Catalytic applications of transition metals in organic synthesis

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Reviewing the literature published between
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Continuing the coverage in *Contemporary Organic Synthesis*, 1995, **2**, 65

1 Introduction

This review highlights the recent advances in transition metal catalysis for the period 1 September 1994 to 31 October 1995. The review deals with homogeneous transition metal catalysed reactions – an area which over the 14 months covered represents a large number of research papers. Consequently, a great deal of high quality chemistry cannot be included in this review, since it cannot be fully comprehensive.

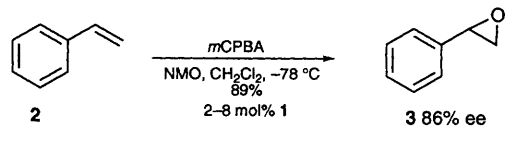
Many transition metal catalysed reactions are being pursued in an asymmetric fashion, and there have been new ligands and new applications of ligands reported in recent months. However, not all research involves asymmetry, and this review has attempted to describe the recent advances in transition metal catalysed reactions as a whole.

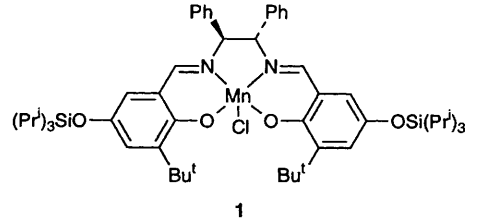
2 Oxidation

There has been a long standing interest in the catalytic oxidation of organic substrates. Catalysis by transition metals allows for stereoselective and chemoselective processes to take place. Each year new advances are made in tuning the selectivity of such catalysed processes. For example, in the last year, several groups have reported allylic oxidation reactions proceeding with good enantioselectivity (see Section 2.3).

2.1 Epoxidation

The use of manganese salen complexes **1** and related sytems for the enantioselective epoxidation of alkenes has continued to be a useful process. Jacobsen and co-workers have reported that with an oxidising system comprising of *m*CPBA (*meta*-chloroperbenzoic acid) and NMO (*N*-methylmorpholine oxide), it is possible to run the epoxidation reactions at low temperatures.[1] The low temperature has a beneficial effect on the enantioselectivity, allowing the epoxidation of styrene **2** to occur with 86% ee in the formation of styrene oxide **3**. This research group has also reported its





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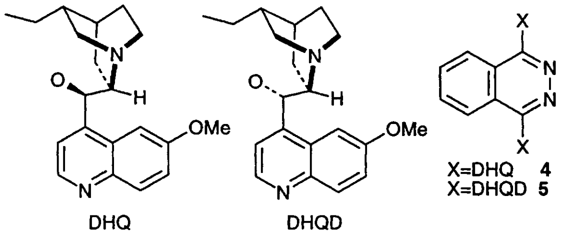
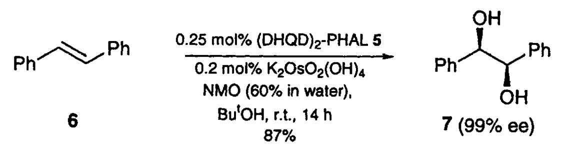
successful results using salen manganese complexes in the asymmetric epoxidation of tetrasubstituted alkenes[2] and in the kinetic resolution of racemic chromenes.[3] Bosquet and Gilheaney have reported that chromium salen complexes are also effective as asymmetric epoxidation catalysts.[4]

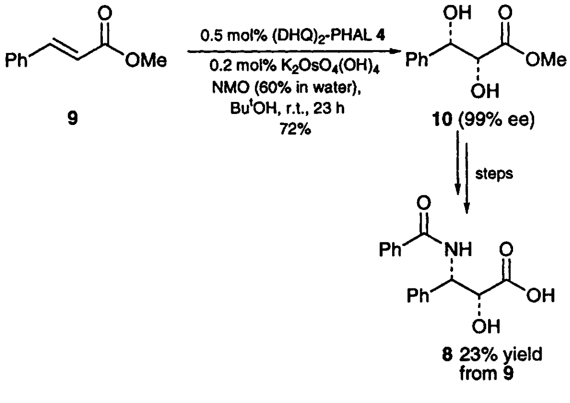
2.2 Dihydroxylation

The asymmetric dihydroxylation (AD) reaction of alkenes now leads the field of asymmetric catalysis in terms of generality and synthetic utility. The asymmetric dihydroxylation reaction is an example of a catalytic reaction which is accelerated by the presence of the ligand, and such reactions have recently been reviewed.[5] The pseudo-enantiomeric ligands **4** and **5** are the most widely employed, although many other variations have also been described. From a practical standpoint, one of the most useful developments of this reaction is the procedure developed by Wang and Sharpless for the conversion of stilbene **6** into the diol **7** with 99% ee and 87% yield on a one kilogram scale.[6] Remarkably, even on this scale, the reaction was achieved in a five-litre flask!!

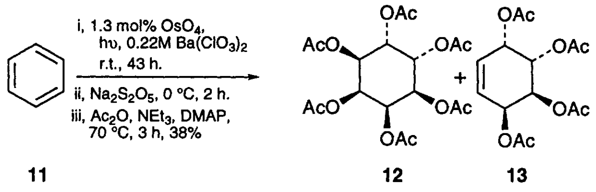




The Sharpless group have also reported a multigram synthesis of the taxol side-chain **8**.[7] Methyl cinnamate **9** underwent asymmetric dihydroxylation to afford the diol **10**, which was further manipulated to provide the taxol side-chain **8**. Additionally, Sharpless and co-workers have reported the selective dihydroxylation of polyenes.[8]

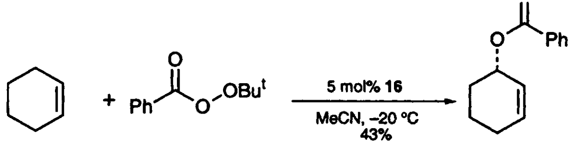


Corey and co-workers have reported that whilst allylic alcohols are not good substrates for asymmetric dihydroxylation reactions, the corresponding methoxybenzoate derivatives can be employed to provide highly enantioselective dihydroxylation.[9] For homoallyl ethers, the methoxyphenyl ether was found to be the best derivative.[10] Warren and co-workers have revealed a racemic version of the Sharpless AD reaction.[11] The alkenes are converted into the corresponding diols upon treatment with $OsCl_3$ and $K_3Fe(CN)_6$ with quinuclidine as the accelerating ligand, using added potassium carbonate and methylsulfonamide in a two-phase system of *tert*-butyl alcohol and water. This can be useful in the preparation of racemic diols which can be used as analytical standards. A remarkable photochemically induced, osmium tetroxide catalysed reaction has been reported by Motherwell and Williams.[12] Benzene **11** was converted into a mixture of *allo*-inositol and conduritol E, which were isolated as their peracylated derivatives **12** and **13**.

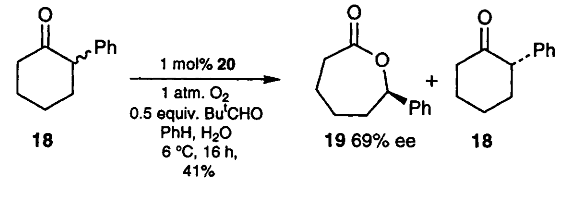


2.3 Other oxidations

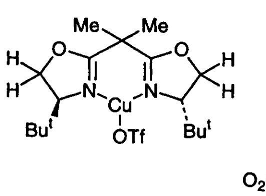
Several groups have independently reported enantioselective allylic oxidation reactions catalysed by copper complexes. Thus, Andrus and co-workers have described the conversion of cyclohexene **14** into cyclohexenyl benzoate **15** with 80% ee in the presence of an enantiomerically pure bis-oxazoline copper complex **16** and the perester **17**.[13] A related system employing bis-oxazolines had also been reported by Pfaltz.[14] Additionally, copper complexes of proline and related amino acids have been employed in asymmetric allylic oxidation reactions[15,16,17]



Enantiomerically pure copper complexes have also been employed in catalytic asymmetric Baeyer–Villiger reactions, such as the conversion of 2-phenylcyclohexanone **18** into the lactone **19**, wherein a kinetic resolution takes place using the catalyst **20**.[18,19] Ruthenium dioxide and manganese dioxide have also been shown to be catalysts for Baeyer–Villiger reactions in the presence of oxygen and benzaldehyde.[20]



18 **19** 69% ee **18**



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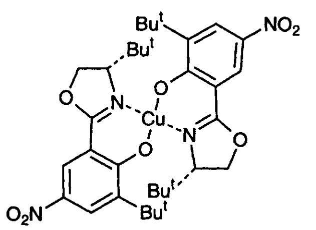

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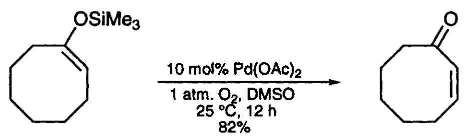
Larock and co-workers have reported an oxidation reaction involving the conversion of silyl enol ethers into α,β-unsaturated carbonyl compounds.[21] For example, the cyclic silyl enol ether **21** was converted into cyclooctenone **22** in high yield upon treatment with catalytic amounts of palladium acetate in the presence of oxygen with Me_2SO as the solvent.



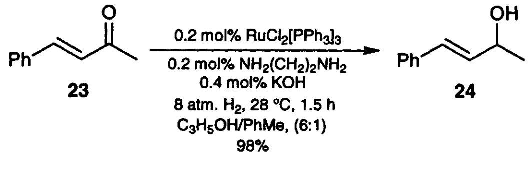
21 **22**

3 Hydrogenation and related processes

Transition metal catalysed hydrogenation reactions are historically amongst the first practical processes which were achieved with homogeneous transition metal catalysts. Hydrogenation and the related processes discussed in this section are still being actively researched, and significant discoveries are still being uncovered.

3.1 Hydrogenation

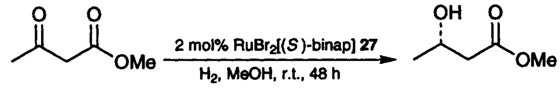
Transition metal catalysed hydrogenation reactions are usually associated with the conversion of alkenes into alkanes, and normally this procedure can be conducted without affecting carbonyl groups. However, Noyori and co-workers have demonstrated that it is possible to selectively hydrogenate aldehydes and ketones in the presence of alkenes![22] Critical to this selectivity is the addition of catalytic amounts of potassium hydroxide and 1,3-diaminopropane to the ruthenium catalyst.[23] Thus, benzylideneacetone **23** is converted into the corresponding alcohol **24**.



23 **24**

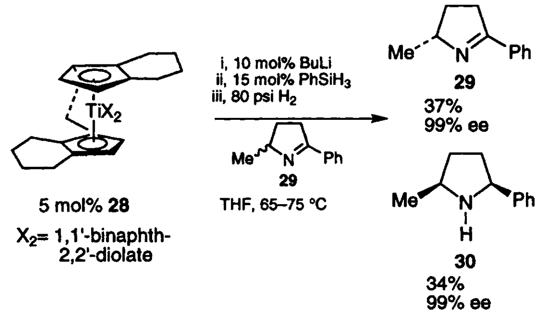
These workers also describe competitive experiments, where acetophenone reacts 1500 times more quickly than α-methylstyrene.

A ruthenium catalysed asymmetric hydrogenation of β-keto esters which proceeds at atmospheric pressure has been reported by Genet and co-workers.[24] Thus the β-keto ester **25** was reduced to the β-hydroxy ester **26** in good yield and enantioselectivity with the ruthenium catalyst **27** under atmospheric pressure of hydrogen. Burk and co-workers also reported mild conditions for the enantioselective ruthenium catalysed hydrogenation of β-keto esters.[25]

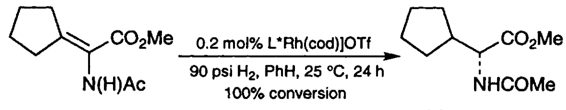


25 **26** 97% ee

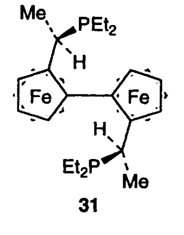
The research group of Buchwald has continued its investigations into the hydrogenation of imines with the enantiomerically pure titanium catalyst **28**.[26,27] For example, this group has performed a kinetic resolution on the racemic pyrroline **29**, one enantiomer of which is selectively hydrogenated to give the *cis*-pyrrolidine **30**.[28]



Interest in the hydrogenation of α-aminoacylacrylates to yield amino acid derivatives is a reaction which has been investigated with many ligands. Recent additions to this research include the use of the ligand **31**,[29] which is proposed to function as a *trans*-chelating ligand, and the ligand **32** employed by Burk and co-workers. Ligand **32** has been used to provide high enantioselectivities in the rhodium catalysed hydrogenation of β-branched substrates, such as **33**, which is converted into a β-branched amino ester derivative **34**.[30] This group have also



33 **34** 97.2% ee



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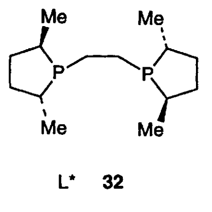
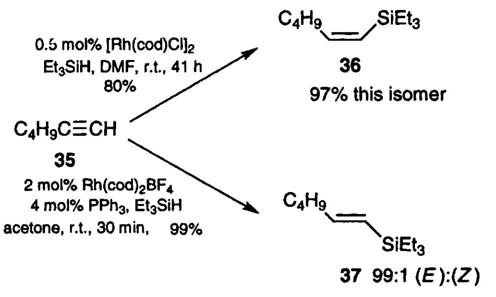


L* **32**

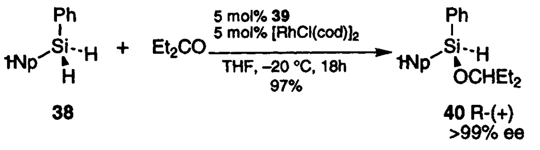
reported related reduction reactions performed in supercritical carbon dioxide.[31] Hydrogenation using two-phase catalysis and glass beads to support one of the phases has been reported. The catalyst is dissolved in a polar phase which binds to the surface of the glass bead, whilst the substrate remains in the organic phase. This overcomes some of the problems associated with catalyst contamination found with conventional homogeneous catalysis. Some of the recent advances have been summarised in a short review.[32]

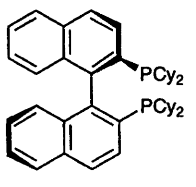
3.2 Hydrosilylation

The stereocontrolled hydrosilylation of terminal alkynes has been reported by Takeuchi and Tanouchi.[33] Depending upon the conditions employed, the reaction pathway could be directed towards the formation of either the (*E*)- or the (*Z*)-vinylsilane. The hydrosilylation of hex-1-yne **35** with $[Rh(cod)Cl]_2$ in the absence of a phosphine affords predominantly the (*Z*)-vinylsilane **36** whereas using a cationic rhodium catalyst in the presence of a phosphine affords predominantly the (*E*)-vinylsilane **37**.

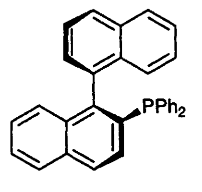


The enantioselective hydrosilylation of prochiral ketones is well known with rhodium catalysts – ligand **31** has recently been used for this purpose.[34] Additionally, Buchwald and co-workers have applied their titanocene derived catalysts **28** to this reaction and obtained excellent enantioselectivity for the reduction of a range of aryl alkyl ketones.[35] Takaya and co-workers have demonstrated that hydrosilylation of symmetrical ketones can lead to excellent asymmetric induction at the silicon centre when a suitable prochiral silane is employed.[36] Treatment of naphthylphenylsilane **38** with pentan-3-one and a catalytic system comprising of the Cybinap ligand **39** and $[Rh(cod)Cl]_2$ affords the hydrosilylation product **40** with >99% ee. Hayashi and co-workers have developed ligands which are indisputably monodentate ligands, and yet still provide very high asymmetric induction in the palladium catalysed hydrosilylation of alkenes.[37] Styrene **2** undergoes hydrosilylation in the presence of 0.1 mol% of a palladium complex of the monodentate phosphine **41** and subsequent conversion into the corresponding alcohol **42** with high levels of asymmetric induction.

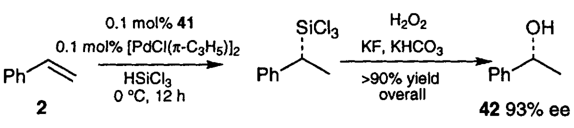




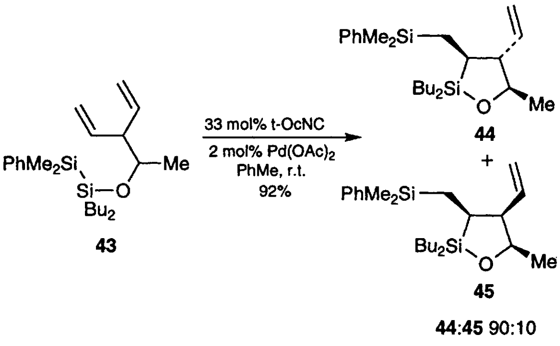
(*R*)-Cybinap **39**

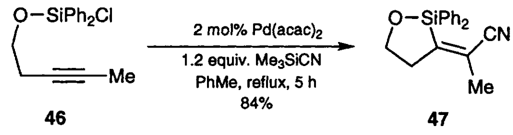


H-MOP **41**



As well as hydrosilylation, bis-silylation reactions are known, and Ito and co-workers have demonstrated that palladium catalysed intramolecular bis-silylation reactions can occur with good diastereocontrol.[38] The single stereocentre of the cyclisation precursor **43** controls the stereochemistry of two further stereocentres formed in the cyclisation products **44** and **45**. Intramolecular cyanosilylation has also been described by Ito and co-workers. The alkyne **46** undergoes palladium catalysed cyanosilylation to afford the silatetrahydrofuran product **47**.[39]

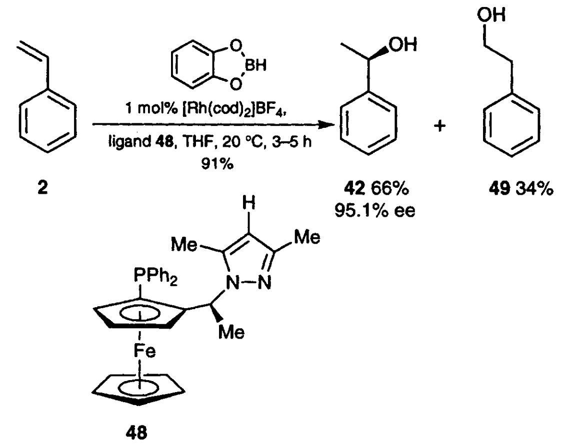




Esters are usually inert to catalysed hydrosilylation reactions. However, Cutler and co-workers have reported that esters can be converted into the corresponding ethers upon treatment with phenylsilane and manganese catalyst.[40]

3.3 Hydroboration

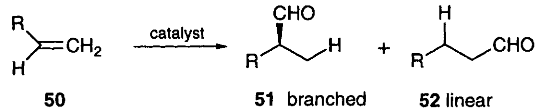
Togni and co-workers have shown that pyrazole-containing ferrocenyl ligands **48** can be used for rhodium catalysed asymmetric hydroboration reactions, as exemplified by the hydroboration of styrene **2**.[41] After oxidative work-up the hydrated



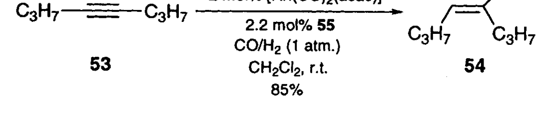
products 42 and 49 are obtained with reasonable regioselectivity and good enantioselectivity.

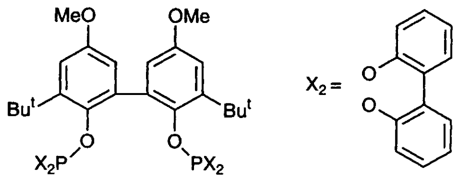
3.4 Hydroformylation

A recent review has provided valuable coverage of the latest developments in enantioselective hydroformylation reactions.[42] The reaction of an alkene **50** with H_2/CO affords the branched aldehyde **51** and linear aldehyde **52**, and the branched chain aldehyde has the possibility of being formed with asymmetric induction. This process has been the subject of much research, and recently, excellent regiocontrol and enantiocontrol have both been achieved. The review describes the factors which affect this stereocontrol.



Buchwald and co-workers have examined the rhodium catalysed hydroformylation of internal alkynes.[43] Under suitable conditions, these workers have been able to form the conjugated aldehyde with only small amounts of isomeric or saturated aldehydes. Oct-4-yne **53** is converted into the unsaturated aldehyde **54** using a rhodium catalyst in conjunction with ligand **55**.





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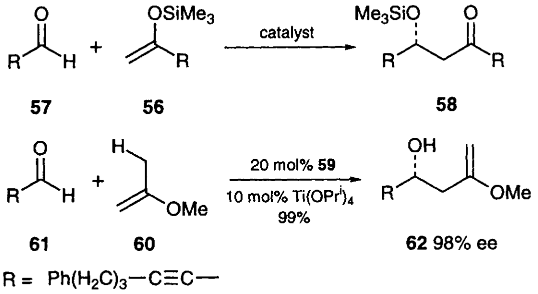
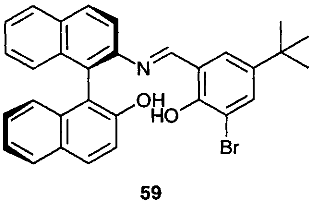
4 Lewis acids

Lewis acids are able to catalyse a wide range of organic transformations. In particular, interest in catalytic asymmetric synthesis with Lewis acids has been great. The Mukaiyama aldol reaction employing silyl enol ethers **56** and a carbonyl compound **57** catalysed by a Lewis acid provides a synthetically useful route to aldol adducts **58**. Many enantiomerically pure ligands have been successfully employed with this reaction, especially titanium catalysts, including ligand **59** recently reported by Carreira and co-workers.[44] Additionally, these workers have described a carbonyl-ene equivalent of this reaction which proceeds with remarkable selectivity, especially for acetylenic aldehydes.[45] In the presence of a titanium complex of ligand **59**, methoxypropene **60** and the aldehyde **61** are converted into the 'aldol adduct' **62** with excellent enantiocontrol and yield. Simple hydrolysis converts the adduct into the corresponding β-hydroxy ketone. Berrisford and Bolm have written a short review detailing some of the current highlights of carbonyl-ene reactions.[46]





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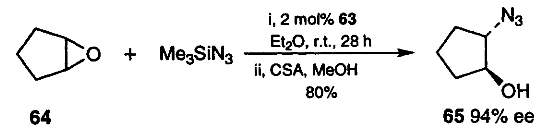
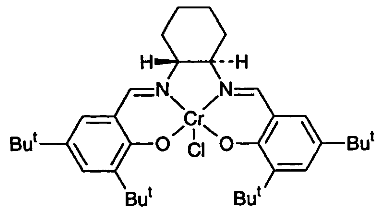
The desymmetrisation of *meso*-epoxides is another reaction which has been catalysed by enantiomerically pure Lewis acids. Jacobsen and co-workers have employed (salen)chromium(III) complexes **63** as Lewis acids to desymmetrise *meso*-epoxides by nucleophilic ring opening with trimethylsilyl azide.[47] For example, cyclopentene oxide **64** was converted [after removal of the silyl group with camphorsulfonic acid (CSA) in methanol], into the azido alcohol **65** with high levels of enantiocontrol.

The allylation of aldehydes such as benzaldehyde **66** with allyltributyltin **67** to give the adduct **68** has been catalysed by a zirconium BINOL complex **69**.[48]

4.1 Diels–Alder reactions

Diels Alder reactions have also been catalysed by transition metal complexes. A lot of research has





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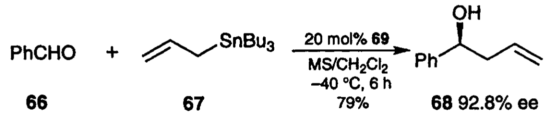

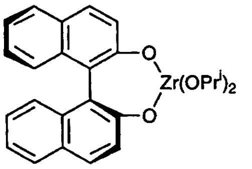

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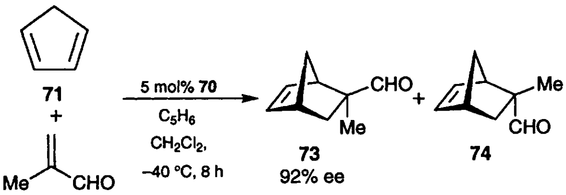
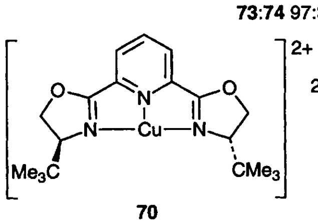
centred around the use of titanium complexes of tartrate-derived TADDOL ligands, and two detailed reports concerning the mechanism of these complexes in Diels–Alder reactions have appeared.[49,50] Evans and co-workers have continued to employ copper(II) bis-oxazoline complexes such as **70** to catalyse Diels–Alder reactions with excellent enantioselectivity, as demonstrated by the catalysed addition of cyclopentadiene **71** to methacrolein **72** to give the cycloadducts **73** and **74**.[51] Mikami and co-workers have shown that the 6,6′-dibromo-BINOL titanium complex **75** provides better results than the parent BINOL titanium complex in catalysed Diels–Alder reactions.[52] The enantiomerically pure iron complex **76** has also been highly successful as an asymmetric Lewis acid catalyst in Diels–Alder reactions,[53] and even oxo(salen)manganese(V) complexes have been used as Lewis acid catalysts for Diels–Alder reactions.[54]





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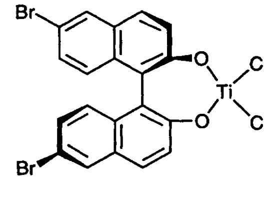
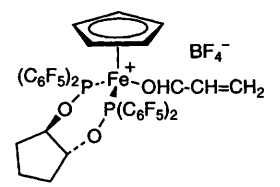
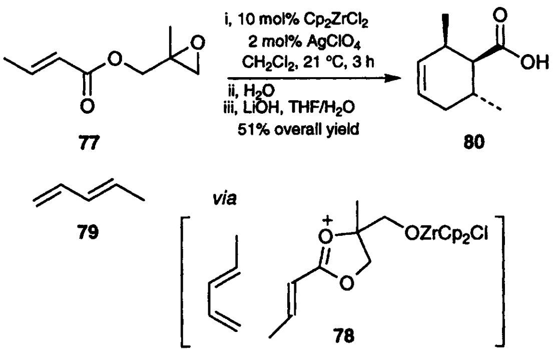




75 **76**

Keck and co-workers have reported a catalytic enantioselective hetero Diels–Alder reaction using titanium BINOL complexes.[55] The adducts are formed with up to 97% ee. The mechanism is probably not concerted and is thought to proceed *via* a two-step aldol–Michael sequence.

Wipf and co-workers have reported an interesting zirconocene catalysed Diels–Alder reaction which does not proceed *via* a simple Lewis acid catalysed mechanism.[56] The dienophile **77** is activated to reaction by the formation of a cationic intermediate **78** which reacts with the diene **79** and after hydrolysis of the cycloadduct esters affords compound **80**.



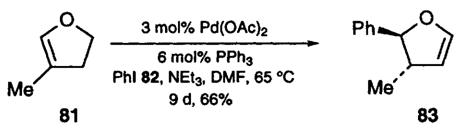
5 Coupling reactions

Transition metal catalysed coupling reactions cover a wide range of synthetically useful processes. Coupling reactions often provide a method for the formation of new C–C bonds, although there are also applications to the formation of carbon–heteroatom bonds. Additionally, many coupling reactions may be conducted in an asymmetric fashion.

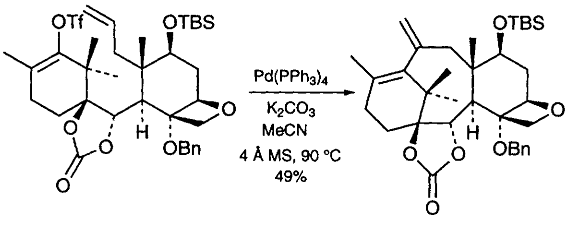
5.1 Heck reactions

The Heck reaction between aryl or vinyl halides with alkenes is a valuable method for the construction of C–C bonds, as are variants of the Heck reaction.

Hillers and Reiser have shown that the Heck reaction of 4-alkyl substituted 2,3-dihydrofurans, such as compound **81**, with a coupling partner such as iodobenzene **82** occurs diastereoselectively to give the *trans*-configured product **83**.[57]

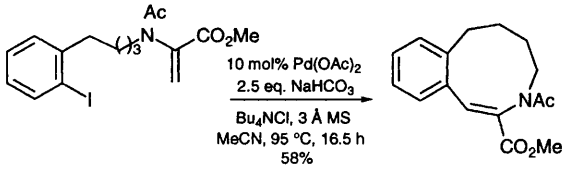


Masters, Danishefsky and co-workers have employed a Heck cyclisation as a key step in the total synthesis of taxol.[58] The vinyl triflate **84** was cyclised to afford the advanced intermediate **85** in a yield of 49%, which is remarkable considering the density of functional groups in this molecule.



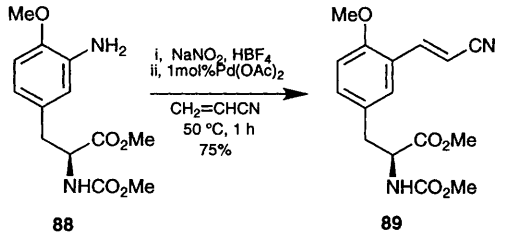
84 **85**

Other Heck cyclisation reactions have been reported. Gibson and co-workers have prepared 7-, 8-, and 9-membered rings by *endo*-Heck cyclisation reactions.[59] Thus, the cyclisation precursor **86** underwent Heck cyclisation to afford the 9-membered ring **87**. Macrocyclisation Heck reactions providing 18-, 20- and 22-membered macrocycles have also been reported.[60]



86 **87**

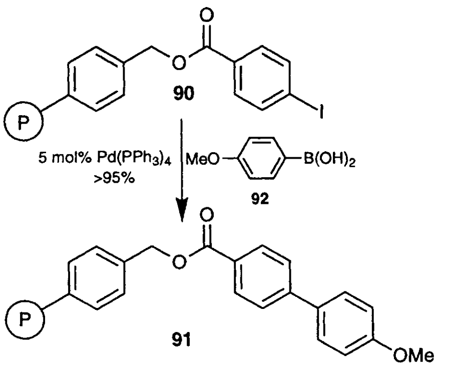
Diazotisation of anilines provides suitable substrates for Heck reactions, and the intermediate diazo compounds can be used without isolation in either a one-pot procedure or by a tandem *in situ* reaction.[61] Sengupta and Bhattacharyya have converted the aniline **88** into the Heck product **89** using the sequential one-pot procedure.[62] Heck reactions of polymer bound aryl iodides with alkenes have been reported, and have applications in combinatorial synthesis.[63,64]



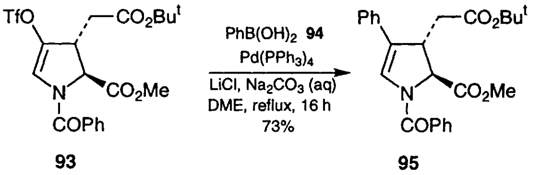
88 **89**

5.2 Suzuki coupling

Polymer bound aryl iodides have also been subjected to Suzuki reactions. This is exemplified in the conversion of the polymer bound aryl iodide **90** into the coupled product **91** on palladium catalysed coupling with the arylboronic acid **92**.[65]

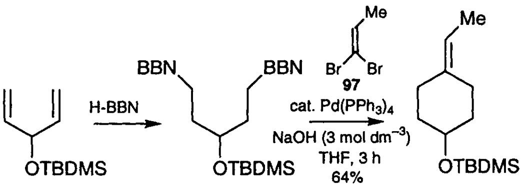


Baldwin and co-workers have used the Suzuki coupling reaction to generate a range of acromelic acid analogues.[66] The vinyl triflate **93** was coupled with arylboronic acids including phenylboronic acid **94**, to give the coupled product **95**. Percec and co-workers have provided a detailed account of the use of nickel catalysts in Suzuki-type reactions of aryl mesylates and aryl arenesulfonates with arylboronic acids.[67]



93 **95**

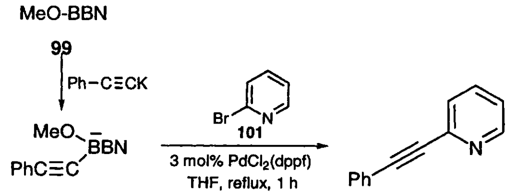
An interesting example of a double Suzuki coupling which results in cyclisation has been reported by Soderquist and co-workers.[68] The diene **96** is doubly hydroborated, and then undergoes a double Suzuki coupling with the dibromoalkene **97**, which affords the cyclic product **98**.



96 **97** **98**

BBN = 9-borabicyclo[3.3.1]nonane

Fürstner and Seidel have described a new approach to the preparation of borates for Suzuki coupling reactions.[69] Rather than adding methoxide to a trialkylboron compound, these workers add polar organometallics to 9-methoxy-9-borabicyclo[3.3.1]nonane **99**. For example, addition of phenylacetylide affords the borate **100**, which was



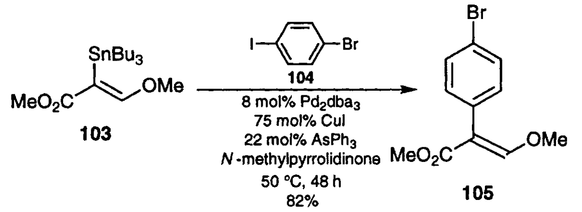
100 **102**

coupled with 2-bromopyridine **101** to give the Suzuki product **102**. By slow addition of the organometallic species, it was possible to use catalytic amounts (30 mol%) of the boron compound **99**.

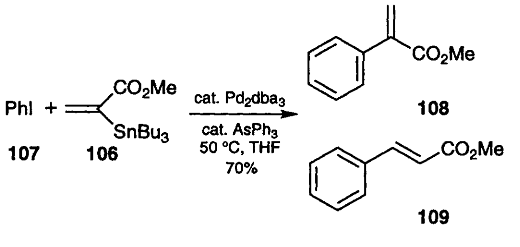
5.3 Stille coupling

The synthetic utility of the Stille coupling is demonstrated by an example reported by Hodgson and co-workers.[70] The functionalised vinyl stannane **103** underwent Stille coupling with various aryl halides including compound **104** to give the product **105**. The presence of copper iodide as a co-catalyst was found to be essential. The role of copper(I) co-catalysts was also discussed in detail elsewhere.[71]

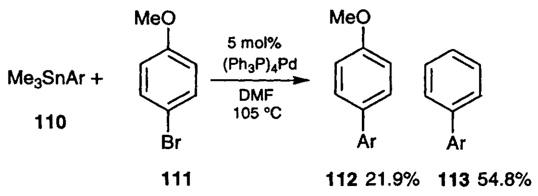
Arylbenzoic acids may be employed without protection in the Stille reaction, and with suitable tin-containing reagents, such reactions can be conducted in water.[72,73]



Sometimes, the Stille reaction produces unexpected coupling products. For example, the coupling of the vinyl stannane **106** with iodobenzene **107** affords very little of the expected product **108**, and instead provides methyl cinnamate **109**.[74] A mechanistic rationale involving the formation of a palladium carbene intermediate is proposed. Chenard and co-workers have reported that phenyl groups from triphenylphosphine can become incorporated into the coupled products *via* a scrambling of aryl groups within the intermediate palladium(II) complex.[75] For electron-rich aryl halides the effect is substantial, and in the coupling of arylstannanes **110** with 4-bromoanisole **111**, the expected product **112** is present in smaller amounts than the 'scrambled' product **113**. Norton and co-workers have described related results.[76]

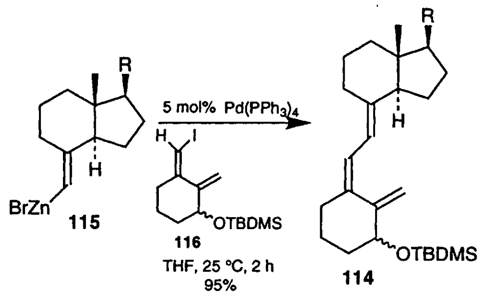


108:**109** 1:254

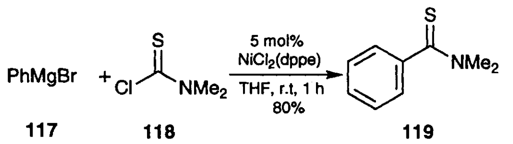


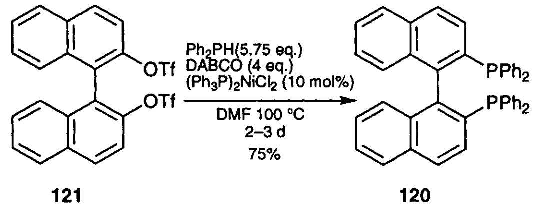
5.4 Other coupling reactions

Very often organozinc reagents prove to be amongst the best partners in metal catalysed coupling processes. In the preparation of the vitamin D skeleton **114** the organozinc derivative **115** was found to provide a higher yield than other organometallics when coupled with the vinyl iodide **116**.[77]

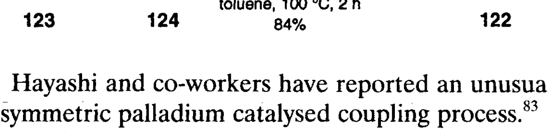


There are also many examples of the use of Grignard reagents in coupling reactions. An interesting method for the preparation of thioamides employs Grignard reagents, as illustrated by the nickel-catalysed coupling between phenylmagnesium bromide **117** and *N*,*N*-dimethylthiocarbamoyl chloride **118** to give the thioamide **119**.[78] Cai and co-workers have reported a useful preparation of BINAP **120** by direct nickel catalysed coupling between binaphthol ditriflate **121** and diphenylphosphine.[79,80] This reaction proceeds without loss of stereochemical integrity.

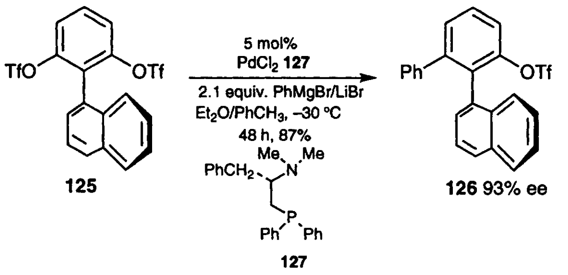




Hartwig and Louie have developed the palladium catalysed synthesis of arylamines **122** from arylbromides **123**.[81] Whilst initial results had required the use of aminostannanes, it has now proved to be possible to use simple amines such as compound **124** as the coupling partner.[82]

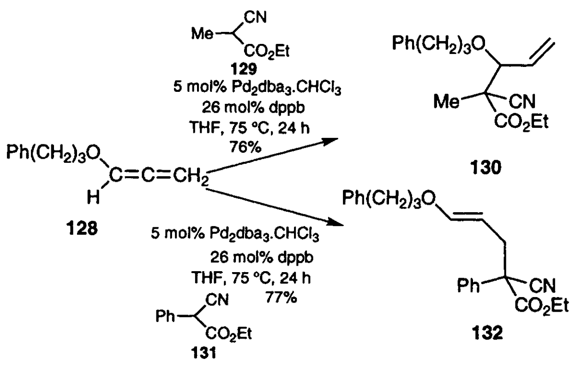


Hayashi and co-workers have reported an unusual asymmetric palladium catalysed coupling process.[83] The achiral precursor **125** undergoes an enantioselective reaction where one of the enantiotopic

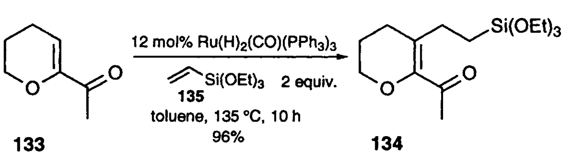


triflate groups undergoes preferential reaction to provide the coupled product **126** with high enantioselectivity in the presence of ligand **127**.

There is a substantial interest in the use of allenes in metal catalysed coupling reactions. The reactivity of the alkoxyallene **128** is particularly interesting because the regioselectivity of the palladium catalysed addition is strongly dependent upon the nucleophile employed.[84] Thus, using the pronucleophile **129** leads to the α-addition product **130**, whereas the use of the pronucleophile **131** affords the alternative γ-addition product **132**.

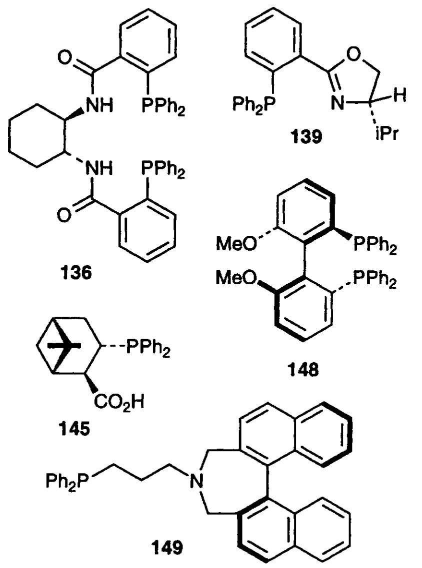


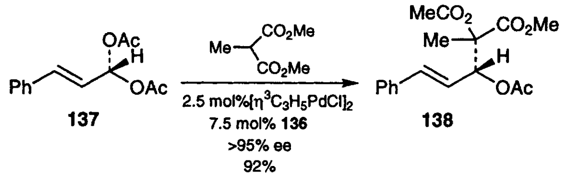
Murai and co-workers have reported the ruthenium catalysed addition of C–H bonds in an enone to an alkene.[85] Thus, the enone **133** undergoes catalysed elaboration into the coupled product **134** on treatment with triethoxyvinylsilane **135** and a ruthenium catalyst. Trost and co-workers have reported related results.[86]



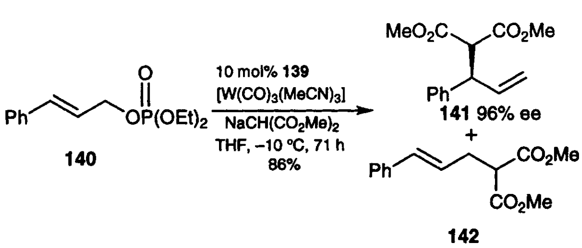
5.5 Allylic substitution reactions

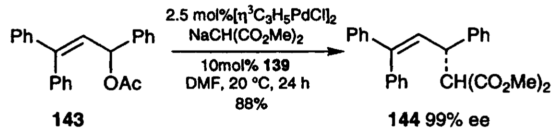
There is still a substantial interest in asymmetric allylic substitution reactions. The ligand **136** has been shown to provide high asymmetric induction in the palladium catalysed formation of cyclic allylic sulfones from cyclic allylic acetates.[87] The same ligand has been used in the asymmetric alkylation of the *gem*-diacetate **137**, which is converted into the substitution product **138**.[88]

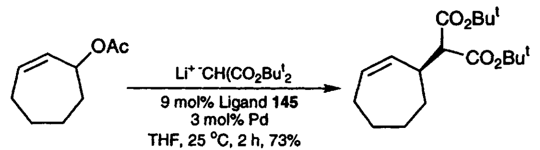




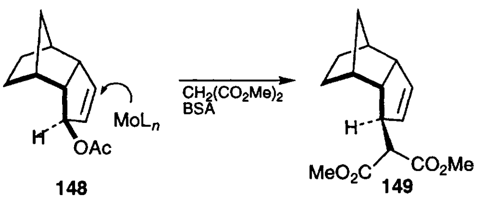
Pfaltz and co-workers have reported the use of ligand **139** in tungsten catalysed allylic substitution reactions.[89] Thus, cinnamyl phosphate **140** is converted into **141** and **142** with excellent enantioselectivity and good regioselectivity. Williams and co-workers have used the same ligand in palladium catalysed asymmetric allylic substitution of the acetate **143** which provides the substitution product **144** with excellent enantioselectivity.[90] Helmchen and co-workers have shown that whilst ligand **139** is not ideally suited to inducing high enantioselectivity for cyclic substrates,[91] the new ligand **145** is outstanding for such reactions. Thus, the cyclic acetate **146** is converted into the substitution product **147** with excellent enantioselectivity.[92] Indeed, there are now many ligands available which provide excellent enantioselectivity for palladium catalysed allylic substitution reactions, including ligands **148**[93] and **149**.[94]







146 **147** >99% ee

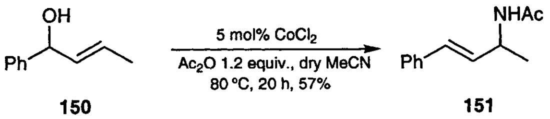


148 **149**

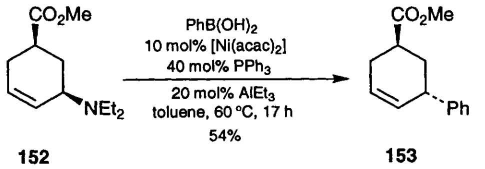
Brandes and Hoffmann have reported a diastereoselective intramolecular palladium catalysed allylic substitution reaction leading to functionalised 9-membered rings.[95]

Kocovsky and co-workers have reported a molybdenum catalysed allylic substitution reaction which proceeds with overall retention of stereochemistry.[96] These workers present evidence for a mechanism which proceeds *via* a *syn*–*syn* pathway, since neither the molybdenum nor the nucleophile are believed to be able to approach from the *endo* face of substrate **148** in its conversion into product **149**.

Iqbal and co-workers have continued their research into cobalt catalysed substitution reactions of allyl alcohols.[97] The allyl alcohol **150** is converted into the amide **151** by treatment with acetonitrile and acetic anhydride in the presence of a cobalt(II) catalyst.[98]



150 **151**



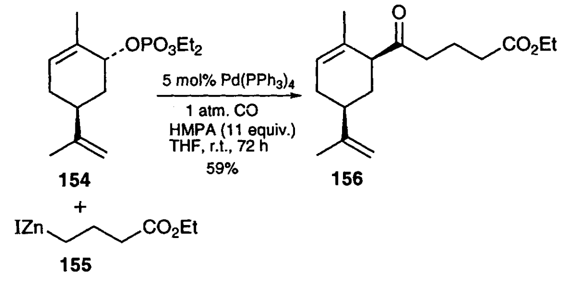
152 **153**

Trost and Spagnol have reported the nickel catalysed reaction between allylamines and boronic acids.[99] Furthermore, they have reported that the reaction proceeds by retention of configuration, as demonstrated by the conversion of the cyclic allylamine **152** into the phenyl-substituted product **153**. The use of soft nucleophiles such as dimethyl malonate in nickel catalysed allylic substitution reactions has also been reported.[100]

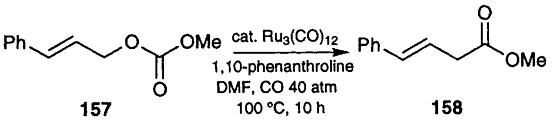
5.6 Carbonylation

Many transition metals bind well to carbon monoxide, and consequently, there is a rich chemistry associated with transition metal catalysed reactions in the presence of carbon monoxide.

Tamaru and co-workers have reported a synthesis of unsymmetrical ketones by carbonylative coupling.[101] For example, the allyl phosphate **154** is coupled with the zinc reagent **155** in the presence of carbon monoxide and a palladium catalyst to give the ketone **156** with inversion of stereochemistry.



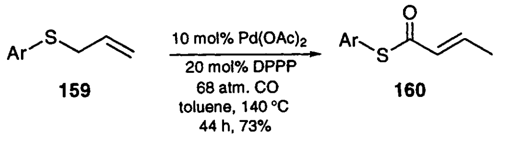
Other carbonylation reactions of allylic compounds have also been reported. Cinnamyl methyl carbonate **157** undergoes ruthenium catalysed carbonylation to give the methyl ester **158**, where the methoxy group has come from the original starting material.[102] Overall, the reaction involves loss of CO_2 and gain of CO.



157 **158**

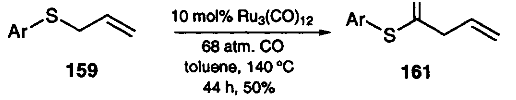
Crudden and Alper have reported the insertion of carbon monoxide into allylic C–S bonds.[103] Using a palladium catalyst, the substrate **159** is converted into the product **160** with concomitant isomerisation of the alkene. However, using a ruthenium catalyst, there is no such isomerisation, and the β,γ-thioester **161** was isolated.

Palladium catalysed carbonylative coupling reactions can provide a useful route to lactones and lactams.[104] Crisp and Meyer have used this strategy in the synthesis of the α,β-unsaturated lactam **162** from the vinyl triflate **163**.[105]

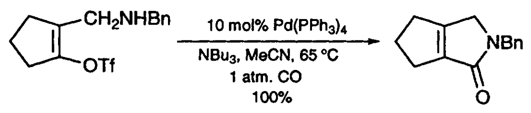


159 **160**

Ar = p-MeC$_6$H$_4$-

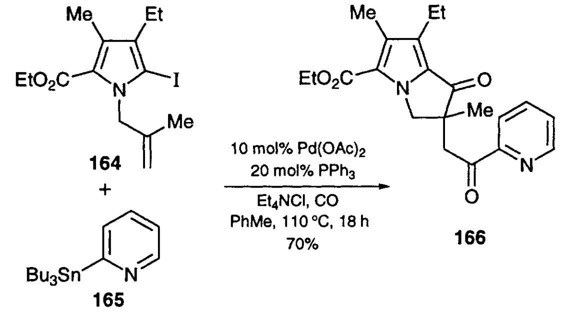


159 **161**



163 **162**

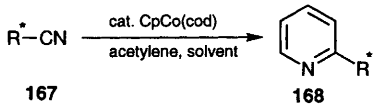
Grigg and co-workers have reported a remarkable cascade reaction involving the incorporation of 2 equiv. of carbon monoxide.[106] The coupling partners **164** and **165** underwent palladium catalysed carbonylation to give the product **166**.



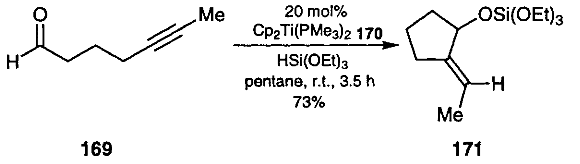
5.7 Cyclisation reactions

In the preceding sections, a number of cyclisation reactions are discussed. However, some cyclisation reactions were not easy to allocate to one section, and so have been included here.

The conversion of enantiomerically enriched nitriles **167** into the corresponding pyridines **168** using cobalt catalysts has been the subject of a review.[107]

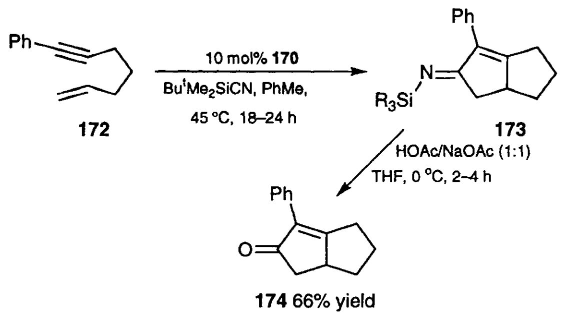


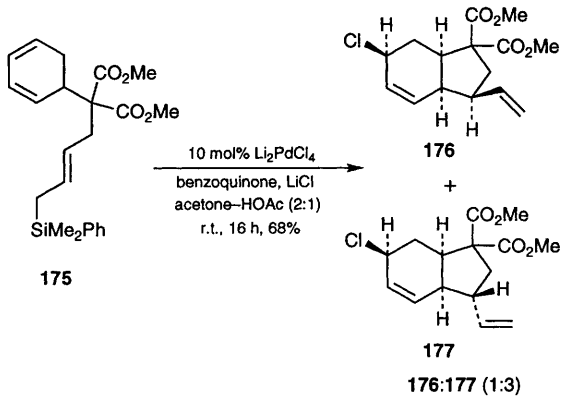
The research groups of Crowe[108] and Buchwald[109] have independently reported the titanium catalysed reductive cyclisation of unsaturated ketones and aldehydes. The aldehyde **169** undergoes reductive cyclisation upon treatment with triethoxysilane and the titanium catalyst **170** to give the cyclisation product **171**.



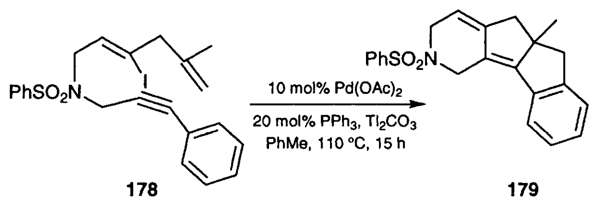
Buchwald and co-workers had earlier reported the use of the same catalyst in the enyne cyclisation reaction where an isocyanide is inserted into the substrate.[110] The enyne **172** is converted into the intermediate **173** which is hydrolysed directly into the bicyclic ketone **174**.

The palladium catalysed 1,4-addition to dienes has been performed in an intramolecular sense,[111] and the latest addition to this family of reactions, involves the use of an allylsilane as the tethered nucleophile.[112] Thus, the allylsilane **175** undergoes palladium catalysed oxidative cyclisation to the diastereomers **176** and **177**.





Grigg and co-workers have reported a cascade cyclisation reaction which terminates in a formal Friedel–Crafts alkylation.[113] The substrate **178** undergoes a cascade cyclisation to afford the tetracyclic product **179**.

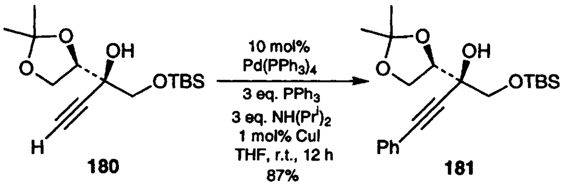


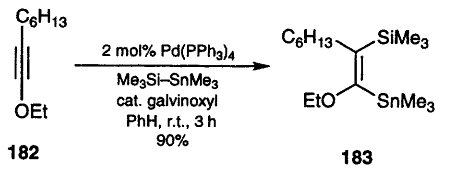
5.8 Reactions involving alkynes

The number of transition metal catalysed reactions involving alkynes is large. This section deals with only a few of these reactions.

Buszek and Jeong have reported the arylation of the propargylic alcohol **180** under cross-coupling conditions.[114] The triphenylphosphine employed as a ligand was found to be the source of the aryl group, and by employing excess triphenylphosphine, a good yield of the arylated product **181** was obtained.

Kocienski and co-workers have reported the silylstannylation of alkoxyalkynes.[115] The ethoxyalkyne **182** was converted into the adduct **183**, which could

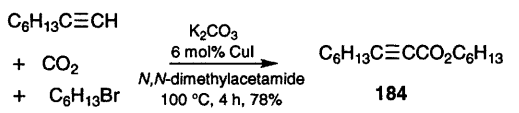




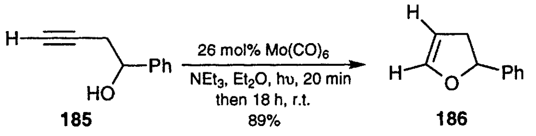
subsequently be employed in Stille coupling reactions.

In addition to the already well-documented hydrometallation reactions of alkynes, Sato and co-workers have reported a titanium catalysed hydrozincation of internal alkynes.[116] The stereo-defined alkenylzinc reagents can be further exploited in palladium catalysed coupling reactions.

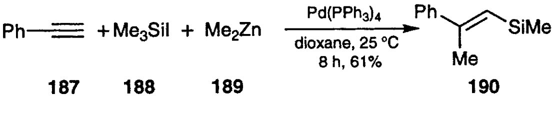
Inoue and co-workers have provided a direct synthesis of alkylalkynoates using copper or silver catalysts.[117] For example, treatment of oct-1-yne with hexyl bromide and carbon dioxide with potassium carbonate and a copper catalyst directly provides the ester **184** without the need for any other co-catalyst.



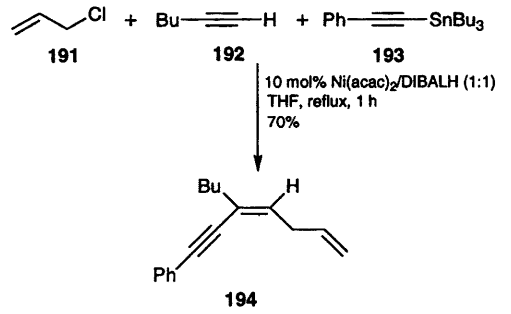
McDonald and Schultz have reported an unusual molybdenum pentacarbonyl catalysed cyclisation of alkynols.[118] The alkynol **185** is treated with the molybdenum catalyst, and undergoes reaction to afford the dihydrofuran **186**. The mechanism is postulated to proceed by intramolecular attack of the hydroxy group on a vinylidene carbene species. In the presence of tributyltin triflate, α-stannyl vinyl ethers can be prepared.[119]

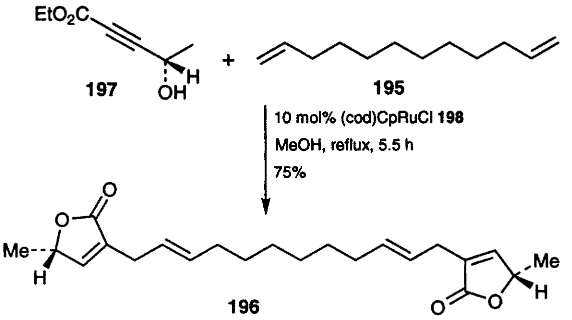


Three-component coupling reactions are always of interest because of the rapid construction of more complex molecules. An example is provided by Murai and co-workers, where the alkyne **187**, trimethylsilyl iodide **188** and dimethylzinc **189** are converted with a palladium catalyst into the coupled product **190**.[120] Another example is provided by Sato and co-workers, who have reported that allyl chloride **191**, hex-1-yne **192** and the alkynyltin compound **193** are coupled with a palladium catalyst to give the product **194**.[121]



Trost and co-workers have reported a ruthenium catalysed synthesis of butenolides.[122] The diene **195** is converted in one step into the bis-butenolide **196** upon reaction with the prop-2-ynylic alcohol **197** in the presence of the ruthenium catalyst **198**.

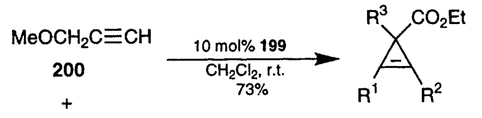


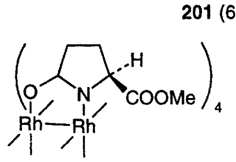


6 Reactions involving metal carbenoids

6.1 Cyclopropanation and related processes

Whilst the enantioselective cyclopropanation of alkenes has become a reasonably familiar reaction over recent years,[123,124] Doyle and co-workers have reported an enantioselective cyclopropenation reaction.[125] Using rhodium MEPY catalyst **199**, they were able to convert the alkyne **200** into the corresponding cyclopropene **201** with reasonably good enantioselectivity.





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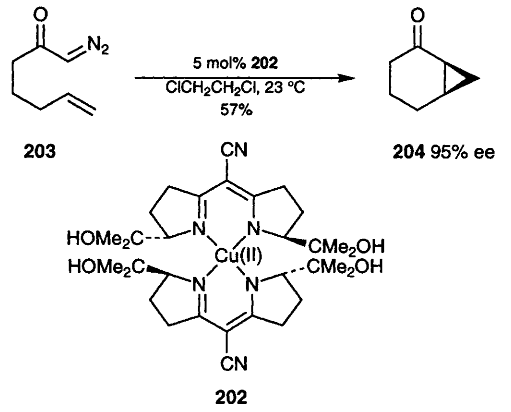
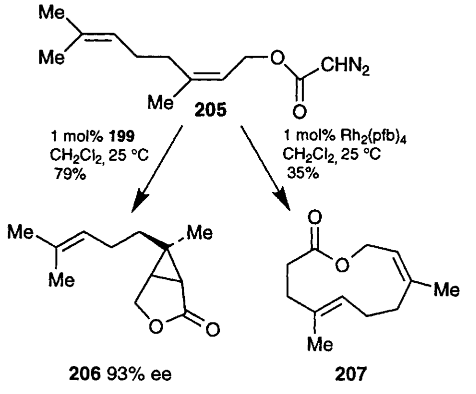
Several groups have reported enantioselective intramolecular cyclopropanation reactions. Pfaltz and co-workers have employed their enantiomerically pure semicorrin copper complexes **202** as catalysts for the conversion of the diazoketone **203** into the bicyclic product **204**.[126] Doyle and Protopopova have used their rhodium MEPY catalyst **199** to effect the intramolecular cyclisation of **205** into the product **206**.[127] Interestingly, when rhodium(II) perfluorobutyrate (pfb) was employed as the catalyst, the reaction pathway changed from intramolecular cyclopropanation to intramolecular C–H insertion, affording the alternative product **207**.

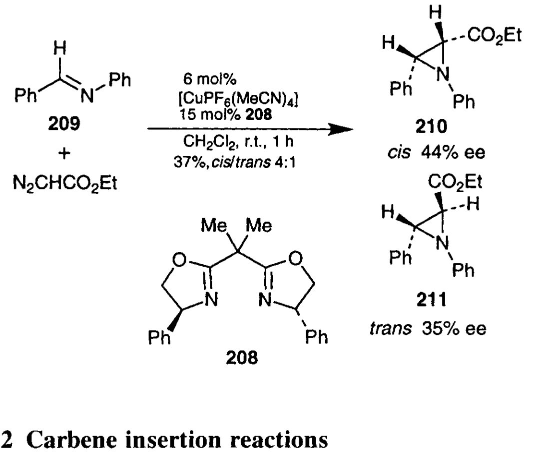




Doyle and co-workers have published other examples of intramolecular cyclopropanation reactions.[128,129]

Two groups have reported the catalytic formation of aziridines from imines and diazo esters. Rasmussen and Jørgensen have shown that using aniline derived imines, they can generate the corresponding aziridines with up to 95% yield.[130]

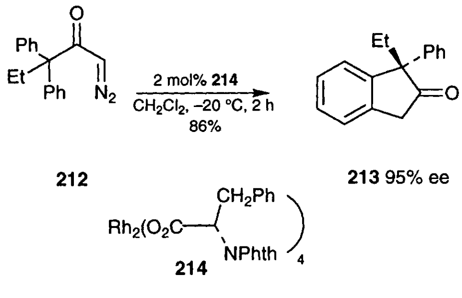
Jacobsen and co-workers have reported an asymmetric variant of this reaction, although the yields and enantioselectvities are only modest.[131] Using the bis-oxazoline **208** and a copper(I) catalyst, the imine **209** was converted into the aziridines **210** and **211**.

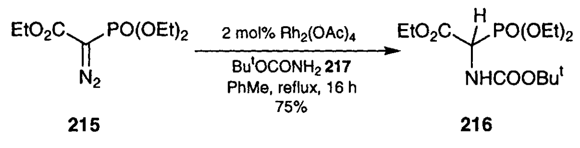


6.2 Carbene insertion reactions

Transition metal catalysed carbenoid reactions may undergo reaction pathways involving addition to double bonds, insertion into single bonds or addition to heteroatoms. Padwa and Austin have provided a useful review discussing the factors which influence the chemoselectivity of these reactions.[132]

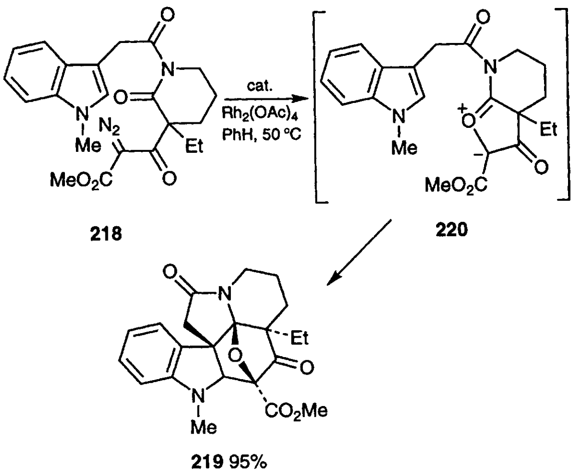
Doyle and co-workers have continued their research into highly enantioselective C–H insertion reactions, including an example of a route to *β*-lactams *via* intramolecular C–H insertion reactions.[133] Hashimoto and co-workers have reported an effective route to the formation of quaternary centres with high asymmetric induction by an enantiotopically selective C–H insertion of the substrate **212** to give the cyclised product **213** catalysed by the rhodium complex **214**.[134] Insertion into other single bonds is also possible, and Moody and Miller have reviewed the synthetic applications of O–H insertion reactions.[135] Additionally, Moody and co-workers have reported an N–H insertion reaction of amides, carbamates and ureas with the diazo compound **215** which affords the *N*-acylaminophosphonoacetate **216** when decomposed in the presence of carbamate **217**.[136] Landais and co-workers have provided another example of a rhodium catalysed Si–H insertion reaction.[137] The vinyldiazocarbonyl compounds employed were found to retain their geometry, thereby providing a stereospecific route to allylsilanes. Katsuki and Ito have used enantiomerically pure bipyridine copper complexes to effect enantioselective C–O insertion reactions.[138]

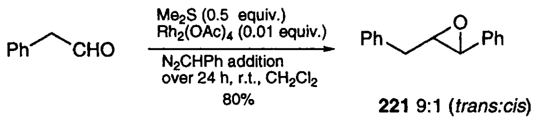




Transition metal carbenoid intermediates can also react with suitable substrates to form 1,3-dipole and ylide intermediates. Padwa and Price have used this to great effect in the rhodium(II) catalysed conversion of **218** into **219**.[139] The reaction is presumed to proceed *via* the intermediate **220**.

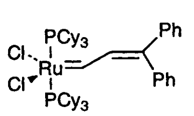
Aggarwal and co-workers have continued to develop their rhodium tetra-acetate catalysed epoxidation reaction of aldehydes using sub-stoichiometric quantities of a sulfide.[140] These reactions probably proceed *via* a sulfur ylide intermediate. These workers have demonstrated that the reaction is suitable for the preparation of epoxides **221** from base-sensitive aldehydes such as phenylacetaldehyde.[141]





6.3 Metathesis reactions

Catalytic ring-closing metathesis reactions have continued to be popular. Schmalz has written a short review of the recent developments.[142] Grubbs and co-workers have reported the ring-closing metathesis of dienynes in the formation of fused bicyclic rings.[143] Thus, treatment of the dienyne **222** with the ruthenium catalyst **223** affords the cyclisation product **224**. This research group has also reported the ring-closing metathesis reaction of dienes in the formation of eight-membered rings.[144] The tungsten catalyst **225**, which is readily prepared from tungsten(VI) oxychloride and 2,6-dibromophenol is also an active catalyst for ring-closing metathesis.[145] This catalyst has been employed in the conversion of the diene **226** into the cyclisation product **227** with little or no loss of enantiomeric purity. The mechanism is believed to proceed *via* tungsten carbene complexes.



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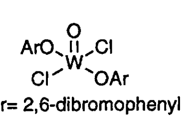

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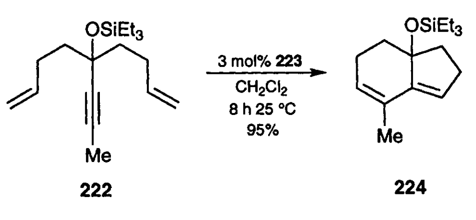
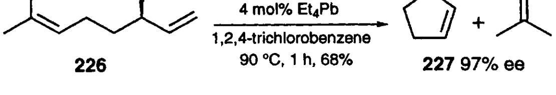


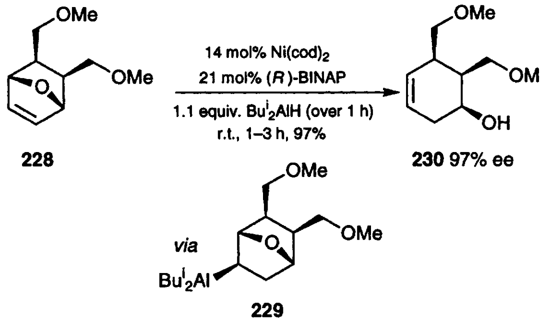


7 Miscellaneous

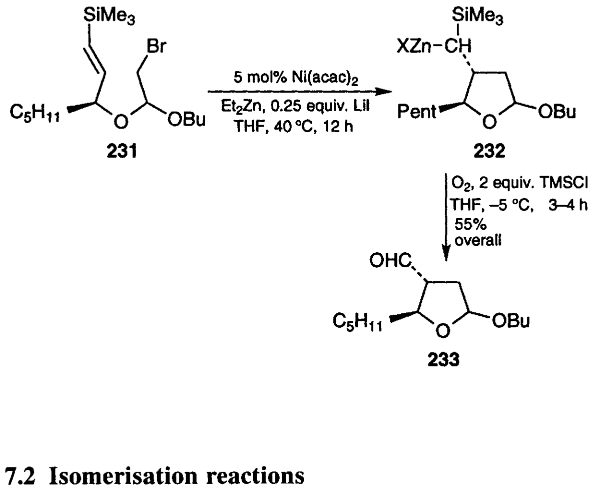
7.1 Alkene hydrometallation and carbometallation

In earlier sections, reactions involving the hydroboration and hydrosilylation of alkenes were discussed. However, the hydrometallation of alkenes can also be catalysed by transition metal catalysts.

Lautens and co-workers have reported the nickel catalysed hydroalumination of the oxabicyclic alkene **228**.[146] With the addition of an enantiomerically pure ligand, the hydroalumination process occurs *via* the intermediate **229**, thereby affording the isolated product **230** also with excellent enantioselectivity.



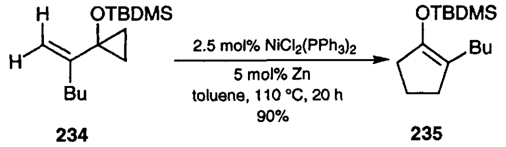
Knochel and co-workers have reported further examples of nickel catalysed hydrozincation,[147] as well as an interesting use of nickel catalysed carbozincation.[148] The bromide **231** is converted into the corresponding zinc reagent which undergoes an intramolecular carbozincation reaction to give the intermediate **232**, which upon treatment with oxygen in the presence of trimethylsilyl chloride affords the cyclic aldehyde **233**.



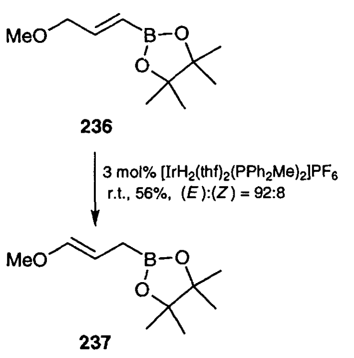
7.2 Isomerisation reactions

Isomerisation reactions encompass a wide range of reaction types. They are particularly appealing in terms of 'atom economy'.[149] Three interesting examples are described in this section.

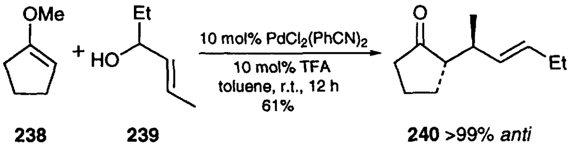
Cyclopropanes are a rich source of isomerisation chemistry. Ryu and Sonoda have reported the nickel catalysed rearrangement of the 1-siloxy-1-vinylcyclopropane **234** into the cyclic silyl enol ether **235**.[150]



Alkenes are also susceptible to isomerisation in the presence of transition metal catalysts. Miyaura and co-workers have employed ruthenium and iridium catalysts in the conversion of the vinylboronate **236** into the allylboronate **237**.[151]

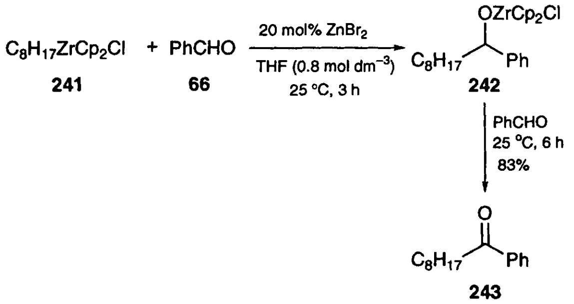


Nakai and co-workers have developed a palladium(II) catalysed Claisen rearrangement in which the enol ether is generated by the addition of trifluoroacetic acid as a co-catalyst.[152] The enol ether **238** and the allyl alcohol **239** were directly transformed into the ketone **240** without isolation of the intermediate enol ether.



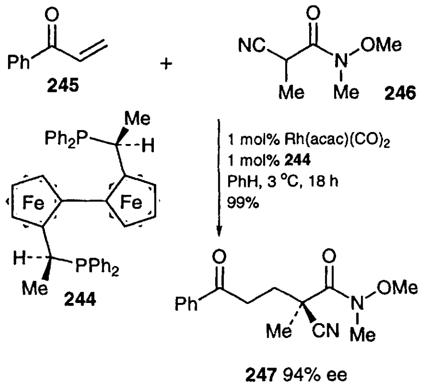
7.3 Conversion of aldehydes to ketones

The *in situ* conversion of aldehydes into ketones has been achieved by Zheng and Srebnik in an interesting manner.[153] As an example, the zinc bromide catalysed addition of the alkylzirconocene chloride complex **241** to benzaldehyde **66** affords an intermediate **242** which in the presence of additional benzaldehyde undergoes an Oppenauer-type oxidation to the ketone **243**.



7.4 Catalysed Michael addition

The *trans*-chelating diphosphine **244** has been used to provide asymmetric induction in a rhodium catalysed Michael addition reaction. The α,β-usaturated ketone **245** undergoes conjugate addition with the α-cyano Weinreb amide **246** with excellent yield and enantioselectivity in the formation of the product **247**.[154]



8 Conclusion

The use of transition metal catalysed reactions is still increasing and transformations are being reported with higher levels of chemoselectivity and enantioselectivity. Some of the excellent chemistry which has been reported in the literature during the period covered by this review clearly demonstrates the vitality of this area of chemistry.

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