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## 1 Introduction

This review covers the literature describing homogeneous transition metal catalysed reactions published during 1998.

Less than one tenth of the relevant published material is covered, and the authors have endeavoured to identify important new transition metal catalysed reactions. The application of known transition metal catalysed processes to noteworthy substrates is also described.

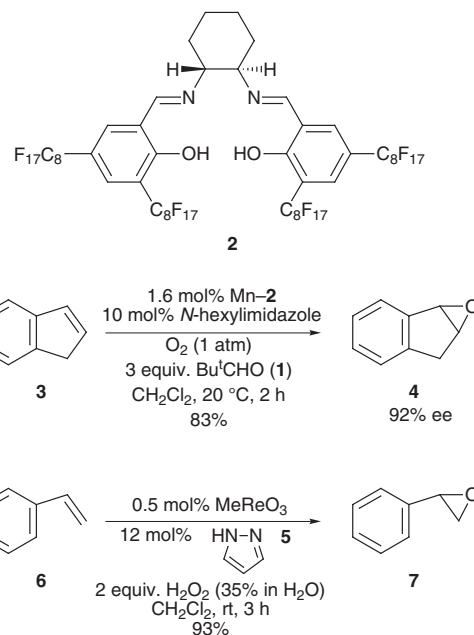
## 2 Oxidation reactions

### 2.1 Oxidation of alkenes

The epoxidation, dihydroxylation and aminohydroxylation reactions of alkenes, especially their asymmetric variants, continue to attract considerable attention. The basic principles were covered in the previous review.<sup>1</sup>

The use of fluoruous solvents has now been demonstrated for many transition metal catalysed reactions. One advantage that they offer for catalytic epoxidation is the fact that molecular oxygen has a high solubility in fluoruous solvents. The combination of O<sub>2</sub> with pivalaldehyde **1** and manganese catalysts has been shown to be effective for epoxidation of alkenes in a racemic<sup>2</sup> and enantioselective<sup>3</sup> sense. The fluoruous soluble ligand **2** afforded a manganese complex which was insoluble in common organic solvents, but soluble in the fluoruous phase. Indene **3** was converted into indene oxide **4** with high enantioselectivity, although other substrates afforded low selectivity (Scheme 1). The fluoruous phase, containing the active catalyst, could be recycled.

Manganese salen complexes have also now been successfully immobilised within polymer supports, and still provide high enantioselectivity.<sup>4</sup>



Scheme 1

Whilst the enantiomerically pure manganese salen complexes are still often the most enantioselective available for epoxidation of unfunctionalised alkenes, alternative systems are often reported. For example, End and Pfaltz have used ruthenium bis(oxazoline) complexes to provide up to 69% ee in the epoxidation of stilbene.<sup>5</sup>

The use of methyltrioxorhenium as a catalyst for epoxidation continues to attract attention. Herrmann and co-workers have shown that a combination of methyltrioxorhenium with pyrazole **5** affords a highly efficient catalyst for the epoxidation of alkenes.<sup>6</sup> Styrene **6** was converted cleanly into styrene oxide **7** with this catalytic combination.

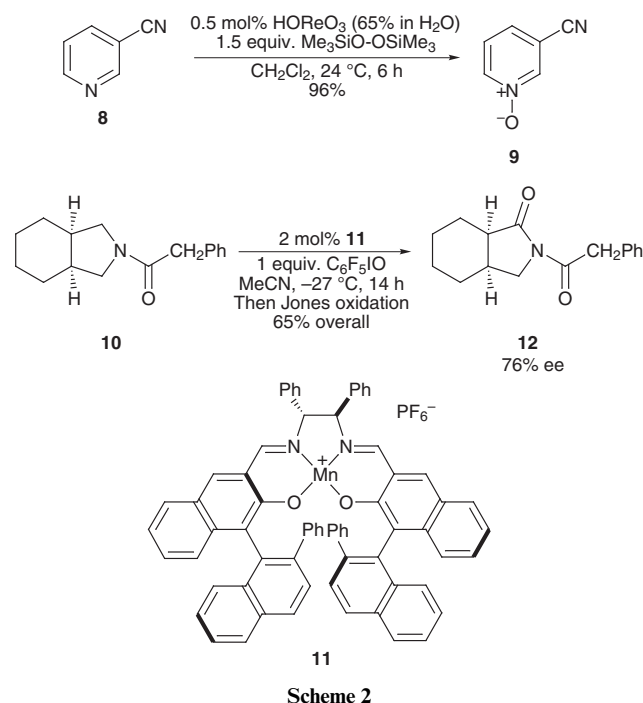
### 2.2 Other oxidation reactions

Various rhenium complexes have been used by Sharpless and co-workers to catalyse the oxidation of pyridines.<sup>7</sup> For example, pyridine 3-carbonitrile **8** was one of many pyridines converted into its corresponding *N*-oxide **9** (Scheme 2).

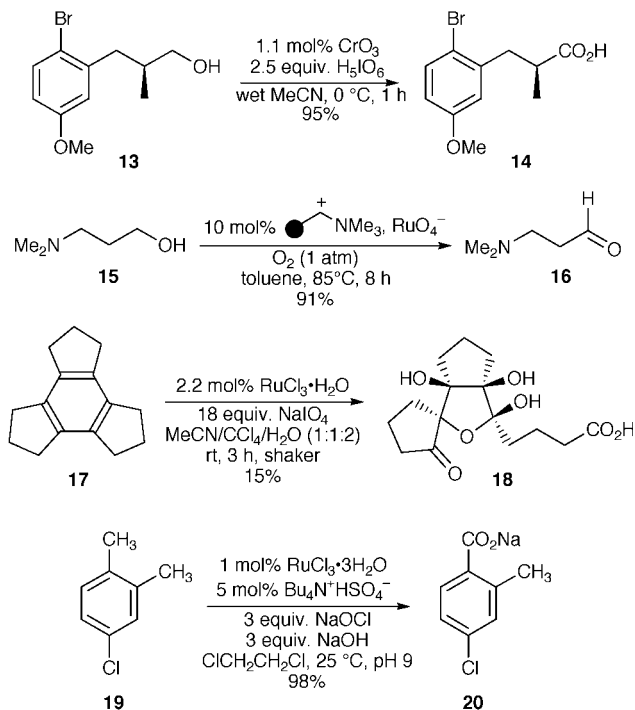
The direct catalytic asymmetric oxidation of hydrocarbons would be an incredible achievement. So far, the oxidation of C–H bonds with nearby functional groups can be accomplished with good enantioselectivity. Very often the yields of such reactions are low,<sup>8</sup> but improvements are steadily being made.

Katsuki and co-workers have oxidised the *meso*-pyrrolidine derivative **10** into a 2-hydroxy compound using the enantiomerically pure salen complex **11** which is oxidised up to the lactam **12** before isolation.<sup>9</sup> In other examples, the yields and enantioselectivities tended to be somewhat lower.

The selective oxidation of alcohols to either aldehydes or carboxylic acids can be achieved using various catalytic



strategies. The use of stoichiometric chromium trioxide as an oxidant (Jones oxidation) is a classic way to oxidise alcohols. Zhao and co-workers have shown how the reaction can be achieved using catalytic chromium trioxide. Thus, the primary alcohol **13** is oxidised into the carboxylic acid **14** using 2.5 equivalents of the stoichiometric oxidant, periodic acid (Scheme 3).<sup>10</sup>



Polymer-supported perruthenate has been reported to catalyse the oxidation of alcohols into aldehydes.<sup>11</sup> The amino alcohol **15** was converted into the amino aldehyde **16** in good yield using molecular oxygen as the oxidant. Work-up involves simple filtration to remove the polymer-supported reagent. Other catalytic strategies using molecular oxygen as the terminal oxidant have also been recently reported.<sup>12,13</sup> Ruthenium catalysts are usually associated with the oxidation of aromatic

groups into carboxylic acids, when used in conjunction with sodium periodate. An extraordinary example of ruthenium catalysed oxidation has been reported for the conversion of trindane **17** into the highly oxygenated product **18**.<sup>14</sup> The product identity was confirmed by X-ray crystallography.

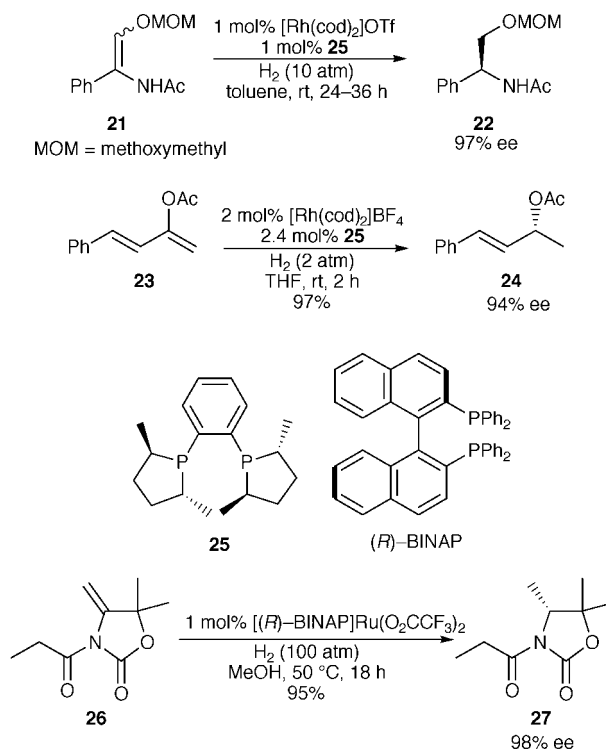
Ruthenium catalysts have also been used in the conversion of methylbenzenes into benzoic acids. In fact, with a phase transfer catalyst, an unusual selective oxidation takes place in the conversion of xylene **19** into the sodium benzoate **20**.<sup>15</sup> As soon as the oxidation has taken place, transport into the aqueous phase prevents over-oxidation.

The Baeyer–Villiger oxidation of ketones into esters using transition metal catalysed reactions has been reviewed by Strukul, one of the leaders in the field.<sup>16</sup>

### 3 Reduction reactions

The reduction of various functional groups can often be achieved using transition metal catalysts and a suitable reducing agent: often molecular hydrogen, silanes, boranes or hydrides. Amongst all of the possibilities, metal-catalysed hydrogenation has been the most widely studied, especially as an asymmetric process.

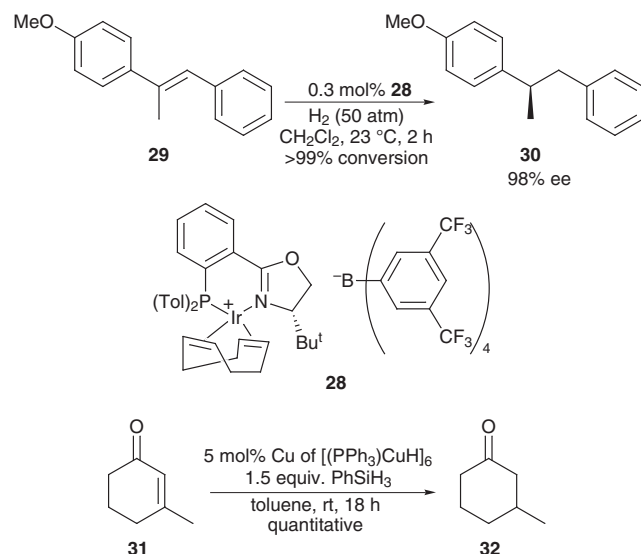
Some recently reported examples of rhodium-catalysed asymmetric hydrogenation of alkenes include the conversion of the enamide **21** into the derivatised amino alcohols **22**,<sup>17</sup> and the regioselective hydrogenation of dienyl acetate **23** into the allyl acetate **24**,<sup>18</sup> both using the Me-DuPhos ligand **25** (Scheme 4). Reports of new ligands for asymmetric hydrogenation of alkenes continue to appear, often providing highly selective examples.<sup>19,20</sup>



Ruthenium catalysed hydrogenation of alkenes is also popular,<sup>21</sup> and an interesting example has been provided by Bruneau, Dixneuf and co-workers.<sup>22</sup> The achiral substrate **26** is hydrogenated with an enantiomerically pure ruthenium complex into compound **27**, which behaves as propionic acid attached to a chiral auxiliary. The achiral auxiliary in the substrate is converted into an enantiomerically enriched one prior to a subsequent auxiliary controlled functionalisation.

Whilst most homogenous catalytic hydrogenation reactions

rely on either rhodium- or ruthenium-based complexes, Pfaltz and co-workers have shown that suitable iridium complexes are able to catalyse enantioselective hydrogenation reactions.<sup>23</sup> Thus complex **28** was used as an analogue of Crabtree's catalyst, in the asymmetric hydrogenation of alkene **29** with up to 98% ee in the best example (Scheme 5).



Scheme 5

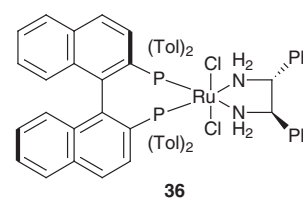
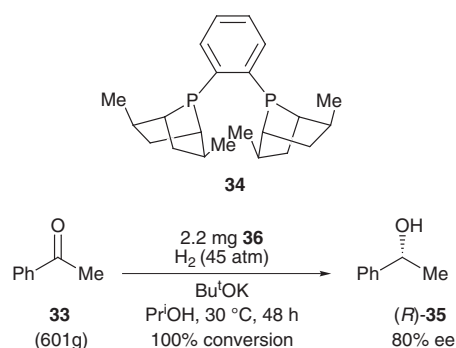
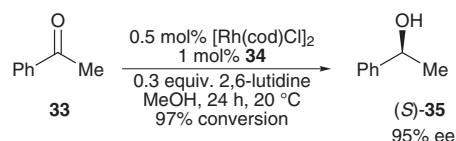
The conjugate reduction of enones can be achieved using Stryker's reagent,  $[(Ph_3P)CuH]_6$ . Usually the reagent is either used in stoichiometric amounts, or as a catalyst under a high pressure of hydrogen. However, Lipshutz and co-workers have published results showing how either  $Bu_3SnH$  or  $PhSiH_3$  can be used as the stoichiometric reductant in catalysed conjugate reduction reactions with Stryker's reagents.<sup>24</sup>

In a typical example, 3-methylcyclohex-2-enone **31** is reduced to the product **32** with quantitative conversion using phenylsilane as the reductant.

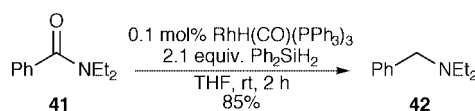
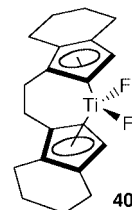
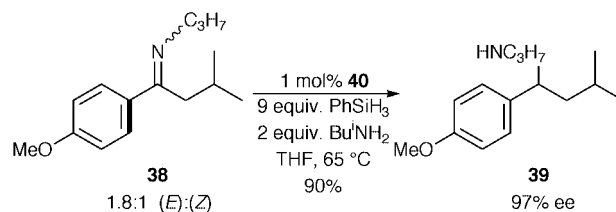
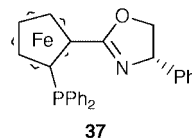
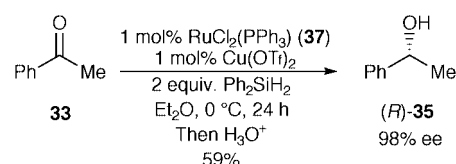
The catalysed hydrogenation of ketones into alcohols is usually achieved with ruthenium catalysts. New ligands for the asymmetric variant generally use ketones which contain neighbouring donor groups in order to obtain high selectivity.<sup>25</sup> Nevertheless, the direct hydrogenation of the simple ketone **33** has recently been achieved with a rhodium catalyst and the PennPhos ligand **34** (Scheme 6).<sup>26</sup> This is an important breakthrough in the asymmetric hydrogenation of simple ketones, and further developments in this area are likely to be useful.

As well as direct hydrogenation, transition metal catalysed transfer hydrogenation reductions of ketones, often with ruthenium complexes, have been of growing interest.<sup>27</sup> Noyori and co-workers have reported a highly selective, highly reactive catalytic system for the hydrogenation of ketones.<sup>28</sup> The reactions appear to have attributes of both direct hydrogenation and transfer hydrogenation. In one especially impressive example, acetophenone **33** was converted into phenethyl alcohol **35** with a turnover number in excess of two million and with good enantioselectivity, using catalyst **36**. The enantioselectivity provided by similar catalysts reached 99% ee, still with a turnover number of 100,000.

Advances have been made in the asymmetric reduction of ketones and imines by hydrosilylation. Uemura and co-workers have employed ferrocenyl phosphinoxazoline ligand **37** to achieve asymmetric ruthenium catalysed hydrosilylation of ketones and imines.<sup>29</sup> In fact, these ligands provide the highest selectivities for ruthenium-catalysed hydrosilylation reactions, as shown by the hydrosilylation of acetophenone **33**, which after acidic hydrolysis affords the alcohol **35** (Scheme 7). The catalyst has also been used in the hydrosilylation of cyclic imines with good selectivities.



Scheme 6



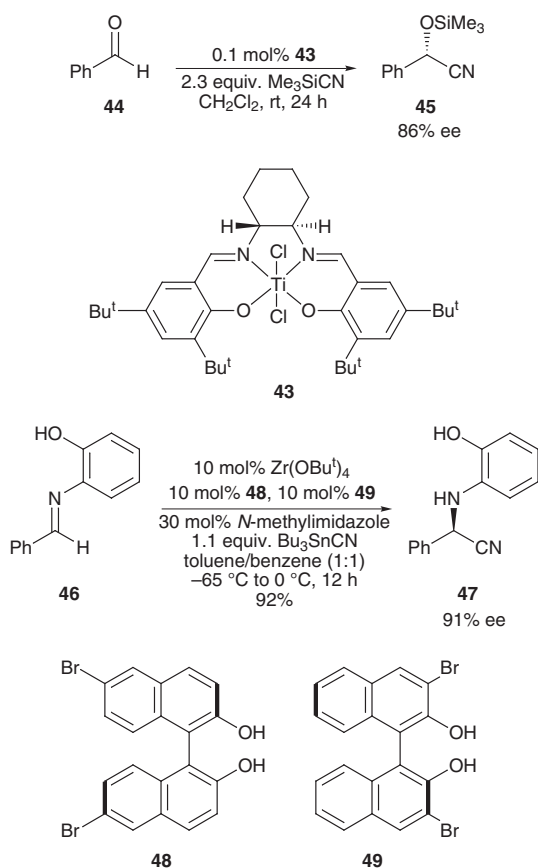
Scheme 7

Buchwald and co-workers have further developed the titanium-catalysed hydrosilylation of imines.<sup>30</sup> The addition of a primary amine expands the scope of the reaction. Of particular note is the fact that the imine geometry does not need to be high in order to achieve high enantioselectivity. Thus imine **38** is converted into product **39** using the titanocene catalyst **40**, which is pre-activated by reaction with silane and piperidine in methanol (Scheme 7).

The hydrosilylation of amides with rhodium complexes provides a method for reduction to amines.<sup>31</sup> For example, amide **41** is reduced to the amine **42** under mild conditions. Under these reaction conditions, amides could be reduced in the presence of esters and epoxides.

#### 4 Lewis acid catalysed reactions

Lewis acids are able to catalyse a wide range of reactions. The addition of cyanide to aldehydes is one such reaction and has been studied by many groups. Recently, North, Belokon and co-workers have used a titanium (salen) complex **43** to catalyse the addition of trimethylsilylcyanide to benzaldehyde **44** with low catalyst loadings.<sup>32</sup> Less work has been reported on the enantioselective addition of cyanide to imines, although it provides a useful route to  $\alpha$ -amino acids (Strecker synthesis). However, there have been several reports of the enantioselective variant of this reaction by aluminium catalysts,<sup>33</sup> non-metallic catalysts,<sup>34</sup> and with the zirconium catalysts, reported here. The imine **46** is converted into the  $\alpha$ -aminonitrile **47** with good yield and enantioselectivity (Scheme 8).<sup>35</sup>

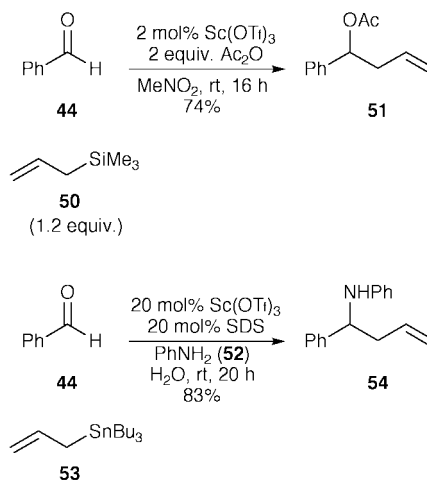


Scheme 8

Scandium triflate is a good catalyst for the allylation of aldehydes with allylsilanes and stannanes. Aggarwal and Vennal have detailed the allylation of aldehydes followed by *in situ* acylation.<sup>36</sup> Benzaldehyde **44**, allylsilane **50** and acetic anhydride undergo coupling to provide the homoallylic acetate **51** with scandium triflate as the catalyst (Scheme 9).

Kobayashi and co-workers have shown that a three component system comprising of benzaldehyde **44**, an amine, such as aniline **52** and allylstannane **53** affords the homoallylic amine **54**.<sup>37</sup> The reaction works more quickly in the presence of sodium dodecylsulfate SDS, which provides a micellar system.

The allylation of isolated imines with enantiomerically pure palladium complexes has been achieved with up to 82% enantiomeric excess.<sup>38</sup>

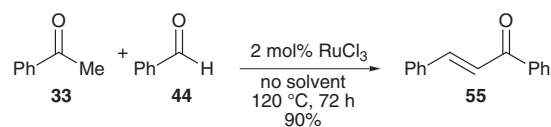


Scheme 9

Throughout the 1990's, developments have taken place with the catalytic aldol reaction.<sup>39</sup> Recently, Kobayashi and Nagayama have employed scandium triflate based micro-encapsulated Lewis acids as a new type of polymer-supported Lewis acid, which have been used to catalyse aldol reactions and other reactions.<sup>40</sup> Platinum complexes have been used as unusual Lewis acids in asymmetric catalytic aldol reactions,<sup>41</sup> whilst palladium complexes have been used to catalyse the addition of silyl enol ethers to activated imines.<sup>42</sup>

Ruthenium trichloride catalyses the cross aldol reaction between ketones and aromatic aldehydes, without the need for activation of the ketone by prior enolate/enol ether formation.<sup>43</sup> Acetophenone **33** reacts with benzaldehyde **44** to give chalcone **55** in good yield (Scheme 10).

In an impressive example of an asymmetric catalytic reaction, Evans and co-workers have achieved a highly enantioselective glyoxylate-ene reaction.<sup>44</sup> In a typical reaction, alkene **56** reacts with ethyl glyoxylate **57** to give  $\alpha$ -hydroxyester **58**, catalysed by the copper bis(oxazoline) complex **59**.



Scheme 10

The ring-opening of epoxides by transition metal catalysts has been further developed by Jacobsen and co-workers. The ring-opening of epichlorohydrin **60** with water is catalysed by the cobalt complex **61**.<sup>45</sup> A remarkable kinetic resolution is achieved where both the recovered starting material and diol **62** are obtained in very high enantioselectivity (Scheme 11).

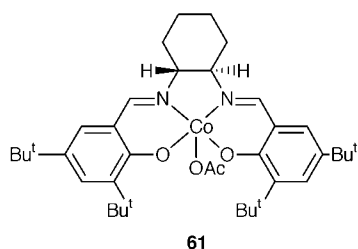
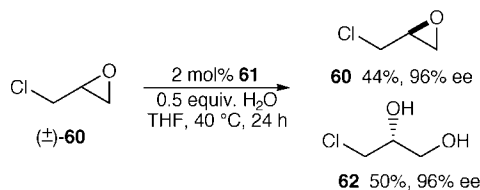
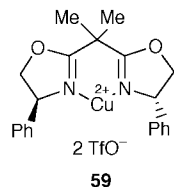
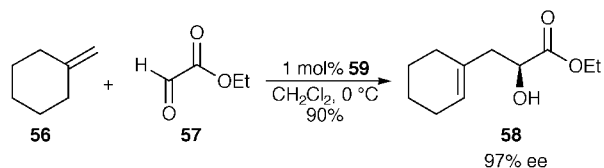
The use of bifunctional nucleophiles<sup>46</sup> and dimeric salen complexes<sup>47</sup> has also provided some advantages. Chromium salen complexes have also been employed for ring-opening epoxides with azide.<sup>48</sup>

#### 5 Catalytic coupling reactions

The formation of C–C bonds, as well as C–X bonds can be catalysed by many transition metals, although palladium complexes seem to have a greater scope than other metals. The use of catalytic coupling reactions to provide biaryls has recently been reviewed.<sup>49</sup>

##### 5.1 Suzuki reactions

The Suzuki reaction is a popular coupling reaction, using boronic acids as the "nucleophilic" component. Examples of the Suzuki reaction in synthetic sequences include the conver-



Scheme 11

sion of the enantiomerically enriched cyclopropyl boronic acid **63** into the coupled product **64**.<sup>50</sup>

Conversion of the enol ether **65** into an intermediate alkyl borane **66** allowed a subsequent Suzuki reaction with enol triflate **67** to give the densely functionalised product **68**, useful in the preparation of fused polyethers (Scheme 12).<sup>51</sup>

White and co-workers have used the Suzuki coupling for the macrocyclisation of compound **69** into the rutamycin B precursor **70**.<sup>52</sup>

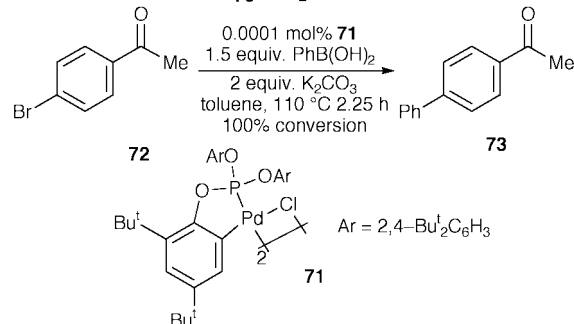
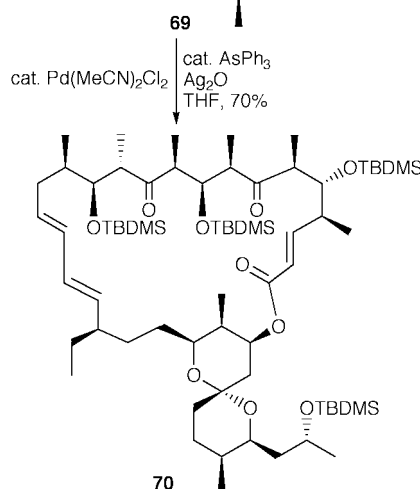
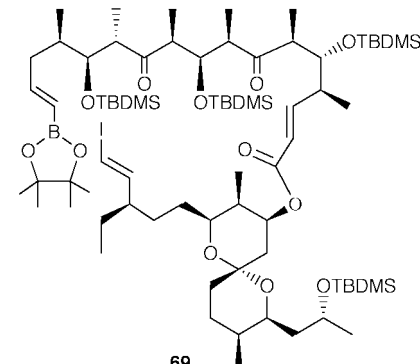
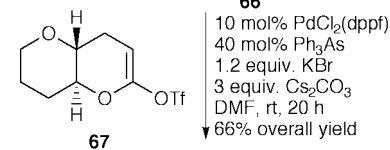
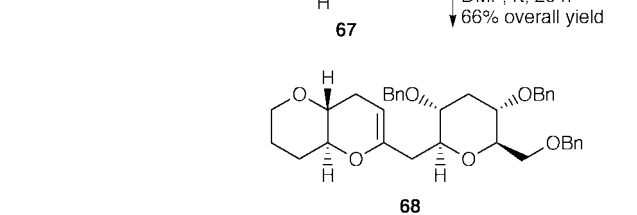
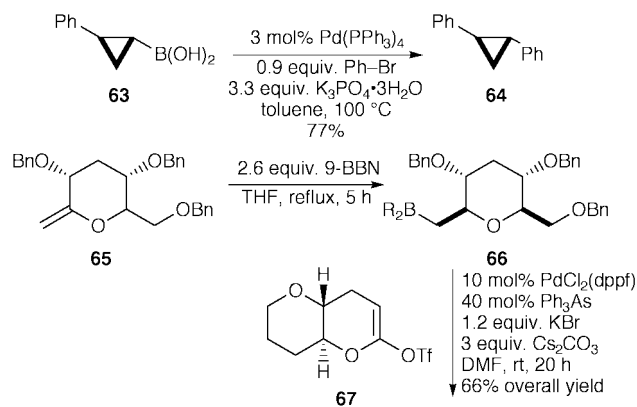
Both the Suzuki coupling and the related Stille coupling benefit from the use of orthopalladated triaryl phosphite complexes **71**, allowing turnover numbers of up to one million.<sup>53</sup> This was shown for the conversion of 4-bromoacetophenone **72** into the coupled product **73** (Scheme 12).

## 5.2 Stille coupling

Each year there are many examples of the Stille coupling in synthesis. Of the many possible examples,<sup>54</sup> the coupling of stannane **74** with vinyl iodide **75** without the use of protecting groups, really shows the synthetic utility of the Stille coupling reaction.<sup>55</sup> A variety of epothilone E analogues was prepared using this strategy.

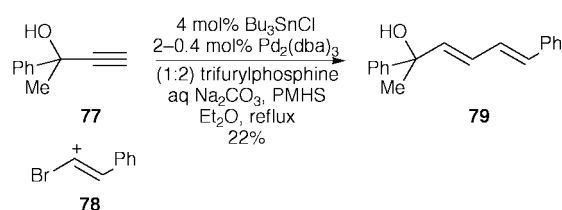
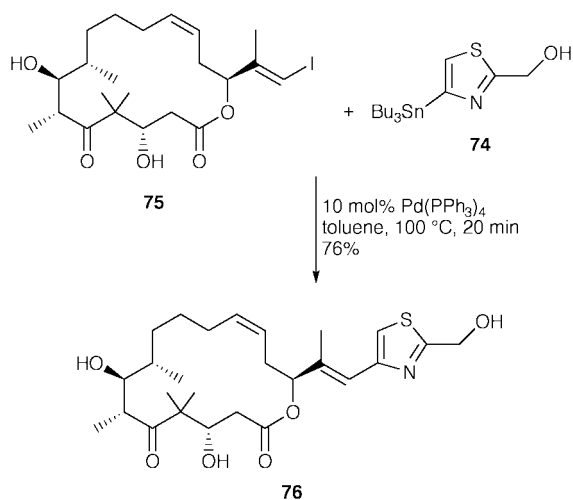
The coupling of stannanes with suitable electrophiles can also be achieved using platinum catalysts<sup>56</sup> or copper catalysts.<sup>57,58</sup>

Maleczka and Terstiege have shown how the Stille reaction can be achieved using *catalytic* amounts of tin.<sup>59</sup> The reaction between alkyne **77** and  $\beta$ -bromostyrene **78** affords the diene **79** under the reaction conditions which employ 4 mol% of  $\text{Bu}_3\text{-SnCl}$  (Scheme 13). The polymethylhydrosiloxane (PMHS) reduces the tin chloride to tin hydride which then adds across the alkyne to provide a vinyl tin species which undergoes the coupling reaction. The tin by-product is recycled to tin hydride, hence allowing the “catalytic-in-tin” conditions. So far, only five turnovers in tin have been achieved, but further development seems likely.

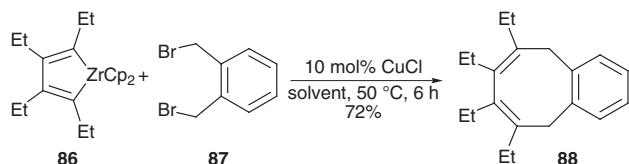
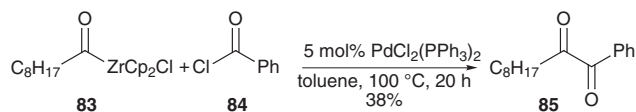
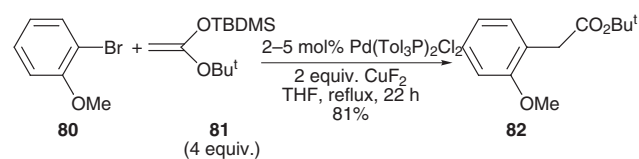


Scheme 12

Agnelli and Sulikowski have published a useful procedure for coupling aryl bromides with enolates.<sup>60</sup> In a typical example, *o*-bromoanisole **80** is coupled with the silylketene acetal **81** to give the product **82** (Scheme 14). The reaction is performed in the presence of cupric fluoride, which provides an *in situ*



Scheme 13



Scheme 14

preparation of the copper(II) enolate. The reaction also works well with electron deficient aryl bromides.

### 5.3 Other C–C coupling reactions

Less conventional catalysts and organometallic coupling partners can be used in coupling reactions. Knochel, Cahiez and co-workers have employed cobalt catalysts to couple organozinc and Grignard reagents with vinyl halides.<sup>61,62</sup> There have also been several reports of the coupling reactions of organometallic reagents based on zirconium.<sup>63</sup> For example, the acylzirconium reagent **83**, which is an “unmasked” acyl anion undergoes palladium catalysed coupling reactions to provide diketones such as compound **85** in moderate yield.<sup>64</sup> Higher isolated yields were observed using allyl halides and related substrates as the electrophilic coupling partner.

Even zirconacyclopentadienes have been used in coupling reactions.<sup>65</sup> Thus the zirconium reagent **86** has been coupled with the dibromide **87** using a copper catalyst to give the eight-membered ring derivative **88** (Scheme 14). Higher yields could be achieved using two equivalents of copper chloride.

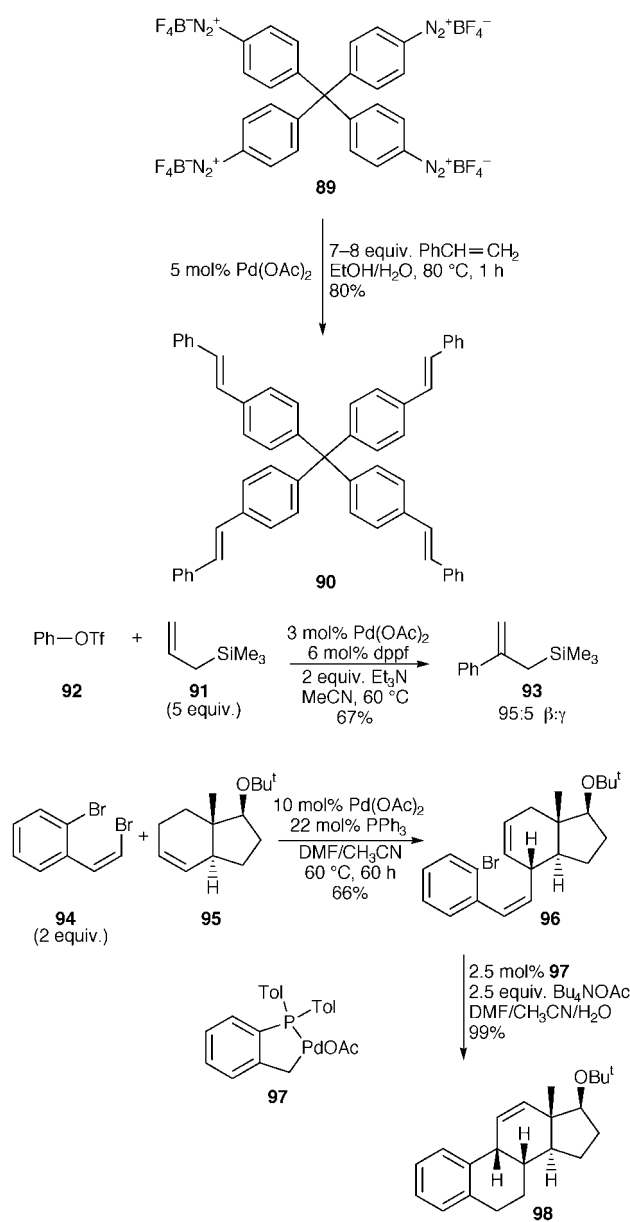
### 5.4 Heck reactions

The Heck reaction is another established favourite amongst transition metal catalysed coupling reactions.

An interesting fourfold Heck reaction of the tetrakis-(diazonium) salt **89** affords the tetravinylated product **90** in good yield.<sup>66</sup>

The Heck arylation of allyltrimethylsilane **91** occurs with very high regioselectivity to afford products where internal arylation has taken place.<sup>67</sup> The regioselectivity is attributed to stabilisation of the electron-deficient centre that develops β- to the silicon atom during the reaction. The coupling reaction with phenyl triflate **92** provides the product **93** with 95/5 selectivity.

The synthetic power of the Heck coupling reaction is demonstrated well by Tietze and co-workers in the conversion of vinyl bromide **94** and alkene **95** into the diene **96**, followed by a second intramolecular Heck reaction using catalyst **97** to give the estrone precursor **98** (Scheme 15).<sup>68</sup>



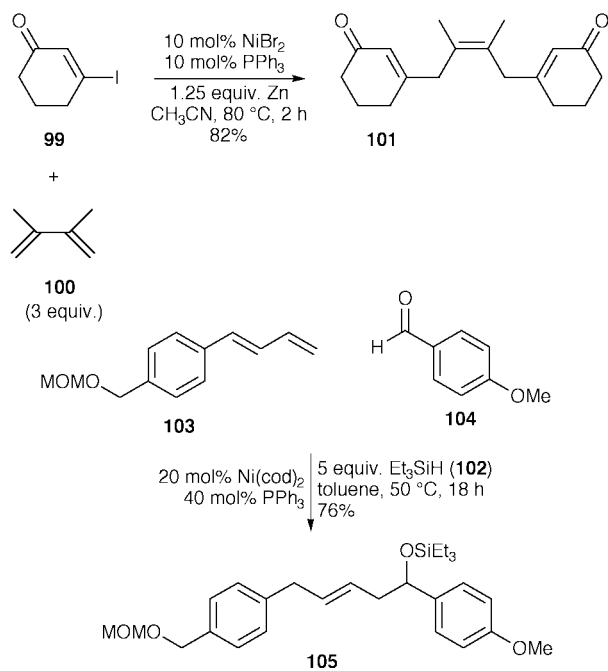
Scheme 15

Two interesting nickel catalysed reactions of dienes, which have no formal connection to the Heck reaction, show interesting synthetic potential.

Firstly, a dialkenylation reaction of 1,3-dienes has been reported by Cheng and co-workers.<sup>69</sup> For example the β-iodo-

enone **99** undergoes a bis-coupling reaction with diene **100** to provide the triene **101** in good yield. The reaction proceeds *via* formation of an alkenyl zinc iodide reagent from the iodide.

Secondly, Mori and co-workers have shown that the nickel-catalysed coupling of dienes with aldehydes in the presence of triethylsilane **102** affords silyl-protected homoallylic alcohols as products.<sup>70</sup> Using this methodology, the diene **103** and aldehyde **104** afford the alkene **105** in good yield with complete control of alkene geometry (Scheme 16).



Scheme 16

## 5.5 Heteroatom coupling reactions

The transition metal catalysed amination of aryl halides continues to be an area of active interest and has been reviewed.<sup>71,72</sup>

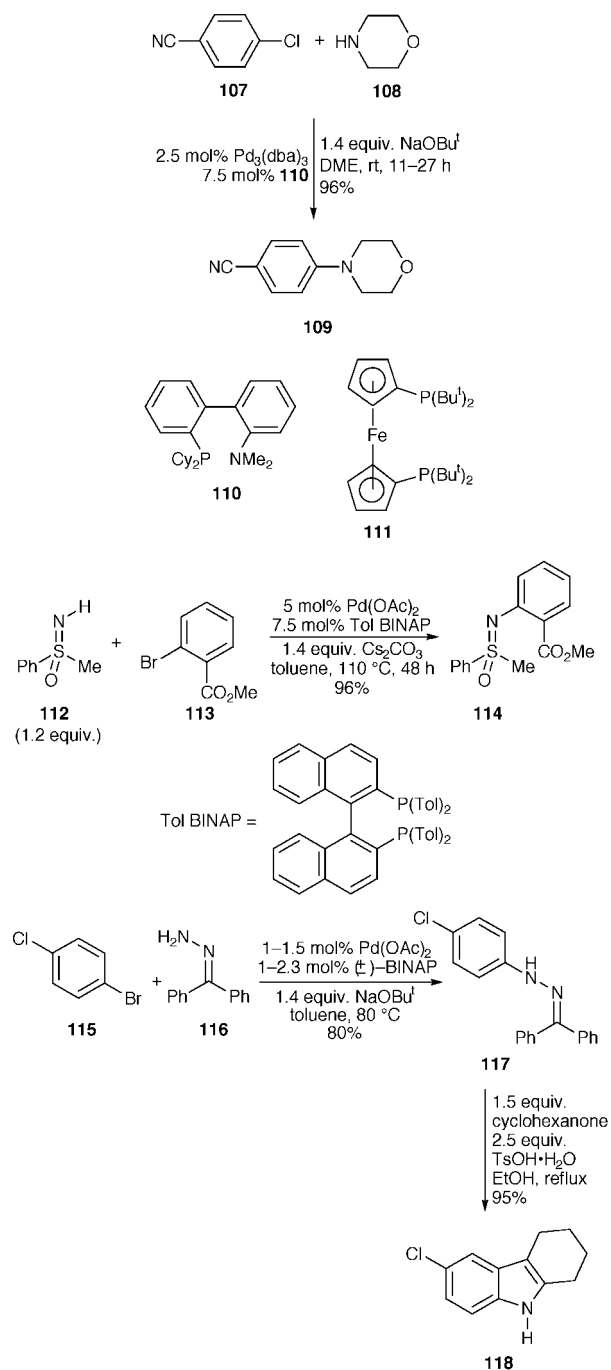
One of the challenges in these reactions has been to find particularly mild conditions for the amination reaction, especially for less reactive substrates such as aryl chlorides. To this end, Buchwald and co-workers have reported that ligand **110** provides an especially active catalytic system.<sup>73</sup> Using an activated aryl chloride **107**, the coupling with morpholine **108** was achieved using a palladium catalyst with ligand **110**. Hamann and Hartwig have used sterically hindered chelating alkylphosphines for amination reactions, including ligand **111**, which provide good rate accelerations in amination reactions.<sup>74</sup>

The amination of aryl chlorides can also be achieved catalytically using nickel–bipyridine complexes.<sup>75</sup> Aryl amination procedures have been employed by Bolm and Hildebrand in the preparation of *N*-arylated sulfoximines.<sup>76</sup> For example, the sulfoximine **112** is coupled to the aryl bromide **113** in excellent yield, using a palladium–TolBINAP catalyst.

Hydrazones have been used as the nitrogen source in an interesting variant of the Fischer indole synthesis.<sup>77</sup> Aryl bromide **115** can be coupled with benzophenone hydrazone **116** under standard conditions to give the *N*-aryl hydrazone **117**. Exchange with an enolisable ketone allowed entry into the Fischer indole synthesis to provide, in this case, indole **118** (Scheme 17).

Heteroatom coupling is not restricted to the use of nitrogen nucleophiles. Thiols can be coupled with aryl triflates to provide a synthesis of aryl sulfides.<sup>78</sup> Under optimised conditions, phenyl triflate **92** and butylthiol **119** are coupled using a palladium catalyst to provide the aryl sulfide **120** (Scheme 18).

Diaryl sulfides have also been prepared by palladium catalysed coupling reactions of aryl halides with aryl thiols.<sup>79</sup>



Scheme 17

Scheme 18

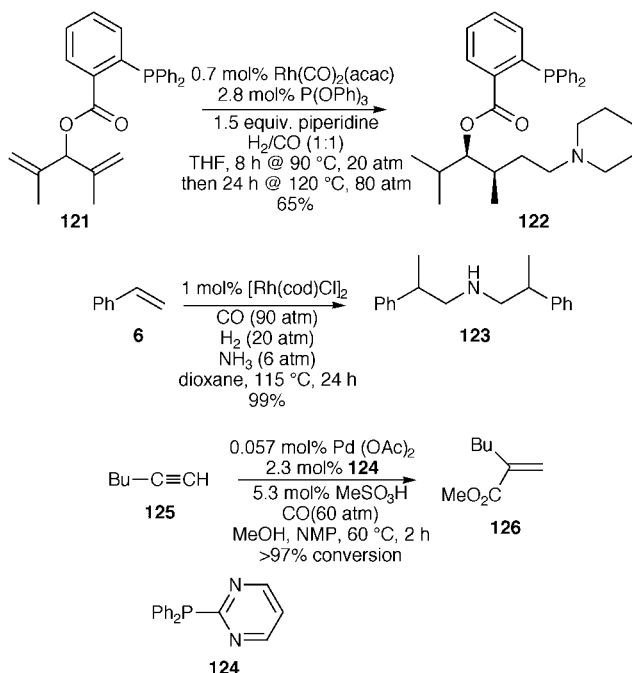
## 5.6 Coupling reactions involving CO

There are many transition metal catalysed reactions which incorporate carbon monoxide into the organic product. The hydroformylation of alkenes is one of the most industrially important examples of the process, and recently asymmetric hydroformylation has been achieved using enantiomerically pure phosphine/phosphite ligands incorporated into a cross-linked polymer matrix.<sup>80</sup>

In the presence of suitable amines, hydroformylation can provide a synthesis of more elaborate amines. Breit has controlled the diastereoselectivity of this process using

substrate **121** with a pendant phosphine group.<sup>81</sup> The reaction proceeds *via* diastereoselective hydroformylation and reductive amination.

Multiple reductive amination with primary amines and ammonia is also possible under hydroformylation conditions.<sup>82</sup> Of the many reported results, the conversion of styrene **6** and ammonia into the secondary amine **123** occurs in especially good yield (Scheme 19). Hydroesterification of alkenes is achieved by carbonylation in the presence of an alcohol. Monteiro and co-workers have shown that molten salts can be used in conjunction with organic solvents to allow for a regioselective synthesis of 2-arylpropionic esters from styrenes.<sup>83</sup>



Scheme 19

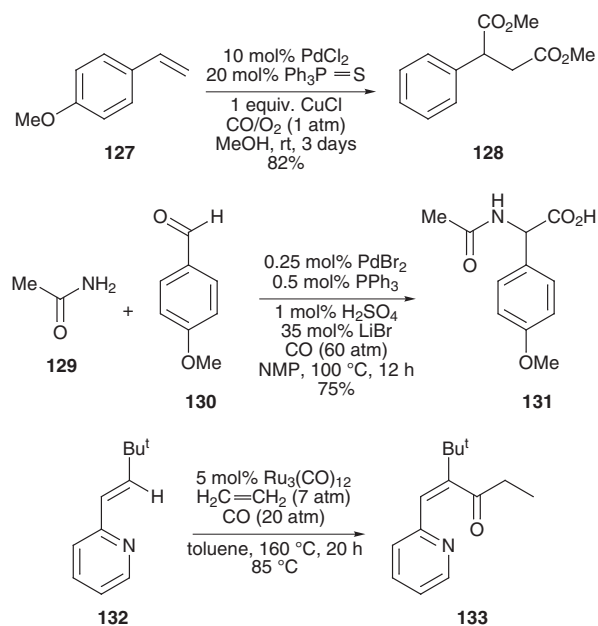
Reetz and co-workers have discovered that palladium complexes which contain four-membered P/N chelates are very active for the hydroesterification of alkynes. The use of ligand **124** provides a catalytic system which allows for the conversion of hex-1-yne **125** into the α,β-unsaturated ester **126**.<sup>84</sup>

An interesting bisalkoxycarbonylation of alkenes has been reported by Hashimoto, Saigo and co-workers, using phosphine sulfides as ligands.<sup>85</sup> The reactions work well for vinylsilanes and styrenes including substrate **127**, which is converted into the succinate **128** under the reaction conditions.

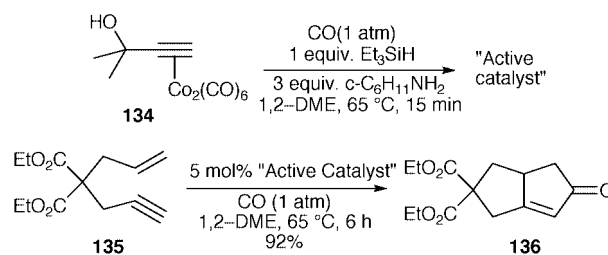
Beller and co-workers have provided further examples of their new procedure for amidocarbonylation.<sup>86</sup> Acetamide **129** and anisaldehyde **130** undergo amidocarbonylation to afford the *N*-acyl-arylglycine **131** (Scheme 20). The reaction conditions are milder than classical conditions using cobalt catalysts.

The carbonylation of C–H bonds is an interesting process, which can be achieved in the presence of a nearby co-ordinating group, as is found in substrate **132**.<sup>87</sup> Carbon monoxide and ethylene are both added to the substrate to give an α,β-unsaturated ketone **133** in good yield, using a ruthenium catalyst.

The Pauson–Khand reaction to give cyclopentenones has been enjoying renewed interest, and recent progress has been reviewed.<sup>88</sup> Belanger and Livinghouse have shown that hexacarbonyldicobalt–alkyne complexes such as complex **134** can be used as convenient catalyst precursors for the catalysed Pauson–Khand reaction.<sup>89</sup> Activation of the complex by treatment with triethylsilane affords an active complex for the relatively mild catalytic Pauson–Khand cyclisation of enyne **135** into cyclopentenone **136** (Scheme 21), as well as several other related examples.



Scheme 20



Scheme 21

Catalysis of the Pauson–Khand reaction with rhodium complexes has also been reported, but more severe conditions were required.<sup>90</sup>

## 5.7 Allylic substitution reactions

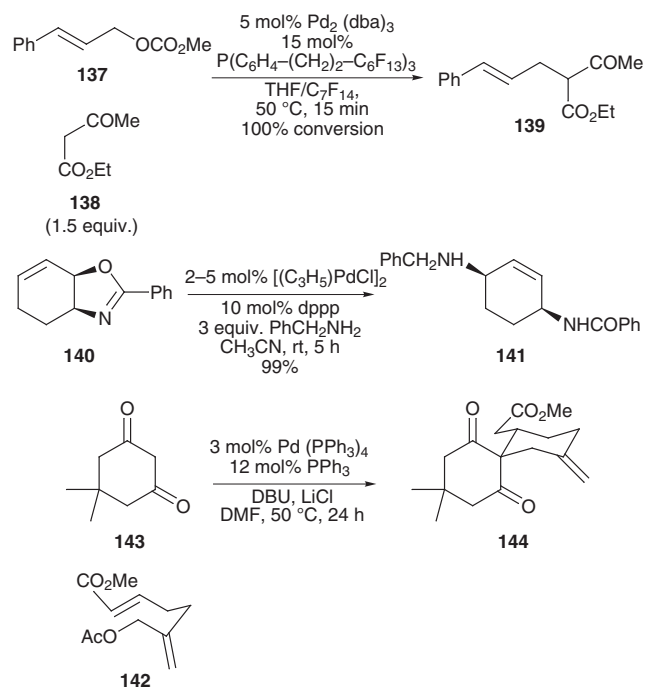
The basic allylic substitution reaction catalysed by palladium(0) complexes involves the substitution of an allyl acetate or allyl carbonate with a mild nucleophile. It is one of the most widely studied transition metal catalysed reactions, at least by academic groups. The use of fluororous phosphine ligands has allowed such reactions to be performed under fluororous biphasic systems.<sup>91</sup> Cinnamyl carbonate **137** and β-ketoester **138** combine to provide the substitution product **139**. The fluororous phase could be re-used to catalyse another batch of substrate.

Cook and Shanker have investigated the reactions of vinyl oxazolidinones, vinyl oxazolines and related substrates.<sup>92,93</sup> The vinyl oxazoline **140** is converted, with retention of stereochemistry into the *cis*-substituted cyclohexene **141**, by the well known double inversion mechanism.

An interesting tandem process involving palladium catalysed allylic substitution followed by Michael addition has been shown for the bis-functional electrophile **142** with dimedone **143** as the nucleophile.<sup>94</sup> Two of the C–C bonds in the new carbocycle **144** are formed during the reaction sequence (Scheme 22).

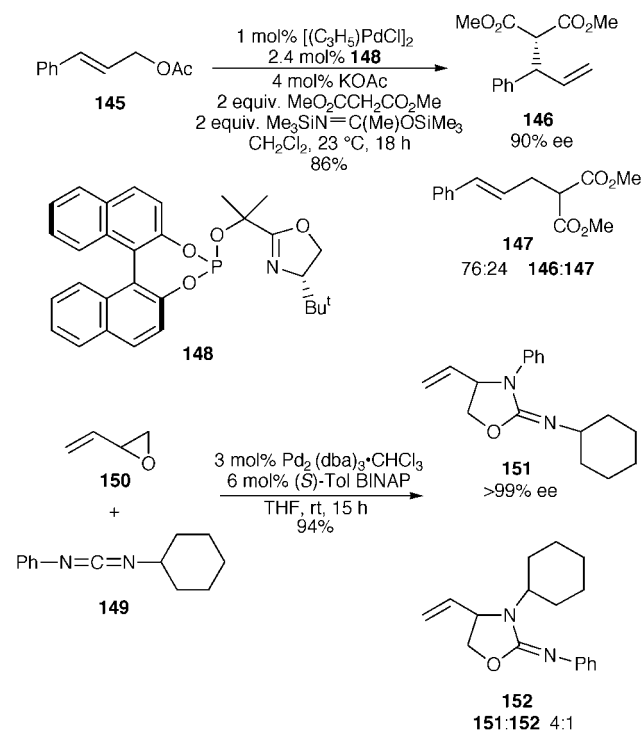
Control of regioselectivity and enantioselectivity has been a major aspect of research into allylic substitution. Prétôt and Pfaltz have combined both of these selectivity issues by investigating the allylic substitution of cinnamyl acetate **145**.<sup>95</sup> The more substituted isomer **146** is obtained in preference to the linear isomer **147** when the enantiomerically pure phosphite **148** is employed in the catalyst. The regioselectivity of the process was dependent upon the electronic nature of the ligand.





Scheme 22

Larksarp and Alper have used unsymmetrical carbodiimides, such as compound **149** as unusual nucleophiles in palladium catalysed asymmetric allylic substitution reactions.<sup>96</sup> The racemic starting material **150** is converted into the oxazolidinone regioisomers **151** and **152** with remarkably high enantioselectivity and reasonable regioselectivity (Scheme 23).



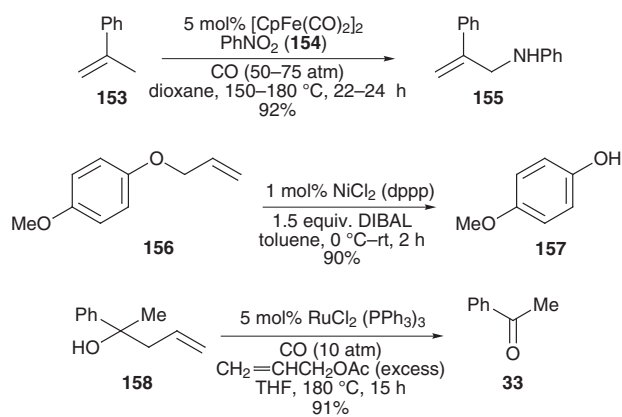
Scheme 23

Many other ligands have been reported to give high enantioselectivity in various allylic substitution reactions,<sup>97–100</sup> including examples where kinetic resolution of racemic starting material is observed.<sup>101</sup>

An allylic amination using iron catalysts in the presence of carbon monoxide allows for the functionalisation of alkenes.<sup>102</sup> The highest yielding example of this unusual reaction involves

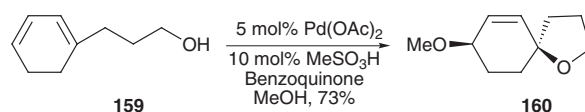
the reaction of  $\alpha$ -methylstyrene **153** with nitrobenzene **154** using an iron catalyst to give the allylamine **155** in good yield. Full mechanistic details have yet to be disclosed.

Another unusual process involving formal allylic substitution is the use of a nickel catalyst and diisobutylaluminium hydride (DIBAL) to cleave allyl ethers.<sup>103</sup> The mechanism is believed to occur *via* the hydroalumination of the alkene, followed by elimination of the alkoxide. The allyl ether **156** undergoes allyl ether cleavage to provide the phenol **157** in good yield (Scheme 24). The methyl ether is not cleaved under these conditions. De-allylation of amines using a similar protocol has also been reported.<sup>104</sup> De-allylation involving cleavage of a C–C bond is a less well known process. Kondo, Mitsudo and co-workers have fragmented homoallylic alcohols using ruthenium catalysts.<sup>105</sup> The homoallyl alcohol **158** is converted into acetophenone **33** under rather forcing conditions.



Scheme 24

Bäckvall and co-workers have investigated the 1,4-oxidation of 1,3-dienes for substrates containing pendant alcohol groups, to give a cyclisation process.<sup>106</sup> The diene alcohol **159** thereby affords the spiro product **160** with excellent *cis*-selectivity (Scheme 25). The reaction mechanism proceeds *via* an allyl-palladium species. Benzoquinone is required in such reactions in order to re-oxidise the palladium(0) to palladium(II). The use of enantiomerically pure benzoquinones which function as both re-oxidant and as a ligand have been shown to provide the basis for an asymmetric 1,4-oxidation of 1,3-dienes.<sup>107</sup>



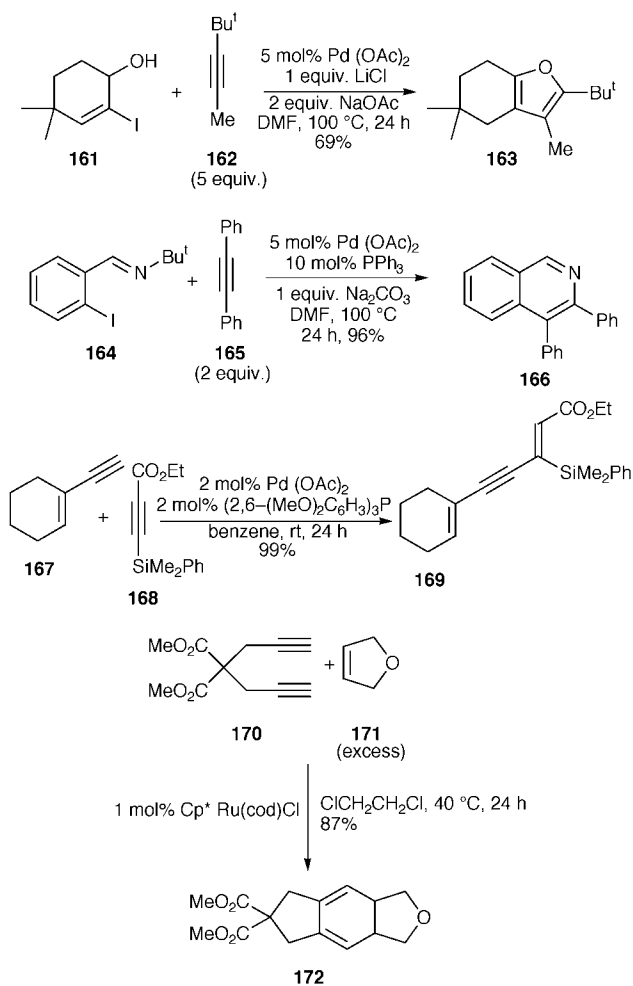
Scheme 25

## 5.8 Reactions involving alkynes

The use of alkynes as substrates in transition metal catalysed reactions has a long history. One of the themes in recent years has been annulation and heteroannulation reactions where one component is an alkyne. Of the many publications in this area, some examples include: the heteroannulation of the iodoalcohol **161** with alkyne **162** to give a substituted furan **163**,<sup>108</sup> the iodoimine **164** reacting with alkyne **165** to provide an isoquinoline **166** in excellent yield (Scheme 26),<sup>109</sup> and the preparation of various fused pyrrolopyridines using similar heteroannulation reactions, starting from 3-iodo-2-aminopyridine derivatives.<sup>110,111</sup>

The addition of one alkyne to another alkyne has been developed by Trost and co-workers. In a recent communication,<sup>112</sup> they report that the donor alkyne **167** reacts with the acceptor alkyne **168** with remarkable selectivity and yield.

Alkynes also undergo a variety of cycloaddition reactions. A ruthenium catalysed [2 + 2 + 2]-cycloaddition of diyne **170**



**Scheme 26**

with alkene **171** has been reported to give the cycloadduct **172**.<sup>113</sup>

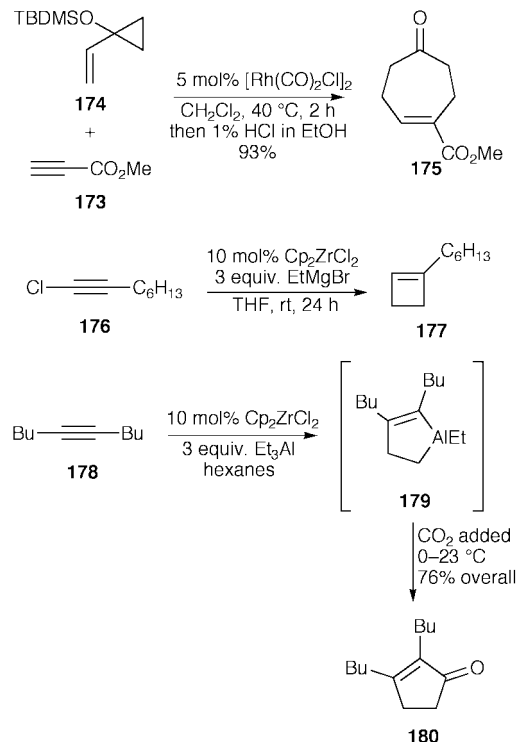
Wender and co-workers have shown that alkynes undergo a rhodium-catalysed [5 + 2]-cycloaddition with vinyl cyclopropanes.<sup>114</sup> For example, the reaction of alkyne **173** with the vinyl cyclopropane **174** affords a seven-membered carbocyclic ring containing a silyl enol ether which is hydrolysed to give the cyclic ketone **175**. Even four-membered rings can be generated from alkynes using catalysis. The chloroalkyne **176** is converted into cyclobutene **177** with ethylmagnesium bromide and a zirconocene catalyst (Scheme 27).<sup>115</sup> Higher yields were obtained using stoichiometric amounts of zirconocene dichloride.

Zirconium catalysts are also well known for their ability to effect carbometallation of alkynes. Negishi and co-workers have shown how the chemistry can be adapted to provide cyclometallation, and thence cyclic organic products.<sup>116</sup> Treatment of dec-5-yne **178** with triethylaluminium and a zirconocene catalyst affords the aluminacyclopentene **179**, which on treatment with carbon dioxide afforded the cyclopentenone **180** in good yield.

### 5.9 Reactions involving allenes

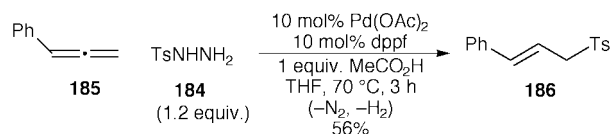
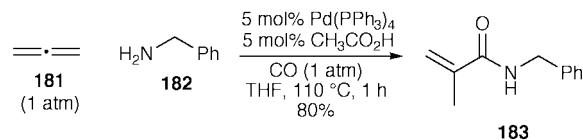
Grigg and co-workers have employed allenes in a useful synthesis of  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>117</sup> The combination of allene **181**, carbon monoxide and a nucleophile, in this case benzylamine **182**, affords a route through to the  $\alpha,\beta$ -unsaturated amide **183**. Many other nitrogen and oxygen nucleophiles were also effective in this process.

The metal-catalysed reactions of allenes often involve nucleophilic addition reactions. Yamamoto and co-workers have reported an unusual example where the nucleophile, tosyl-



**Scheme 27**

hydrazine **184**, fragments (Scheme 28).<sup>118</sup> Allene **185** undergoes hydrosulfination, and nitrogen and hydrogen are released, providing a synthesis of allylsulfone **186**.



**Scheme 28**

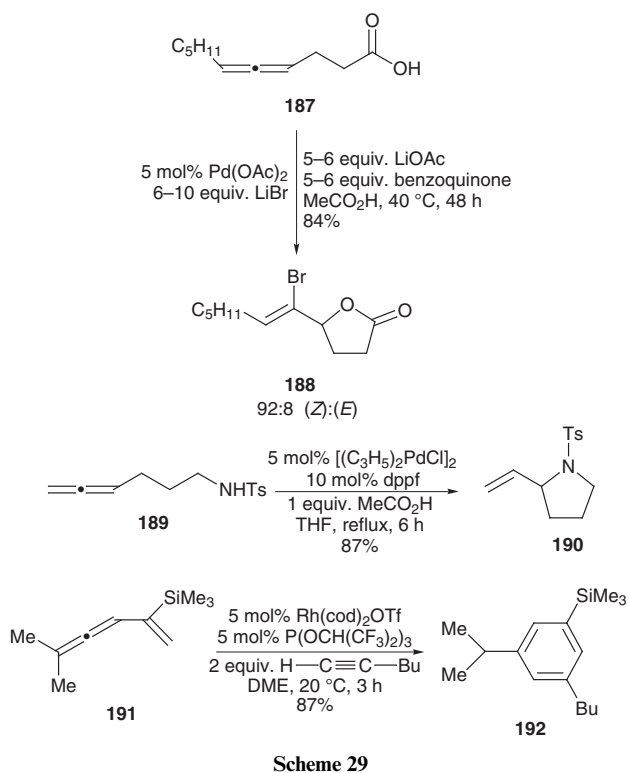
Cyclisation reactions involving allenes can be synthetically useful. Examples of intramolecular cyclisation reactions include the 1,2-oxidation of allenes reported by Jonasson and Bäckvall<sup>119</sup> and an intramolecular hydroamination of allenes reported by Meguro and Yamamoto.<sup>120</sup> Specific examples include the cyclisation of allene **187** into the lactone **188**, and the cyclisation of allene **189** into the vinylpyrrolidine **190** (Scheme 29).

Allenes can also participate in intermolecular cyclisation reactions. The allene **191** undergoes a rhodium-catalysed [4 + 2] cycloaddition to provide the arene **192**.<sup>121</sup> Various other di-, tri- and tetra-substituted arenes were prepared using a similar methodology.

Rhodium-catalysed reactions have also been exploited in the ring expansion reactions of allenylcyclopropanes into methylenecyclopentenes.<sup>122</sup>

## 6 Reactions involving metal carbenoids

Dihydrodium(II) carboxylates and related complexes hold a privileged position amongst catalysts for reactions proceeding *via* metal carbenoids. Cyclopropanation and bond insertion reactions with these catalysts are well documented. Marsden and Pang have used such catalysts for the C–H insertion reaction of



Scheme 29

silylated diazoacetates.<sup>123</sup> The silylated diazoacetate **193** undergoes a C–H insertion reaction to provide the  $\alpha$ -silylated lactone **194** as a single diastereomer.

The use of parallel synthesis and high throughput methods in the search for asymmetric catalysts is a research area of current interest.<sup>124</sup> Moody and co-workers have applied parallel synthesis methods to the identification of asymmetric catalysts for Si–H insertion reactions.<sup>125</sup> Screening of dirhodium carboxylate complexes produced from a range of structurally diverse enantiomerically pure carboxylic acids enabled a good catalyst to be identified. The insertion of diazoester **195** into silane **196** was achieved using the rhodium complex of ligand **197**, providing the insertion product **198** with up to 76% ee (Scheme 30).

Platinum complexes have been used to catalyse the insertion of carbenes into the O–H bonds of alcohols,<sup>126</sup> whilst copper complexes have been used for insertion into the O–H bond of carboxylic acids.<sup>127</sup> In a typical example, the acid **199** and diazo compound **200** undergo copper-catalysed conversion into the  $\alpha$ -acyloxyketone **201**.

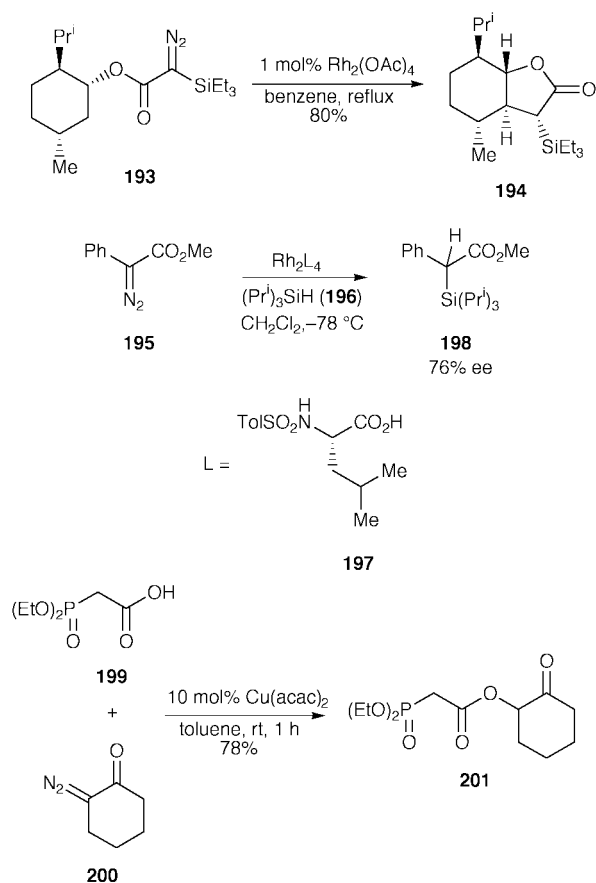
## 7 Alkene metathesis reactions

Alkene metathesis reactions, and in particular, ring-closing alkene metathesis (RCM) reactions have been quickly adopted by organic chemists as powerful synthetic methodology. Two reviews have been published discussing applications of the methodology to organic synthesis.<sup>128,129</sup>

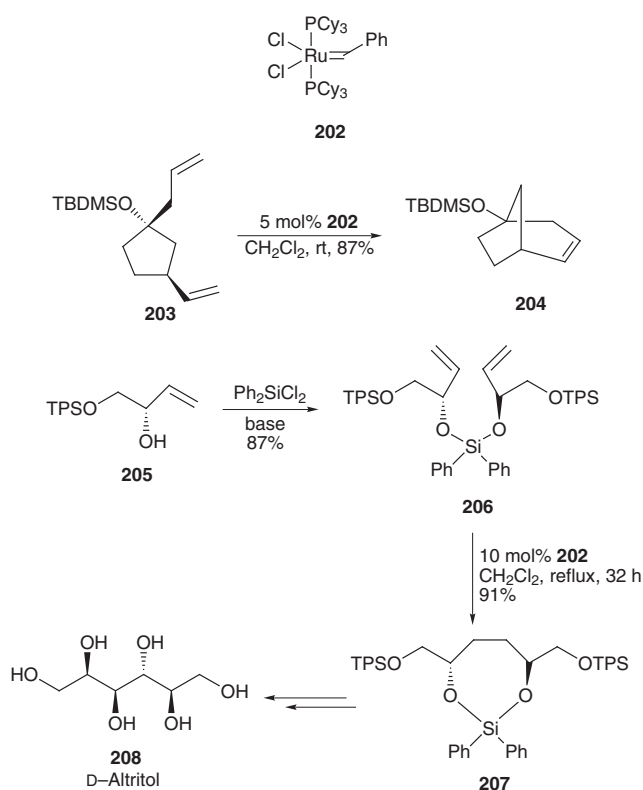
The most commonly used catalyst for ring-closing metathesis reactions is the Grubbs catalyst **202**, although other catalysts may have advantages in some situations.<sup>130</sup> Morehead and Grubbs have applied ring-closing metathesis to the formation of bridged bicycloalkenes.<sup>131</sup> The diene **203** is converted into the bicyclic structure **204** in good yield.

Evans and Murthy have coupled enantiomerically pure allyl alcohols using a temporary silicon tether to facilitate the metathesis process.<sup>132</sup> Tethering of the allylic alcohol **205** affords the diene **206**, which undergoes straightforward ring-closing metathesis to give the seven-membered heterocycle **207**. Further diastereoselective elaboration and removal of protecting groups affords D-altritol **208** (Scheme 31).

Synthetic sequences involving ring-closing metathesis and



Scheme 30

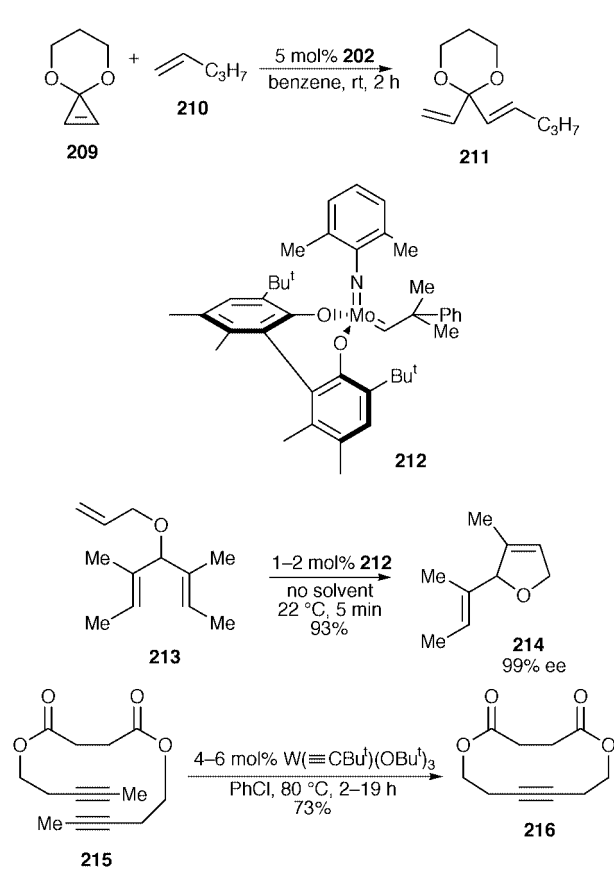


Scheme 31

subsequent intramolecular Heck reactions have been reported as an efficient route to polycycles.<sup>133</sup>

Cyclopropenone ketal **209** undergoes a ring-opening cross metathesis with other alkenes in high yield.<sup>134</sup> Often cross metathesis reactions present problems of giving mixed products, but

in this case the selectivity is normally high. Metathesis with pent-1-ene **210** affords the protected divinyl ketone **211** as the product (Scheme 32).



Scheme 32

Enantiomerically pure molybdenum complexes **212** have been used by Hoveyda, Schrock and co-workers in the enantioselective desymmetrisation of compound **213**.<sup>135</sup> The kinetic resolution of racemic dienes by ring-closing metathesis with complex **212** has also been achieved.

The metathesis of alkynes is not such a widely studied area of research, but Fürstner and Seidel have demonstrated the ring-closing metathesis of diynes using tungsten complexes.<sup>136</sup> For example, the diyne **215** is converted into the cycloalkyne **216**. Many other macrocyclic alkynes were generated in a similar fashion, and this new methodology holds real promise for further applications.

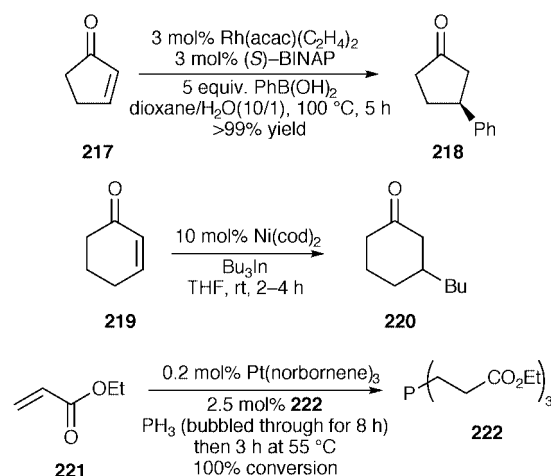
## 8 Conjugate addition reactions

The copper-catalysed conjugate addition of organozincs and other nucleophiles has recently been achieved with very high enantioselectivity, and progress in this area has recently been reviewed.<sup>137</sup> As well as reports of new ligands for the copper-catalysed reactions,<sup>138</sup> remarkable reports of the asymmetric rhodium-catalysed addition of aryl and alkenylboronic acids to enones have been published by Hayashi and co-workers.<sup>139,140</sup> Cyclopentenone **217** is usually a poor substrate for highly enantioselective conjugate addition reactions, but with the new rhodium-catalysed reaction, very high enantiomeric excess is observed in the product **218**. Excellent asymmetric induction was also observed with acyclic enones.

Bis(cyclooctadiene)nickel is a good catalyst for the conjugate addition of organoindium reagents to cyclohexenone **219** and other electron deficient alkenes.<sup>141</sup> Both alkyl and aryl triorganoindium reagents can be employed in these reactions, such as the use of tributylindium in the formation of conjugate addition product **220**.

The conjugate addition of  $\text{PH}_3$  to ethyl acrylate **221** is

catalysed by platinum(0) complexes. Multiple reaction affords the phosphine **222** as the product (Scheme 33).<sup>142</sup>



Scheme 33

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