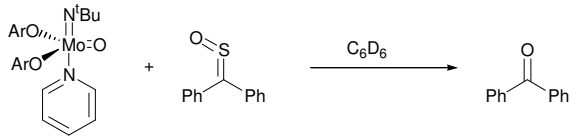
The complex $CpReO_3$ **189** was also reacted with diphenylsulfine **183** in a Young's NMR tube and monitored for several days (Scheme 65). The reaction was analysed by ^{1}H NMR and ^{13}C NMR. After one week at 40 °C the concentration of benzophenone **180** increased from 4% to 81% compared to the diphenylsulfine **183**. In addition, the concentration of the complex had decreased as by ^{13}C NMR the cyclopentadienyl ring was no longer visible and only a small amount was visible by ^{1}H NMR. This suggested the complex **189** had degraded with time.



Scheme 65

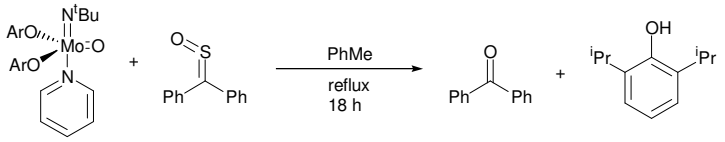
The MoO(N^{t}Bu)(2,6-$^{i}Pr_2C_6H_3O)_2$py **127a** complex was reacted in deuterated benzene with diphenylsulfine **183** in a Young's NMR tube (Scheme 66). The reaction again showed the concentration of diphenylsulfine **183** decreased. The concentration of benzophenone **180** increased form 5% to 72% over six days. In this reaction the complex did not degrade to the free phenol **206a** and suggested the complex **127a** was still present by ^{1}H NMR and ^{13}C NMR. Therefore the MoO(N^{t}Bu)(2,6-$^{i}Pr_2C_6H_3O)_2$py **127a** complex was reacted on a larger scale with diphenylsulfine **183** and refluxed in toluene over night (Scheme 67). The ^{1}H NMR and ^{13}C NMR of the reaction showed the sulfine

183 had been consumed as it was no longer present. The sulfine **183** appeared to have been fully converted to benzophenone **180** as this was the only observed new product. Again the complex **127a** was still present by ^{1}H and ^{13}C NMR however approximately 16% of the complex had been degraded to the phenol **206a**.



127a **183** **180**

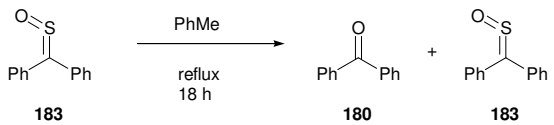
Scheme 66



127a **183** **180** **206a**

Scheme 67

The reaction of diphenylsulfine **183** with metal-oxo complexes appeared to show the conversion of the sulfine **183** to benzophenone **180**. However to confirm the participation of the metal-oxo complex, a control reaction was performed. The diphenylsulfine **183** was refluxed in toluene over night (Scheme 68). It was analysed by ^{1}H and ^{13}C NMR and showed a slight increase in benzophenone **180** compared to diphenylsulfine **183** (4% to 9%). However it was a much slower conversion compared to when a metal-oxo complex was present.



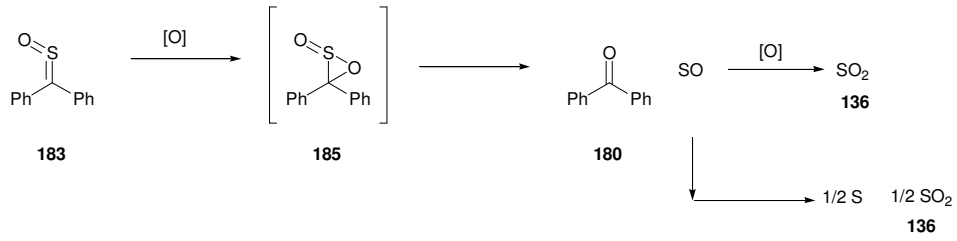
183 **180** **183**

Scheme 68

The diphenylsulfine **183** was also reacted with (4-*tert*-butylpyridine)methyltrioxorhenium **82**, (4,7-diphenyl-1,10-phen)ReO_3Br **197**,

(4,7-diphenyl-1,10-phen)ReO_3Cl **198** and $MoO_2(2,6\text{-}Me_2C_6H_3O)_2py_2$ **208**. Again the same result was observed where the diphenylsulfine **183** was converted to benzophenone **180**.

It is believed the conversion of the sulfine **183** to benzophenone **180** occurs due to oxo-transfer which creates an unstable intermediate called a sultine **185** (Scheme 69). This was reported by Espensen in 1999 while investigating sulfine synthesis from thioketones using methyltrioxorhenium **82** with hydrogen peroxide.[52b] The sultine **185** formed by oxidation of the sulfine **183** can degrade to sulfur monoxide and benzophenone **180**. The transfer of a metal-oxo ligand needed in the oxidation of sulfine **183** to sultine **185** also explains the degradation of the metal complex. With this result the investigation into the catalytic Wittig reaction using sulfur reagents was halted.



Scheme 69

Chapter 3: Conclusion & Further Work

3.1 Conclusion

Our investigation into the catalytic Wittig reaction using sulfur reagents has proved that sulfur ylides and sulfines will not produce the desired catalytic cycle.

Generally the dimethylsulfoxonium methylide **145** produced degradation when reacted with our metal-oxo complexes. Often the reaction of diphenylsulfonium benzylide **177** resulted in no reaction with our metal-oxo complex. The diphenylsulfide **173** observed at the end of the reaction suggests the ylide **177**, which is unstable, decomposed on warming to room temperature to produce diphenylsulfide **173** and potentially toluene which would be removed under vacuum.

The reaction of diphenylsulfine **183** with metal-oxo complexes led to the oxidation of the sulfine **183** which produced benzophenone **180**. This was unfortunate as we had wished to directly compare this compound with the results obtained for diphenylketene **128**. This did show the difference in the two compounds as the diphenylketene **128** had been shown to react in a [3+2] reaction with rhenium complexes and potentially a [2+2] with the oxo-imido molybdenum complexes. Our investigation with diphenylsulfine **183** with these metal complexes showed formation of **180** which we attribute to metal-oxo transfer across the C=S bond to produce an unstable sultine intermediate **185** which degrades to sulfur monoxide and benzophenone **180**.

3.2 Further work

To conclude this project there are several experiments which could be performed. The experiments up until this point had been looking for the loss of a metal-oxo bond by IR. Therefore the IR for the reactions with diphenylsulfine should be performed to ascertain whether the loss of an oxo bond is observed. In addition the oxidation state of the metal at the end of the reaction with dimethylsulfoxonium methylide **145**, diphenylsulfonium benzylide **177** and diphenylsulfine **183** could be determined by the characterisation of an isolable complex if possible.

Chapter 4: Experimental

4.1 General Experimental Details

All experimental procedures were performed under an atmosphere of dry, oxygen free argon using an M-BRAUN Uni Lab glove box, and standard Schlenk techniques. All glassware was oven dried and flame dried prior to use. Cooling to 0 °C was achieved using an ice-water bath. Cooling to temperatures below 0 °C was achieved by using dry ice/acetone mixtures.

Purification of Solvents and Reagents:

The lithium aryloxides Li(2,6-$^{i}Pr_2C_6H_3O$) **204a** and Li(2,6-$Me_2C_6H_3O$) **204b** were prepared from ^{n}BuLi and the appropriate aryl alcohol **206** in hexane at -78 °C. Commercial solvents and reagents were used as supplied or purified in accordance with standard procedures, as described below.

Solvents were either dried by passing through activated alumina (THF, diethyl ether, toluene, hexane and pentane) or distilled and dried using: Et_3N (CaH_2), THF (Na/Benzophenone), DCM (CaH_2), Pyridine (CaH_2), DMSO (CaH_2). When necessary DMF, Et_3N and pyridine were stored under Ar and over 4Å molecular sieves (activated by heating (250 ºC) under vacuum (0.1 mbar) for 24 h).

The compounds styrene oxide **172**,[42] MoO(N^{t}Bu)Cl_2dme **203**,[67] MoO_2Cl_2dme,[68] Mo($N^{t}Bu)_2Cl_2$dme[68] and $CpSnBu_3$ **188**[69] were prepared by literature methods.

Characterisation:

Solid IR spectra were recorded using an Avatar 320 FTIR. All NMR spectra were recorded on Bruker AM-400 and DRX-500 NMR spectrometer. The chemical shifts were recorded relative to the solvent standard or tetramethylsilane. NMR spectra were recorded using $CDCl_3$ (δ_H = 7.27, δ_C = 77.1 ppm) or C_6D_6 (δ_H = 7.16, δ_C = 128.6 ppm). Multiplicities for coupled signals are denoted as: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad. All resonances that were recorded were in parts per million (ppm). All coupling constants (*J*) were recorded in Hertz (Hz). Elemental analysis was performed by the School of Chemistry, University of Nottingham on an Exeter Analytical CE-440 elemental analyser. Melting points are uncorrected and were recorded on a Gallenkamp melting point apparatus.

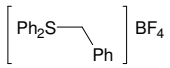
4.2 Experimental Procedures

Dimethylsulfoxonium methylide (145) in tetrahydrofuran[43]

145

To 95% dry NaH (350 mg, 8.75 mmol, 1.10 equiv) was added THF (40 mL) and trimethylsulfoxonium chloride **170** (1.00 g, 7.8 mmol, 1.00 equiv) at rt. The suspension was heated to reflux for 4 h and then cooled to rt before being filtered into a clean Schlenk. The solution was calibrated by titration with 0.1 M HCl and phenolpthalien. Typically showed a concentration of ~ 0.16-0.21 M.

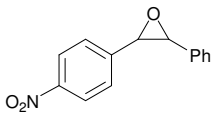
Diphenylbenzylsulfonium tetrafluoroborate (176)[47]



176

Compound **176** prepared according to the literature procedure to yield $(Ph_2SCH_2Ph)BF_4$ **176** as an off-white solid (5.14 g, 55%, lit.[47] 90%); m.p. 89 °C (lit.[70] 102.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.85 (4H, m, *m*-Ph-H), 7.66-7.55 (6H, m, *o/p*-Ph-H), 7.35-7.20 (5H, m, SCH_2-Ph-H), 5.35 (2H, s, SCH_2-Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 134.6, 131.3, 131.1, 131.0, 130.2, 129.4, 129.2, 128.4, 127.8, 127.0, 126.2, 123.7, 51.0 (SCH_2).

***p*-Nitrostilbene oxide (179)**[57]



179

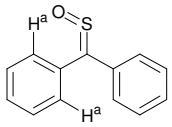
To an off-white suspension of $[Ph_2SCH_2Ph]BF_4$ **176** (1.0 g, 2.75 mmol, 1.00 equiv) in THF (25 mL) at -70 °C under an argon atmosphere was added solid $KN(SiMe_3)_2$ (559 mg, 2.80 mmol, 1.02 equiv). The yellow suspension was warmed to -30 °C and a solution of *p*-nitro-benzaldehyde **178** (415 mg, 2.75 mmol, 1.00 equiv) in THF (10 mL) was added slowly over 10 min. The solution was stirred at -30 °C for 1 h and slowly warmed to rt over 2 h. The reaction was stirred at rt for 1 h before being quenched with water (50 mL) and extracted with Et_2O (3 x 50 mL). The organic phase was dried ($MgSO_4$), filtered and solvent removed under vacuum to obtain a yellow residue (1.40 g). The residue was purified by silica column chromatography (10% EtOAc/Hex) to give *p*-nitrostilbene oxide **179** as a solid (363 mg, 55%, 9.4:1, trans:cis); ^{1}H NMR^{trans} (400 MHz, $CDCl_3$) δ 8.28 (2H, dd, *J*=6.8, 2.0, C<u>H</u>CNO$_2$), 7.53 (2H, dd, *J*= 6.8, 2.0, CC<u>H</u>CHCNO$_2$), 7.45-7.35 (5H, m, Ph), 3.99 (1H, d, *J*=1.6, OC<u>H</u>), 3.87 (1H, d, *J*=2.0, OC<u>H</u>); ^{1}H NMR^{cis} (400 MHz, $CDCl_3$) δ 8.04 (2H, dd, *J*=7.0, 1.8, C<u>H</u>CNO$_2$), 7.39-7.33 (2H, m, CC<u>H</u>CHCNO$_2$), 7.23-7.14 (5H, m, Ph-<u>H</u>), 4.47 (1H, d, *J*=4.0, OC<u>H</u>), 4.42 (1H, d, *J*=4.4, OC<u>H</u>) – Data was identical to that reported in the literature.[71]

Thiobenzophenone (182)[58]

182

Compound **182** was prepared according to literature procedure to yield thiobenzophenone **182** as a blue semi-solid (886 mg, 81% lit.[58] 98%)[60]; b.p. 175 °C at 0.1 Torr (lit.[60] b.p. 170 °C at 0.1 Torr); IR ν_{max} (solid) 1594, 1500, 1446, 1319, 1309, 1297, 1266, 1227, 1175, 1158, 1122, 1096, 1047, 1020, 999, 920, 890, 832, 805, 777, 758 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (4H, m, *o*-H), 7.60 (2H, m, *p*-H), 7.40 (4H, m, *m*-H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 238.6 (C=S), 147.4 (C), 132.1(*m*-CH), 129.7 (*p*-CH), 128.0 (*o*-CH).

Diphenylsulfine (183)[52]



183

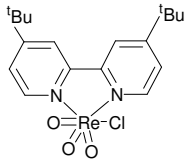
Compound **183** was prepared according to the literature procedure to obtain diphenylsulfine **183** as a yellow oil (798 mg, 83% lit.[52] 90%); IR ν_{max} (liquid film) 3057, 3031, 1658, 1597, 1574, 1489, 1448, 1317, 1306, 1277, 1220, 1186, 1109, 1077, 1034, 1007, 922, 907 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (2H, m, H^a), 7.03 (4H, m, Ar-H), 6.94 (4H, m, Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 188.6 (C=S), 134.6, 131.4, 130.9, 130.1, 129.7, 129.5, 129.0, 128.7.

Cyclopentadienyltrioxorhenium (189)[61]

189

Compound **189** was prepared according to the literature procedure to yield cyclopentadienyltrioxorhenium **189** as a yellow solid (0.49 g, 40%, lit.[61] 80%); IR ν_{max} 3102 (Ar-CH), 1429, 1066, 1057, 1017, 922, 883(Re-O), 851, 799, 780, 773, 766, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (5H, s, C<u>H</u>); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 113.9 (CH).

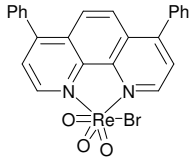
(4,4'-Di-*t*-Butyl-2,2'-bipyridyl)(Cl)ReO_3 (193)[62]



193

Compound **193** was prepared according to literature procedure to yield [(4,4'-Di-*t*-Butyl-2,2'-bipyridyl)(Cl)ReO_3] **193** (2.02 g, 91%, lit.[62] 90%) m.p. >300 °C (decomp); IR ν_{max} (Solid) 1615 (Ar-C-H), 1412 (Alk-C-H), 1252, 1026, 943, 920 (Re-O), 907, 891(Re-O), 862 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (2H, d, *J*=5.6, NC<u>H</u>), 8.17 (2H, d, *J*=2.0, NCC<u>H</u>C), 7.74 (2H, dd, *J*=6.0, 2.0, NCHC<u>H</u>C), 1.48 (18H, s, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR (100.6 Hz, $CDCl_3$) δ 166.7, 151.5, 150.1, 125.0, 119.6, 36.0 (<u>C</u>(CH$_3$)$_3$), 30.4 (C(<u>C</u>H$_3$)$_3$).

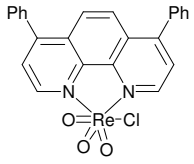
(4,7-Diphenyl-1,10-phenanthroline)(Br)ReO_3 (197)[63]



197

To a solution of Re_2O_7 **186** (73 mg, 0.15 mmol, 1.00 equiv) in THF (15 mL) was added bromotrimethylsilane **198** (39 μL, 0.30 mmol, 2.00 equiv) at rt under argon. Immediately 4,7-diphenyl-1,10-phenanthroline **196** (100 mg, 0.30 mmol, 2.00 equiv) was added to the yellow solution and the solution changed colour to orange. The solution was stirred for 30 min before solvent was removed under vacuum to yield [(4,7-diphenyl-1,10-phenanthroline)(Br)ReO_3] **197** as an orange solid (181 mg, 93%, lit.[63] 44%). m.p. >300 °C (decomp) (lit.[63] m.p. 240 °C (decomp.)); IR ν_{max} (solid) 1622, 1600, 940 (Re-O), 921, 897 (Re-O), 854, 770 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.70 (2H, d, *J*=5.5, *o*-H), 8.16 (2H, s, Ar-H), 8.02 (2H, d, *J*= 5.5, *m*-H), 7.64 (6H, m, Ph-H) 7.60 (4H, m, Ph-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 151.1, 142.2, 135.2, 130.3, 129.6, 129.4, 128.9, 126.5, 125.9.

(4,7-diphenyl-1,10-phenanthroline)(Cl)ReO_3 (198)



198

To a solution of Re_2O_7 **186** (364 mg, 0.75 mmol, 1.00 equiv) in THF (30 mL) was added chlorotrimethylsilane **191** (190 μL, 1.50 mmol, 2.00 equiv). Immediately the 4,7-diphenyl-1,10-phenanthroline **196** (500 mg, 1.50 mmol,

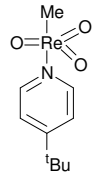
2.00 equiv) was added to the yellow solution. The solid dissolved in the solution before a precipitate formed. The suspension was stirred for 1 h and the precipitate was collected *via* canula filtration. The precipitate was washed with hexane (3 x 10 mL) and dried under vacuum to obtain (4,7-diphenyl-1,10-phenanthroline)(Cl)ReO_3 **198** as an off-white solid (678 mg, 75%) m.p. >300 °C (decomp); IR ν_{max} (solid) 2989, 2901, 1625, 1604, 1559, 1521, 1431, 1403, 1238, 1066, 942 (Re-O), 922, 911, 900 (Re-O), 855, 840, 811, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.70 (2H, d, *J*=5.6, *o*-H), 8.15 (2H, s, Ar-H), 8.02 (2H, d, *J*=5.6, *m*-H), 7.68-7.55 (10H, m, Ph-H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 153.5, 150.9, 142.2, 135.2, 130.3, 129.7, 129.4, 128.9, 126.4, 125.8; Anal. Calcd for $C_{24}H_{16}ClN_2O_3Re$: C, 47.84; H, 2.68; N, 4.65. found: C, 48.61; H, 2.83; N, 4.55.

Methyltrioxorhenium (82)[64]

82

Compound **82** was prepared according to literature procedure to obtain clear crystals of methyltrioxorhenium **82** (856 mg, 77%, lit.[64] 76%) m.p. 108 °C (lit.[64] m.p. 108 °C); IR ν_{max} (solid) 2986, 2900, 1359, 1206, 1066, 966(Re-O) 958, 948 (Re-O) cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.35 (3H, s, Re-C$\underline{H}_3$); ^{13}C NMR (100.6 MHz, C_6D_6) δ 17.75 (Re-$\underline{C}H_3$).

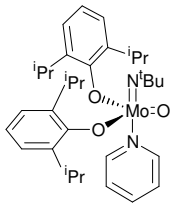
Methyltrioxorhenium(4-*tert*-butylpyridine) (202)[65]



202

Compound **202** was prepared according to literature procedure to obtain methyltrioxorhenium(4-*tert*-butylpyridine) **202** (307 mg, 82% lit.[65] 52%); m.p. 119 °C; IR ν_{max} (solid) 2969, 1613, 1420, 1071, 1019, 926 (Re-O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (2H, dd, *J*=5.2, 1.6, *o*-H-py), 7.37 (2H, dd, *J*=5.2, 1.6, m-H-py), 1.88 (3H, s, Re-CH_3), 1.30 (9H, s, $C(CH_3)_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 163.6 (NCH), 146.5 (N(CH)(CH)(C)), 122.2 (N(CH)(CH)), 35.1 ($C(CH_3)_3$), 30.4 ($C(CH_3)_3$), 25.4 (Re-CH_3).

MoO(N^{t}Bu)(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$py (127a)[41]

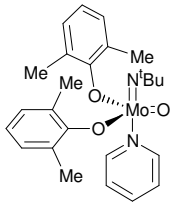


127a

Compound **127a** was prepared according to literature procedure to obtain yellow crystals of **127a** (412 mg, 31% lit.[41] 48%); m.p. 125 °C (lit.[41] m.p. 117-121 °C); IR ν_{max} (solid) 2962, 1603, 1444, 1426, 1381, 1358, 1326, 1252, 1215, 1193, 1153, 1114, 934, 899 (Mo-O), 798, 767, 753 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 9.26 (2H, brd, *J*= 4.4, *o*-H-py), 7.13 (4H, d, *J*= 7.6, *m*-H-Ar), 6.97 (2H, t, *J*= 7.6, *p*-H-Ar), 6.84 (1H, t, *J*= 7.6, *p*-H-py), 6.66 (2H, dd, *J*=7.2, 6.6, *m*-H-py), 3.95 (4H, sept, *J*= 6.8, $CH(CH_3)_2$), 1.38 (12H, d, *J*=6.8,

CH(C<u>H</u>$_3$)$_2$), 1.37 (12H, d, *J*=6.8, CH(C<u>H</u>$_3$)$_2$), 0.75 (9H, s, NC(C<u>H</u>$_3$)$_3$); ^{13}C NMR (100.6 MHz, C_6D_6) δ 165.3 (C-O), 149.2, 137.6, 136.2, 124.0, 123.1, 121.6, 72.7 (N<u>C</u>(CH$_3$)$_3$), 28.9, 27.4, 23.3, 23.1.

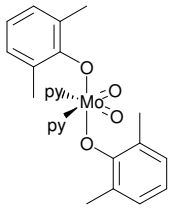
MoO(N^{t}Bu)(2,6-Me$_2$C$_6$H$_3$O)$_2$py (127b)[41]



127b

Compound **127b** was prepared according to literature procedure to obtain yellow crystals of **127b** (284 mg, 39%, lit.[41] 45%); m.p. 125 °C (lit.[41] m.p. 122-126 °C); IR ν_{max} (solid) 2974, 2925, 1602, 1466, 1423, 1358, 1265, 1237, 1200, 1160, 1092, 1072, 1038, 1011, 902 (Mo-O), 856, 775, 760, 743, 709 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 9.11 (2H, brd, *J*=4.4, *o*-<u>H</u>-py), 6.97 (4H, d, *J*=7.6, *m*-<u>H</u>-Ar), 6.88 (1H, t, *J*=7.6, *p*-<u>H</u>-py), 6.78 (2H, t, *J*=7.4, *p*-<u>H</u>-Ar), 6.62 (2H, m, *m*-<u>H</u>-py), 2.57 (12H, s, Ar-C<u>H</u>$_3$), 0.70 (9H, s, NC(C<u>H</u>$_3$)$_3$); ^{13}C NMR (100.6 MHz, C_6D_6) δ 167.9, 149.3, 138.1, 137.2, 126.1, 124.0, 121.2, 72.5 (N<u>C</u>(CH$_3$)$_3$), 28.51 (NC(<u>C</u>H$_3$)$_3$), 17.51 (Ar-<u>C</u>H$_3$).

MoO_2(2,6-$Me_2C_6H_3O)_2py_2$ (208)[66]



208

Compound **208** was prepared according to literature procedure to obtain orange crystals of MoO_2(2,6-$Me_2C_6H_3O)_2py_2$ **208** (187 mg, 22%, lit.[66] 37%); m.p. 100 °C (lit.[66] m.p. 62-63 °C); IR ν_{max} (solid) 1604, 1478, 1445, 1327, 1264, 1195, 1090, 1040, 1014, 934 (Mo-O), 901 (Mo-O), 869, 847, 760 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 8.33 (4H, d, *J*=4.4, *o*-H-py), 6.82 (4H, d, *J*=6.8, *m*-H-Ar), 6.71 (2H, t, *J*=7.6, *p*-H-Ar), 6.69 (2H, t, *J*=6.8, *p*-H-py), 6.39 (4H, t, *J*=6.6, *m*-H-py), 2.41 (12H, s, Ar-CH_3); ^{13}C NMR (100.6 MHz, C_6D_6) δ 149.3 136.7, 129.1, 128.4, 127.8, 127.6, 126.8, 123.8, 122.2, 17.0 (CH_3).

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