

Catalytic applications of transition metals in organic synthesis

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Reviewing the literature published between 1 September 1993 and 31 August 1994

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1 Introduction

This review highlights the advances in transition metal catalysis made in the period 1 September 1993 to 31 August 1994. During this period, there have been many advances in the field of homogeneous transition metal catalysed reactions. One of the most prominent areas of research within the field has been the further development of asymmetric catalysis using enantiomerically pure ligands associated with

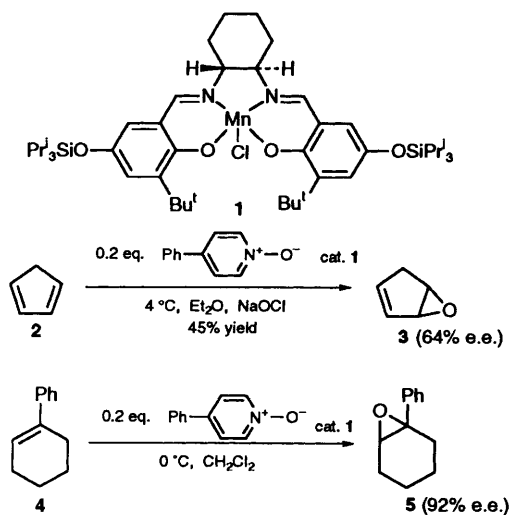
transition metal catalysts. There are a growing number of catalytic reactions in which the enantiomeric excess of the product is > 90%. There has been such a huge volume of publications concerned with transition metal catalysts that it is not possible to provide a fully comprehensive account. We have endeavoured, however, to summarize current areas of interest and to provide commentary on the important advances. Only homogeneous applications have been considered for this review.

2 Oxidation

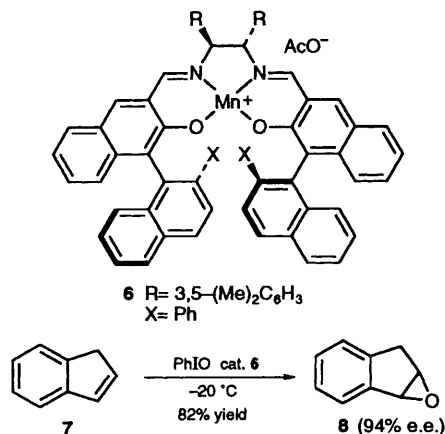
Two important objectives with oxidation reactions are selectivity and efficiency. There are examples here of transition metal catalysed oxidation reactions which are chemoselective as well as stereoselective. The cheapest oxidant is air, and catalytic systems which employ air as the stoichiometric oxidant are especially appealing.

2.1 Epoxidation

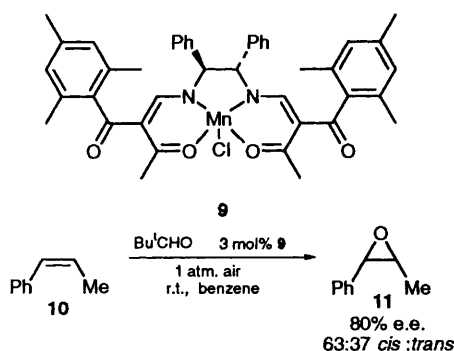
Further developments within asymmetric epoxidation using enantiomerically pure manganese salen complexes have been reported. Jacobsen and co-workers have described the sterically and electronically optimized (salen)Mn complex **1**, which was employed in the catalytic oxidation of the diene **2** to the monoepoxide **3**¹ and also of 1-phenylcyclohexene (**4**) to the corresponding epoxide **5**.²



The related catalyst **6** has been prepared by Katsuki and co-workers, and has provided high levels of asymmetric induction for the epoxidation of conjugated *cis*-alkenes, such as the conversion of **7** into **8**.³

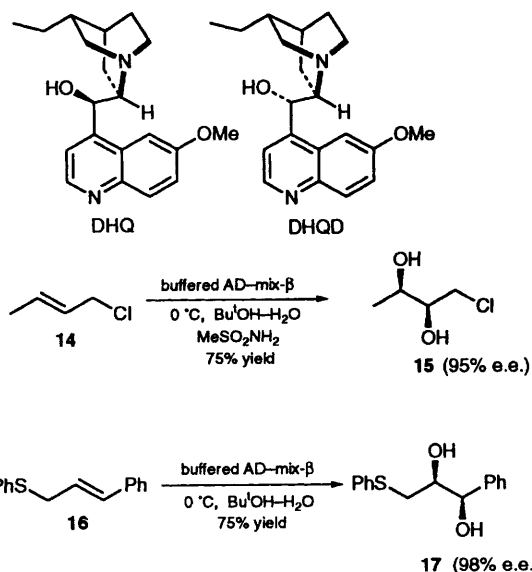
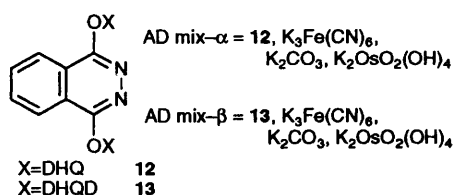


A remarkable enantioselective aerobic epoxidation of alkenes catalysed by the manganese complex **9** has been reported.⁴ The (*Z*)-alkene **10** is converted into the epoxide **11** with 80% e.e. in the presence of oxygen and pivalaldehyde. However, the yield and diastereoselectivity of the reaction are less satisfactory.

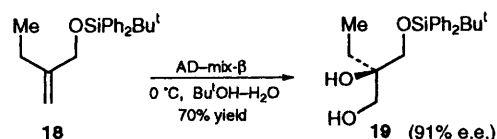


2.2 Dihydroxylation

There still remains considerable debate over the precise mechanism of the enantioselective osmium-catalysed dihydroxylation of alkenes in the presence of cinchona-derived catalysts **12** and **13**.⁵⁻⁷ However, the synthetic importance of this reaction is evident from the increasing range of substrates which have been successfully employed. The Sharpless group have provided many examples recently, including the conversion of the allyl halide **14**⁸ and the allyl sulfide **16**⁹ into the corresponding diols **15** and **17** with excellent levels of asymmetric induction.

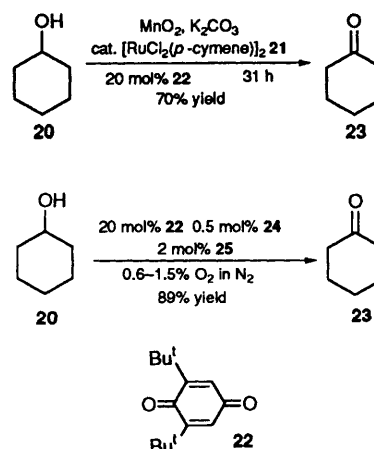


Hale and co-workers have reported that the conversion of the silyl protected allyl alcohol **18** into the product **19** occurs with good enantioselectivity, but with an opposite sense of asymmetric induction to that predicted based solely on the steric demands of the substituents on the alkene.¹⁰



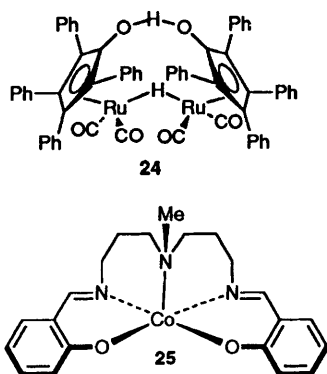
2.3 Oxidation of alcohols

Bäckvall's group has provided two interesting examples of the transition metal catalysed oxidation of secondary alcohols to the corresponding ketones. Treatment of cyclohexanol (**20**) with manganese dioxide and potassium carbonate and catalytic amounts of both the ruthenium complex **21** and the quinone **22**, afforded cyclohexanone (**23**).¹¹



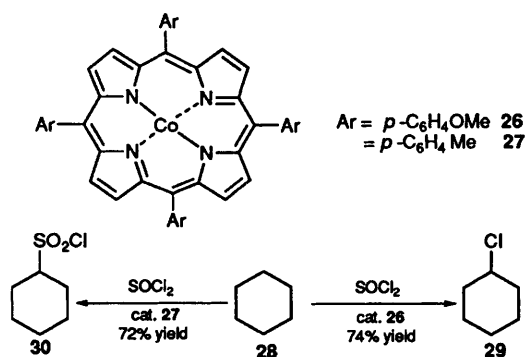
In a related system, it was possible to use air as the stoichiometric oxidant, in conjunction with an additional catalyst **25**. The alternative ruthenium

catalyst **24** was employed, and cyclohexanol was converted into cyclohexanone in 89% yield with this unusual triple catalytic system.¹²



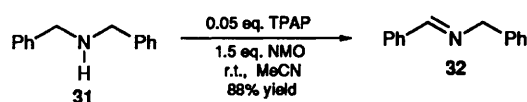
2.4 Oxidation of hydrocarbons

Selective oxidation of alkanes is a daunting objective, and whilst there is still some way to go before chemo- and stereo-selective oxidation of alkanes can be reliably achieved with high efficiency, there are a few examples of highly selective reactions. For example, the functionalization of alkanes with sulfonyl chloride, catalysed by the cobalt complexes **26** and **27**, has been described.¹³ These reagents are highly chemoselective, with catalyst **26** converting cyclohexane (**28**) into the chloride **29**, whilst the use of catalyst **27** affords the chlorosulfonate **30**.



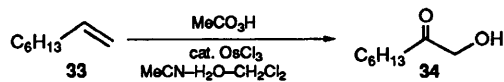
2.5 Other oxidations

Goti and Romani have described a catalytic oxidation of secondary amines into the corresponding imines,¹⁴ a reaction which has received much less attention than the related oxidation of alcohols to ketones. The secondary amine **31** was converted into the imine **32** by treatment with *N*-methylmorpholine *N*-oxide (NMO) and catalytic amounts of tetra-*n*-propylammonium perruthenate (TPAP).



Murahashi and co-workers have reported the osmium trichloride catalysed oxidation of alkenes with peracetic acid to afford α -ketols. These workers

indicate how this is quite different from the osmium tetroxide catalysed oxidation of alkenes to afford diols.¹⁵ Oct-1-ene (**33**) was converted into the α -ketol **34** by treatment with peracetic acid in the presence of catalytic amounts of OsCl_3 .

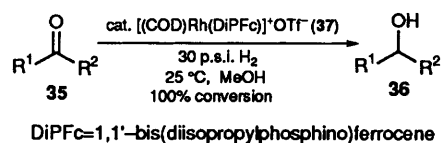


3 Hydrogenation and related processes

Transition metal catalysed hydrogenation reactions have been known for a long time, and even asymmetric variations of this reaction are over twenty years old. There is still room for progress, however, as the following examples illustrate.

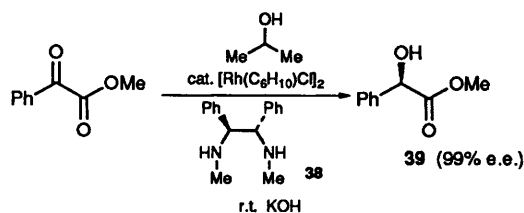
3.1 Hydrogenation

The effective cationic rhodium catalyst **37** for the hydrogenation of aldehydes and ketones **35** under mild conditions into the corresponding alcohols **36** has been reported by Burk and co-workers.¹⁶

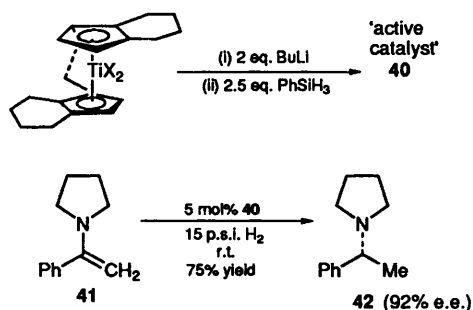


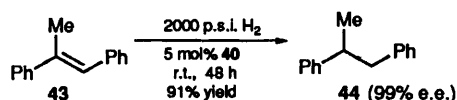
DiPFc = 1,1'-bis(diisopropylphosphino)ferrocene

Lemaire and co-workers have demonstrated that the ligand **38** is effective in the rhodium-catalysed transfer hydrogenation of methyl benzoylformate to the product **39** giving over 99% e.e. and 100% conversion.¹⁷ Other substrates, however, afforded lower levels of asymmetric induction.

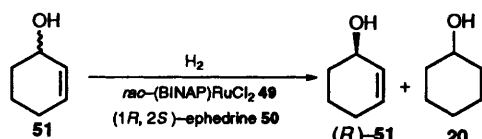
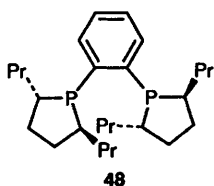
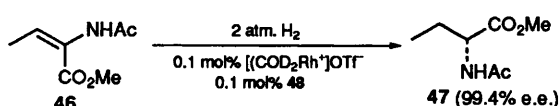
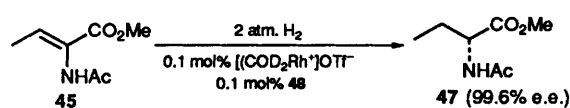


The range of substrates which are efficiently hydrogenated in the presence of the titanocene catalyst **40** has been extended.¹⁸ The enamine **41** is converted into the amine **42** with 92% e.e.,¹⁹ and the alkene **43** is hydrogenated to **44** with 99% e.e.²⁰

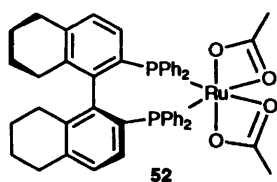
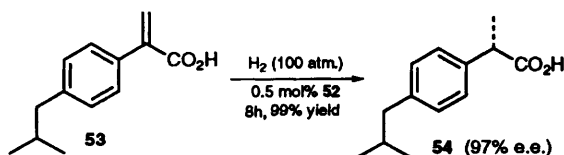




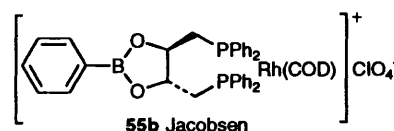
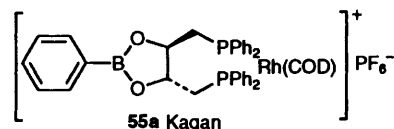
Burk and co-workers have also reported the synthesis of a range of amino acid derivatives via asymmetric hydrogenation with DuPHOS rhodium catalysts.²¹ The (*E*)- and (*Z*)-enamides **45** and **46** were both converted into the same enantiomer of product **47** with very high enantioselectivity upon treatment with ligand **48** and a rhodium catalyst under two atmospheres of hydrogen. Fallér and Tokunaga have provided a further example of chiral poisoning.²² Treatment of the racemic ruthenium complex **49** with (1*R*,2*S*)-ephedrine (**50**) deactivates one of the enantiomers of the catalyst. The unpoisoned enantiomer remains available to effect a kinetic resolution in the hydrogenation of racemic cyclohexenol **51**. At 77% conversion, recovered cyclohexenol **51** was found to have > 95% e.e.



Takaya and co-workers have shown that the H₈-BINAP ruthenium complex **52** is an effective asymmetric hydrogenation catalyst.²³ For example, the alkene **53** was converted into the anti-inflammatory drug (*S*)-ibuprofen (**54**) with 97% e.e. In some cases this catalyst proved to be superior to the more normal BINAP derived catalysts.

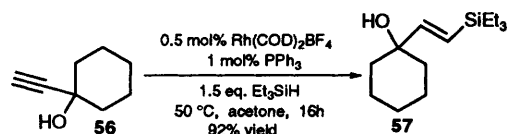


Kagan²⁴ and Jacobsen,²⁵ with their respective co-workers have independently described enantiomerically pure bimetallic complexes, **55a** and **55b**. These complexes are anticipated to afford two-point binding for suitable substrates, and the Kagan group have shown that catalyst **55a** is able to catalyse asymmetric hydrogenation reactions. It may be possible to use such bimetallic complexes to provide highly selective reactions, and it seems likely that this design strategy will afford interesting results in the future.

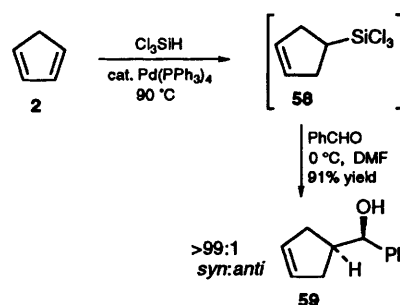


3.2 Hydrosilylation

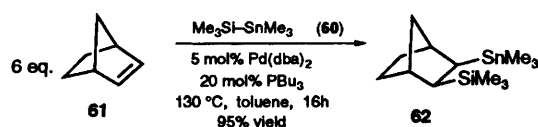
Takeuchi and co-workers have reported a highly selective hydrosilylation of propynylic alcohols with complete control over regiochemistry and alkene geometry.²⁶ Alkyne **56** was converted into the vinyl silane **57** with 92% yield.



Kobayashi and Nishio have described a one-pot preparation of homoallylic alcohols from 1,3-dienes via a hydrosilylation–aldehyde-coupling sequence.²⁷ Cyclopentadiene (**2**) is reacted with trichlorosilane and a palladium catalyst, and the intermediate allylsilane **58** is reacted with benzaldehyde to form the alcohol **59** with high yield and excellent *syn* selectivity.

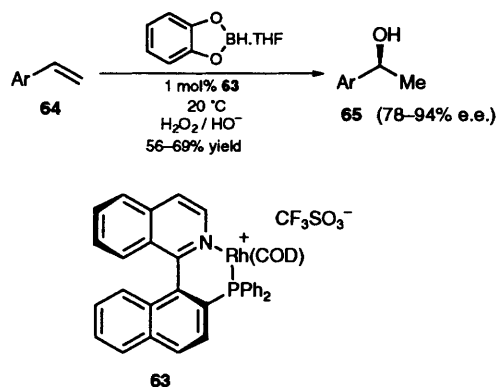


A palladium-catalysed silylstannylation of alkenes has been reported.²⁸ For example, treatment of the silylstannane **60** and norbornene (**61**) with a palladium catalyst affords the derivative **62** in 89% yield.

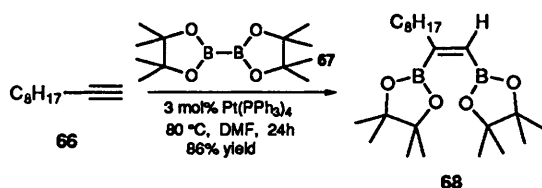


3.3 Hydroboration and diboration

Brown and co-workers have reported that the rhodium complex **63** is able to effect hydroboration of styrenes **64** with good enantioselectivities, as determined after conversion into the corresponding alcohols **65**.²⁹



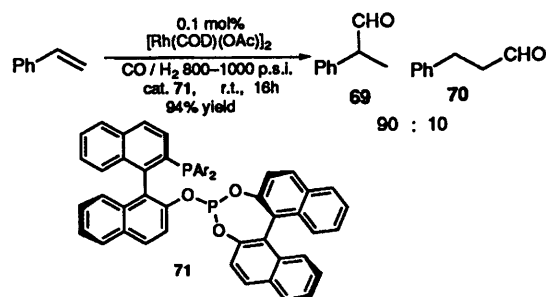
An unusual platinum(0)-catalysed diboration of alkynes has been described.³⁰ The reaction of alkyne **66** with the diboron species **67** with 3 mol% of $\text{Pt}(\text{PPh}_3)_4$ affords the addition product **68** in 86% yield.



3.4 Hydroformylation

Doyle and co-workers have reported a highly regioselective hydroformylation of alkenes catalysed by $[\text{Rh}(\text{COD})(\text{OAc})]_2$.³¹ Thus styrene is hydroformylated to afford a 96:4 ratio of the branched to linear aldehydes **69** and **70**.

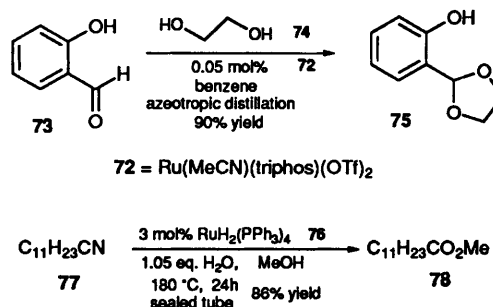
Takaya and co-workers have shown that in the same process the phosphinephosphite ligand **71** provides good enantioselectivity in the reaction, but with a 90:10 ratio of the branched to linear aldehydes.³²



4 Lewis acids

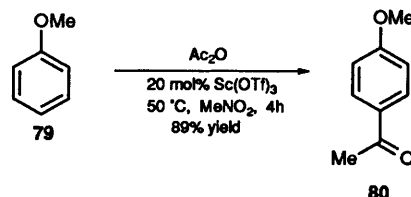
Ruthenium complexes have continued to be used as Lewis acids. Ma and Venanzi have used the ruthenium catalyst **72** to effect the acetalization of

o-salicaldehyde (**73**) with 1,2-ethanediol (**74**) to afford the 1,3-dioxolane **75**.³³ The same workers have also reported the hydrolysis of acetals, including 1,3-dioxolanes by the use of a ruthenium catalyst.³⁴ Nitriles are converted into esters on reaction with an alcohol in the presence of the ruthenium catalyst **76**.³⁵ For example, the nitrile **77** and methanol are converted into the methyl ester **78** in 86% yield. The same catalyst in the presence of water converts nitriles into the corresponding primary amides.³⁶



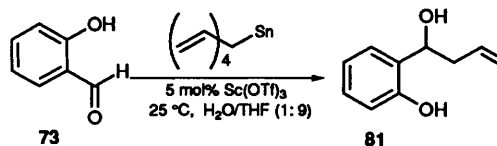
4.1 Friedel-Crafts

The use of scandium triflate as a catalyst has been further developed. This catalyst has been applied to Friedel-Crafts acylation reactions. Thus, treatment of anisole (**79**) and acetic anhydride with 20 mol% scandium triflate afforded the acetylated product **80** in 89% yield.³⁷ The use of 1 mol% catalyst under otherwise identical conditions afforded a 62% yield of product. The catalyst could be recovered from the aqueous layer by simple extraction.

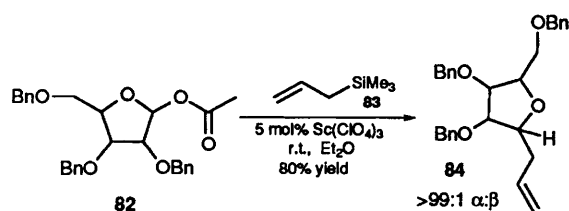


4.2 Allylation

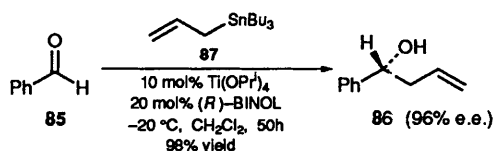
Scandium triflate has also been reported to catalyse the allylation of carbonyl compounds with tetraallyltin.³⁸ Thus, treatment of *o*-salicaldehyde **73** with tetraallyltin in water/tetrahydrofuran (1:9) and 5 mol% scandium triflate affords the adduct **81**. It would be expected that most other Lewis acids would not tolerate the presence of water or the presence of the phenol.



The related catalyst, scandium perchlorate, has been employed in the *C*-glycosidation reaction between **82** and **83** to afford the product **84** with excellent α -selectivity.³⁹

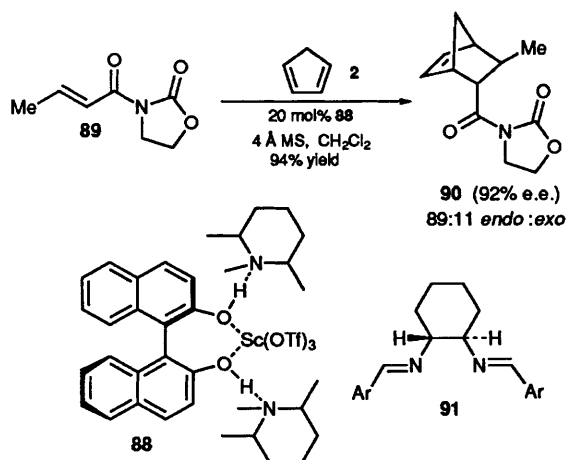


Keck and Geraci have reported a simple procedure for the enantioselective allylation of aldehydes with allyltributylstannane **87** using catalytic amounts of pre-mixed titanium tetraisopropoxide and (*R*)-BINOL.⁴⁰ Using this methodology, benzaldehyde (**85**) was converted into the product **86** with 96% e.e.

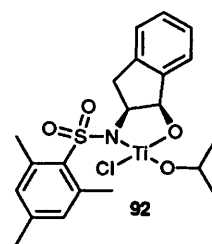
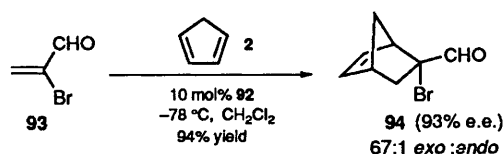


4.3 Diels–Alder

Asymmetric catalysis with scandium reagents has been achieved in the Diels–Alder reaction.⁴¹ A catalyst **88**,⁴² derived from scandium triflate, (*R*)-(+)-1,1'-bi-2-naphthol, and *cis*-1,2,6-trimethylpiperidine, was employed in catalytic amounts in the enantioselective Diels–Alder reaction of the dienophile **89** and cyclopentadiene (**2**) to afford the cycloadduct **90**. Evans and co-workers have employed catalysts based upon copper(II) triflate and the diimine **91** to catalyse Diels–Alder reactions on similar substrates with 83–94% e.e.⁴³

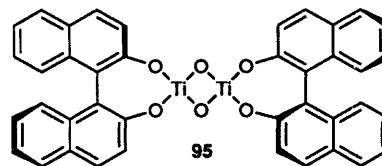
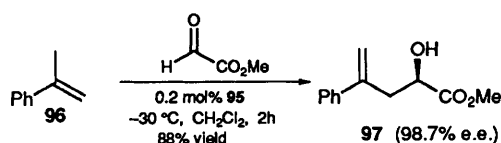


Corey and co-workers have employed the titanium catalyst **92** in the enantioselective Diels–Alder reaction between 2-bromoacrolein (**93**) and cyclopentadiene (**2**) which affords the cycloadduct **94** in 93% e.e.⁴⁴

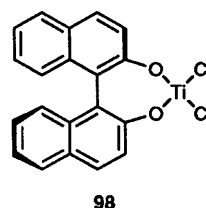
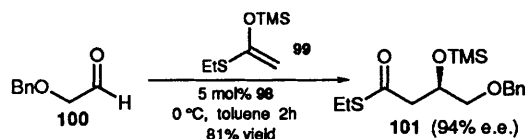


4.4 Carbonyl-ene reactions

Terada and Mikami have used the μ -oxo complex **95** to catalyse the carbonyl-ene reaction between α -methylstyrene (**96**) and methyl glyoxylate to afford the product **97** with very high enantioselectivity.⁴⁵ The same group have also further developed the use of the complex **98** to a more extensive range of substrates.⁴⁶



Mikami and Matsukawa have described an aldol-type reaction between the ketene silyl acetal **99** and the aldehyde **100** catalysed by titanium complex **98** to afford the product **101** with high enantioselectivity.⁴⁷ Whilst the outcome of this reaction indicates an aldol reaction, these authors postulate that the reaction pathway may in fact involve a silatropic ene reaction.



5 Coupling reactions

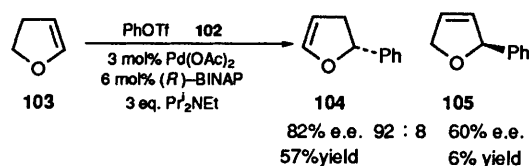
There have been many hundreds of examples of metal-catalysed coupling reactions reported recently, which is a testament to the synthetic utility of these reactions. Palladium has a dominant position as the main metal of choice for conventional coupling reactions, such as the Stille reaction and carbonylation

reactions. However, other transition metals have been examined, and as described here provide useful methods for what have been collected together as 'coupling reactions'.

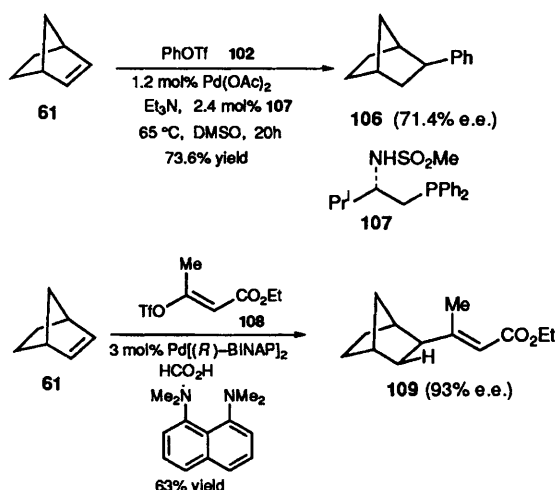
5.1 Heck reactions

Various methods for optimizing Heck reactions have been described. For example, it has been reported that Heck reactions are accelerated by high pressure conditions.⁴⁸ Jeffery has reported that Heck reactions can take place in water in the presence of added tetrabutylammonium salts.⁴⁹

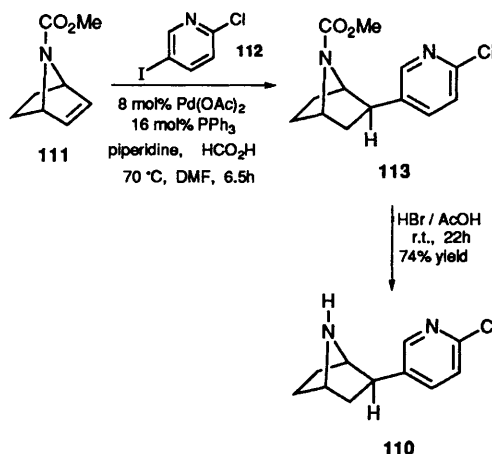
Japanese workers have provided a detailed account of their work on the enantioselective intermolecular Heck reaction.⁵⁰ The reaction of phenyl triflate (**102**) with 2,3-dihydrofuran (**103**) in the presence of catalytic amounts of palladium acetate and (*R*)-BINAP affords the products **104** and **105** with configurations opposite to each other.



Achiwa and co-workers have achieved good enantioselectivity in a related reaction employing phenyl triflate (**102**) and norbornene **61** as coupling partners to afford the product of hydroarylation **106** in the presence of a palladium catalyst and the ligand **107**.⁵¹ Ozawa, Hayashi, and co-workers looked at a similar reaction using the vinyl triflate **108** as the coupling partner to afford the product of hydroalkenylation **109** in 93% enantiomeric excess.⁵²

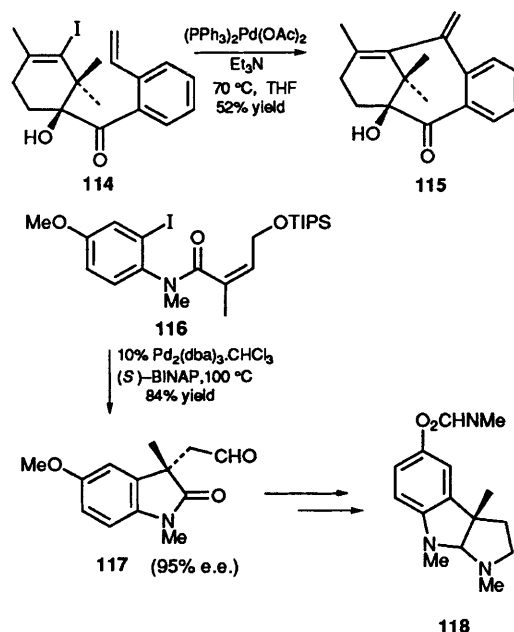


Clayton and Regan have reported the synthesis of racemic epibatidine (**110**), an alkaloid which has received much synthetic attention recently. The key step in their synthesis is a reductive palladium-catalysed Heck-type coupling.⁵³ The reaction between compounds **111** and **112** using a palladium catalyst with piperidine and formic acid afforded the coupled product **113**, which was



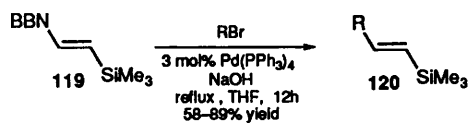
transformed into (\pm)-epibatidine (**110**) upon treatment with HBr/acetic acid.

The Heck reaction has provided some useful examples of cyclization reactions on complex substrates.⁵⁴ For example, Masters and co-workers obtained a 52% yield in the Heck cyclization of precursor **114** into the taxol analogue **115**.⁵⁵ Overman and co-workers have provided another example of an enantioselective intramolecular Heck reaction: treatment of compound **116** with an enantiomerically pure palladium catalyst, followed by acidic hydrolysis afforded the cyclization product **117** in high enantiomeric excess.⁵⁶ This compound was converted into the naturally occurring alkaloid (–)-physostigmine (**118**).

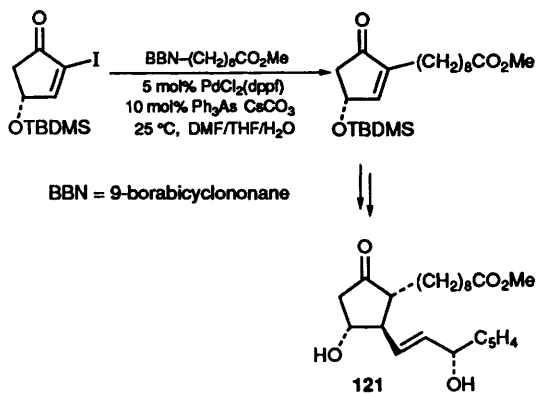


5.2 Suzuki coupling

Wallow and Novak have reported increased catalytic efficiency by using phosphine-free palladium sources in Suzuki coupling reactions.⁵⁷ Soderquist and Colberg have shown that the silylated vinylborane **119** could be converted into *trans*-vinylsilanes **120** via Suzuki coupling in good yields.⁵⁸



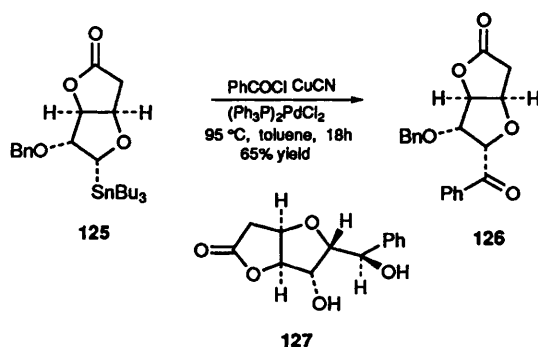
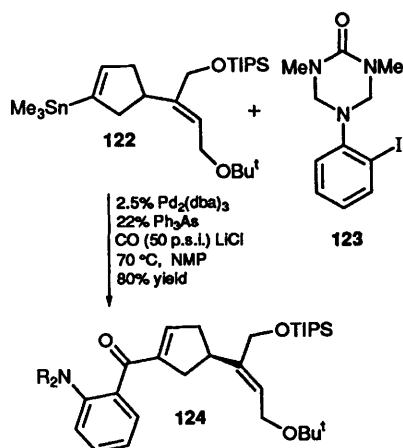
Johnson and Braun have employed a Suzuki coupling reaction in the preparation of the prostaglandin PGE₁ methyl ester **121**.⁵⁹ Treatment of a suitable vinyl iodide and borane with a palladium catalyst afforded the coupled product, which was converted into prostaglandin PGE₁ methyl ester **121** in two further steps (73% yield).



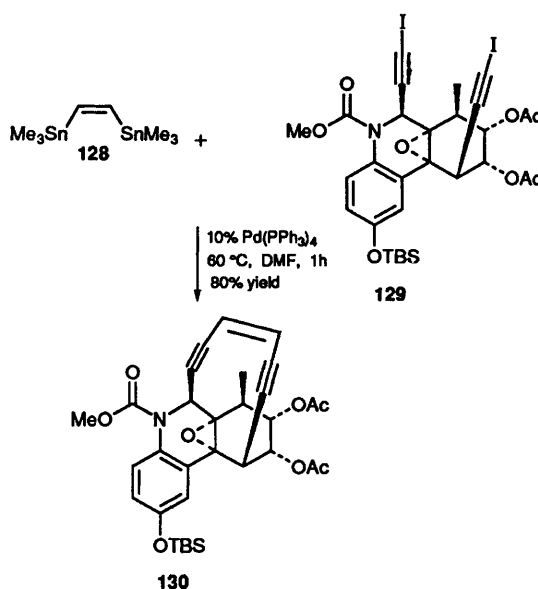
5.3 Stille coupling

The Stille coupling process has provided efficient synthetic routes to many natural products. Indeed there have been several recent examples which demonstrate the versatility of this powerful reaction.

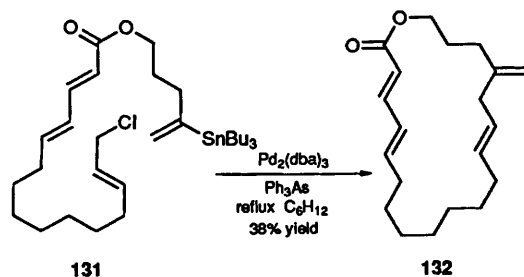
Overman and co-workers employed a Stille coupling between the vinyl stannane **122** and the aryl iodide **123** to afford the coupled product **124** which they use in the total synthesis of (–)-strychnine.⁶⁰ Falck and co-workers converted the stannane **125** into the ketone **126** on treatment with benzoyl chloride and a palladium catalyst.⁶¹ Stereoselective reduction and debenzoylation afforded the natural product goniofufurone (**127**). Similar acyclic examples were also reported to proceed with retention of configuration.⁶²



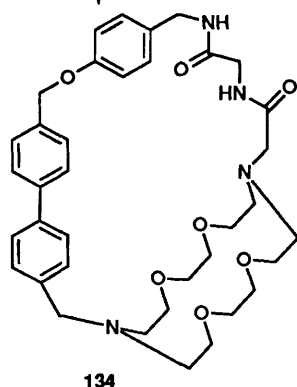
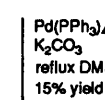
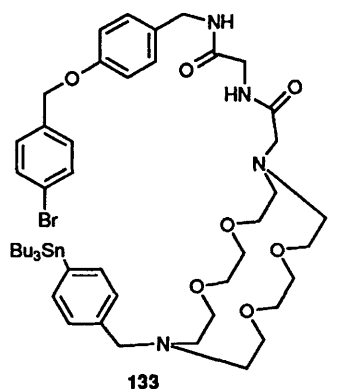
Danishefsky and co-workers have reported an extraordinary palladium-catalysed coupling between (*Z*)-bis(trimethylstannyl)ethylene (**128**) and the bis(iodoalkyne) **129** to afford the cyclic enediyne **130** in an incredible 80% yield!⁶³



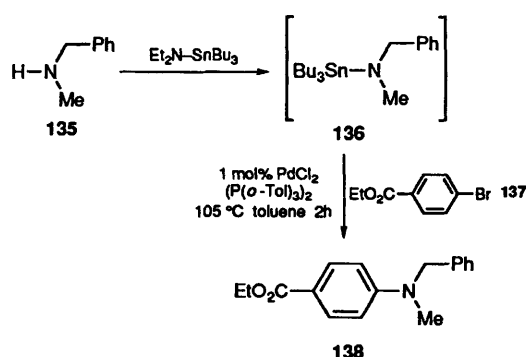
Boden and Pattenden have reported a macrocyclization strategy based on the intramolecular Stille coupling of a vinylstannane with an allyl chloride.⁶⁴ Thus, substrate **131** undergoes macrocyclization on treatment with a palladium catalyst to afford the product **132** in 38% yield.



Kilburn and co-workers have described an unusual Stille-type 4,4'-biaryl formation as a macrocyclization step.⁶⁵ Treatment of substrate **133** with a palladium catalyst afforded the macrocycle **134**, albeit in modest yield.

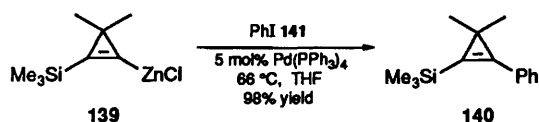


In a process somewhat related to the Stille coupling, Hartwig⁶⁶ and Buchwald,⁶⁷ with their respective co-workers, have independently reported the coupling between arylbromides and aminostannanes. For example, the *in situ* conversion of the secondary amine **135** into the aminostannane **136** upon treatment with (*N,N*-diethylamino)tributyltin, and subsequent reaction with the aryl bromide **137** in the presence of a palladium catalyst affords the tertiary amine product **138**.

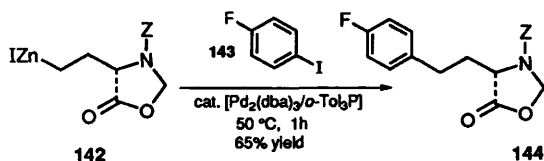


5.4 Coupling of other organometallics

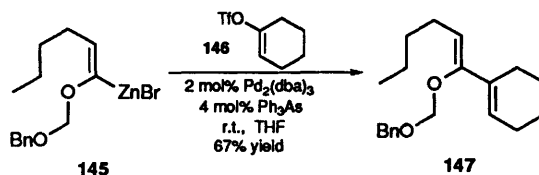
Untiedt and de Meijere have shown that the palladium-catalysed coupling of the unusual zinc reagent **139** proceeds efficiently to afford the phenyl derivative **140** in excellent yield, when treated with iodobenzene (**141**) and a palladium catalyst.⁶⁸



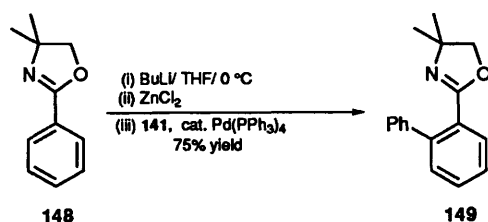
An application of zinc reagents to the preparation of homophenylalanine derivatives has been provided by Jackson and co-workers.⁶⁹ The reaction of zinc reagent **142** with the aryl iodide **143** in the presence of a palladium catalyst affords the homophenylalanine derivative **144** in 65% yield.



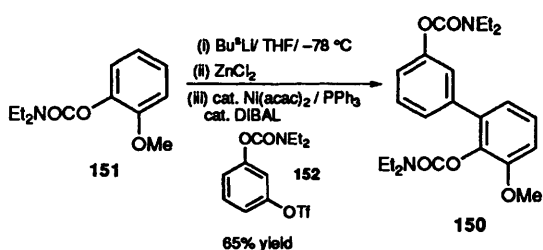
Casson and Kocienski have shown that α -alkoxyalkenylzinc reagents such as **145** are suitable for palladium-catalysed reactions with various coupling partners, including the vinyl triflate **146** to give the coupled product **147**.⁷⁰



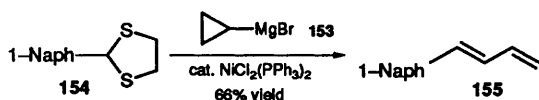
Two groups have employed *ortho*-directing groups to prepare zinc reagents, and coupled these organometallics with aryl triflates. Koch and co-workers *ortho*-lithiated the aryl oxazoline **148**, generated the zinc reagent via transmetalation, and coupled this to iodobenzene (**141**) using palladium catalysis, thereby obtaining the product **149** in 75% yield.⁷¹



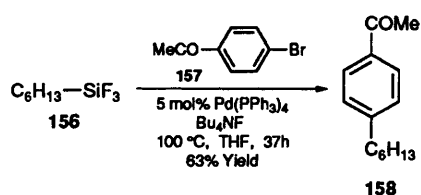
A similar strategy was employed by Snieckus and co-workers to form the coupled product **150** from the carbamate **151** and the aryl triflate **152**. Both groups found that this strategy was effective with other *ortho*-directing groups.⁷²



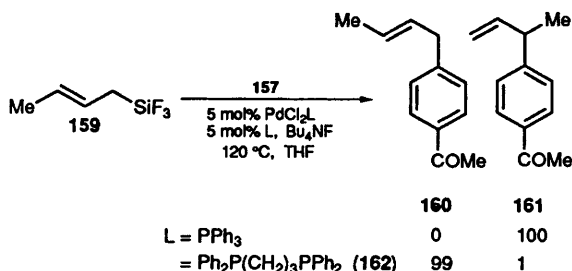
An unusual coupling involving cyclopropyl Grignard reagents **153** with benzylic dithioacetals **154** has been reported.⁷³ The rearrangement of an intermediate cyclopropylcarbinylnickel intermediate accounts for the observed product **155**.



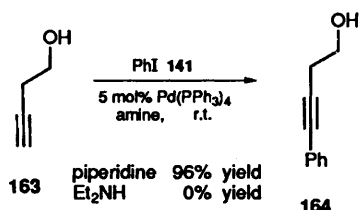
Hiyama and co-workers have employed alkyltrifluorosilanes as coupling partners.⁷⁴ For example, the palladium-catalysed reaction between hexyltrifluorosilane (**156**) and *p*-bromoacetophenone (**157**) is promoted by tetrabutylammonium fluoride to give the coupled product **158** in 63% yield.



The regiochemistry of coupling reactions involving an allyltrifluorosilane **159** with *p*-bromoacetophenone (**157**) was found to be highly dependent upon the ligand employed.⁷⁵ The use of triphenylphosphine as the ligand afforded the γ -product **161**, whereas the use of the bidentate ligand dppp [$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (**162**)] afforded predominantly the α -product **160**.

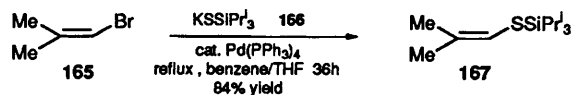


A French group has reported an efficient palladium-catalysed reaction between terminal alkynes and vinyl and aryl halides.⁷⁶ Iodobenzene (**141**) was coupled to the alkyne **163** to afford the product **164** in 96% yield. The added base was critical to the success of the reaction. Piperidine as the added base afford this high yield, whereas the use of either triethylamine or diethylamine gave no product!

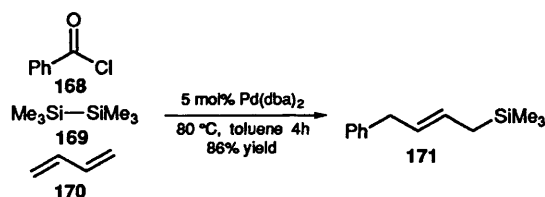


Soderquist and co-workers have demonstrated that thiolates may be employed as coupling partners in the palladium-catalysed cross-coupling between the vinyl

bromide **165** with potassium triisopropylsilanethiolate (**166**) to afford the vinyl silane **167**.⁷⁷ Coupling reactions between aryl halides and **166** were also achieved.

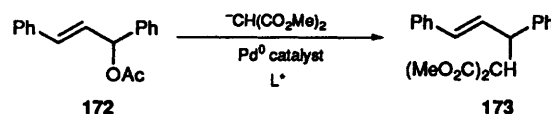


An unusual palladium-catalysed decarbonylative coupling reaction has been investigated by Tsuji and co-workers.⁷⁸ Benzoyl chloride (**168**), hexamethyldisilane (**169**), and butadiene (**170**) are coupled together by a palladium catalyst to afford the allylsilane **171** in which decarbonylation has occurred.

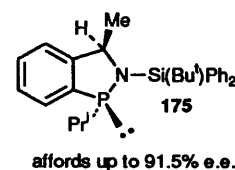
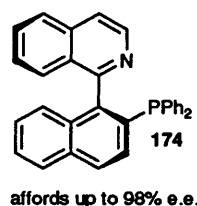


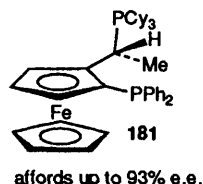
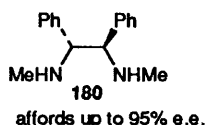
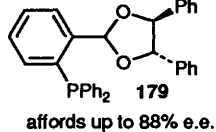
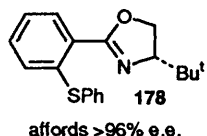
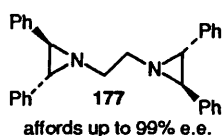
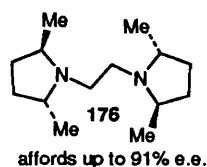
5.5 Allylic substitution

The main interest in allylic substitution has been in enantioselective palladium-catalysed allylic substitution. The conversion of acetate **172** into the substitution product **173** upon treatment with dimethylmalonate and a palladium catalyst with a suitable ligand has been achieved with high enantioselectivity by a number of research groups.

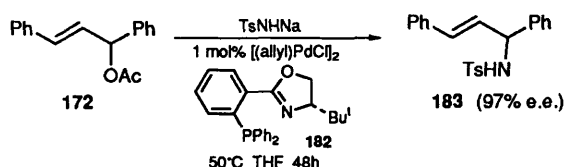


Brown and co-workers have developed the QUINAP ligand **174**,⁷⁹ whilst Wills and co-workers have shown that a monodentate ligand **175** is also effective.⁸⁰ Koga and co-workers employed the C_2 symmetric bis(pyrrolidines) **176**,⁸¹ whereas Tanner and co-workers have used C_2 symmetric bis(aziridines) **177**.⁸² Williams and co-workers have examined the use of ligands **178**⁸³ and **179**.⁸⁴ The diamine ligand **180**⁸⁵ has also been applied to this process, whilst Togni and co-workers have demonstrated that the chelating diphosphine ligand **181** is a useful ligand for a number of catalytic processes, including palladium-catalysed allylic substitution.⁸⁶

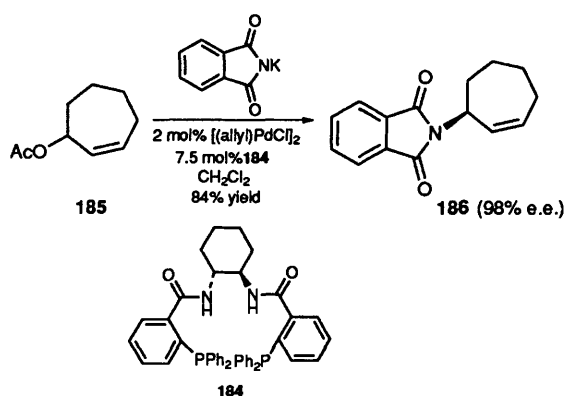




Helmchen, Pfaltz, and co-workers have extended the use of the ligand **182** to palladium-catalysed allylic amination.⁸⁷ Thus, treatment of the same allylic acetate **172** with a variety of nitrogen nucleophiles, including the sodium salt of *p*-toluenesulfonamide, afforded the allylic substitution product **183** with excellent levels of asymmetric induction.

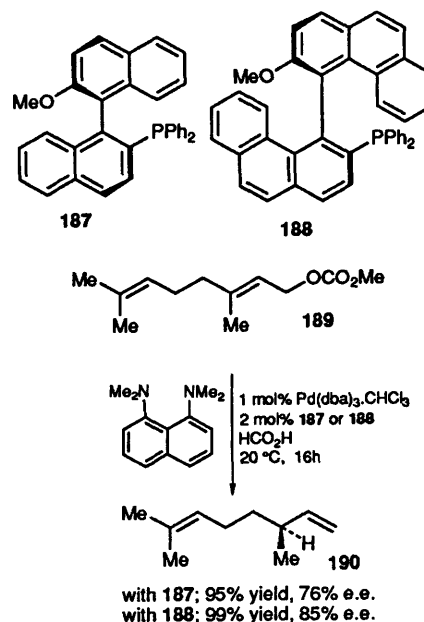


Trost and Bunt have shown that the ligand **184** is particularly effective in enantioselective reactions involving 3-(acyloxy)cycloalkenes. For example, the reaction of the allyl acetate **185** with potassium phthalimide in the presence of a palladium catalyst and an enantiomerically pure ligand afforded the substitution product **186** with very high enantioselectivity.⁸⁸ These workers have also shown that, in some cases, the addition of some tetraalkylammonium salts can have a remarkably beneficial effect on product enantioselectivity.⁸⁹

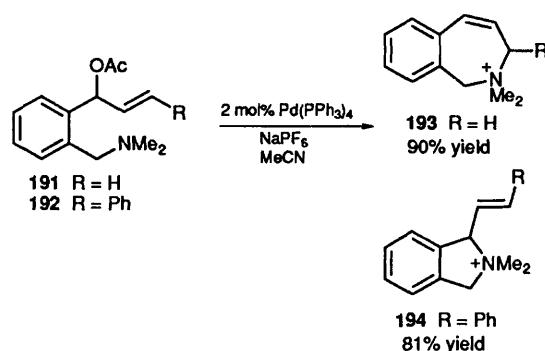


Hayashi and co-workers have also employed the ligands **187** and **188** in the palladium-catalysed reduction of allylic esters.^{90,91} Treatment of the allyl carbonate **189** with formic acid and a base, under

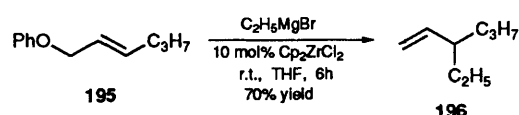
palladium catalysis in the presence of these ligands, afforded high levels of enantioselectivity in the product **190**.

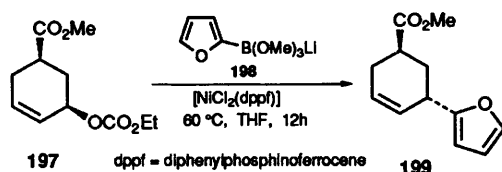


The cyclization of allyl acetates **191** and **192** under palladium-catalysed allylic substitution conditions has been shown to afford either the benzazepinium salt **193** or the alternative five-membered ring compound **194**.⁹² The preference for one regioisomer over the other was found to be due to thermodynamic control.



Whilst allylic substitution reactions catalysed by metals other than palladium continue to receive less attention, Takahashi and co-workers have provided examples of a regioselective carbon-carbon bond-forming reaction between an allyl ether **195** and a Grignard reagent catalysed by zirconocene dichloride to afford the product **196**.⁹³ Kobayashi and Ikeda have shown that the allylic carbonate **197** reacts with 2-furylborate **198** in the presence of a nickel catalyst to give **199**.⁹⁴

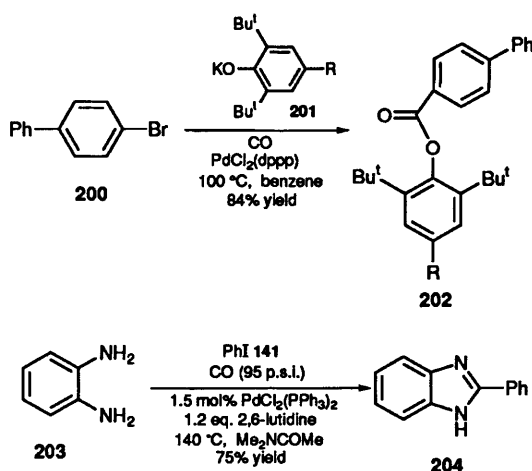




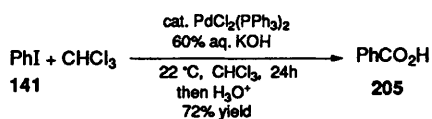
5.6 Carbonylation and related reactions

The aryloxy carbonylation of 4-bromobiphenyl (**200**) with the phenoxide **201** has been reported as an efficient synthesis of the hindered esters **202**.⁹⁵

Perry and Wilson have used a palladium-catalysed carbonylation protocol in the preparation of 2-arylbenzimidazoles.⁹⁶ For example, the palladium-catalysed reaction between iodobenzene (**141**) and *o*-phenylenediamine (**203**) affords 2-phenylbenzimidazole (**204**). The reaction proceeds via a monoamide, which cyclizes *in situ*.



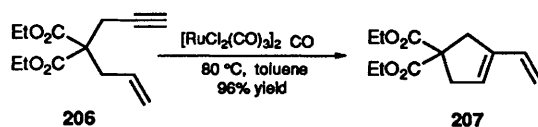
An interesting variant on standard carbonylation procedures has been devised by Grushin and Alper.⁹⁷ The carbon monoxide is generated *in situ* from chloroform and hydroxide. In a typical reaction, iodobenzene (**141**) and chloroform are treated with a palladium catalyst and potassium hydroxide, which after acidic work-up affords benzoic acid (**205**) in 72% yield.



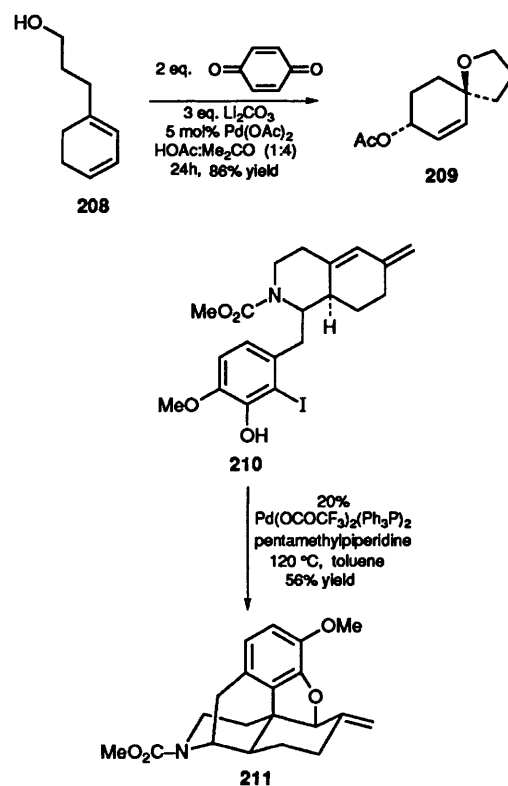
5.7 Cyclizations

There are many possible cyclization reactions which rely upon the previously described coupling processes. A few examples are given here.

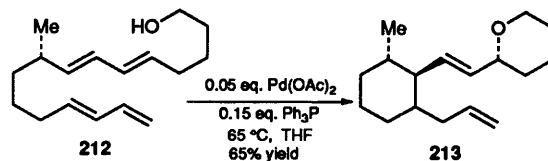
Murai and co-workers have reported the cyclization of the enyne **206** with a ruthenium catalyst to afford the product **207** in which a skeletal rearrangement has taken place.⁹⁸



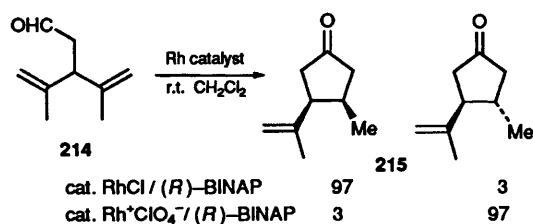
The palladium-catalysed oxaspirocyclizations of substrates such as **208** has been reported by Swedish workers.⁹⁹ The reaction with a palladium catalyst affords the spiro-product **209** with high diastereoselectivity using acetate as the external nucleophile. Hong and Overman have used a palladium-catalysed cyclization reaction in the construction of the pentacyclic opiate **211** (which can be converted into morphine) from the precursor **210**.¹⁰⁰



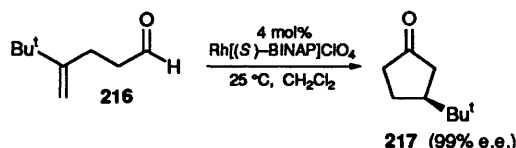
Takacs and Chandramouli have reported a highly diastereoselective palladium-catalysed tetraene cyclization.¹⁰¹ The enantiomerically pure substrate **212** was cyclized to the product **213** as a single diastereomer.



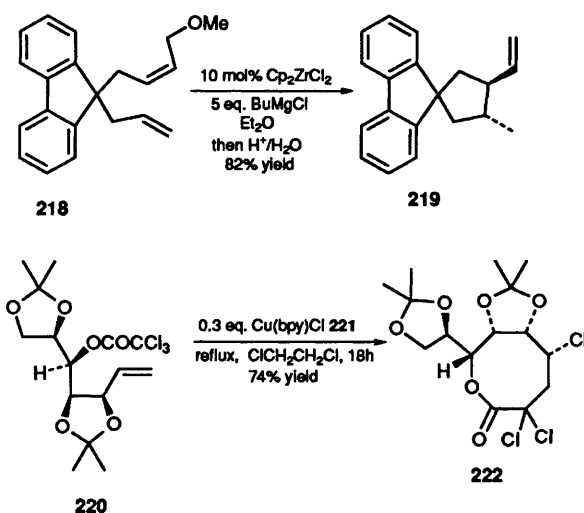
A highly stereoselective cyclization of the unsaturated aldehyde **214** into the cyclopentanone **215** using a cationic BINAP-derived rhodium complex with $>99\%$ e.e. and high *trans*-selectivity has been reported.¹⁰² The use of a neutral rhodium complex afforded a *cis*-selective reaction.



In a related study, Bosnich and co-workers have cyclized the substrate **216** into the cyclopentanone **217** with > 99% e.e. using a similar cationic rhodium complex.¹⁰³



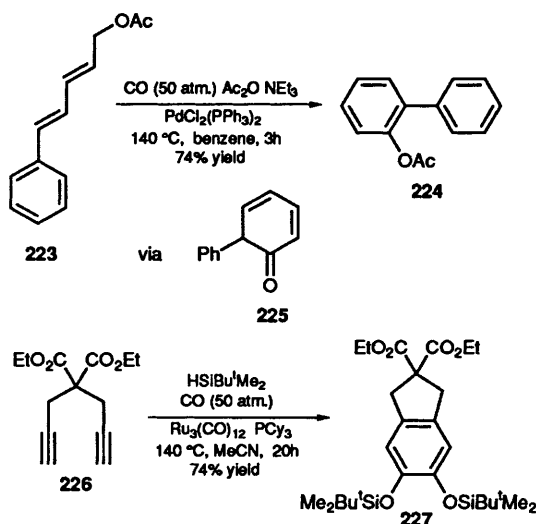
The *trans*-selective zirconocene-catalysed cyclization of the diene **218** into the cyclopentane **219** with the *trans*-isomer predominating has been reported by Knight and Waymouth.¹⁰⁴ Hiemstra, Speckamp, and co-workers have examined a copper-catalysed cyclization of trichloroacetates which takes place via a chlorine-transfer process.¹⁰⁵ Treatment of the trichloroacetate **220** with the copper catalyst **221** affords the eight-membered lactone **222** as a single diastereomer in 74% yield.



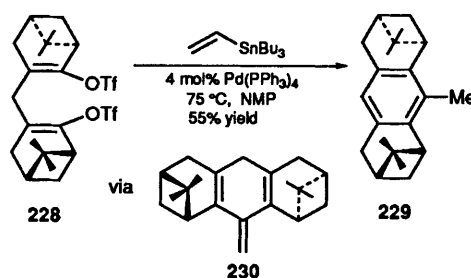
5.8 Cyclizations to form aryl rings

Cyclizations in which aryl rings are formed are particularly impressive. In retrosynthetic planning, most research groups consider modification rather than construction of aryl groups, although with the increasing number of transition metal catalysed aryl-forming reactions this situation may start to change. Hidai and co-workers have carbonylated the dienyl acetate **223** in the presence of acetic anhydride and triethylamine, and isolated 2-acetoxybiphenyl

(**224**) in 74% yield.¹⁰⁶ The reaction proceeds via the carbonylated, cyclized intermediate **225**, which tautomerizes and is acetylated under the reaction conditions. An aromatization reaction involving the incorporation of two equivalents of carbon monoxide has been reported by Murai and co-workers.¹⁰⁷ Thus, the diyne **226** is cyclized to the aromatic compound **227** upon treatment with a ruthenium catalyst in the presence of carbon monoxide and a silane.



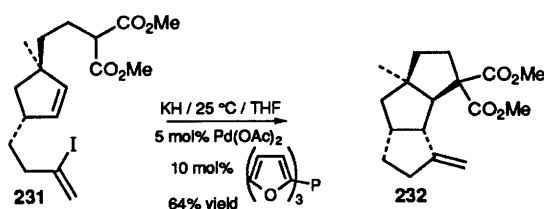
Barry and Kodadek have designed an aromatization of the bis-vinyltriflate **228**. Treatment with tributylvinylstannane and a palladium catalyst affords the aromatic compound **229**. The reaction proceeds via a Stille coupling to one vinyl triflate and a Heck coupling to the other vinyl triflate to give the intermediate **230** which tautomerizes to the product.¹⁰⁸



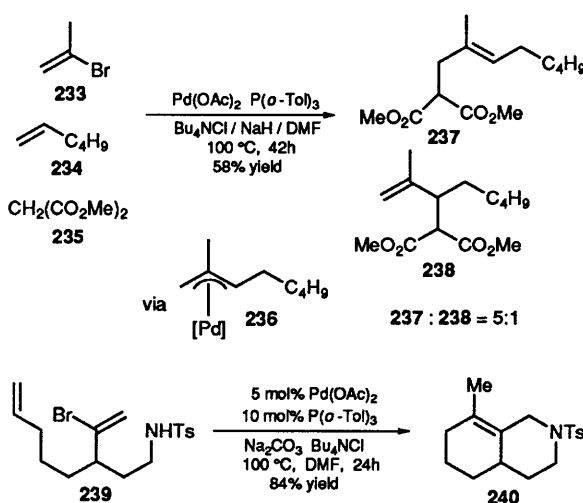
5.9 Tandem and cascade reactions

Tandem and cascade reactions provide an opportunity for transition metal catalysts to effect remarkable transformations. The standard coupling reactions can be linked together in a sequence to afford products in which many new bonds have been created. Some of the synthetic applications recently achieved are reviewed here.

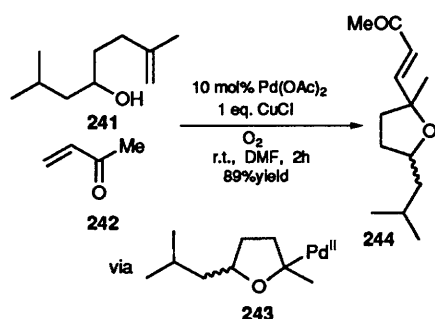
Palladium catalysis has been exploited by Balme and Bouyssi for the cyclization of the alkene **231**, which affords the tricyclic product **232**, which was subsequently converted into capnellene.¹⁰⁹



Weinreb and co-workers have examined the three component coupling between the vinyl bromide **233**, the alkene **234**, and dimethylmalonate (**235**), which is deprotonated under the reaction conditions.¹¹⁰ Initially, the bromide and alkene undergo a Heck coupling to form a palladium allyl intermediate **236**, which undergoes nucleophilic addition by the malonate to afford the products **237** and **238**. In an intramolecular variation of this reaction, where the nucleophilic component is a tethered sulfonamide **239**, the reaction proceeds to afford the bicyclic product **240**.¹¹¹

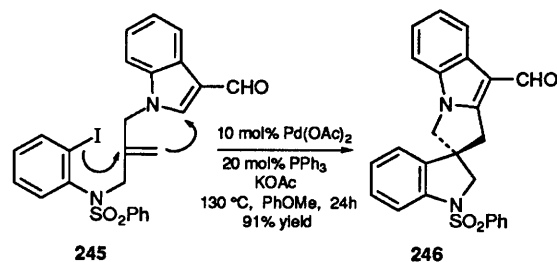


A catalytic tandem oxy-palladation, vinylation reaction has been reported by Semmelhack and Epa.¹¹² The hydroxy alkene **241** is treated with catalytic palladium acetate in the presence of copper chloride and air as re-oxidant. This affords the intermediate **243**, which is trapped with the alkene **242** in Heck fashion to afford the reaction product **244**.

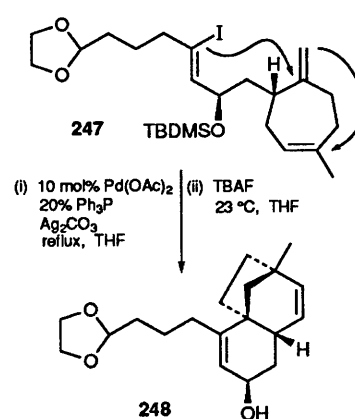


Grigg and co-workers have reported more examples of palladium-catalysed reactions leading to polycyclic products.¹¹³ For example, treatment of the indole **245**

with a palladium catalyst afforded the spiro product **246** obtained in a remarkable 91% yield.¹¹⁴ The starting material undergoes initial oxidative addition with the Pd⁰ catalyst (formed *in situ*), followed by the stitching indicated to provide the expected product.



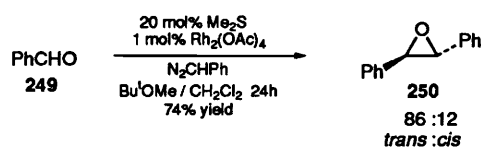
Overman and co-workers have designed an impressive palladium-catalysed bis-Heck cyclization which takes place with complete stereocontrol.¹¹⁵ The vinyl iodide **247** cyclizes as indicated to afford the tricyclic product **248** as a single diastereomer in 82% yield.



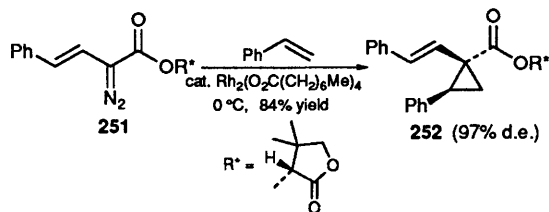
6 Reactions involving metal carbenoids

Rhodium and copper are the most commonly used metals for effecting reactions which proceed via metal carbenoids. Ironically, the metal carbenoids of copper and rhodium are too unstable to isolate, and so the exact structures of such species can only be assumed. Nevertheless, the behaviour of catalytic reactions involving metal carbenoids is now becoming fairly well rationalized.

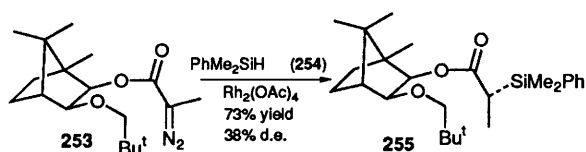
An interesting synthesis of epoxides from aldehydes has been provided by Aggarwal and co-workers.¹¹⁶ Dirhodium tetraacetate catalyses the formation of sulfur ylides from diazo-compounds and sulfides. The so-formed sulfur ylide reacts with the aldehyde to form an epoxide and regenerates the sulfide, which can therefore be used catalytically. For example, benzaldehyde (**249**) was converted into stilbene oxide (**250**) in 74% yield.



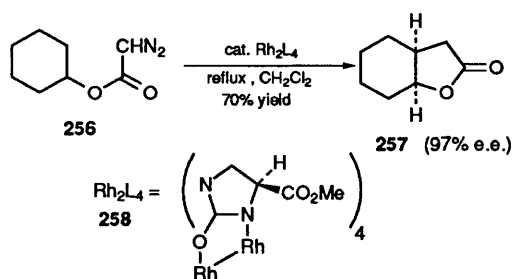
Several diastereoselective rhodium-catalysed transformations controlled by chiral auxiliaries have been reported.¹¹⁷ Davies and co-workers used the pantolactone ester **251** in a diastereoselective cyclopropanation reaction, to afford the product **252**.¹¹⁸



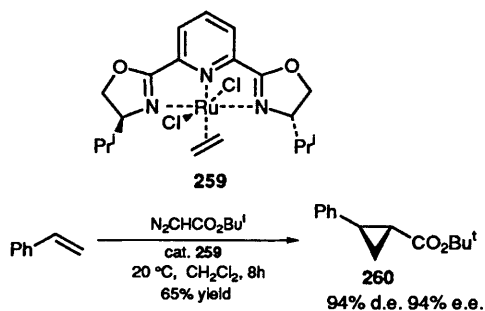
Landais and Planchenault have examined diastereoselective rhodium-catalysed insertions into the Si-H bond. The rhodium-catalysed reaction of the diazoacetate **253** with a silane **254** affords the product **255** with moderate diastereoselectivity.¹¹⁹



A C-H insertion reaction which proceeds with very high diastereocontrol and enantiocontrol has been reported by Doyle, Müller, and co-workers.¹²⁰ The diazoacetate **256** cyclizes to the product **257** on treatment with the rhodium catalyst **258** with 98% d.e. and 97% e.e.

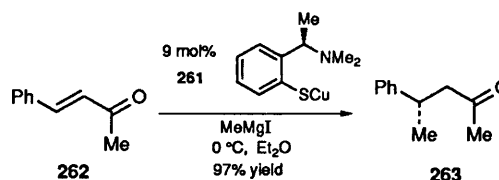


The enantioselective cyclopropanation of alkenes with diazoacetates catalysed by the ruthenium complex **259** has been reported.¹²¹ Styrene is converted into the cyclopropane **260** with high enantioselectivity and diastereoselectivity.

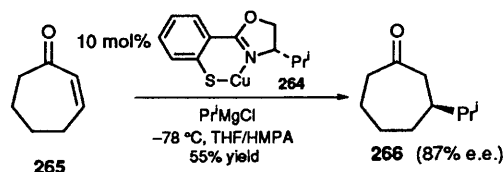


7 Conjugate addition and substitution

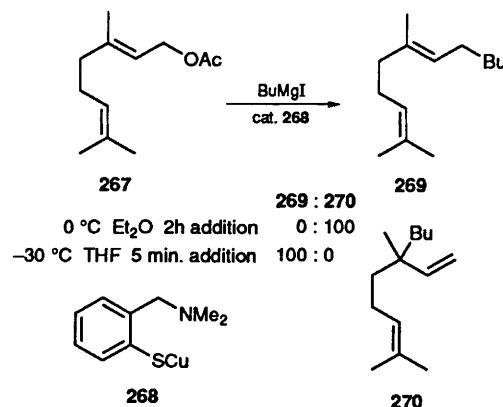
Van Koten and co-workers have further developed the use of enantiomerically pure arenethiolatocopper(I) complexes **261** as catalysts for enantioselective conjugate addition.¹²² In the presence of catalyst **261**, methylmagnesium iodide can be added to the α,β -unsaturated ketone **262** to afford the product of 1,4-conjugate addition **263** with high enantioselectivity.



Zhou and Pfaltz have used the related copper catalyst **264** to provide asymmetric induction in the addition of isopropylmagnesium chloride to 2-cycloheptenone (**265**), which affords the product **266**.¹²³

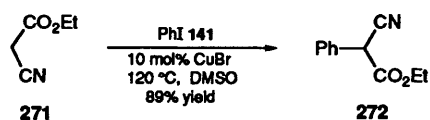


Bäckvall, van Koten, and co-workers have reported the extraordinary finding that treatment of geranyl acetate **267** with the achiral catalyst **268** and butylmagnesium iodide (addition over 120 min.) affords the product of γ -substitution **270** when conducted in diethyl ether at 0°C , whilst the product of α -substitution, **269**, was obtained when the reaction was conducted in THF at -30°C (with Grignard addition over 5 min.).¹²⁴

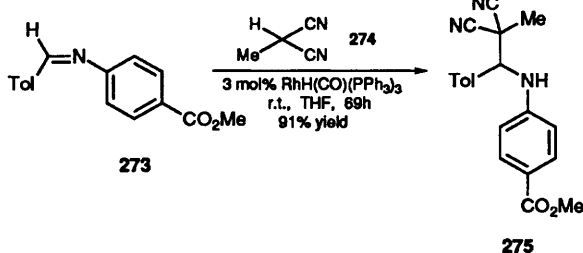


8 Catalysed nucleophilic additions

Miura and co-workers have reported the copper-catalysed reaction of aryl iodides with active methylene compounds.¹²⁵ For example, the reaction between iodobenzene (**141**) and ethylcyanoacetate (**271**) affords the substituted aromatic compound **272** in 89% yield.

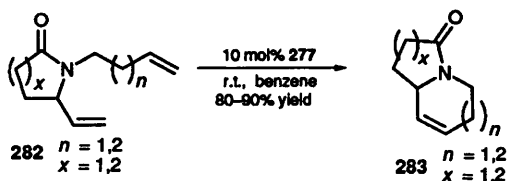
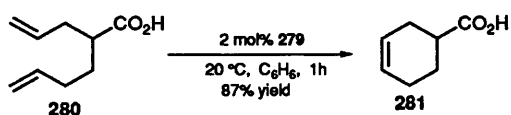
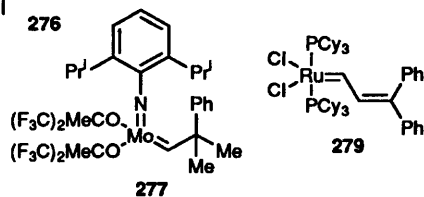
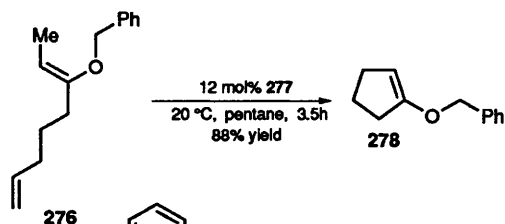


Rhodium catalysts have been employed to effect nucleophilic additions to imines.¹²⁶ Thus, the reaction between the imine **273** and the methylmalonitrile **274** affords the product of nucleophilic addition **275** using a rhodium catalyst. A palladium(0) catalyst was also found to be effective.

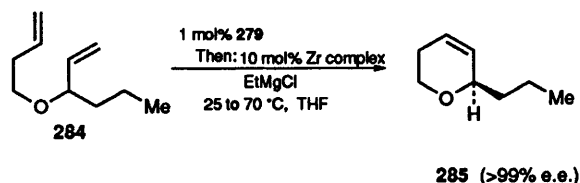


9 Metathesis

Grubbs and co-workers have extended their ring-closing metathesis methodology to include a wider range of substrates. The reaction of enol ether **276** with the molybdenum catalyst **277** affords the ring-closed product **278** in 88% yield.¹²⁷ The ruthenium catalyst **279** was also found to be able to catalyse ring-closing metathesis reactions, including the conversion of **280** into **281**.¹²⁸ Martin and co-workers have used similar methodology to afford fused nitrogen-heterocycles.¹²⁹ Thus, treatment of the diene **282** with catalyst **277** affords the products **283** in 80–90% yields.

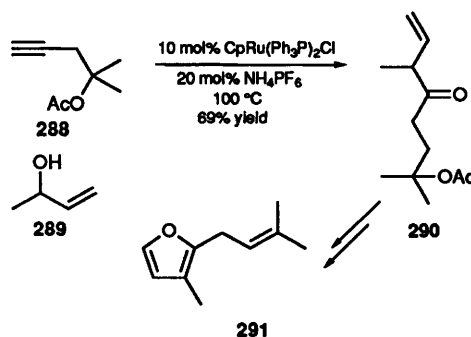
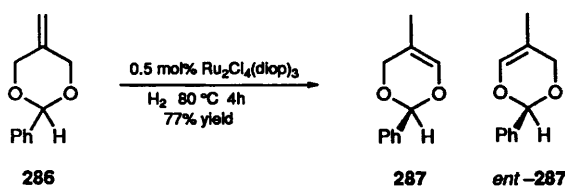


Hoveyda and co-workers have provided a further example of a metathesis/cyclization reaction, using the ruthenium catalyst **279**.¹³⁰ The diene **284** is cyclized to the racemic pyran **285**. By treatment of the so-formed reaction mixture with an enantiomerically pure zirconium catalyst and ethylmagnesium chloride, a kinetic resolution process takes place, allowing recovery of the pyran **285** as a single enantiomer.

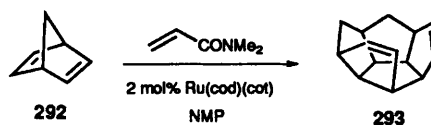


10 Miscellaneous

Frauenrath and Kaulard have examined an interesting asymmetric isomerization of the achiral substrate **286** into the enantiomers **287** and *ent*-**287**.¹³¹ Using an enantiomerically pure ruthenium catalyst, the product is obtained with modest enantioselectivity. Trost and co-workers have continued to find synthetic applications for the unusual ruthenium-catalysed addition of alcohols and acetylenes.¹³² For example, the reaction of the alkyne **288** with allyl alcohol **289** with a ruthenium catalyst affords the addition product **290**, which was further elaborated to rosefuran (**291**).¹³³



A Japanese group has reported the remarkable ruthenium-catalysed dimerization of norbornadiene (**292**) to pentacyclotetradecadiene (**293**) in 85% yield.¹³⁴ It has been assumed that this reaction proceeds by repeated activation of one or more C–C bonds.



11 Conclusion

Transition metal catalysed reactions have continued to grow in importance. The areas of asymmetric catalysis, and the development of tandem and cascade sequences are examples which demonstrate the efficiency of transition metal catalysed reactions, both in terms of potential and of the tremendous achievements already attained.

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