Catalytic applications of transition metals in organic synthesis

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Reviewing the literature published between 1 July 1992 and 31 August 1993

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1 Introduction

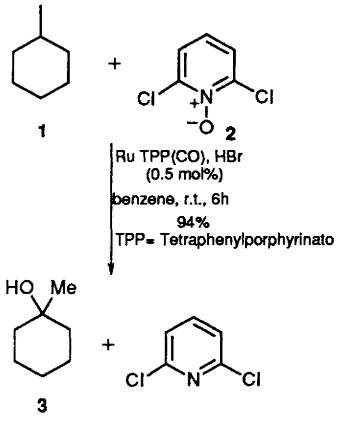
This review highlights significant advances in transition metal catalysis during the period 1 July 1992 to 31 August 1993. The growing body of information in the area enables predictions to be made about the chemoselectivity and stereoselectivity of many homogeneous transition metal catalysts for particular substrates.

There has been such a huge volume of publications concerned with transition metal catalysts that it is not possible to provide a comprehensive account. However, we have endeavoured to summarize current areas of interest and to provide commentary on the important advances. Only homogeneous applications have been considered for this review.

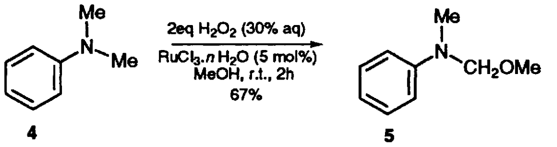
2 Oxidation

2.1 Oxidation of C–H bonds

The direct oxidation of alkanes by catalysis continues to attract attention. Hirobe and co-workers have reported the oxidation of methylcyclohexane **1** into 1-methylcyclohexanol **3** using 2,6-dichloropyridine *N*-oxide **2** and a ruthenium porphyrin catalyst.[1]

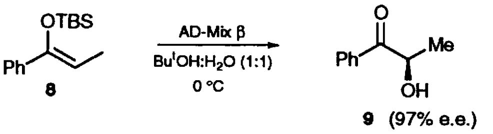


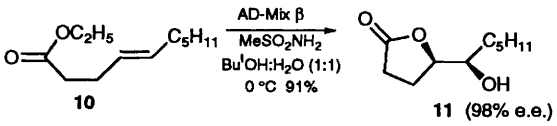
Similarly, Murahashi and co-workers have detailed the ruthenium-catalysed α-methoxylation of tertiary amines[2] and also the direct oxidation of alkanes to alcohols and ketones.[3] Thus, treatment of dimethylaniline **4** with 30% hydrogen peroxide solution and a ruthenium catalyst in methanol afforded the methoxymethylamine **5**. Murahashi and co-workers have also reported the oxidation of alkanes using molecular oxygen in the presence of catalytic copper salts.[4]



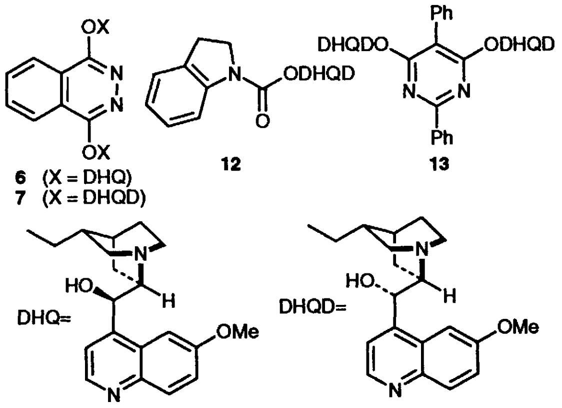
2.2 Dihydroxylation

The asymmetric osmium-catalysed dihydroxylation of alkenes has recently been reviewed.[5] Crystal structures and synthetic details of the cinchona alkaloids used as ligands for this reaction have appeared.[6] Sharpless and co-workers have demonstrated many synthetic applications of the dihydroxylation process using the commercially available AD-mix-α and AD-mix-β reagents. [These mixtures contain $K_3Fe(CN)_6$, K_2CO_3, $K_2OsO_2(OH)_4$, and either $(DHQ)_2PHAL$ **6** (for AD-mix-α) or $(DHQD)_2$-PHAL **7** (for AD-mix-β).[7]] For example, the dihydroxylation of enol ether **8** affords α-hydroxy ketone **9**,[7] and the dihydroxylation of β,γ-unsaturated ester **10** affords the hydroxy lactone **11**.[8,9]



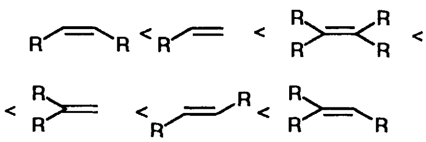


There have been numerous reports of other synthetic applications both by the group of Sharpless and by others. Fine-tuning of the ligand has been achieved to accommodate the enantioselective dihydroxylation of *cis*-disubstituted alkenes using the indolinyl ligand **12**.[10] Similarly, the pyrimidine ligand **13** has been used for improved enantioselectivity in asymmetric dihydroxylations of terminal alkenes.[11]



6 (X = DHQ)
7 (X = DHQD)
12
13

Dihydroxylation of non-symmetrical dienes[12] and rate studies on different categories of olefin have revealed a reactivity hierarchy, as illustrated in **Scheme 1**.[13] The anomalous position of the tetra-substituted olefin is a consequence of the steric demands of the $(DHQD)_2PHAL$ ligand. However, in the presence of the achiral catalyst quinuclidine, tetra-substituted alkenes are the most reactive category of alkene.



Scheme 1

The kinetic resolution of alkenes which already contain a chirality centre has been reported using the asymmetric dihydroxylation process.[14,15]

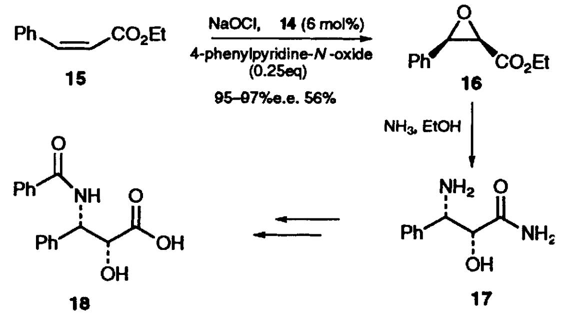
2.3 Epoxidation

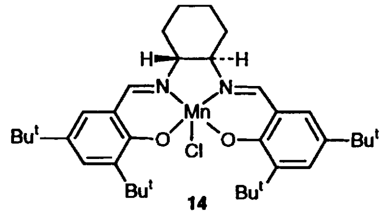
There has been a continued interest in the development of novel catalysts for epoxidation of alkenes. Catalysts which can operate with cheap oxidants and those which can provide asymmetric induction are particularly useful.

Mukaiyama and co-workers have reported the oxidation of alkenes into epoxides with molecular oxygen, catalysed by a Co^{II} complex, using propionaldehyde diethyl acetal as the reductant,[16] in an extension of previous reports employing aldehydes as the reductant.[17] An asymmetric variant of this process has been reported using enantiomerically pure manganese complexes to achieve up to 84% e.e. in the epoxidation of alkenes.[18]

Enantiomerically pure ruthenium catalysts have been employed to give 50–80% e.e. in the epoxidation of styrene with iodosylbenzene, but with low yields (12–38%).[19] Collman and co-workers have prepared threitol-strapped manganese porphyrins which are capable of catalysing epoxidation with up to 88% e.e.[20]

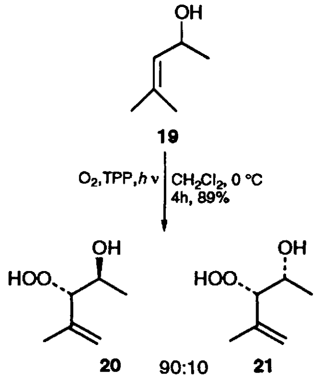
Deng and Jacobsen have used the (salen)Mn^{III} complex **14** as a catalyst for the epoxidation of (*Z*)-ethyl cinnamate **15** to give the product **16** with very high enantioselectivity. Treatment with ammonia afforded the ring-opened amide **17** which was readily converted into **18**, the side chain of taxol.[21]



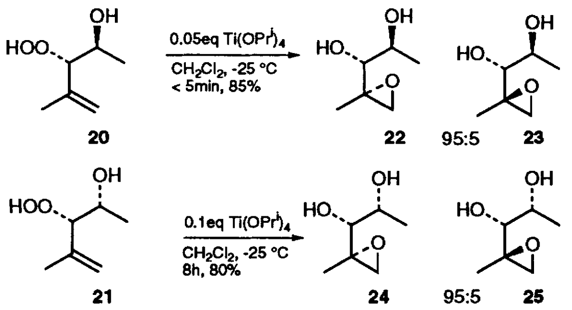


14

Adam and Nestler have developed an interesting titanium-catalysed epoxy-hydroxylation of allylic alcohols.[22,23] Photo-oxygenation of the allyl alcohol **19** affords a 90 : 10 mixture of the diastereomeric hydroperoxy homoallylic alcohols **20** and **21**.

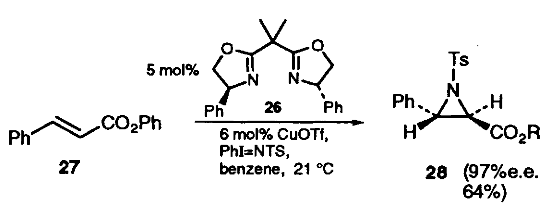


However, upon treatment with catalytic amounts of titanium tetraisopropoxide, the major diastereomer **20** rearranges more quickly to the epoxy diol products **22** and **23** (95 : 5) than the minor diastereomer **21** does to the alternative epoxy diols **24** and **25**.

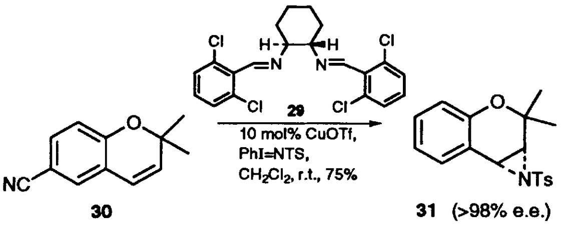


2.4 Aziridination

Transition metal catalysed aziridination of alkenes has been known for several years. However, the recent demonstration of the ability of Cu^I or Cu^{II} salts to catalyse aziridination of alkenes with [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane, PhI = NTs,[24] has led to reports of asymmetric variants of this reaction by the groups of Evans and Jacobsen. Evans and co-workers report the use of the bis(oxazoline) ligands **26** in the presence of a copper catalyst and the cinnamate **27** with PhI = NTs, to afford the aziridine **28** with excellent enantioselectivity (97% e.e.).[25] Jacobsen and co-workers report that whilst salen ligands were found to afford poor results, the diimine ligand **29** was effective for providing asymmetric aziridination under conditions similar to those used by Evans.

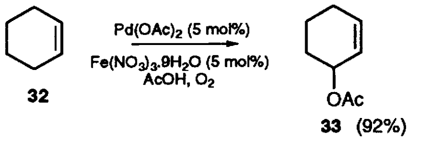


For the chromene **30**, asymmetric induction in the product **31** was very high (> 98%).[26] However, not all of the substrates examined by these groups gave such high levels of enantioselectivity. Furthermore, Katsuki and co-workers have reported that the use of enantiomerically pure (salen)manganese(III) complexes for asymmetric aziridination gives moderate levels of enantioselectivity, but poor yields.[27]

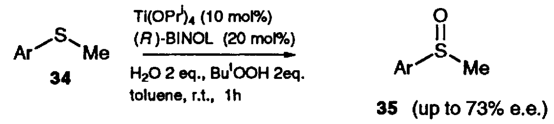


2.5 Other oxidations

Larsson and Åkermark have reported a catalytic system for allylic acetoxylation. Cyclohexene **32** is oxidized to cyclohexenyl acetate **33** in the presence of catalytic palladium acetate and ferric nitrate in acetic acid under an atmosphere of oxygen.[28]



Uemura and co-workers have shown that sulfides **34** may be catalytically converted into sulfoxides **35** using titanium tetraisopropoxide in the presence of (*R*)-BINOL {(*R*)-1,1′-bi-2-naphthol}.[29] In an alternative procedure, Jacobsen and co-workers have used (salen)manganese complexes **14** to catalyse the asymmetric oxidation of sulfides (up to 68% e.e.).[30]

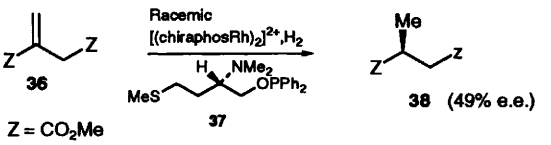


3 Hydrogenation and related processes

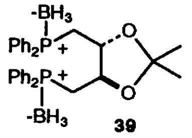
This section includes recent advances in catalytic hydrogenation, hydroboration, and hydrosilylation. Additionally, hydroformylation and silylformylation are described here.

3.1 Hydrogenation

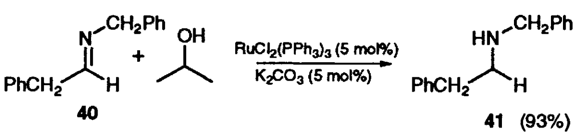
Faller and Parr have demonstrated the use of chiral poisoning as a novel strategy for asymmetric synthesis.[31] Asymmetric rhodium-catalysed hydrogenation was chosen as the example. A mixture of [(*S*,*S*)-chiraphosRh]$^+$ and [(*R*,*R*)-chiraphosRh]$^+$ was employed as the catalyst, and would be expected to afford racemic products in the hydrogenation of dimethylitaconate **36**. However, in the presence of a chiral 'poison' **37**, one enantiomer of catalyst is deactivated preferentially, and thus asymmetric induction is now observed in the product **38**.



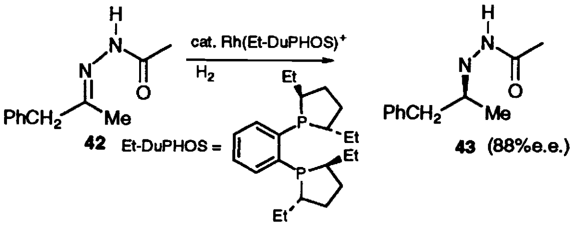
Phosphine–borane complexes provide a method for stabilizing phosphines to oxidation. A recent report describes the direct use of phosphine–borane complexes in asymmetric synthesis. The (−)-DIOP-borane complex **39**, upon treatment with $[(COD)RhCl]_2$ and DABCO affords a catalyst which is competent for asymmetric hydrogenation reactions.[32]

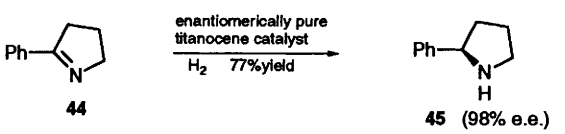


Wang and Bäckvall have reported the ruthenium-catalysed hydrogenation of imines. Thus, the reaction between isopropanol and the imine **40** in the presence of ruthenium catalyst and base affords the amine **41** as the product.[33]

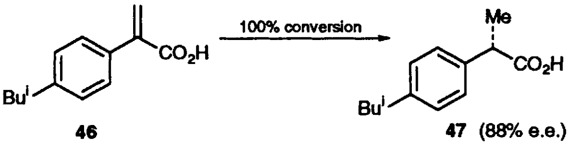


Whilst highly enantioselective hydrogenations of ketones and alkenes have been known for a long time, it is only recently that reports of highly enantioselective reductions of imines have been reported. Burk and Feaster have demonstrated the ability of rhodium DuPHOS complexes to catalyse the hydrogenation of *N*-aroylhydrazones **42** with the formation of product **43** in 72–97% e.e.[34] Willoughby and Buchwald have employed enantiomerically pure titanocene complexes for the hydrogenation of imines **44** with the formation of product **45** in 53–98% e.e.[35]





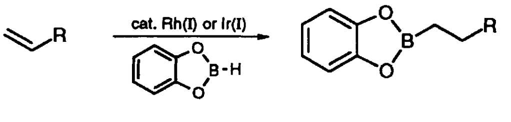
The highly successful ruthenium-BINAP reagents introduced by Noyori and co-workers are now routinely employed for the asymmetric reduction of ketones and alkenes.[36] A recent development is the *in situ* formation of the catalyst. A methanolic solution of $Ru(acac)_3$ and (*S*)-BINAP were treated with hydrogen at 1000 psi, followed by the introduction of the alkene **46**. The product, ibuprofen **47** was formed with 88% e.e.[37]



Reagents: cat. $Ru(acac)_3$, cat. (*S*)-BINAP, MeOH, 1000 p.s.i. H_2

3.2 Hydroboration

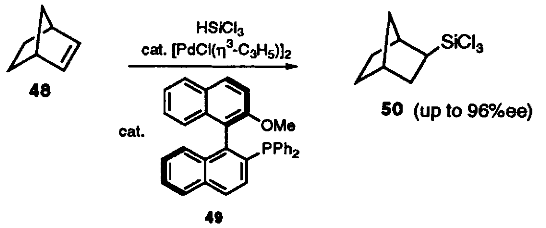
Investigations into the rhodium- and iridium-catalysed hydroboration of alkenes (**Scheme 2**) have been further documented, in terms of synthetic utility[38] and mechanism.[39–41] These papers effectively summarize and review the catalytic hydroboration process, and the reader is directed to these reports for further information.



Scheme 2

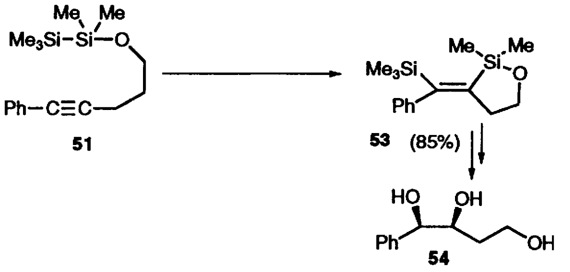
3.3 Hydrosilylation

Asymmetric hydrosilylation of norbornenes[42] and dihydrofurans[43] using an enantiomerically pure palladium catalyst has been reported to give hydrosilylation products of up to 96% e.e. Treatment of norbornene **48** with trichlorosilane in the presence of a palladium catalyst and the enantiomerically pure ligand **49** affords the product **50** with very high enantiocontrol.

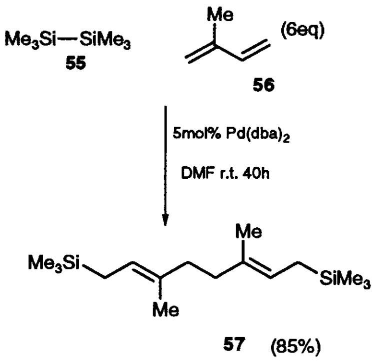


Ito and co-workers have employed an intramolecular palladium-catalysed bis-silylation of alkenes as a route to polyol synthesis.[44] The reaction of the alkyne **51** with catalytic palladium acetate and isocyanide **52** affords the bis-silylated adduct **53** in 85% yield. Hydrogenation and oxidation leads to the formation of 1,2,4-triols **54**.[45]

The palladium-catalysed dimerization/double silylation of 1,3-dienes under ambient conditions has been reported. The reaction of disilane **55** with diene **56** in the presence of a palladium catalyst affords the product **57** in a remarkable 85% yield.[46]

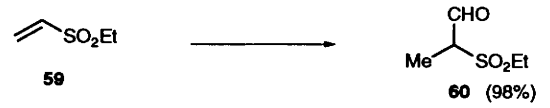


Reagents: $Pd(OAc)_2$ (0.7–2 mol%), $Me_3CCH_2C(Me)_2NC$ **52**(0.1-0.3equiv), toluene,111 °C 2h

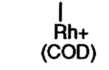


3.4 Hydroformylation

Totland and Alper have investigated the hydroformylation of vinyl sulfones and vinyl sulfoxides catalysed by the zwitterionic rhodium complex **58**.[47] The reaction of ethyl vinyl sulfone **59** with carbon monoxide and hydrogen using catalytic **58** and dppb affords exclusively the branched chain product **60** in 98% yield.



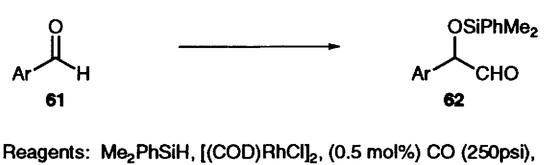
Reagents: CO/H_2 (600 psi), cat. dppb, CH_2Cl_2, 75 °C, cat.



58

Takaya and co-workers have reported an enantioselective rhodium-catalysed hydroformylation of olefins.[48]

Recent reports of silylformylation of aldehydes and epoxides[49] have appeared. Wright and Cochran have shown that treatment of aldehydes **61** with dimethylphenylsilane in the presence of catalytic amounts of $[(COD)RhCl]_2$ affords the corresponding α-silyloxy aldehydes **62** in 60–90% yield.[50]



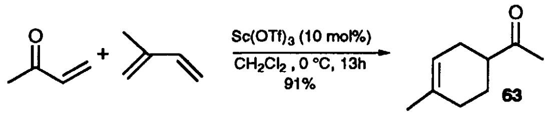
Reagents: Me_2PhSiH, $[(COD)RhCl]_2$, (0.5 mol%) CO (250psi), 23 °C, 24 h, THF 60–90%

4 Lewis acids

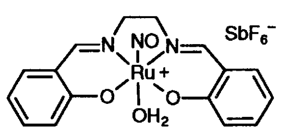
Transition metal reagents such as titanium tetrachloride have been familiar Lewis acids for a long time. However, there is a growing tendency to exploit the properties of the later transition metals as Lewis acids, since advantages in terms of catalytic turnover and ligand design may be afforded.

4.1 Diels–Alder and related processes

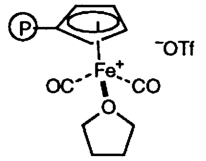
Kobayashi and co-workers have reported the use of scandium trifluoromethylsulfonate as a reusable catalyst for the Diels–Alder reaction.[51] For example, the reaction of isoprene with methyl vinyl ketone afforded the Diels–Alder adduct **63** in 91% yield using scandium trifluormethylsulfonate as a catalyst.



Other examples of transition metal catalysed Diels–Alder reactions include reactions mediated by the ruthenium catalyst **64**,[52] developed by Bosnich and co-workers, and the polymer-bound, iron-based Lewis acid catalyst **65**.[53]

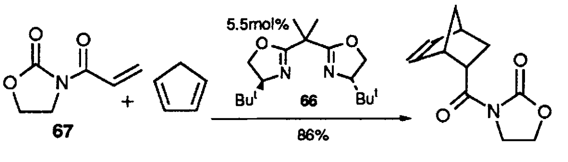


64



65

Evans and co-workers have prepared enantiomerically pure bis(oxazoline) ligands **66** for use in copper(II) triflate catalysed Diels–Alder reactions.[54] High levels of enantioselectivity were reported for the catalysed reaction between cyclopentadiene and oxazolidinone **67** to afford the Diels–Alder adduct **68**.

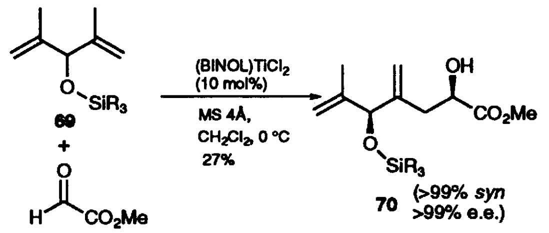


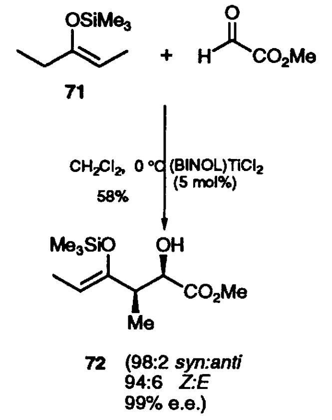
68 (>98% e.e. 98:2 *endo:exo*)

Reagents: 5mol% $Cu(OTf)_2$, CH_2Cl_2, -78 °C, 18h

Further advances in the use of enantiomerically pure titanium catalysts for the carbonyl-ene reaction have been described.[55] Mikami and co-workers have demonstrated an asymmetric desymmetrization of **69** into **70**, catalysed by a chiral titanium complex previously developed by this group.[56] The product was obtained with very high enantioselectivity and very high diastereoselectivity.

Interestingly, the reaction of the silyl enol ether **71** with methyl glyoxylate and the same catalyst affords the ene-type product **72**, rather than a Mukaiyama aldol reaction. Furthermore, remarkably high enantioselectivity and diastereoselectivity is obtained in the aldol-like product.[57]

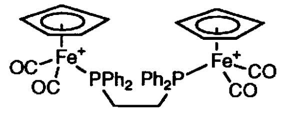




4.2 Aldol reactions

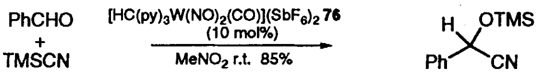
As well as the highly stereoselective example cited above, more conventional Mukaiyama aldol reactions have recently been reported to be catalysed by scandium trifluoromethanesulfonate,[58] ruthenium catalysts **64**,[59] mercuric iodide,[60] the titanium and zirconium catalysts **73** and **74**[61] and also the unusual binuclear iron complex **75**,[62] which offers the possibility of bis-coordination to the carbonyl substrate.

$Cp_2Ti(OTf)_2$
73
$Cp_2Zr(OTf)_2THF$
74

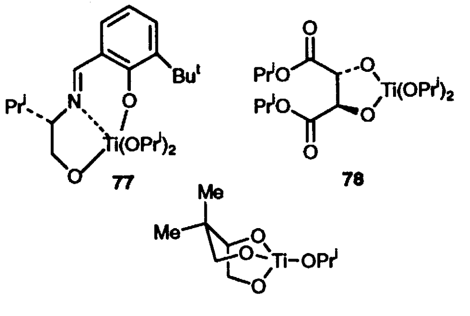

75

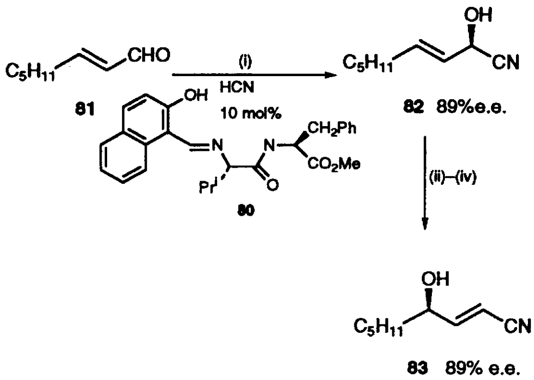
4.3 Hydrocyanation and silylcyanation

Faller has used the unusual tungsten complex **76** as a Lewis acid precursor. Upon loss of CO, a potent Lewis acid is formed, which catalyses the addition of trimethylsilyl cyanide to aldehydes.[63]



Asymmetric trimethylsilylcyanation of aldehydes has been achieved with the titanium based catalysts **77**,[64] **78**,[65] and **79**.[66] Inoue has exploited titanium complexes of the peptide **80** as catalysts for the asymmetric addition of hydrogen cyanide to aldehydes.[67] In the case of α,β-alkenyl aldehydes **81**, the product cyanohydrin **82** was acetylated, treated with catalytic bis(acetonitrile)palladium dichloride, and hydrolysed to afford the rearranged product **83**.[68]

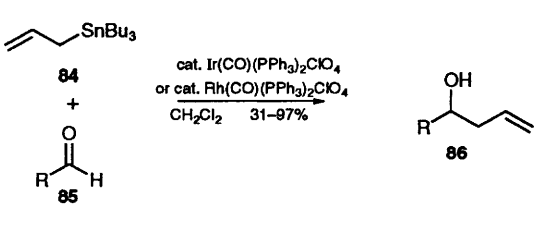




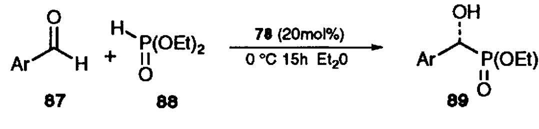
Reagents: (i) Ti(OEt)$_4$ (10 mol%); (ii) Ac$_2$O, C$_5$H$_5$N; (iii) 10 mol%PdCl$_2$(CH$_3$CN)$_2$ THF; (iv) hydrolysis

4.4 Other nucleophilic additions

Nuss and Rennels have employed cationic iridium and rhodium catalysts for the addition of allyltributyltin **84** to aldehydes **85** to afford the homoallylic alcohols **86**.[69] In the presence of enantiomerically pure catalysts, a small but promising degree of asymmetric induction was observed.



Shibuya and co-workers have devised an enantioselective hydrophosphonylation of aldehydes **87** which uses diethylphosphonate **88** and a titanium catalyst **78** to afford α-hydroxyphosphonates **89**.[70] Whilst the enantioselectivities reported are modest (up to 53% e.e.), there is potential for the improvement of this process.

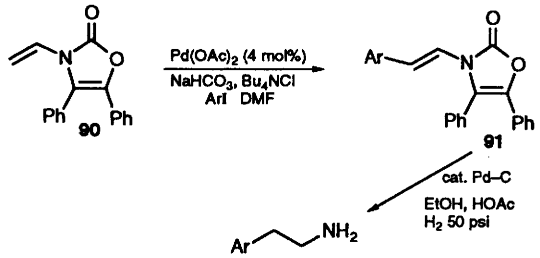


5 Coupling reactions

This large section contains a multitude of reactions which are often identified as coupling reactions. Many of these catalysed processes involve the formation of new C–C bonds, and are therefore of great synthetic utility. Only representative examples have been chosen for this section due to the enormous amount of research activity in the area.

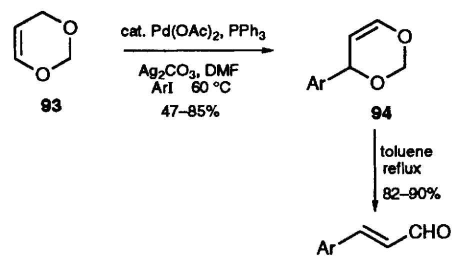
5.1 Heck reactions

Busacca and co-workers have developed an interesting new vinylamine equivalent for use in the Heck reaction.[71] Heck reaction between aryl iodides and the vinyloxazolone **90** affords the Heck adducts **91**. Hydrogenation affords the corresponding phenethylamines **92**.



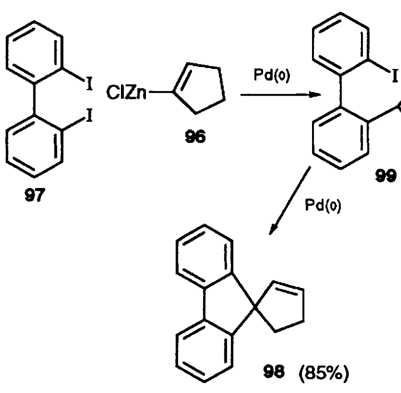
92

Another application of the Heck reaction is in the arylation of 4*H*-1,3-dioxin **93**.[72] The arylated product **94** can be converted into cinnamaldehydes **95** upon heating (*via* a retro Diels–Alder reaction).

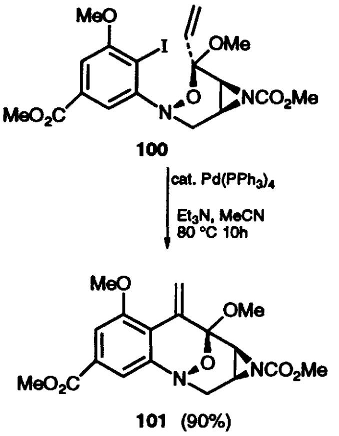


95

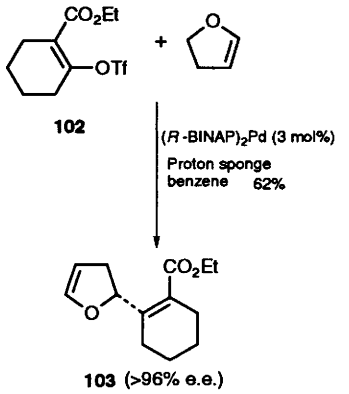
An interesting example of a palladium-catalysed reaction between cyclopentenylzinc chloride **96** and diiodobiphenyl **97** affords the cyclization product **98**.[73] The reaction is believed to proceed *via* the coupled intermediate **99**, which is able to undergo an intramolecular Heck reaction.



McClure and Danishefsky have reported an intramolecular Heck reaction on the highly functionalized substrate **100** to afford the cyclized product **101**, showing the remarkable chemoselectivity afforded by the Heck arylation reaction.[74]



Asymmetric Heck reactions may be achieved for certain substrates. The use of a palladium BINAP complex as a catalyst for the reaction between dihydrofuran and the alkenyl triflate **102** affords the product **103** in 62% yield and with > 96% e.e.[75]

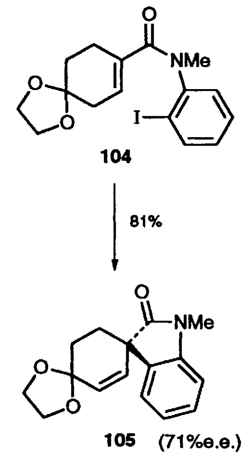


Hillers and Reiser have demonstrated that the enantioselectivity and regioselectivity of related reactions are pressure dependent.[76]

Ashimori and Overman have reported the asymmetric Heck cyclization of the aryl iodide **104**.[77] Using a palladium BINAP catalyst in the presence of a silver salt, they obtain the product **105** with up to 71% e.e. However, in the presence of 1,2,2,6,6-pentamethylpiperidine, and the absence of silver salts, the other enantiomer of the cyclization product is obtained with 66% e.e.!

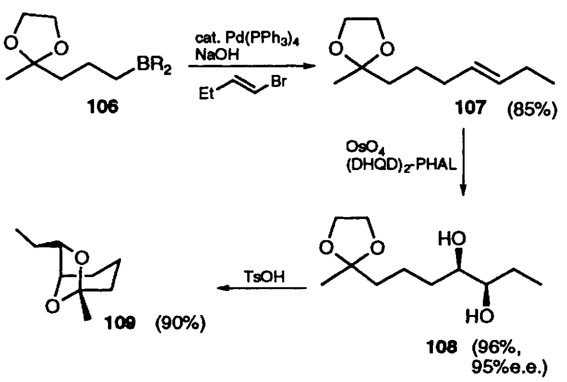
5.2 Suzuki-type coupling

The coupling of boron compounds with organic halides is frequently called the Suzuki coupling. The reaction is also effective using organic triflates as one of the coupling partners.[78] Soderquist and Rane have reported a synthesis of (+)-*exo*-brevicomin **109** which relies upon a Suzuki coupling followed by an osmium-catalysed asymmetric dihydroxylation.[79]

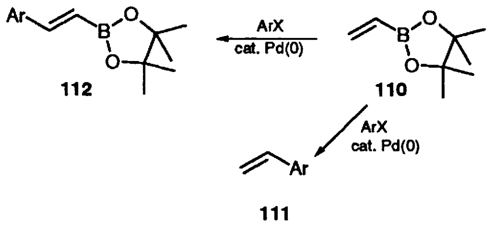


Reagents: $Pd_2(dba)_3$ (5 mol%), R-(+)BINAP (10 mol%), 1–2eq. Ag_3PO_4, $MeCONMe_2$, 80 °C, 26h

Coupling of the borane **106** with (*E*)-1-bromobut-1-ene affords the isomerically pure alkene **107**. Asymmetric dihydroxylation affords the diol **108** which is readily cyclized to **109**.



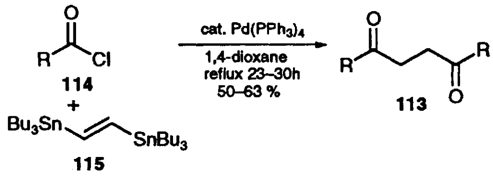
Whiting and co-workers have examined the reaction of the vinylborate ester **110** with aryl iodides in the presence of a palladium catalyst.[80] There are two possible outcomes and either the Suzuki product **111** or the Heck product **112** could be obtained. The Heck product appears to be kinetically preferred, although minor changes in conditions affected the product ratio.



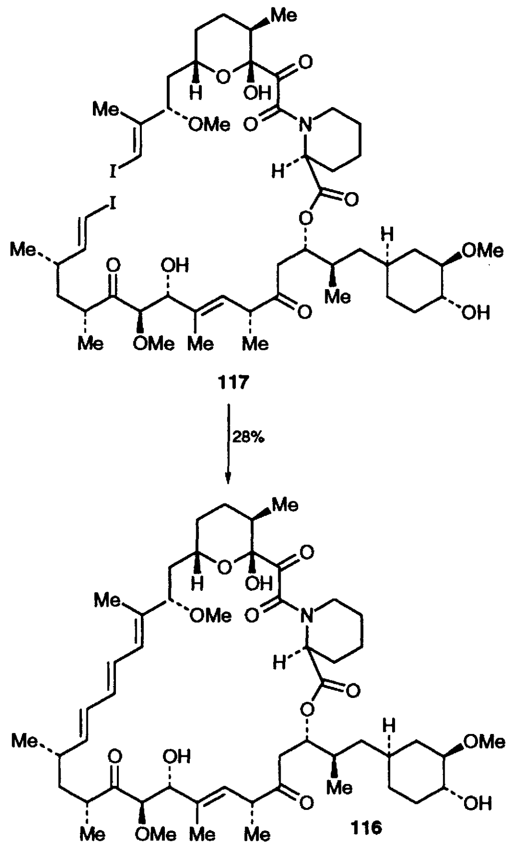
5.3 Stille-type coupling

Mitchell has recently reviewed the palladium-catalysed reactions of organotin compounds.[81] The Stille reaction has been widely exploited recently, and only a tiny selection of such applications can be reported here.

Eschavarren and co-workers have prepared 1,4-diketones **113** by the palladium-catalysed reductive coupling of acid chlorides **114** with (*E*)-1,2-bis(tri-n-butylstannyl)ethene **115**. Thus, in order to produce these diketones, the alkene has been reduced under the reaction conditions.[82a]



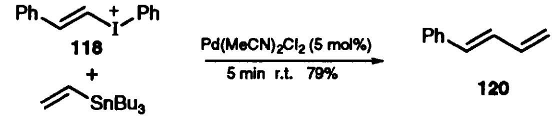
Nicolaou and co-workers have reported an exciting example of the use of the Stille coupling for the last step in the total synthesis of the macrocycle rapamycin **116** from the acyclic precursor **117** and (*E*)-1,2-bis(tri-n-butylstannyl)ethene **115**.[82b] This remarkable cyclization process demonstrates the chemoselectivity of reactions of this type.

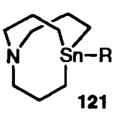


Reagents: **115** (1.2 eq.), Pr^i_2EtN (1.5 eq.), $Pd(MeCN)_2Cl_2$ (20 mol%), DMF/THF (1:1), 25 °C, 24h

Moriarty and Epa have demonstrated that alkenyl iodonium salts are reactive components for the Stille coupling.[83] Thus, the reaction between the iodonium salt **118** and tributylvinyltin **119** affords the coupled product **120** in 5 minutes at room temperature using bis(acetonitrile)palladium dichloride as catalyst.

Vedejs and co-workers have demonstrated that tin reagents **121** are unusually reactive in the Stille coupling, and can be used for the selective transfer of primary alkyl groups.[84]

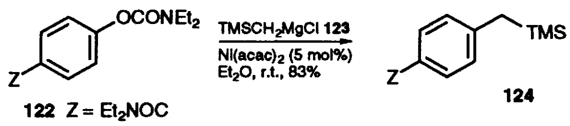



121

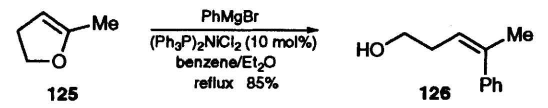
5.4 Coupling reactions of other nucleophiles

Apart from the use of boron and tin reagents for coupling reactions, other reagents can be employed, including Grignard reagents, organozincs, and other organometallic species.

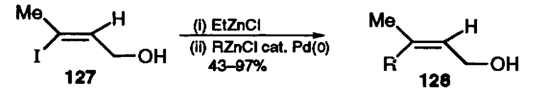
Snieckus and co-workers have employed nickel catalysis for the reaction between arylcarbamates or aryl triflates and Grignard reagents.[85] Many examples are reported, including the nickel-catalysed coupling of the carbamate **122** with Grignard reagent **123** which affords the coupled product **124** in 83% yield.



Kocienski and co-workers have shown that the nickel-catalysed coupling of Grignard reagents with 5-alkyl-2,3-dihydrofurans is also effective.[86] Thus, the reaction of **125** in the presence of catalytic $(Ph_3P)_2NiCl_2$ and phenyl magnesium bromide affords homoallylic alcohol **126** as the product with 96% isomeric purity.



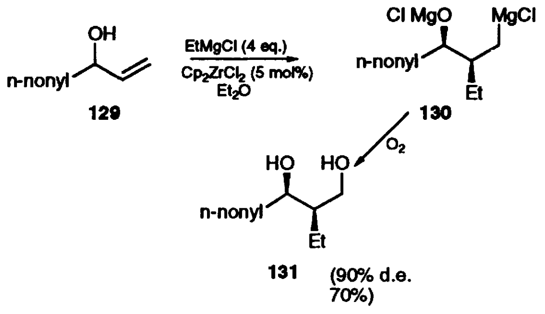
One recent application of the cross-coupling of organozinc reagents has been reported by Negishi and co-workers.[87] Treatment of the vinyl iodide **127** with ethylzinc bromide afforded a zinc alkoxide which could then be coupled with another alkylzinc halide using palladium catalysts to generate the product **128**.



Larock and co-workers have reported the coupling of aryl and vinyl halides or triflates with vinylic epoxides,[88] vinylic oxetanes,[89] and vinylic azetidinones.[90]

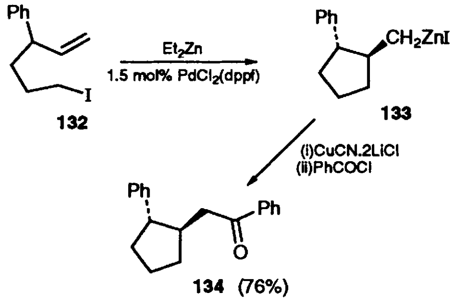
5.5 Carbometallation

Hoveyda and co-workers have continued a study of the zirconium-catalysed ethylmagnesation of alkenes. The reaction of allyl alcohol **129** with four equivalents of ethylmagnesium chloride and 5 mol% of Cp_2ZrCl_2 affords the intermediate **130**, which upon treatment with oxygen affords the diol **131** with 90% d.e.[91]



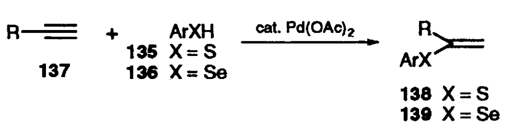
Conversion of the allylic alcohol into the corresponding methyl ether affords the alternative diastereomer as the major product (78% d.e.). Furthermore, the use of enantiomerically pure zirconocene catalysts leads to highly enantioselective reactions.[92]

Knochel and co-workers have reported a novel palladium-catalysed intramolecular carbozincation of alkenes.[93] The reaction of **132** with diethylzinc and 1.5 mol% of $PdCl_2$(dppf) gives the cyclized organozinc species **133**. Transmetallation with CuCN·2LiCl and trapping with benzoyl chloride affords the functionalized cyclopentane **134** in 76% yield.

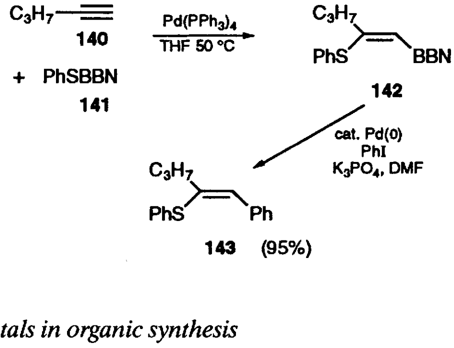


5.6 Reactions involving alkynes

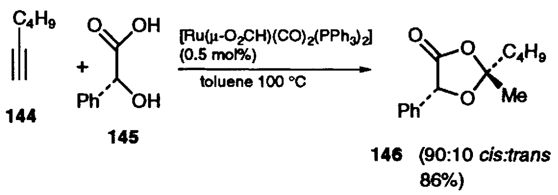
Ogawa, Sonoda, and co-workers have reported the palladium acetate catalysed addition of aromatic thiols **135**[94] and benzeneselenol **136**[95] to acetylenes **137** to give the products **138** and **139**. In neither case was the catalyst poisoned by the reagent.



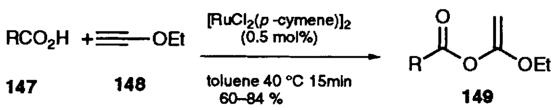
The palladium-catalysed thioboration of terminal alkynes has also been reported.[96] Thus, treatment of pent-1-yne **140** with 9-(phenylthio)-9-BBN **141** affords the intermediate **142**, which can be converted *in situ*, by addition of iodobenzene, into the coupled product **143** in 95% yield with 99% isomeric purity.



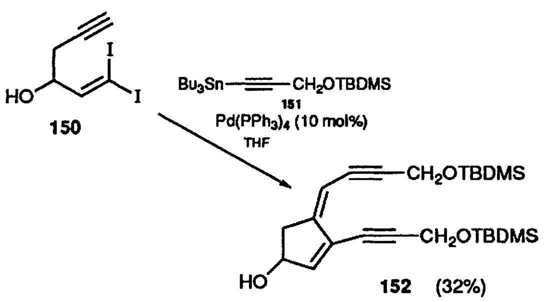
Dixneuf and co-workers have investigated the stereoselective addition of carboxylic acids to alkynes.[97] They have also reported that in the presence of the binuclear catalyst precursor $[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$, hexyne **144** and mandelic acid **145** are converted into the 1,3-dioxolan-4-one **146**.[98]



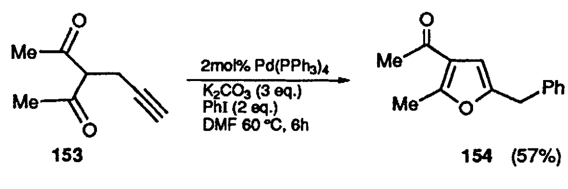
Kita and co-workers have shown that whilst standard catalysts for the addition of carboxylic acids to alkynes are ineffective in the case of alkoxyalkynes, catalytic amounts of $[RuCl_2(p\text{-cymene})]_2$ were effective for the addition of various carboxylic acids **147** to ethoxyacetylene **148**, thereby affording ethoxyvinyl ester **149**.[99]



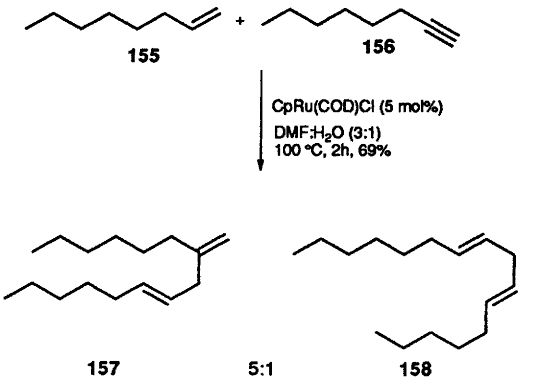
Nuss and co-workers have reported the palladium-catalysed reaction between di-iodoenyne **150** and five equivalents of the alkynyl stannane **151** to afford the product **152** in 32% yield, in which three new C–C bonds have been formed.

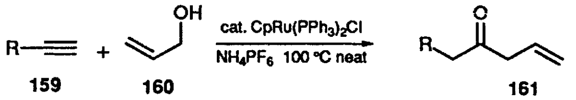


Larock, Cacchi, and co-workers have exploited palladium catalysts for the formation of furans.[100] Reaction of the alkyne **153** with iodobenzene in the presence of a palladium catalyst directly affords the furan **154** in 57% yield.



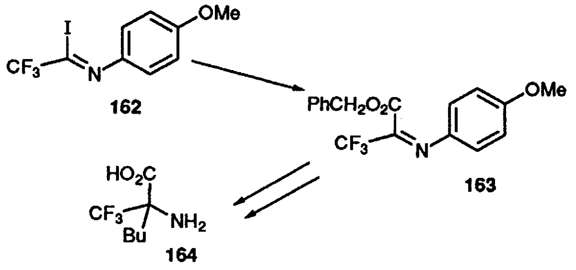
Trost and Indolese have reported the novel ruthenium-catalysed addition of alkenes to alkynes.[101] Thus, the reaction of oct-1-ene **155** and oct-1-yne **156** with a ruthenium catalyst afforded a 69% yield of the branched diene **157** and the linear diene **158** (**157**:**158**, 5:1). Trost and co-workers have further documented the use of the ruthenium-catalysed 'reconstitutive condensation' of acetylenes **159** with allyl alcohols **160** to afford the ketone **161**. Evidence has been presented to support the proposed mechanism for the catalytic cycle.[102] Applications to the functionalization of steroidal side chains have been reported.[103]





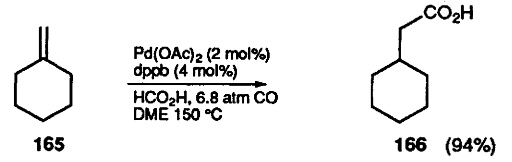
5.7 Hydroxycarbonylation and alkoxycarbonylation

An interesting approach to α-amino perfluoroalkanoic acids has been designed by Uneyama and co-workers.[104] Palladium-catalysed carbonylation of the imidoyl iodide **162** in the presence of benzyl alcohol affords the corresponding α-imino ester **163**, with further transformation giving the α-amino acid **164**.

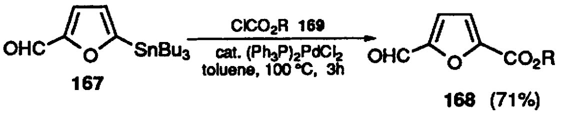


Reagents: CO(1atm), $Pd_2(dba)_3CHCl_3$, $PhCH_2OH$, K_2CO_3, toluene

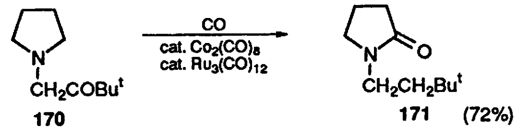
Ali and Alper have reported a highly regioselective catalytic process for the hydrocarboxylation of methylenecycloalkanes.[105] The reaction of methylenecyclohexane **165** with two equivalents of formic acid in the presence of catalytic amounts of 1,4-bis(diphenylphosphino)butane and palladium acetate under 6.8 atmospheres of carbon monoxide afforded the product **166** in 94% yield. The choice of ligand was crucial for high yields of product.



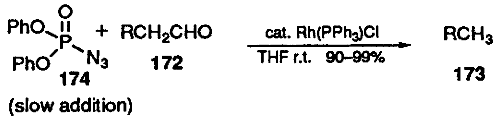
Alkoxycarbonylation can be achieved using chloroformates as the coupling partner. We are reminded of this in the conversion of the stannylfuran **167** into the corresponding ester **168**, which occurs upon treatment with chloroformate **169** under palladium catalysis.[106]



Wang and Alper have reported an unusual rearrangement reaction to afford lactam products.[107] Treatment of the ketone **170** with catalytic amounts of $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ affords the rearranged product **171** in 72% yield.



O'Connor and Ma have described a useful method for the metal-catalysed decarbonylation of aldehydes **172** into alkanes **173** at room temperature.[108] The method relies upon the presence of stoichiometric amounts of diphenylphosphoryl azide **174**, which prevents the rhodium catalyst from forming inactive carbonyl complexes.

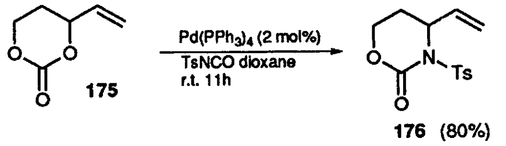


5.8 Allylic substitution

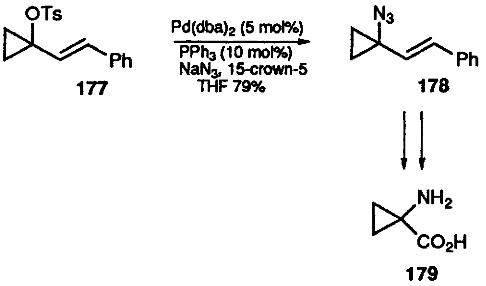
The majority of research in the area of catalysed allylic substitutions is currently centred around palladium catalysis, and has recently been reviewed.[109]

The use of triphenylsilanol as an oxygen nucleophile has been used for the selective 1,4-opening of vinyl epoxides.[110] Trimethylsilyl cyanide successfully delivers cyanide as a nucleophile in palladium-catalysed allylic substitution.[111]

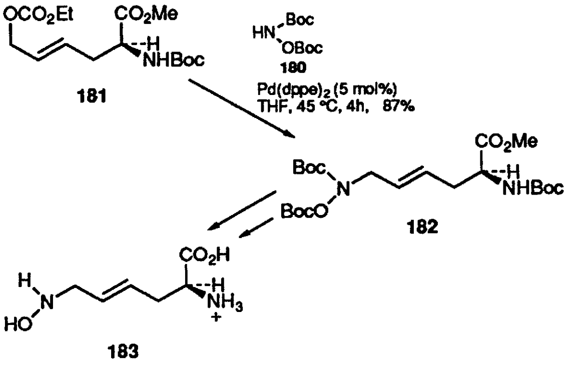
Tamaru and co-workers have employed cyclic carbonates **175** as substrates.[112] By using isocyanates as the incoming nucleophiles, a highly regioselective amination occurs by pre-coordination of the nucleophile to give the product **176**. For other nucleophiles, the regiochemistry would be expected to involve nucleophilic addition to the less sterically encumbered allyl terminus.[113]



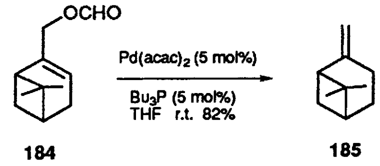
Palladium-catalysed azidation of 1-alkenylcyclopropyl tosylate **177** affords the azide substituted product **178** with the indicated regiochemistry.[114] Functional group manipulation affords 2,3-methanoamino acid **179**.



Genet and co-workers have reported the use of N,O-bis-t-Boc protected hydroxylamine **180** as a nucleophile for palladium-catalysed allylic substitution.[115] Thus the allyl carbonate **181** is converted into the substitution product **182**, which is further transformed into (+)-N^6-hydroxylysine **183**.

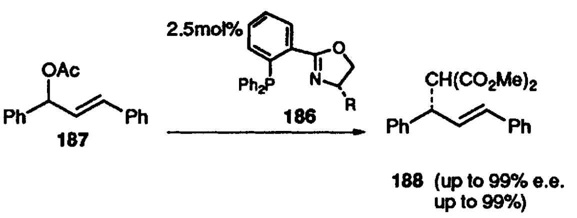


The use of palladium acetate or palladium acetylacetonoate in combination with tributyl phosphine has been recommended as a particularly active catalyst,[116] and has been used in the introduction of exocyclic methylene groups. For example, myrtenyl formate **184** selectively affords β-pinene **185** upon treatment with this catalyst.[117]



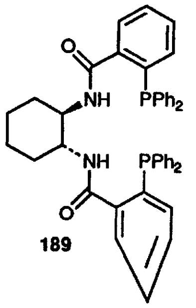
Three groups have reported the use of the ligand **186** for enantioselective palladium-catalysed allylic substitution.[118-120] This ligand provides higher enantioselectivities than previous ligands for some reactions. For example, the reaction of allyl acetate **187** with dimethylmalonate affords the allylic substitution product **188** with up to 99% e.e. These, and related ligands appear to rely upon a disparity in the electronic/steric properties of the two donor atoms.[121]

Trost and Van Vranken report the use of palladium-catalysed allylic substitution in the synthesis of aminocyclopentitol glycosidase inhibitors.[122] They are pursuing asymmetric variants of these syntheses



Reagents: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1 mol%), KOAc,BSA (2 mol%), $H_2C(CO_2Me)_2$, CH_2Cl_2, 23 °C

using highly effective ligands exemplified by structures **189** and **190**.[123,124]



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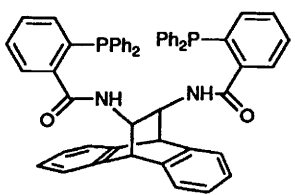
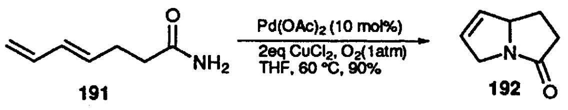


190

Bäckvall's group has demonstrated the synthetic power of the palladium-catalysed 1,4-oxidation of conjugated dienes, a reaction which also proceeds *via* π-allylpalladium intermediates.[125] A recent development has been the use of tethered nucleophiles which are able to add to both ends of the diene. For example, the reaction of the dienamide **191** with catalytic palladium acetate and excess cupric chloride using oxygen as the primary oxidant afforded the pyrrolizidinone **192** in 90% yield.

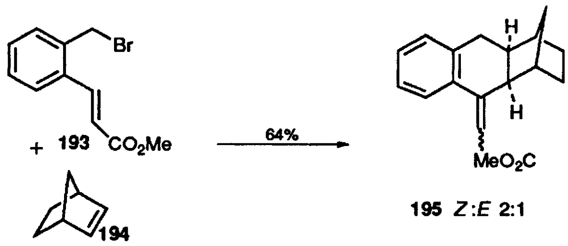


5.9 Tandem and cascade processes

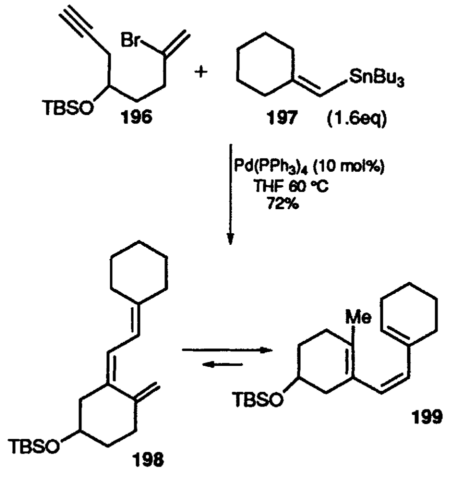
There are a growing number of tandem and cascade processes being reported wherein the catalyst triggers a series of reactions on one molecule. The various components of these reactions are familiar catalytic reactions, such as those that we have seen in the preceding sections.

Grigg's research group has accessed various polycyclic structures by identifying various 'starter components' for catalytic cascade reactions. For example, the reaction of benzylic bromide **193** with norbornene **194** affords the cyclized product **195**.[126] Intermediate palladium alkyl species can also be trapped by hydride ion capture[127] or cyanide ion capture.[128]

The research groups of Nuss[129] and Trost[130] have both reported palladium-catalysed tandem reactions as an entry into vitamin D derivatives. Thus, Nuss and co-workers have shown that the palladium-catalysed reaction between the vinyl bromide **196** and the vinyl stannane **197** afforded the cyclized and coupled product **198**, which is in equilibrium with **199** *via* a [1, 7] H shift.



Reagents: $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), 2eq. K_2CO_3, Et_4NCl (1eq.), C_6H_6, 80 °C, 18h.

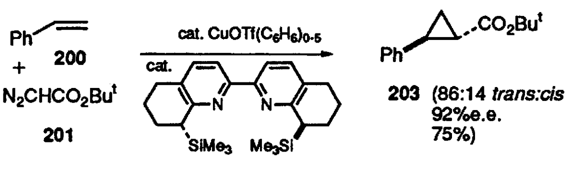


6 Reactions involving metal carbenoids

Whilst many transition metals are believed to catalyse reactions which proceed *via* intermediate carbenes or carbenoids, the majority of work has been centred around rhodium- and copper-catalysed reactions. The behaviour and chemoselectivity of these carbenoids are becoming more well understood.[131] There are increasingly complex cascade reactions which begin with metal carbenoids and lead to polycyclic products.[132]

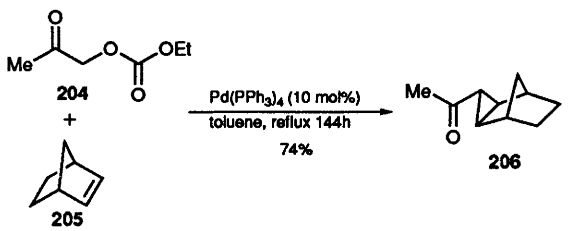
6.1 Cyclopropanation

Katsuki and co-workers have reported the use of bipyridine ligands for copper-catalysed asymmetric cyclopropanation.[133,134] Cyclopropanation of styrene **200** with t-butyl diazoacetate **201** in the presence of catalytic copper triflate and the ligand **202** afforded the *trans* cyclopropane **203** selectivity with 92% e.e.



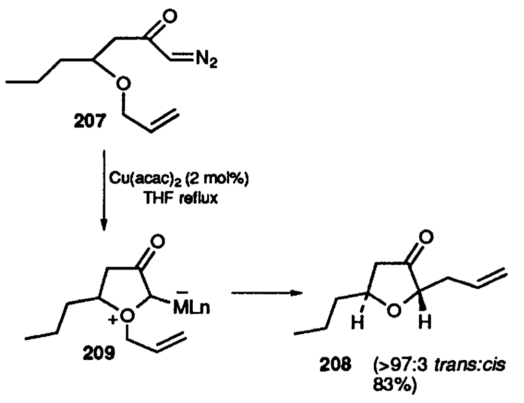
Enantioselective intramolecular cyclopropanations have also been reported with enantiomerically pure copper[135] and rhodium[136] catalysts. Enantiomerically pure polyethylene-bound rhodium(II) complexes have also been developed, and are especially efficient for enantioselective intramolecular cyclopropanations.[137]

Not all metal-catalysed cyclopropanation reactions proceed *via* carbenes. Murai and co-workers have reported the palladium-catalysed reaction of ketone α-carbonates **204** with norbornenes **205** to afford cyclopropane products **206**.[138] The reaction is believed to proceed *via* an oxa-π-allylpalladium intermediate rather than *via* a palladium carbene.

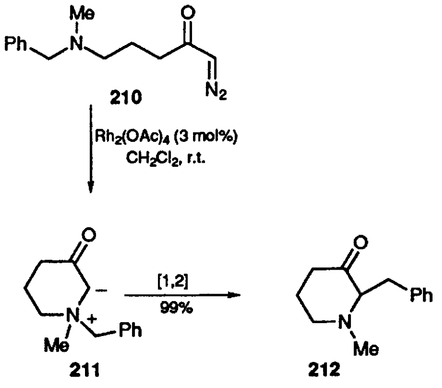


6.2 Insertion reactions

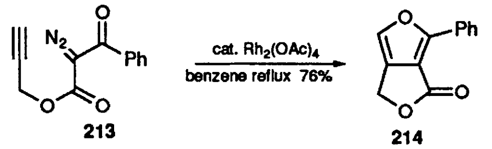
Clark has shown that $Cu(acac)_2$ is superior to $Rh_2(OAc)_4$ for the conversion of **207** into **208**.[139] The mechanism is suggested to occur through a metal bound oxonium ylide **209**, since variation in the catalyst results in differing levels of diastereoselectivity in the product.

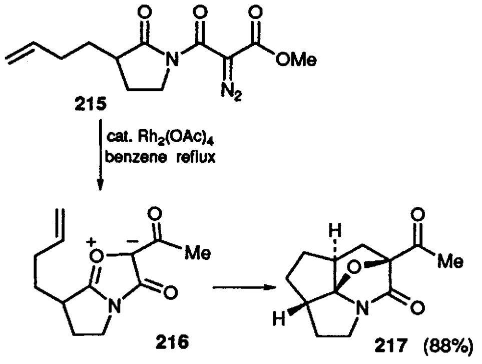


Reactions involving the corresponding ammonium ylide have been reported by West and Naidu.[140] Thus cyclization of **210** in the presence of catalytic rhodium(II) acetate affords the intermediate **211**, which undergoes a Stevens [1, 2] shift to afford the piperidine **212** in 99% yield. Alternative C–H insertion reactions were not observed.

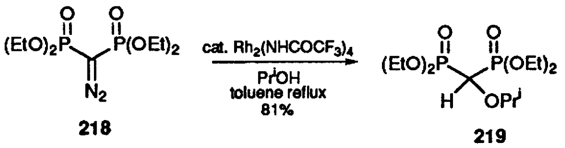


Padwa and Kinder have reported the rhodium(II) acetate catalysed formation of substituted furans.[141] Treatment of the diazo precursor **213** affords the bicyclized product **214** in 76% yield. A range of similar cyclizations were also reported. Padwa's group has continued its investigations into tandem rhodium-catalysed cyclization/1,3-dipolar cycloaddition processes.[142] In particular, an intramolecular system **215** has been reported to proceed *via* the intermediate **216** to afford the tetracyclic product **217** in 88% yield.[143]





Moody and co-workers have reported the benefits of using rhodium(II) trifluoroacetamide as a catalyst for O–H insertion reactions.[144] The diazobisphosphonate **218** afforded none of the desired O–H insertion product **219** in the presence of rhodium(II) acetate. However, the use of rhodium(II) trifluoroacetamide as the catalyst afforded an 81% yield of product **219**.

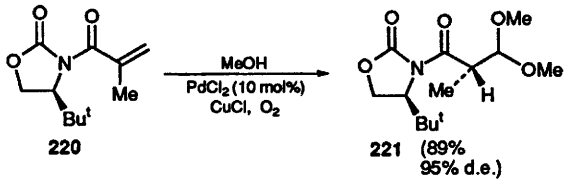


7 Miscellaneous

This last section contains a pot-pourri of interesting reactions which do not readily fall into one of the major categories. In some cases, the difficulty of categorization is a reflection of the novelty of the reaction concerned.

7.1 Acetalization

A diastereoselective palladium-catalysed acetalization of alkenes has been reported.[145] The greatest diastereoselectivity was observed with the t-butyl substituted oxazolidinone **220**. Treatment of **220** with methanol, palladium chloride catalyst, and stoichiometric cuprous chloride under an atmosphere of oxygen afforded the product **221** with 95% d.e.



7.2 Thioether formation

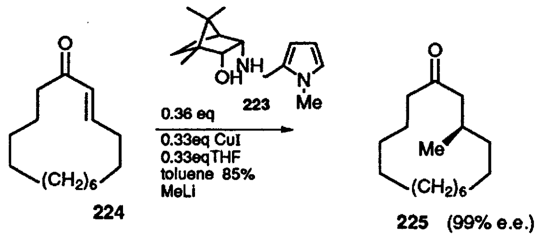
Bulman Page and co-workers have reported an unusual reaction involving the platinum-catalysed formation of thioethers from thiols and alkyl halides.[146] For example, treatment of butane thiol, iodobutane, and sodium carbonate with a platinum catalyst affords dibutylsulfide **222** in 80% yield.

$$\mathrm{BuSH} + \mathrm{BuI} \xrightarrow[\mathrm{Na_2CO_3}\quad 80\%]{(\mathrm{dppm})\mathrm{PtCl_2}\,(5\,\mathrm{mol}\%)} \mathrm{BuSBu}$$

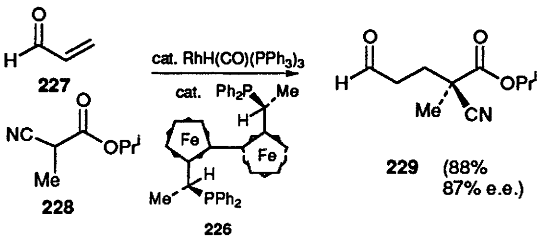
222

7.3 Conjugate addition

Tanaka and co-workers have developed the use of the ligand **223** for catalytic enantioselective conjugate addition. The reaction of **224** with methyllithium in the presence of 0.36 equivalents of the ligand **223** and 0.33 equivalents of copper iodide and 0.33 equivalents of THF afford the conjugate addition product, muscone **225** with 99% e.e.[147] Such high levels of enantioselectivity hold great promise for reactions involving less catalyst.

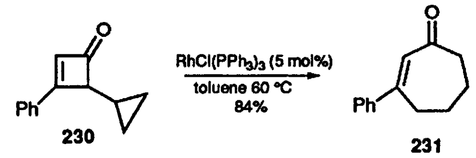


Ito and co-workers have employed the *trans* chelating ligand **226** for a rhodium-catalysed addition of α-cyano carboxylates to Michael acceptors. Thus the reaction between **227** and **228** in the presence of catalytic amounts of $\mathrm{RhH(CO)(PPh_3)_3}$ and ligand **226** affords the addition product **229** with 87% e.e.[148]

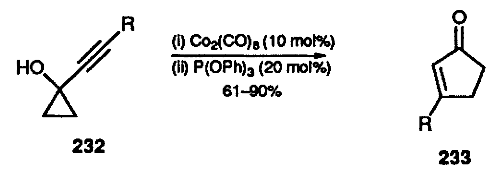


7.4 Ring fusion and expansion

Huffman and Liebeskind have designed a novel intramolecular carbocyclic ring-fusion process.[149] Treatment of 4-cyclopropyl-2-cyclobutenone **230** with 5 mol% $\mathrm{RhCl(PPh_3)_3}$ affords the cycloheptadienone **231** in 84% yield.

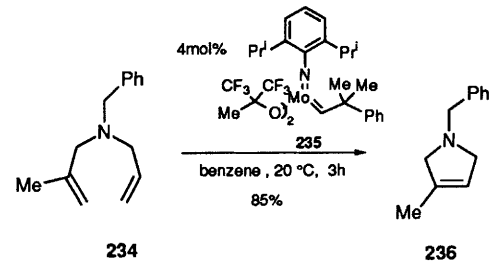


Iwasawa and Matsuo have reported the ring expansion of 1-alkynylcyclopropanols **232** into cyclopentenones **233** on treatment with 10 mol% $\mathrm{Co_2(CO)_8}$ followed by 20 mol% $\mathrm{P(OPh)_3}$.[150]



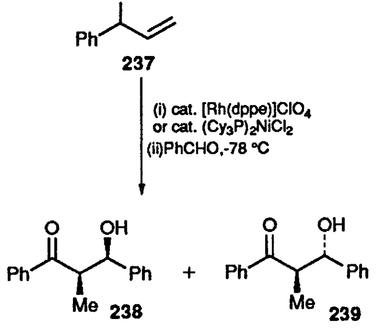
7.5 Metathesis

The catalytic ring-closing of dienes has been pursued by Fu and Grubbs.[151] For example, the reaction of the diene **234** in the presence of the catalyst **235** affords an 85% yield of pyrroline **236**.



7.6 Isomerizations

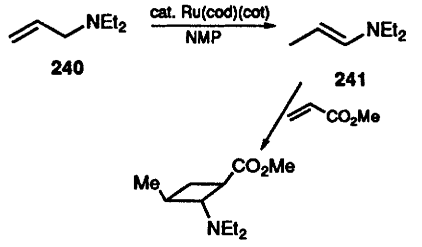
It is well known that transition metals are able to isomerize alkenes. Particularly useful are the isomerizations of allyl alcohols[152,153] and allyl amines, as these next examples illustrate. Motherwell and Sandham have demonstrated the nickel-catalysed transformation of allylic alkoxides **237** into enolates, and their use in an aldol reaction with benzaldehyde to afford the aldol products **238** and **239**.[154]



84% 8.6 : 1 (Rh)
81% 6.6 : 1 (Ni)

Additionally, it has been reported that treatment of diethylallylamine **240** with *N*-methylpiperidine and a ruthenium catalyst affords the isomerized enamine

241, which is trapped with methyl acrylate to afford the cycloaddition product **242**.[155]



242 (85%)

8 Conclusion

The use of transition metals as catalysts is becoming increasingly popular with synthetic organic chemists. Many catalytic systems offer the advantages of chemical selectivity, mild reaction conditions, and can additionally provide regiocontrol, diastereocontrol, and enantiocontrol. The future development of new reactions and catalytic pathways is still an exciting prospect.

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