Catalytic applications of transition metals in organic synthesis

Louise Tonks and Jonathan M. J. Williams

Department of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY

REVIEW PERKIN 1

Covering: 1 November 1996 to 31 December 1997
Previous review: *Contemp. Org. Synth.*, 1997, 4, 353

1 Introduction

This review highlights advances in homogeneous transition metal catalysed reactions in the fourteen month period up to 31 December 1997. Some very recently developed reactions, including metal-catalysed ring closing metathesis and palladium catalysed amination of aryl halides, have already become part of the standard repertoire for organic chemists. It is no longer possible to detail every paper involving such topics, which is a testament to their utility. Newly emerging reactions, including the Sharpless aminohydroxylation reaction and Jacobsen ring-opening of epoxides look set to follow a similar trend over the coming years.

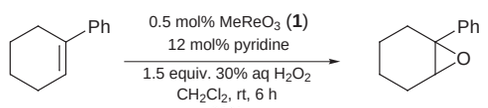
The authors have endeavoured to cover as many areas of transition metal catalysed organic synthesis as possible, within the space constraints imposed, but with an emphasis on newer methods.

2 Oxidation reactions

Many transition metals catalyse oxidation reactions, but in order to be synthetically useful, selective oxidation is a requirement. Selectivity for particular functional groups and, of increasing importance, enantioselectivity are useful features in an oxidation process.

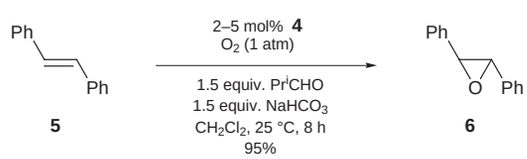
2.1 Epoxidation

The epoxidation of alkenes with aqueous hydrogen peroxide can be catalysed by methyltrioxorhenium **1** and is accelerated by pyridine[1] or 3-cyanopyridine.[2] The reaction can be performed at high concentration, and is illustrated by the conversion of 1-phenylcyclohexene **2** into the corresponding epoxide **3**. The reaction has been performed on aliphatic alkenes and dienes, also with high yields. This new catalytic system has much to offer; acid sensitive epoxides do not undergo rearrangement or ring-opening reactions, the only by-product is water, and isolation is straightforward.[3] The use of bis(trimethylsilyl) peroxide has been shown to have advantages over hydrogen peroxide in terms of catalyst stability.[4]



2 **3**

Epoxidation reactions of alkenes using molecular oxygen in the presence of an aldehyde have considerable synthetic utility. The latest addition to this family of reactions employs the ruthenium catalyst **4** to catalyse the conversion of stilbene **5** into stilbene oxide **6**.[5]



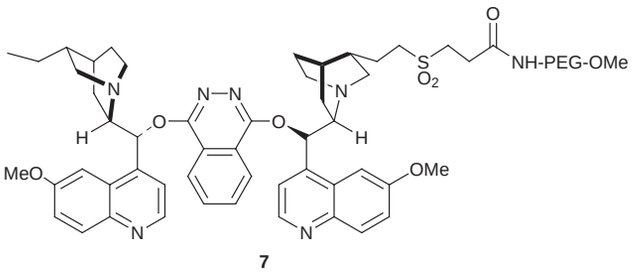
5 **6**

4

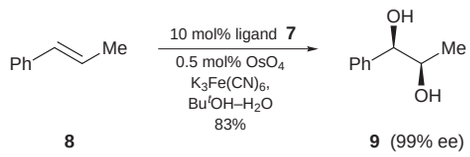
2.2 Dihydroxylation and aminohydroxylation

Asymmetric dihydroxylation reactions continue to occupy a position of synthetic importance. Janda and Han have reported the use of the soluble polymer bound ligand **7** for this reaction, which facilitates ligand recovery and product isolation.[6] Levels of enantioselectivity are very similar to those obtained using conventional ligands. Alkene **8** is converted into the diol **9** in good yield, and with the expected high enantioselectivity. The same workers have also reported the combination of using ligand **7** with polymer-supported substrates.[7]

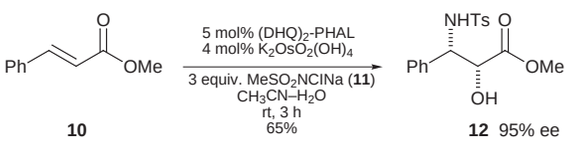
The Sharpless asymmetric aminohydroxylation reaction has seen some exciting developments.[8] The reaction works particularly well on cinnamate substrates such as methyl cinnamate **10**. Using the chloramine salt **11**, the asymmetric aminohydroxylation reaction affords the hydroxysulfonamide product **12** with very high enantioselectivity.[9] Subsequent papers demonstrated that alternative nitrogen sources led to even more efficient



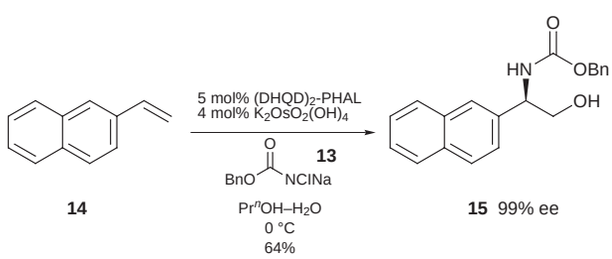
7



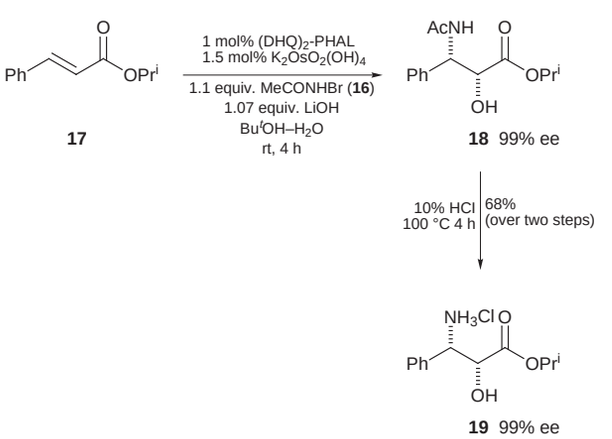
8 **9** (99% ee)



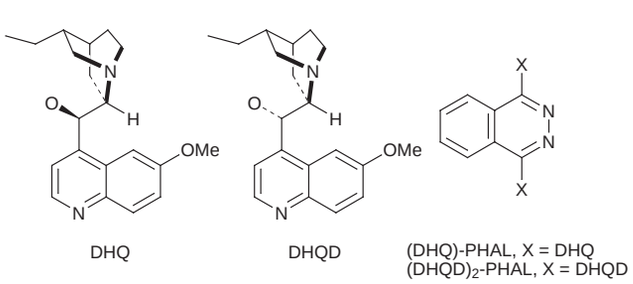
10 **12** 95% ee



14 **15** 99% ee

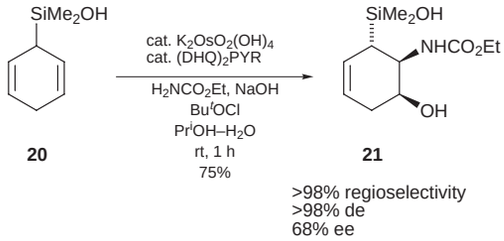


17 **18** 99% ee **19** 99% ee



asymmetric aminohydroxylation reactions. Thus, the *N*-chlorocarbamate salt **13** provides the basis for the conversion of vinylnaphthalene **14** into the product **15**.[10] *N*-Bromoacetamide **16** has also been exploited with great effect.[11] Thus, cinnamate **17** was converted into the amido alcohol **18**, which was hydrolysed to give 3-phenylisoserine hydrochloride **19** in good yield and excellent enantiomeric excess.

Landais and co-workers have already exploited the asymmetric aminohydroxylation reaction in a synthetic sequence leading to aminocyclitols.[12] The dienylsilane **20** is converted



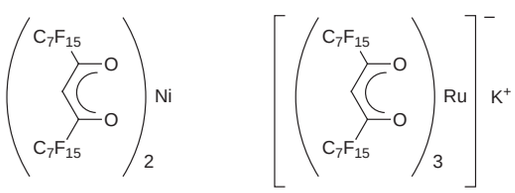
20 **21**

regioselectively, diastereoselectively and enantioselectively into the product **21** in good yield!

Iqbal and Das have reported a one-pot conversion of alkenes into *trans* amino alcohol derivatives, which proceeds *via* cobalt catalysed epoxidation and ring-opening with a nitrogen nucleophile.[13]

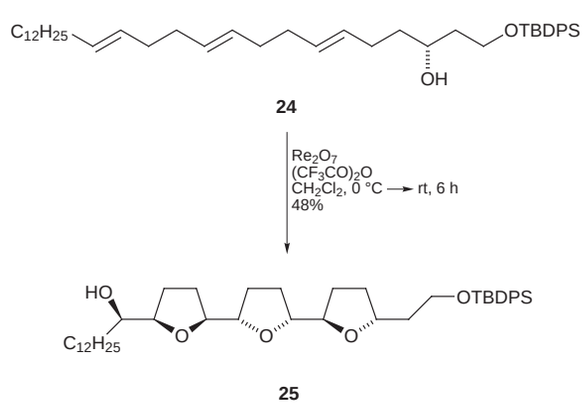
2.3 Other oxidations

The use of perfluorinated solvents is of interest in many aspects of catalysis and organic chemistry in general. Knochel and co-workers have described oxidations of aldehydes to acids, and sulfides to sulfoxides using the perfluorinated nickel complex **22**.[14] The perfluorinated ruthenium complex **23** was employed for catalytic epoxidation reactions. The organic phase (toluene) and fluorous phase ($C_8F_{17}Br$) are separate at room temperature, but form a single phase at 60 °C. This allows easy separation and re-use of the catalysts.



22 **23**

An interesting, highly selective triple oxidative cyclisation of triene **24** using a rhenium(VII) reagent has been reported, which although not catalytic is sufficiently noteworthy that it is included here. The product **25** is isolated in 48% yield as a single diastereomer.[15]



24 **25**

TBDPS = tert-butyldiphenylsilyl

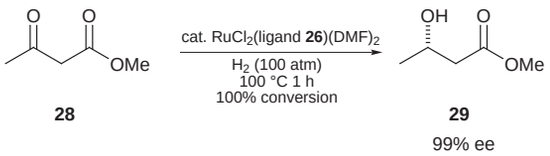
3 Hydrogenation and related reactions

As with oxidation reactions, it is the selectivity of reduction reactions which can be of utmost importance. Transition metals are often able to provide a chemoselective reduction reaction, especially in the field of hydrogenation reactions, and related processes. Again, enantioselectivity is often an important factor to be considered in such reactions.

3.1 Hydrogenation

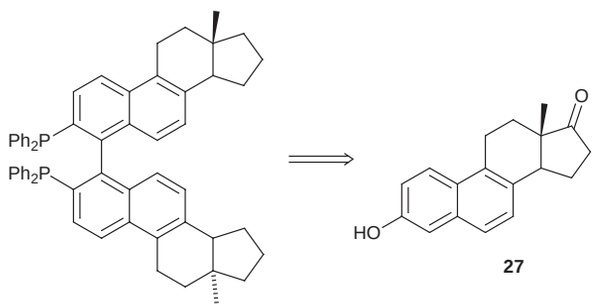
Asymmetric hydrogenation of carbonyl groups and of alkenes using suitable ruthenium and rhodium catalysts is a well-

documented area of research, and many new ligands are reported each year for such reactions. An appealing ligand which caught the attention of the authors is the bis-steroidal phosphine **26** which is prepared in a few steps from the steroidal precursor equilenin **27**.[16] The ligand worked well in the asymmetric reduction of β-keto ester **28** providing the β-hydroxy ester **29** with high selectivity.



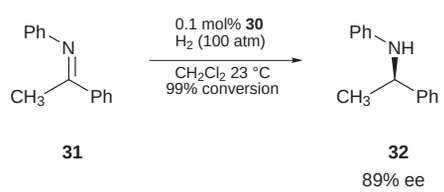
28 **29**

99% ee



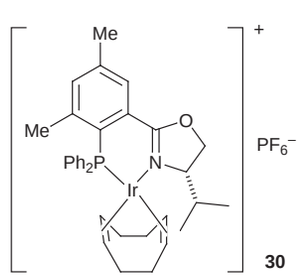
26 **27**

Pfaltz and co-workers have reported the enantioselective hydrogenation of imines with the iridium catalyst **30**.[17] Thus, imine **31** was reduced to the amine **32** with up to 89% ee under optimised conditions. The enantioselectivity was found to be highest when high dilution conditions were employed.



31 **32**

89% ee



30

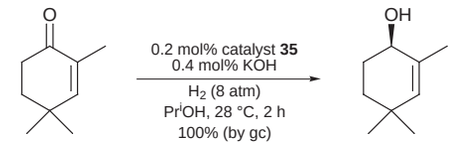
3.2 Transfer hydrogenation

Noyori's research team has shown how ruthenium catalysed transfer hydrogenation can be used both chemoselectively and enantioselectively. Thus, the cyclic enone **33** was reduced to the alcohol **34** with high enantioselectivity and no conjugate reduction, using catalyst **35**.[18] Even α,β-acetylenic ketones are only reduced at the carbonyl group, as illustrated by the conversion of ketone **36** into alcohol **37** using the 'Noyori catalyst' **38**.[19]

The reduction of acetophenone **39** to 1-phenylethanol **40** is a standard reaction, against which new ligands can be tested. (Phosphinoferrocenyl)oxazoline **41** was employed as a ligand by Sammakia and Strangeland.[20] Wills and co-workers used commercially available amino-indanol **42**.[21]

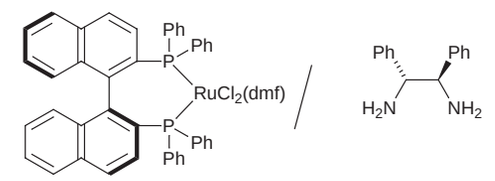
3.3 Hydroboration

Horváth, Gladysz and Juliette have exploited fluorous biphase chemistry in rhodium catalysed hydroboration reactions.[22] The fluorous phosphine **43** is soluble in $CF_3C_6F_{11}$ and co-ordinates

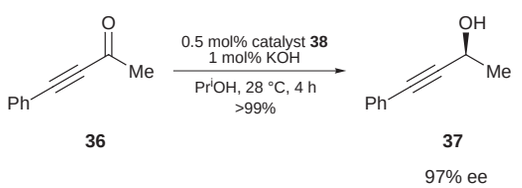


33 **34**

(95% ee)

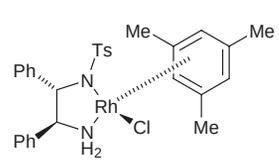


Catalyst **35**

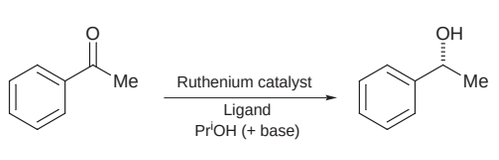


36 **37**

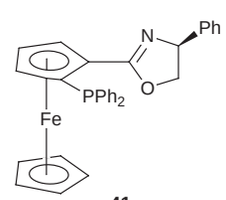
97% ee



Catalyst **38**

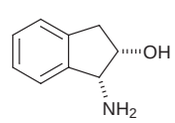


39 **40**



41

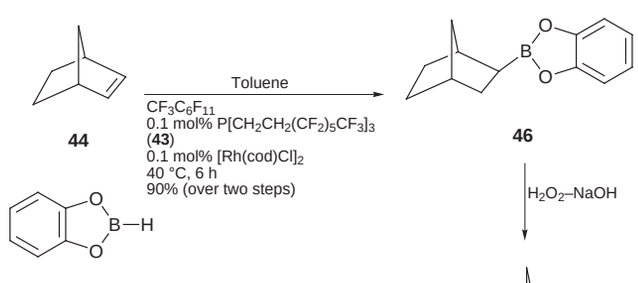
(provides up to 96% ee)



42

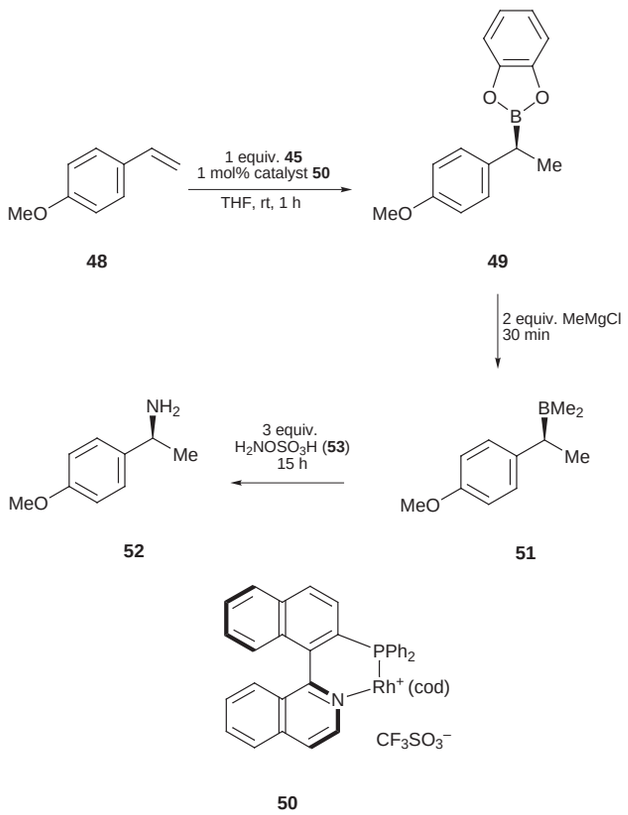
(provides up to 95% ee)

to the rhodium catalyst. The organic reactants, norbornene **44** and catecholborane **45** remain in the organic layer and react to form the organoborane **46**. The organic phase could be separated and the borane converted into the alcohol **47**. The fluorous phase (containing the rhodium catalyst) could be separated and recycled.



44 **45** **46** **47**

J. M. Brown and co-workers have reported a synthetically useful manipulation for the products of hydroboration reactions with catecholborane.[23] Hydroboration of 4-methoxystyrene **48** with catecholborane **45** affords the intermediate **49**, using the rhodium catalyst **50**. Such intermediates cannot be directly converted into amines, which is why they are always isolated as the corresponding alcohols. However, by treatment with two equivalents of methylmagnesium chloride, the borane **51** is formed, which can now be converted into the amine **52** using the aminating agent **53**.



48 **49** **52** **51** **50**

4 Catalytic coupling reactions

Transition metals are able to catalyse the coupling of many organic compounds. Most typically, such reactions involve palladium and the formation of C–C bonds. Nevertheless, there are many synthetically useful processes which fall outside of this window, providing a greater range of chemical transformations.

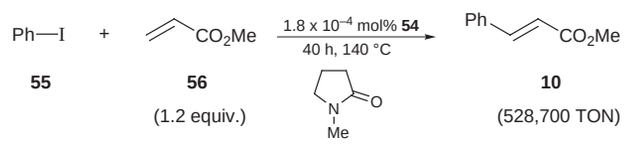
4.1 Heck reaction

Milstein and co-workers have shown that the palladium catalyst **54** is highly active in the Heck coupling reaction. Very high turnover numbers (TON) (in excess of half a million!) have been achieved in the reaction between iodobenzene **55** and methyl acrylate **56** to give the coupled product **10**.[24]

Nickel catalysts have also been employed in Heck reactions, including the reaction of the iodoarene **57** with ethyl acrylate **58**, which affords the coupled product **59** in good yield.[25]

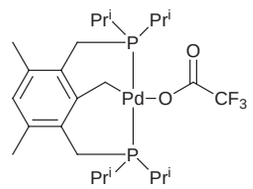
Heck reactions have been performed using glass bead technology.[26] The palladium catalyst is complexed to a polar phosphine which resides in an ethylene glycol film coating the surface of a porous glass bead. The reactants are in the bulk organic solvent and the products can be isolated with very low levels of palladium contamination. A heterogenous catalyst of palladium associated directly on to porous glass has also been reported,[27] as well as the use of palladium complexes associated to a phosphine-containing dendrimer.[28]

An interesting Heck-type reaction on the allylsilane **60** leads to the formation of two new cyclopentane rings in the product

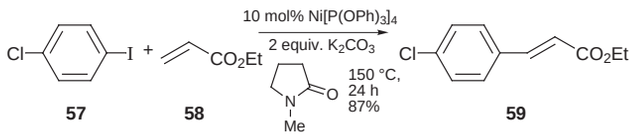


55 **56** (1.2 equiv.) **10** (528,700 TON)

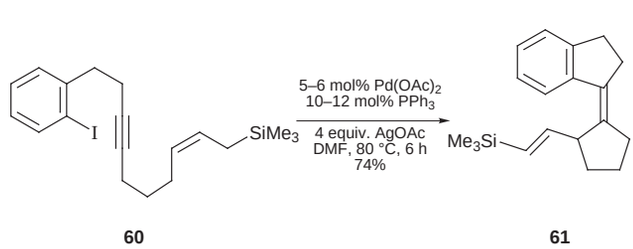
45% (by gc)



54



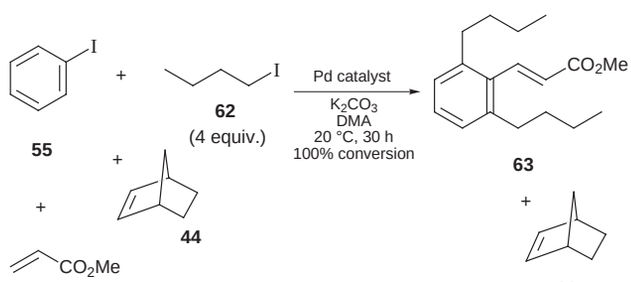
57 **58** **59**



60 **61**

61.[29] The authors refer to this process as the allylsilane terminated domino Heck reaction.

A Heck reaction between iodobenzene **55** and methyl acrylate **56** in the presence of butyl iodide **62** and norbornene **44** affords the dibutyl-substituted Heck product **63**.[30] The norbornene is involved in the mechanism, but is not incorporated into the final product. A complex catalytic cycle was proposed to rationalise the synthetic outcome.

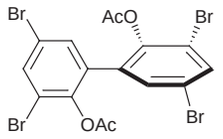


4.2 Stille reaction

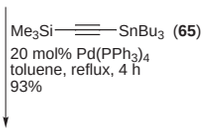
The Stille coupling reaction has found widespread use in synthesis. The tin reagents have considerable stability compared with some other organometallic reagents. An unusual example of a multiple Stille coupling has been reported by Echavarren and co-workers.[31] The tetrabromide **64** is coupled with the alkynylstannane reagent **65** under Stille coupling conditions to give the tetralkynyl derivative **66** in a remarkable 93% yield.

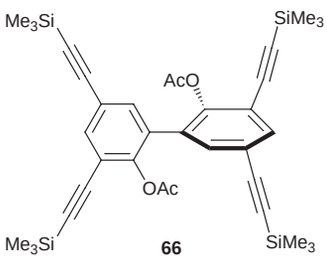
Nicolaou and co-workers have shown that cyclic ketene acetal phosphates (derived from lactones) are good coupling partners in Stille reactions.[32] Thus, the phosphate **67** and tin reagent **68** are coupled to give the highly oxygenated product **69** in excellent yield.

The use of fluorous phase chemistry has also been applied to the Stille coupling.[33] Microwave irradiation was found to accelerate the fluorous Stille coupling.[34] For example, the fluor-

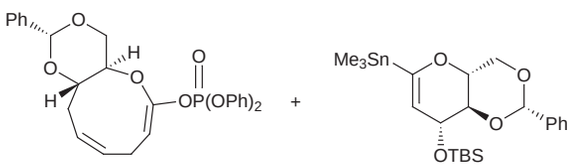


64

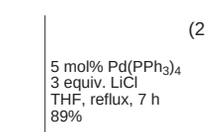


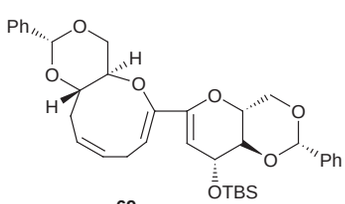


66



67 68 (2 equiv.)

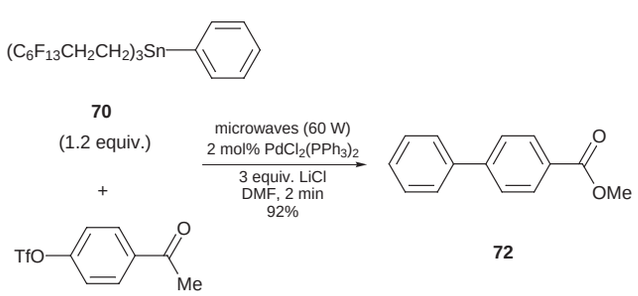




69

TBS = tert-butyldimethylsilyl

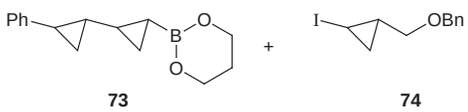
ous tin reagent **70** was coupled with the aryl triflate **71**, which under Stille coupling/microwave irradiation conditions afforded the product **72** in just two minutes! Product isolation is achieved by partitioning between aqueous, organic and fluorous layers, and isolation of the organic layer.



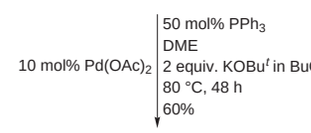
Although palladium catalysts are usually employed for Stille coupling reactions, Kang and co-workers have reported the use of copper-catalysed and manganese-catalysed variants.[35] Shirakawa and co-workers have reported an analogous nickel-catalysed variant.[36]

4.3 Suzuki reaction

Like its cousin, the Stille reaction, the Suzuki reaction deserves a special mention amongst catalytic coupling reactions. It can be the method of choice for the coupling of complex structures. Nicolaou and co-workers have recently reported the use of this reaction in the formation of a biaryl construction in studies towards the synthesis of vancomycin.[37] The Suzuki coupling has recently been applied to the synthesis of structures containing contiguous cyclopropane units.[38] The boronate ester derivative **73** was coupled with the iodocyclopropane **74** under Suzuki coupling conditions to give the tris-cyclopropyl product **75**.

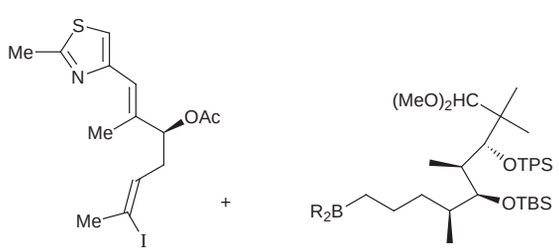


73 74



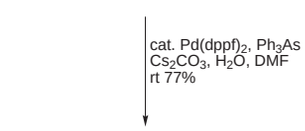
75

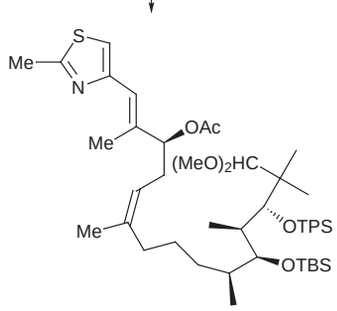
Danishefsky and co-workers have used a Suzuki coupling to construct two major fragments in the synthesis of the anti-tumour agent, epothilone.[39] The vinyl iodide **76** and borane **77** were coupled in good yield to give the product **78**.



76 77

dppf = 1,1′–bis(diphenylphosphino)ferrocene





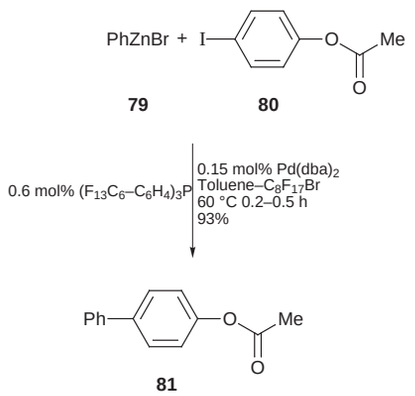
78

TPS = triphenylsilyl

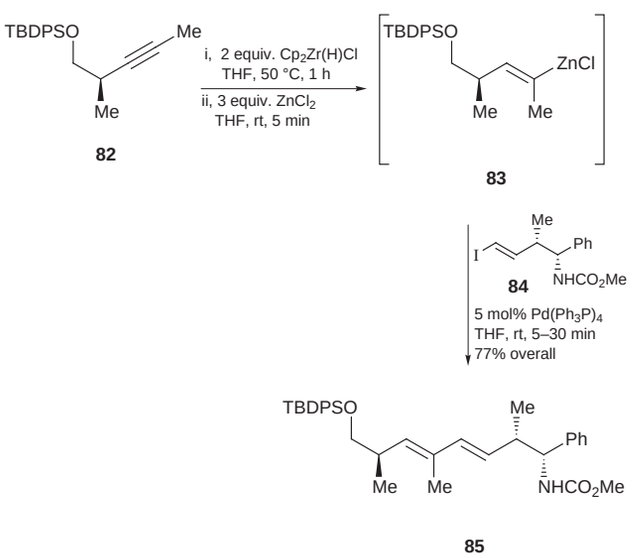
4.4 Other coupling reactions

Apart from the organotin and organoboron compounds described in the last two sections, many other organometallic reagents undergo coupling reactions. Organozinc reagents are especially popular, since they offer a balance between good reactivity in the coupling step, and enough stability that they are compatible with many functional groups.

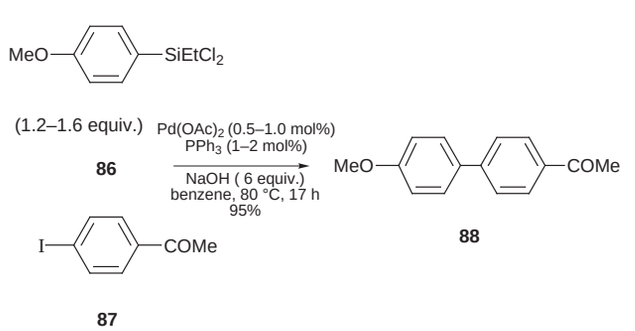
Betzemeier and Knochel have investigated the use of organozinc reagents with a fluorous phase palladium catalyst.[40] Thus, phenylzinc bromide **79** and aryl iodide **80** were coupled using a fluorinated phosphine in a biphasic system of toluene with 1-bromoperfluorooctane, which afforded the product **81**.



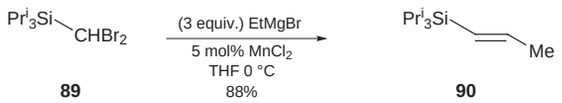
Organozinc reagents were prepared indirectly by Panek and Hu, who use a hydrozirconation/transmetallation sequence to prepare vinylzinc reagents with high selectivity.[41] Alkyne **82** is converted *in situ* into the zinc reagent **83**, which is then coupled with the vinyl iodide **84** to give the coupled product **85** in good yield.



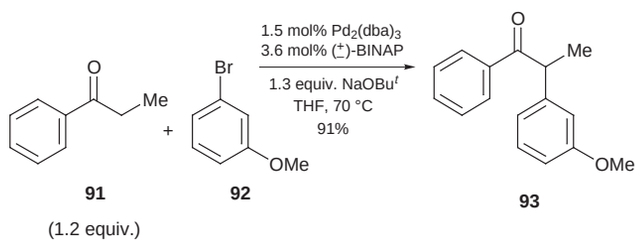
Although organosilicon compounds are not commonly used in cross-coupling reactions, such reactions can occur by the formation of an intermediate pentacoordinate silicate, by the addition of a suitable nucleophile. In the presence of sodium hydroxide the dichlorosilane **86** is coupled with aryl iodide **87** to give the product **88** in good yield.[42] A similar strategy using aryltrialkoxysilanes in the presence of tetrabutylammonium fluoride has also been reported.[43]



Oshima and co-workers have demonstrated the catalytic ability of manganese chloride in the preparation of vinylsilanes.[44] For example, the *gem*-dibromo compound **89** is converted into vinylsilane **90** on treatment with ethylmagnesium bromide and catalytic manganese chloride.



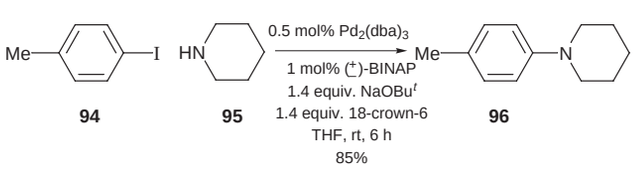
The α-arylation of ketones *via* enolates is often a difficult synthetic problem due to the lack of good electrophilic aryl sources. The groups of Buchwald[45] and Hartwig[46] have independently reported a palladium-catalysed α-arylation of ketones. Ketone **91** is arylated by 3-bromoanisole **92** in the presence of sodium *tert*-butoxide and a palladium catalyst to give the substituted product **93**.



An intramolecular α-arylation of a ketone with an aryl triflate has also been reported by Muratake and Natsume using base and a palladium catalyst.[47] Miura and co-workers have outlined a palladium catalysed diarylation of 1,3-diphenylpropanone.[48]

4.5 Catalytic synthesis of carbon–heteroatom bonds

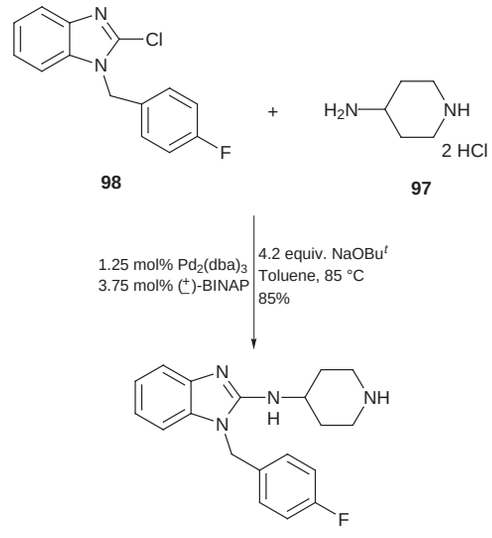
The palladium catalysed amination of aryl halides is becoming an increasingly well developed reaction. Wolfe and Buchwald have shown how the addition of 18-crown-6 leads to an amination procedure which can be performed at room temperature.[49] 4-Iodotoluene **94** was coupled to piperidine **95** to give the coupled product **96** under mild conditions. The same workers have used caesium carbonate as the base, instead of sodium *tert*-butoxide.[50] This latter modification provides a wider range of functional group compatibility.



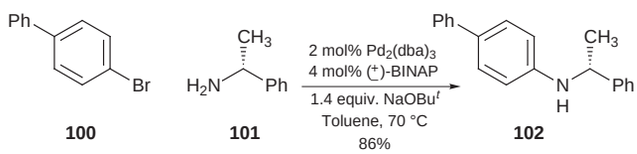
Senanayake and co-workers have used palladium catalysed amination in the preparation of the H_1-antihistaminic agent Norastemizole.[51] 4-Aminopiperidine hydrochloride **97** reacts selectively (18 : 1) through the primary amine with the chlorobenzimidazole derivative **98** to give the product Norastemizole **99**.

Aryl triflates are also suitable substrates for palladium catalysed amination reactions, and these reactions have been independently described by the groups of Buchwald[52,53] and Hartwig.[54] Amination of aryl chlorides can be achieved with palladium[55,56] or nickel[57] catalysis, but these reactions require more vigorous conditions.

In principle, palladium catalysed amination of enantiomerically pure amines could lead to racemisation, although Buchwald and co-workers have shown that, under appropriate conditions, the coupling can take place without any erosion of enantiomeric excess.[58] For example, aryl bromide **100** is coupled to the enantiomerically pure amine **101**, which provides the aniline derivative **102**.



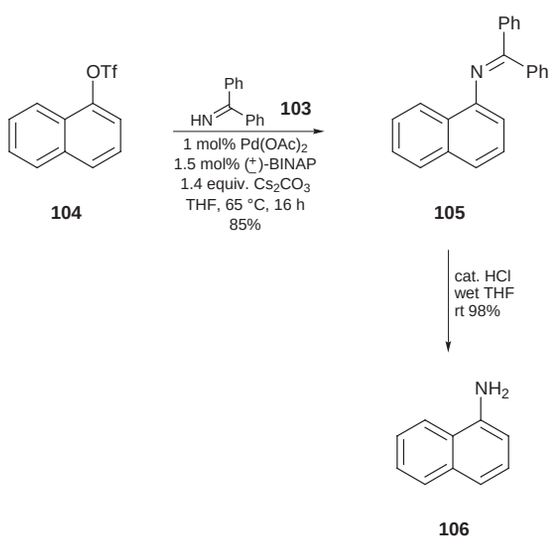
98 **97** **99**



100 **101** **102**

For most amination reactions of aryl halides, there is no scope for asymmetric induction. However, a team from Merck has shown that kinetic resolution of a racemic dibromoparacyclophane (which possesses planar chirality) can take place using an enantiomerically pure palladium catalyst.[59]

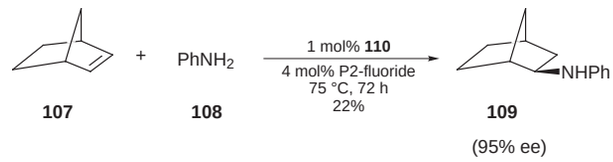
Benzophenone imine **103** has been used as an ammonia equivalent in palladium catalysed amination reactions.[60] Triflate **104** is readily converted into the imine **105**, which is then hydrolysed to give 1-aminonaphthalene **106**.



104 **105** **106**

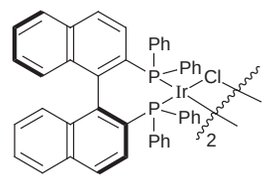
Another emerging area of catalysis with amines involves alkene hydroamination. Togni and co-workers have reported some very encouraging results in this area.[61] Norbornene **107** undergoes hydroamination with aniline **108** to give the adduct **109** with very high enantioselectivity using the iridium catalyst **110** in the presence of fluoride.

The use of diboron reagents, such as compound **111** has provided a new method over the last few years for the formation of carbon–boron bonds. Miyaura and co-workers have extended this reaction to the use of aryl triflates as the electrophile.[62] For example, triflate **112** is coupled with diboron compound **111** to

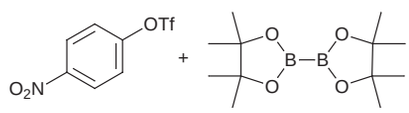


107 **108** **109**

(95% ee)

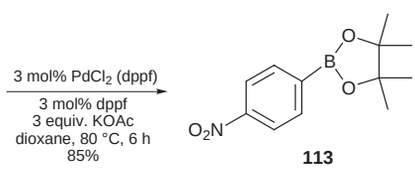


110



112 **111**

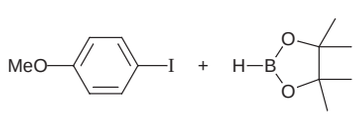
(1.1 equiv.)



113

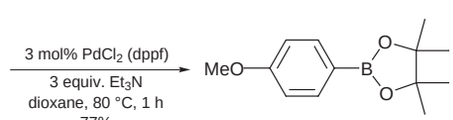
give the arylboronate **113**. It has been shown by Giroux and co-workers that arylboronates can be formed *in situ*, and further reacted by Suzuki reaction to give a new C–C bond.[63]

An interesting development in this area comes from the research group of Masuda.[64] Using the simple hydroborane **114**, direct formation of arylboronates has been achieved. 4-Iodoanisole **115** is readily converted into the boronate **116** using this method.



115 **114**

(1.5 equiv.)

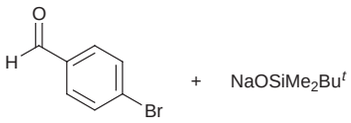


116

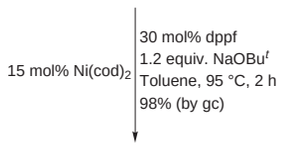
Carbon–oxygen bonds have been prepared using catalytic coupling reactions.[65,66] An example from Mann and Hartwig involves the nickel catalysed coupling of 4-bromobenzaldehyde **117** with sodium *tert*-butyldimethylsiloxide **118** giving the silyl ether product **119** in good yield.[67] In another example, Buchwald and co-workers couple bromonaphthalene **120** with cyclohexanol **121** using palladium catalysis to give the aryl ether **122**.[68]

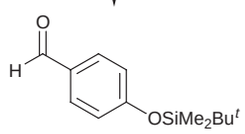
Oxygen nucleophiles are also important in Wacker oxidation. In a Wacker-type cyclisation, very high levels of asymmetric induction have been achieved.[69] Phenol **123** undergoes an oxidative cyclisation to give the dihydrobenzofuran derivative **124** in high enantiomeric excess using ligand **125**, a palladium catalyst and benzoquinone as the stoichiometric oxidant.

Aryl iodides have been converted into arylsilanes using triethoxysilanes and palladium catalysed coupling.[70] Carbon–phosphorus bonds have also been prepared by nickel catalysed

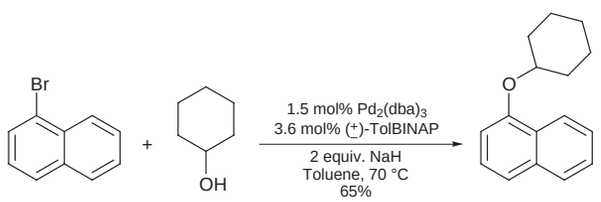


117 **118**

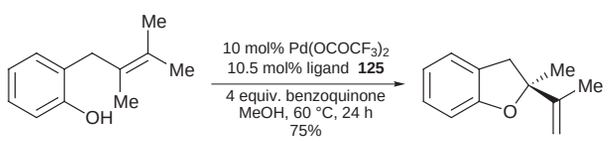




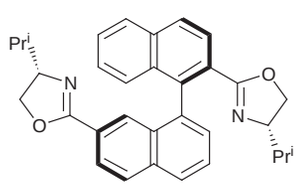
119



120 **121** (1.2 equiv.) **122**



123 **124** (96% ee)



125

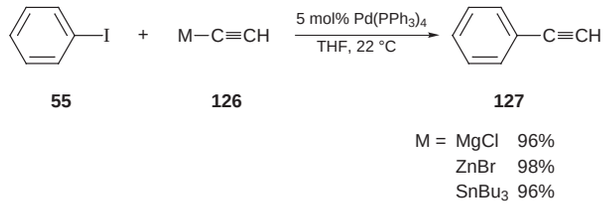
coupling, using Ph_2PZnCl (prepared *in situ*) with aryl halides and triflates.[71]

4.6 Reactions involving alkynes

Catalytic reactions involving alkynes appear in many of the sections of this review. The examples described here also have some cross-over with other sections. Negishi and co-workers have compared the use of various ethynyl metals in the cross-coupling reactions with aryl and alkenyl halides.[72] The example reaction between iodobenzene **55** and ethynyl metal **126** affords phenylacetylene **127**. Sodium, lithium and borate salts were found to be unsuitable (essentially no yield of coupled product). Grignard reagents, organozinc halides and organotin compounds all gave a high yield of product (96–98%), although the tin reagent was the slowest to react. The conclusion of the study is that commerically available HC≡CMgBr is a good starting point, but that in more demanding cases, HC≡CZnBr may be better.

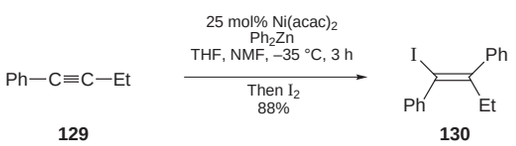
Stüdemann and Knochel have employed a nickel-catalysed carbozincation strategy in a very short synthesis of (*Z*)-Tamoxifen **128**.[73] Carbozincation of alkyne **129**, followed by an iodine quench affords the vinyl iodide **130**, which undergoes coupling with a suitable organozinc halide **131** to give, after protonation, Tamoxifen **128**.

Alkynes undergo a palladium catalysed borylsilylation reaction with reagent **133**. The reaction in the conversion of oct-1-yne **134** into product **135** is remarkably regioselective.[74]

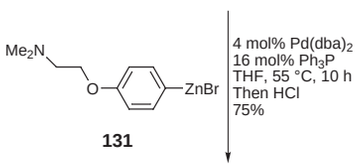


55 **126** **127**

M = MgCl 96%
ZnBr 98%
$SnBu_3$ 96%



129 **130**



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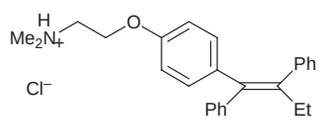
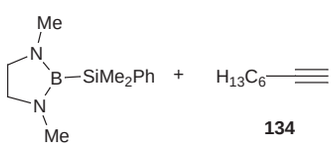
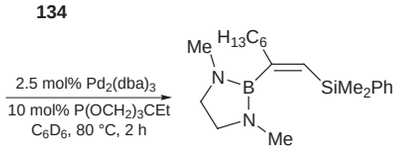


128

acac = acetylacetonate

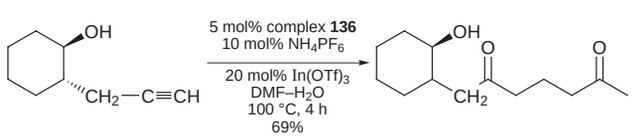


133 **134**

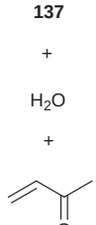


135

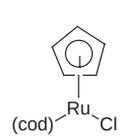
Trost and co-workers have continued their research into ruthenium-catalysed reactions of alkynes.[75] Ruthenium complex **136** catalyses a three component addition of alkyne **137** with methyl vinyl ketone **138** and water to give diketone **139** as the product.



137 **139**



138

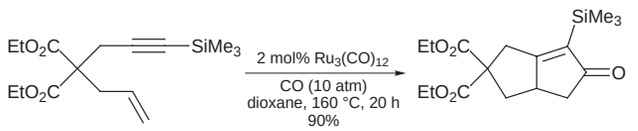


136

4.7 Cyclisation reactions

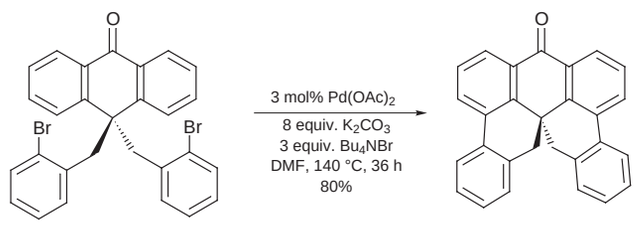
Many transition metal catalysed reactions have a variant which leads to a cyclisation process. The Pauson–Khand reaction, however, is a cyclisation process itself, and the intramolecular variant leads to bicyclisation.

A ruthenium catalysed variant of the Pauson–Khand reaction has been reported independently by two research groups.[76,77] For example, the enyne **140** undergoes a bicyclisation reaction to give the enone **141** in good yield using a ruthenium catalyst.



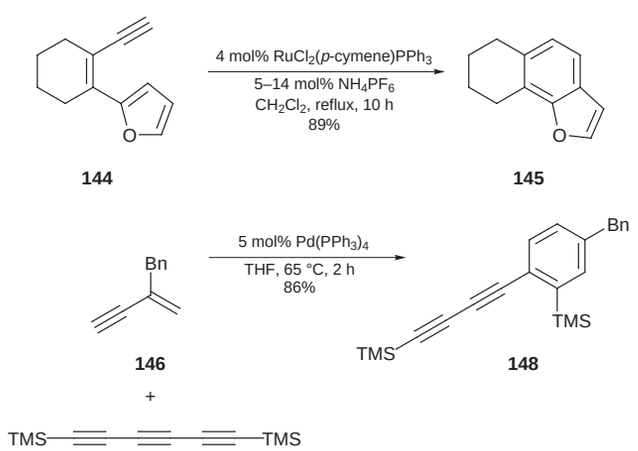
140 **141**

An example of a bis-cyclisation involving the formation of two new aryl–aryl bonds has been provided by Echavarren and co-workers.[78] The dibromide **142** is converted into the product **143** in surprisingly good yield.



142 **143**

Cyclisations of substrates containing polyene/alkyne units can lead to interesting products.[79] In some cases, new aromatic rings are formed, as illustrated by the work of Merlic and Pauly.[80] Benzofuran derivative **145** was prepared by the cyclisation of the dienylalkyne **144**. Another example of cyclisation to afford an aromatic compound has been reported by Yamamoto and co-workers.[81] For example, the palladium catalysed coupling of enyne **146** with triyne **147** affords the benzannulation product **148**.



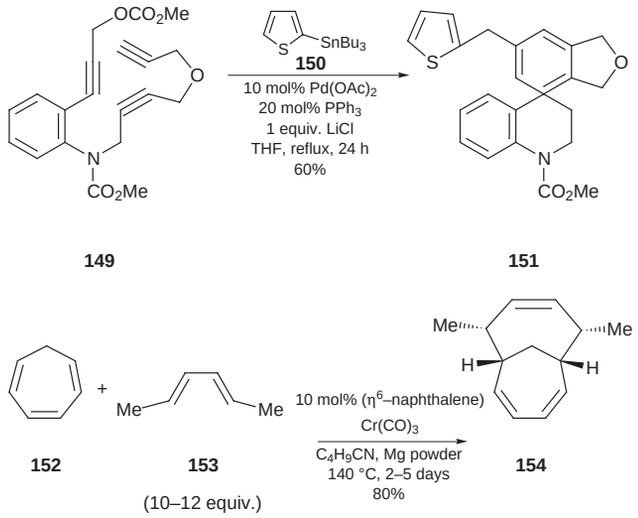
144 **145**

146 **148**

147

Grigg's research group has continued its research into queuing cascade reactions with examples of benzannulation reactions.[82] The triyne **149** is treated with stannane **150**, which under palladium catalysis affords the isobenzofuran derivative **151**.

Rigby and Fiedler have demonstrated the use of chromium(0)-catalysed [6π + 4π]-cycloaddition reactions.[83] Thus, cycloheptatriene **152** and diene **153** react stereoselectively to give the cycloaddition product **154**. The reaction is believed to proceed *via* an (η^6-cycloheptatriene) chromium tricarbonyl complex.

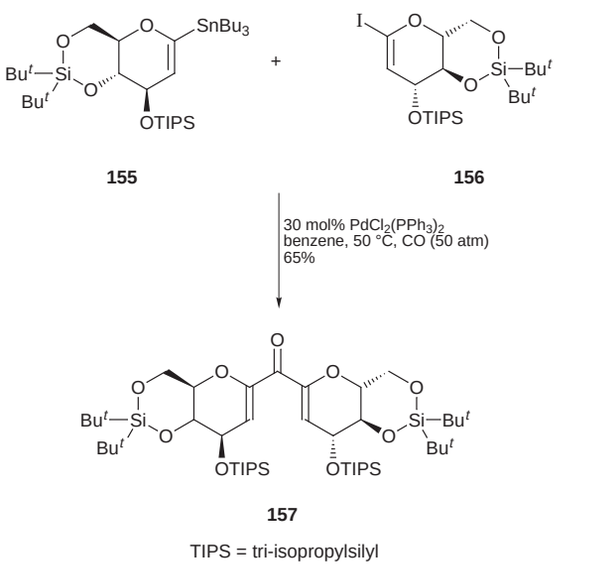


149 **151**

152 **153** (10–12 equiv.) **154**

4.8 Carbonylation and related reactions

Transition metal catalysed coupling reactions run under a pressure of carbon monoxide have the capacity to incorporate a carbonyl group into the final structure. Depending on whether the nucleophile is carbon, hydrogen or oxygen based, the product may be a ketone, aldehyde, ester or other derivative. An interesting example of a carbonylative Stille coupling has been provided by Vogel and co-workers.[84] Thus, stannane **155** and iodide **156** were coupled under CO pressure to give the ketone **157**.

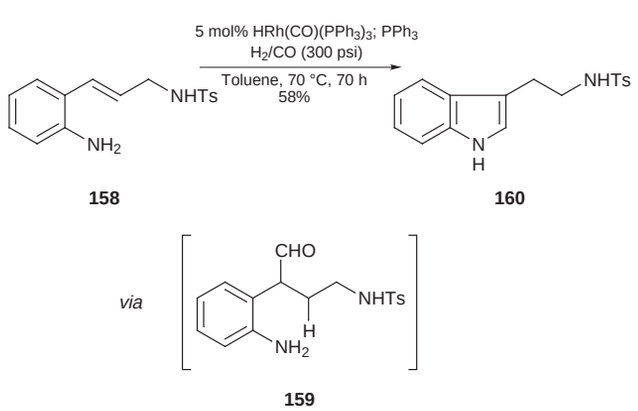


155 **156**

157

TIPS = tri-isopropylsilyl

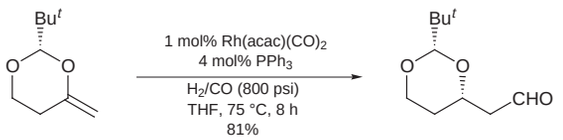
In the presence of hydrogen, carbonylation reactions can afford the hydroformylation product when an alkene is used as substrate. Dong and Busacca have used this approach in an indole synthesis.[85] The aniline derivative **158** undergoes hydroformylation, presumably to give intermediate **159**, which closes to give indole **160**.



158 **160**

159

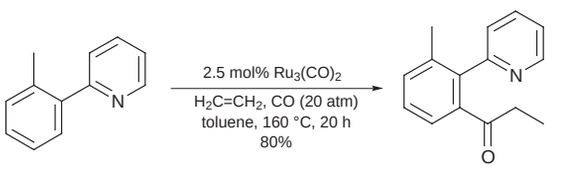
Leighton and O'Neil have investigated the diastereoselective hydroformylation of enol ethers, typified by compound **161**.[86] The product **162** is obtained with complete control of diastereoselectivity, and good control of regioselectivity (linear : branched, 12 : 1).



161 **162**

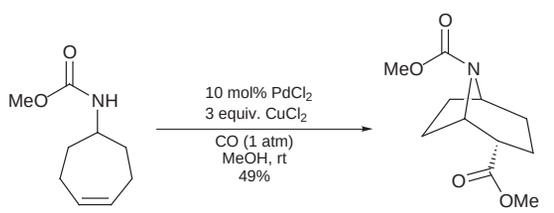
12:1 linear branched

A direct carbonylation of a benzene ring has been reported by Murai and co-workers using a ruthenium catalyst, in the presence of carbon monoxide and ethylene.[87] The pyridine group in compound **163** directs the reaction to the only remaining *ortho*-position, providing the ketone product **164**.



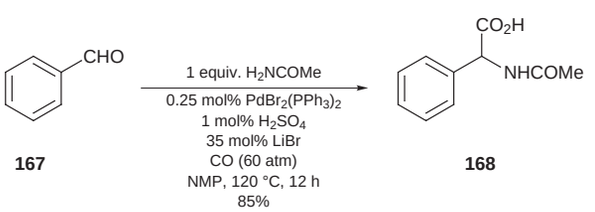
163 **164**

Carbonylation of the alkene **165**, which has a pendant carbamate group affords the cyclised product **166**, where the carbonyl group has been trapped with methanol.[88]

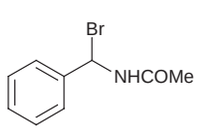


165 **166**

Beller and co-workers have described a useful procedure for the conversion of aldehydes, including benzaldehyde **167**, into racemic *N*-acetylphenylglycine **168**.[89] It is suggested that the reaction proceeds *via* carbonylation of the compound **169**, present in a pre-equilibrium under the reaction conditions.

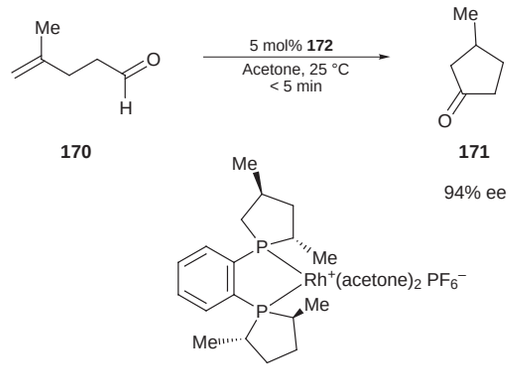


167 **168**



169

Hydroacylation reactions do not involve carbon monoxide, and are mechanistically quite distinct from carbonylation processes, but since the reaction products are ketones, these reactions are discussed here. The intramolecular hydroacylation of unsaturated aldehydes is a known process, and Bosnich and co-workers have reported an enantioselective variant.[90] The enal **170** is converted into 3-methylcyclopentanone **171** with good enantioselectivity using rhodium complex **172**.

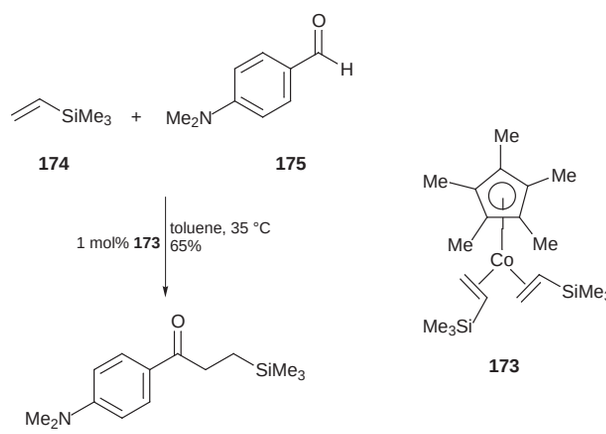


170 **171**

94% ee

172

Lenges and Brookhart have employed the cobalt complex **173** to catalyse the intermolecular hydroacylation of trimethylvinylsilane **174** by 4-dimethylaminobenzaldehyde **175**, which gives the ketone product **176**.[91] Jun and co-workers have reported rhodium catalysed intermolecular hydroacylation reactions using 2-amino-3-picoline as a co-catalyst.[92]



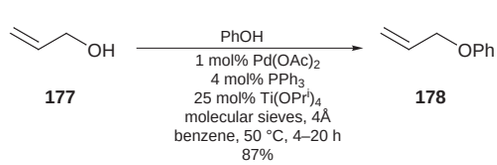
174 **175** **173**

176

4.9 Reactions involving allyl intermediates

Palladium catalysed allylic substitution reactions usually require an activated allylic substrate in order for the intermediate allylpalladium species to be formed.

Miura and co-workers have employed allyl alcohol **177** as the substrate, but in the presence of molecular sieves and sub-stoichiometric quantities of titanium tetraisopropoxide, palladium catalysed allylic substitution with phenol proceeded smoothly, to give the product **178** in 87% yield.[93]

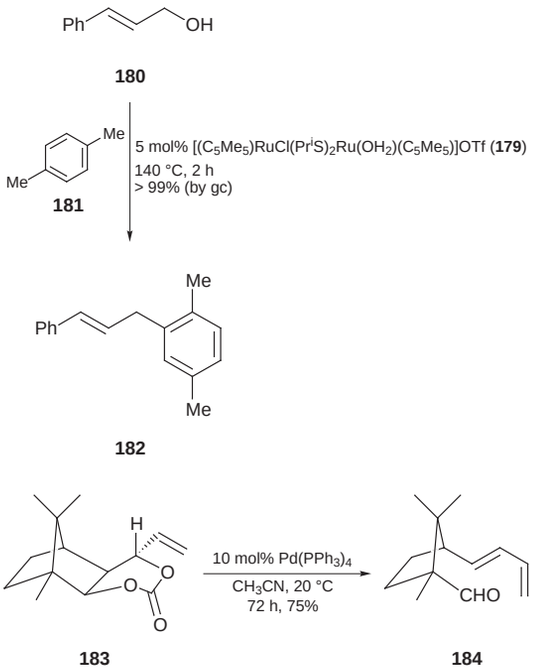


177 **178**

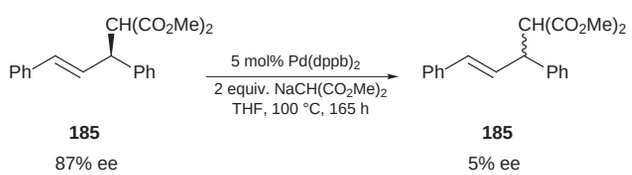
The thiolate-bridged ruthenium complex **179** acts as a catalyst for the allylation of activated arenes.[94] Treatment of cinnamyl alcohol **180** with *p*-xylene **181** as solvent affords the substitution product **182** in high conversion.

An unusual fragmentation reaction of the carbonate **183** occurs in the presence of a palladium catalyst, to afford the dienal **184**.[95] Other related examples were also reported.

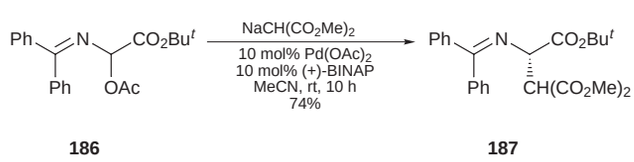
Enantioselective palladium catalysed allylic substitution reactions continue to attract attention, and several new mono-



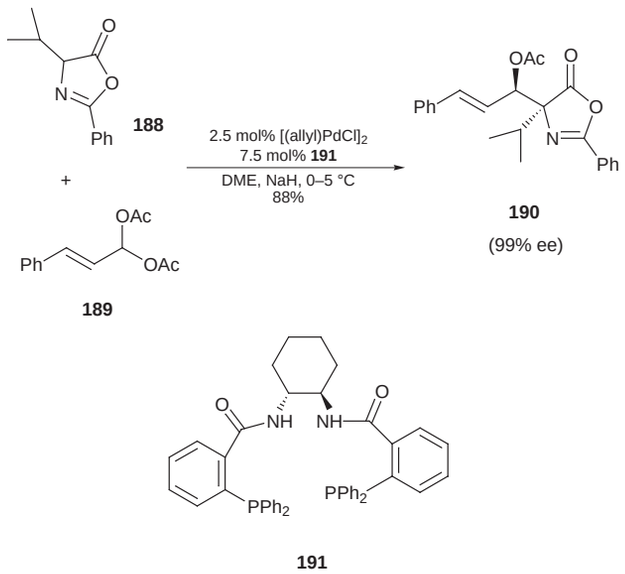
dentate ligands,[96,97,98] as well as other ligands,[99] have been reported to give high levels of enantioselectivity. Of relevance to these asymmetric reactions, is that under sufficiently harsh conditions, the product experiences racemisation (presumably by loss of the malonate as a leaving group). Mortreux and co-workers have shown that enantiomerically enriched allylic substitution product **185** undergoes racemisation.[100]



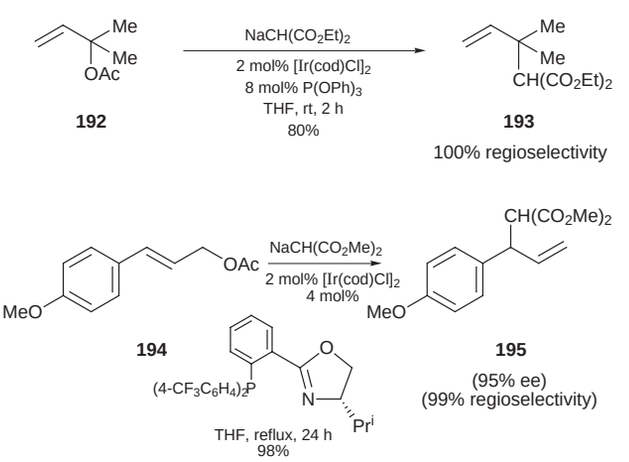
Substrate **186** is an aza-analogue of a conventional allylic acetate substrate, and O'Donnell and co-workers have demonstrated that, using an enantiomerically pure palladium catalyst, the substitution product **187** can be obtained with good enantioselectivity.[101] The azlactone **188** participates in palladium catalysed allylic substitution reactions, and Trost and Ariza have provided an enantioselective and diastereoselective example of this reaction.[102] In the best example, azlactone **188** and allylic acylal **189** react to provide the substitution product **190**, using the ligand **191** for asymmetric control. Trost and co-workers have reported similar results by β-keto esters as an alternative prochiral nucleophile.[103]



As cited above, allylic substitution reactions are not confined to palladium-catalysed examples. Kocovsky and co-workers have shown that molybdenum(II) triflate complexes catalyse allylic substitution reactions using silyl enol ethers as nucleophiles.[104] The use of nickel-based catalysts allows for the use of allyl amines as substrates in allylic substitution.[105] Furthermore, using nickel catalysts, Grignard reagents can be used as the nucleophile. Nomura and RajanBabu have reported that Grignard reagents can be used in asymmetric nickel-catalysed allylation reactions.[106]



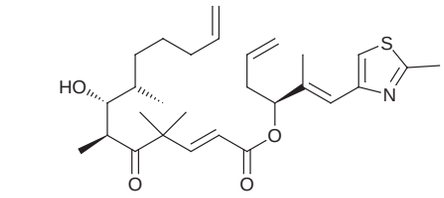
Iridium-catalysed allylic substitution reactions are emerging as a useful synthetic method. Takeuchi and Kashio have shown that allyl acetate **192** undergoes iridium-catalysed allylic substitution to give the product **193** with complete regiocontrol, where the nucleophile has attacked at the more substituted terminus of the allyl intermediate.[107] Janssen and Helmchen have developed an asymmetric variant of this reaction.[108] The best result was obtained when the allyl acetate **194** underwent allylic substitution with sodium dimethyl malonate to give the product **195** with very high enantioselectivity, yield and regioselectivity.



5 Alkene metathesis reactions

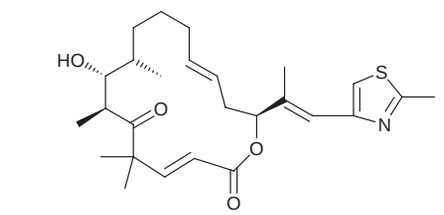
Alkene metathesis reactions, and especially ring-closing metathesis reactions have enjoyed considerable attention from chemists over the last few years.[109] Some examples of ring-closing metathesis applications in synthesis are given here, although many others have been published during the period covered by this review. Nicolaou and co-workers have used the ruthenium catalyst **196** for the conversion of the substrate **197** into the ring-closed product **198**.[110] It is noteworthy that the conjugated alkenes are not affected. Crimmins and Choy have ring-closed the functionalised diene **199** to provide the eight-membered ring compound **200**.[111] Fuchs and co-workers have used ring-closing metathesis to prepare the macrocyclic *ansa*-bridge of roseophilin.[112]

Cross-metathesis reactions can also be synthetically useful reactions, although mixed products are usually obtained. Gibson and co-workers have performed cross-metathesis reactions on homoallylglycine derivatives, including compound

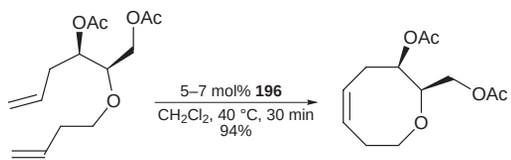


197

10 mol% **196**, CH_2Cl_2, 25 °C, 12 h, 86%

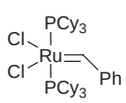


198



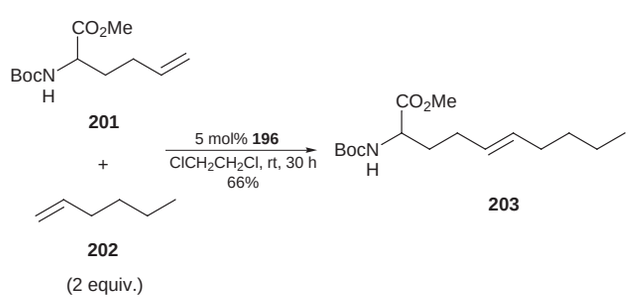
5–7 mol% **196**, CH_2Cl_2, 40 °C, 30 min, 94%

199 **200**



196

201.[113] Using hex-1-ene **202** as the metathesis partner, up to 66% yield could be obtained for the cross-metathesis product **203**. Blechert and co-workers have examined a series of cross-metathesis reactions, including the reaction of alkenes **204** and **205**, which provide the cross-metathesis product **206**.[114] The same research group has also used cross-metathesis to attach alkenes to a resin bound allylsilyl linker.[115]



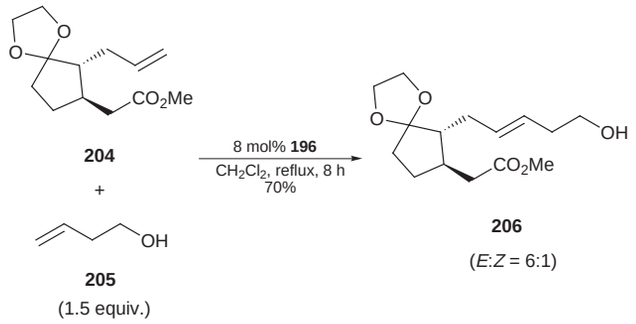
201 **202** (2 equiv.) **203**

5 mol% **196**, $ClCH_2CH_2Cl$, rt, 30 h, 66%

The combination of metathesis reactions with solid phase synthesis provides a useful method for the cleavage of substrates from resin. For example, Piscopio and co-workers have used this approach to release compound **207** from the resin-bound diene **208**.[116] Peters and Blechert have employed a slightly different concept to liberate alkenes **209** from resin-bound dienes **210**.[117]

Other advances in metathesis reactions include the demonstration, by Grubbs and co-workers, of template-directed ring-closing metathesis, using Li^+ as a template to close crown ethers.[118]

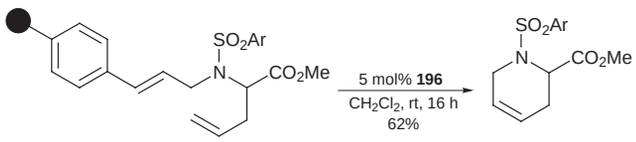
Mori and co-workers have investigated the metathesis of alkynes with ethylene.[119] For example, alkyne **211** undergoes



204 + **205** (1.5 equiv.)

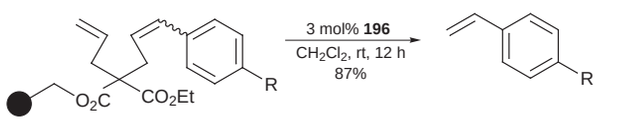
8 mol% **196**, CH_2Cl_2, reflux, 8 h, 70%

206 (*E*:*Z* = 6:1)



208 **207**

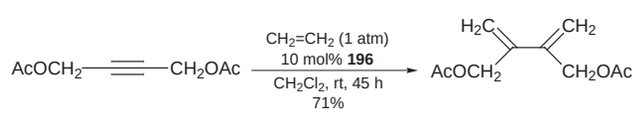
5 mol% **196**, CH_2Cl_2, rt, 16 h, 62%



210 **209**

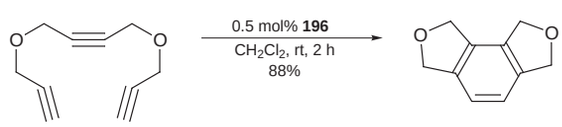
3 mol% **196**, CH_2Cl_2, rt, 12 h, 87%

metathesis with ethylene to afford the diene **212** as product. The triyne **213** undergoes a benzannulation process to give the product **214** in good yield.[120]



211 **212**

$CH_2{=}CH_2$ (1 atm), 10 mol% **196**, CH_2Cl_2, rt, 45 h, 71%



213 **214**

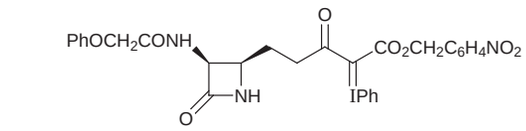
0.5 mol% **196**, CH_2Cl_2, rt, 2 h, 88%

6 Reactions involving metal carbenoids

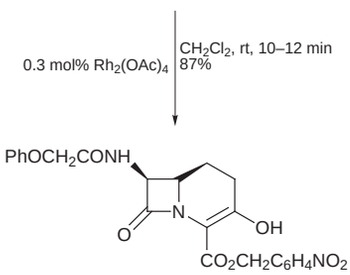
The usual precursors to metal carbenoids are organic diazo compounds. However, Vaid and Hopkins chose to use the iodonium ylide **215** as a precursor in the N–H insertion reaction to form the bicyclic product **216**.[121] Sheehan and Padwa have demonstrated a new route to 2-pyridones using a rhodium(II)-catalysed reaction of diazo compound **217** in the presence of methyl acrylate **56**.[122] The initially formed isomünchnone ring is trapped by the alkene to give intermediate **218**. Loss of $PhSO_2H$ affords the product **219**.

Asymmetric reactions involving metal carbenoids are still very popular. In most examples, an enantiomerically pure metal complex is used to provide the enantioselectivity. However, Aggarwal and co-workers have used enantiomerically pure sulfides to provide asymmetry in carbenoid reactions.[123] Cyclopropanation of enone **220** was achieved using compound **221**, sulfide **222** and a rhodium catalyst to give the product **223** with impressive enantioselectivity.

Asymmetric reactions catalysed by enantiomerically pure rhodium complexes have been reported for Si–H insertion reactions (up to 95% ee),[124] and even intermolecular C–H insertion reactions.[125] In this latter case, insertion into cyclopentane **224** with diazo-compound **225** affords the product **226** with remarkable enantiomeric excess using the rhodium catalyst



215



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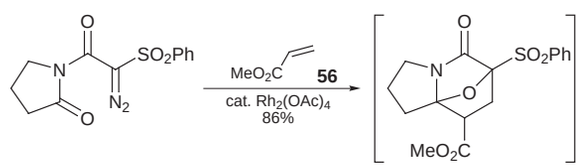
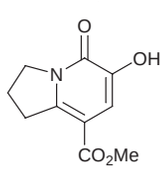
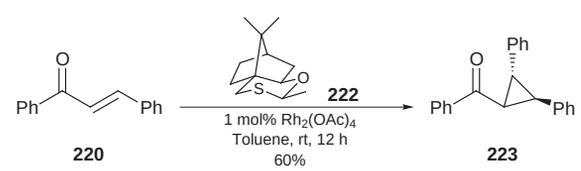


217 **218**



219



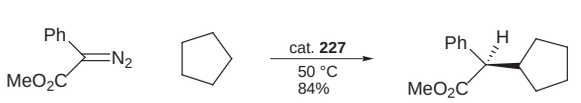
220

$PhCHN_2$

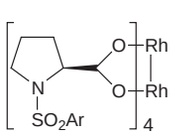
221

(syringe pump addition)

227. Enantioselective carbonyl ylide formation, followed by either cycloaddition[126] or rearrangement[127,128] has also been reported.



225 **224** (solvent) **226** (87% ee)



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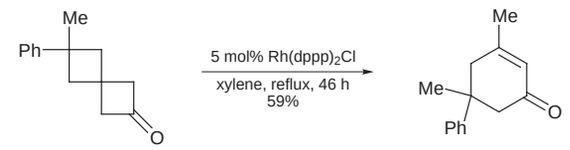
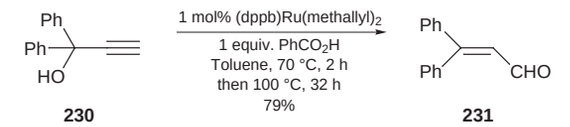
7 Isomerisations

Strained molecules have a major driving force to rearrange into more stable compounds. Transition metals are often able to catalyse such processes. For example, the spiro compound **228** undergoes an unusual rhodium-catalysed rearrangement to give the cyclohexenone **229**.[129]

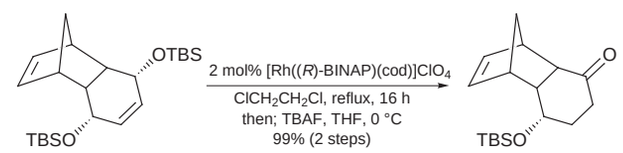
Dixneuf and co-workers have employed a ruthenium complex to catalyse the isomerisation of prop-2-ynyl alcohols, including compound **230** into the corresponding α,β-unsaturated aldehyde **231**.[130]



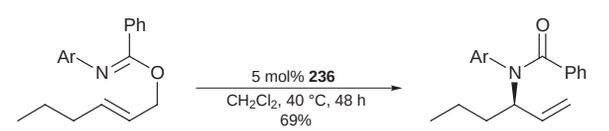
228 **229**



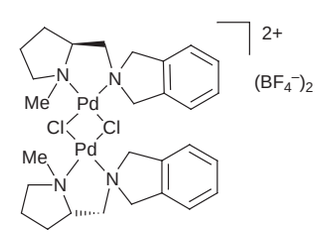
230 **231**



232 **233**



234 **235** (55% ee)



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The *meso*-compound **232** has been reported to undergo an enantioselective isomerisation to a silyl enol ether, which is immediately converted into the ketone **233**.[131]

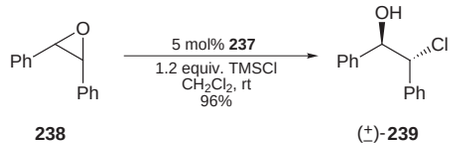
Overman and co-workers have provided the first examples of an enantioselective rearrangement of allylic imidates to allylic amides.[132,133] Imidate **234** is converted into amide **235** using the palladium catalyst **236**.

8 Miscellaneous catalysed reactions

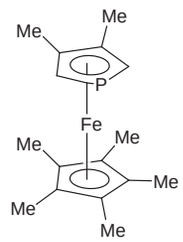
8.1 Ring-opening of epoxides

Garrett and Fu have used phosphaferrocene **237** as a catalyst for the ring-opening of epoxides, including compound **238**, with TMSCl to give the chlorohydrin product **239**.[134]

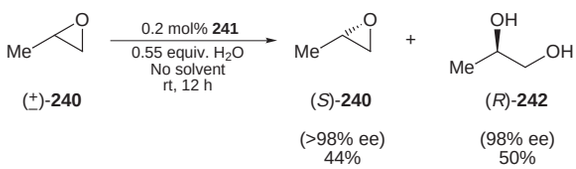
In one of the most interesting papers from 1997, Jacobsen and co-workers have reported an impressive kinetic resolution of terminal epoxides by catalytic hydrolysis.[135] Propylene oxide **240** is hydrolysed by the cobalt complex **241** to give recovered starting material and diol **242**, both with excellent yield and enantioselectivity. The reaction has also been extended to the ring-opening of epoxides by carboxylic acids.[136]



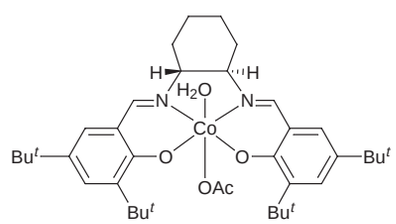
238 (±)-**239**



237



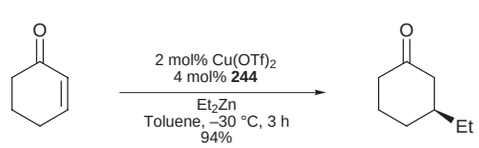
(±)-**240** (*S*)-**240** (>98% ee) 44% (*R*)-**242** (98% ee) 50%



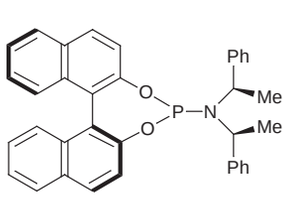
241

8.2 Conjugate addition

Feringa and co-workers have discovered a highly enantioselective copper-catalysed conjugate addition reaction.[137] Thus, cyclohexenone **243** is treated with diethylzinc, ligand **244** and a copper catalyst. The product **245** is obtained with excellent enantiomeric excess.



243 **245** (>98% ee)



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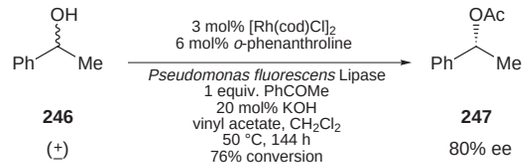
8.3 Enzyme and transition metal combinations

Enzymes and transition metals both offer selectivity in catalysed organic reactions. The combination of the two may provide further opportunities.[138] Williams and co-workers have combined an enzyme catalysed acylation reaction with a transition metal catalysed racemisation of the starting material **246**. The product **247** is therefore obtained by dynamic kinetic resolution.[139] Bäckvall and co-workers have reported an improvement on this reaction using a ruthenium catalyst.[140] Although a heterogeneous catalyst is employed, Reetz and

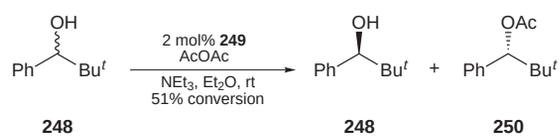


246 (±) **247** 80% ee

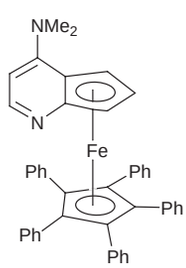
Schimossek have reported a related amine acylation reaction using a combination of enzyme with palladium on carbon.[141]

8.4 Kinetic resolution of alcohols

Kinetic resolution of alcohols by non-enzymatic methods has been achieved with previously ummatched selectivities by Fu and co-workers.[142] In the best case, racemic alcohol **248** undergoes acetylation catalysed by ferrocene derivative **249** to give the ester **250** and unreacted alcohol with good enantioselectivity.



248 **248** (92.2% ee) **250**



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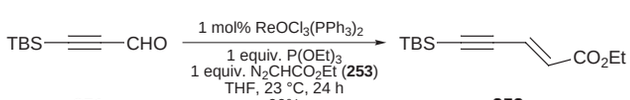
8.5 Catalytic synthesis of alkenes

Ledford and Carreira have demonstrated an unusual alternative to the Wadsworth–Horner–Emmons reaction.[143] The aldehyde **251** is converted into the enoate ester **252** on treatment with ethyl diazoacetate **253** and a rhenium catalyst. Several examples were given with *E*:*Z* selectivities ranging from 3:1 to 20:1.



251 **252** (*E*:*Z*, 7:1)

Acknowledgements

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