Main group organometallics in synthesis

MARTIN WILLS

Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

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1 Introduction

As with previous reviews the emphasis will be on synthetic aspects, rather than mechanistic and structural properties, of the organometallic compounds in the following discussion.

2. Group 1

2.1 Lithium

2.1.1 Lithium amides and enolates

Under certain conditions, and provided β-hydrogen atoms are available, lithiated amines can act as reducing agents; this aspect of their reactivity has been reviewed recently.[1] The use of homochiral lithium amides in asymmetric deprotonation chemistry is now a mature area of research and most reports now detail refinements and improvements to known systems. A striking recent application of this methodology has been in the asymmetric *ortho*-lithiation of certain activated arene–chromium tricarbonyl complexes, where enantiomeric excesses (ee's) of up to 90% have been recorded.[2]

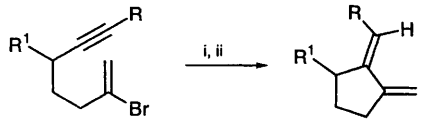
Lithium enolate chemistry is pivotal to organic synthesis and a comprehensive coverage would not be possible in a review of this type. However attention will be drawn to recent developments in the area of asymmetric protonations of racemic enolates, which have in some cases been refined to give ee's of up to 98%.[3] With the aid of an appropriate chiral ligand, similar selectivities may be achieved in alkylation reactions of certain compounds.[4]

2.1.2 Non-stabilised organolithium reagents

Due to their high reactivity, organolithium compounds are rarely used in catalytic asymmetric reactions, since reaction acceleration is difficult to achieve. This feature is reflected in the report by Denmark on the asymmetric addition of alkyllithiums to imines catalysed by diamines, in which ee's of up to 82% are achieved, but only when a stoichiometric amount of ligand is employed.[5] Whilst halide–lithium exchange reactions remain the predominant method for formation of complex organolithium building blocks,[6] the use of lithium metal, together with a catalytic amount of a polyaromatic, is gaining popularity. In a recent development it has been demonstrated that aryl sulfones can serve as suitable precursors for this chemistry.[7] The same Barbier-type process can be achieved using sonochemical methods.[8]

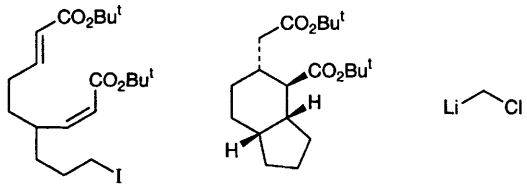
In recent years intramolecular cyclisations of organolithiums onto unactivated double[9] or triple[10] bonds has been developed into a versatile and reasonably general procedure. In one example a very simple diene synthesis has been achieved

(**Scheme 1**).[10a] Related cyclisations onto activated multiple bonds are also synthetically valuable, especially when the process can be achieved in a tandem sense by setting up an appropriate sequence of five- and six-membered rings. This has been illustrated by the stereoselective conversion of iodide **1** into the bicycle **2** upon treatment with butyllithium.[11]



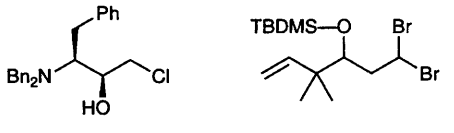
Reagents: i, 2.0 eq. Bu^tLi, C_5H_{12}, Et_2O, –78 °C to r.t.; ii, H_3O^+

Scheme 1

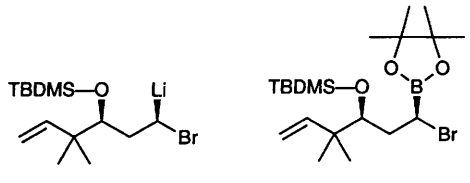


1 **2** **3**

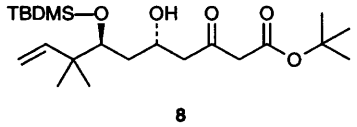
Lithium anions may be created adjacent to heteroatoms by a variety of methods. In a large scale (2.2 kg) example of the 'reductive' method, an excess of lithium metal is employed to generate **3** and subsequently **4** upon reaction with the appropriate chiral aldehyde.[12] This synthesis clearly underlines the value of such methodology to process development as well as to small scale synthetic work. In other cases, however, the process of lithium–bromine exchange *via* the use of an alkyllithium is favoured.[13] In some cases this can be a stereoselective process, as illustrated by the low temperature reaction of **5** with butyllithium to give predominantly the isomer **6**, which was trapped as a boronic ester derivative **7**.[13b] This reaction formed the basis for the synthesis of the bryostatin subunit **8** *via* reaction with the dianion of *tert*-butyl acetoacetate. The corresponding reaction of butyllithiums with alkyl chlorides does not result in lithium–chlorine exchange; deprotonation adjacent to the chlorine is favoured. This process may also be employed to synthetic advantage.[14]



4 **5**



6 **7**



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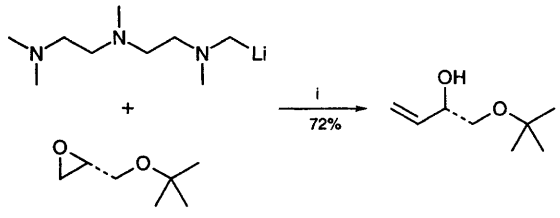
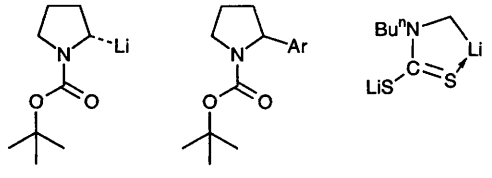
Lithiation may be achieved by deprotonation α- to a nitrogen atom;[15] however some form of activation or a directing group is invariably required. In some cases polyamines, which are often employed to activate alkyllithium bases, can direct their own self-lithiation. In some cases this can be a troublesome side reaction, as illustrated by a report of tetramethylethylenediamine (TMEDA) lithiation,[16] but may also be employed to useful effect, for example in a methylene transfer reaction (**Scheme 2**).[17] Carbamates are perhaps the most widely used directing groups for lithiation adjacent to nitrogen,[18] and a full paper has appeared describing formation and applications of enantiomerically enriched complexes such as **9**. These valuable homochiral building blocks are formed by the action of butyllithium complexed with a chiral ligand such as the diamine sparteine.[19] Applications of these and related compounds have been extensively explored; however a very attractive recent addition to the repertoire is a very valuable palladium coupling with aryl halides to give the 2-aryl derivatives **10**.[20] Directed lithiation adjacent to a nitrogen atom may also be achieved by using a complex with carbon disufide, as in **11**, which collapses back to the amine upon work-up of the reaction.[21]



Reagent: i, pentane, 0 °C

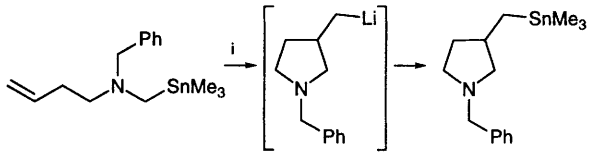
Scheme 2



9 **10** **11**

Trialkyltin–lithium exchange is another of the popular methods for formation of lithiated anions adjacent to nitrogen.[22] Rather milder conditions are required to achieve this than for direct deprotonation, which has obvious advantages. This

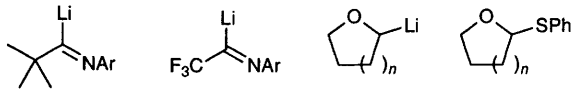
process has formed the basis of an interesting cyclisation reported by Coldham, in which a five-membered heterocycle formation is terminated by re-addition of trimethyltin (**Scheme 3**).[23] As well as the bonus that is afforded by the further manipulation of the trialkyltin group (for example to give an acetal), the process also benefits from the fact that only a catalytic amount of methyllithium is required.



Reagent: i, MeLi

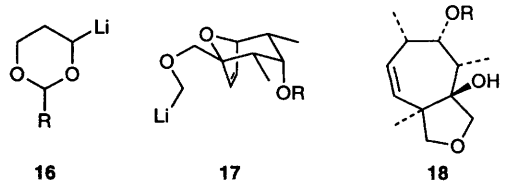
Scheme 3

Formyl anion equivalents[22c] are of great use in synthesis and will feature at various points throughout this report. Less common however are the nitrogen equivalents – imines lithiated at the α-position such as **12**.[24] Such compounds may be simply generated by the addition of *tert*-butyllithium to the appropriate isonitrile and, in the example referenced here, add to carbon monoxide and then cyclise in an intramolecular sense onto the aromatic ring to form indoles. The trifluoroacetimidoyl lithium compounds **13** may be generated from the corresponding iodides using butyllithium[25a] and a related compound has been prepared by a similar treatment of a trialkylstannane precursor.[25b]



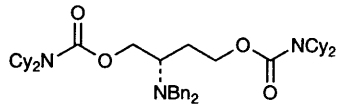
12 **13** **14** *n* = 1,2 **15** *n* = 1,2

Much of the discussion above is also applicable to the preparation and use of lithium anions adjacent to oxygen. Reductive methods using lithium metal and catalytic amounts of a polyaromatic are again popular, and have been successfully employed for the formation of lithiated tetrahydrofurans and pyrans **14** from the precursors **15** in high yields.[26] Useful chiral building blocks such as **16** are available in the same way.[27] Whatever the method of generation, anions adjacent to oxygen atoms have been employed extensively in Wittig rearrangements to great effect,[28] as illustrated by the impressive ring expansion of **17** to give the bicyclic product **18** (the lithiated species is generated from the trimethyltin precursor).[28a]



16 **17** **18**

Hoppe has reported further results from his studies on the asymmetric directed lithiations of carbamates using the chiral base sparteine as a directing group.[29] Such reactions show remarkable dependence on the nature of the deprotonation conditions and the nature of additives. Reaction of **19** with 1.5 equiv. of *sec*-butyllithium in ether at −78 °C involves a directing effect by the dibenzylamine group to give the lithiated species **20**. In contrast, use of the same conditions in the presence of 1.5 equiv. of (−)-sparteine gives the regioisomeric complex **21** (sparteine is omitted for clarity), presumably due to the overriding directing effect of the chiral diamine–alkyllithium complex.[29a]



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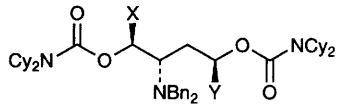
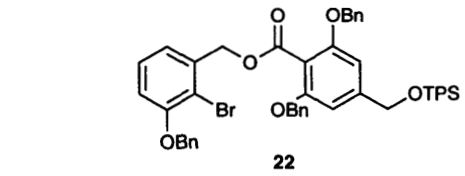


20 X = Li, Y = H
21 X = H, Y = Li

2.1.3 Lithiated aromatic and heteroaromatic groups

Of all the functional groups known to be effective at directing the *ortho*-lithiation of aromatic rings, methoxy and amide groups are two of the most effective. However even a catalytic amount of TMEDA can generate a dramatic rate increase in this process, an effect which has been studied in detail recently.[30] The presence of a *para*-fluoro atom has also been shown to provide a dramatic rate enhancing effect, presumably due to activation *via* inductive electron withdrawal.[31] Bromine–lithium exchange provides a milder alternative to deprotonation and is the method of choice provided a suitable substrate is available. In the total synthesis of balanol, Nicolaou employed such a process to convert ester **22** to the ketone **23** *via* an intramolecular reaction initiated by treatment with butyllithium.[32] After oxidation with TPAP and further steps, **23** was converted to the side chain of the synthetic target molecule. In another intramolecular example, rapid bromine–lithium exchange outpaces attack by phenyllithium on the epoxide in **24**, allowing intramolecular ring opening to be achieved to give the product **25**.[33]

The relatively facile 2-lithiation of furan rings has been studied in some detail. This process has been employed recently in a key step in the total synthesis of salinomycin, where fragment **26** was coupled cleanly with another of equal complexity to provide the C(11)–C(30) portion of the target molecule.[34] One-pot furan lithiation and acylation may also be achieved using the sonochemical Barbier reaction in



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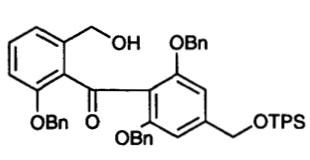

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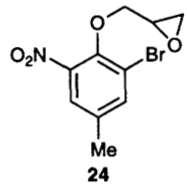

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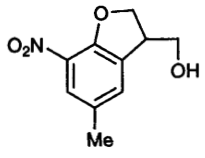

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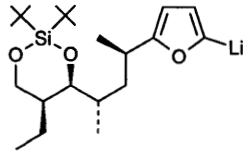

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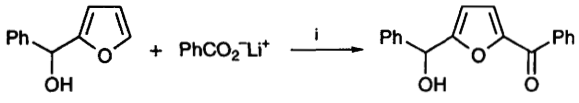
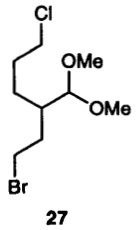


Reagent: i, Bu^{t}Cl, TMEDA, THF,))), r.t., 15 min.

Scheme 4

which the lithium salt of a carboxylic acid is irradiated in the presence of *tert*-butyl chloride and lithium metal, presumably resulting in *in situ* formation of *tert*-butyllithium (**Scheme 4**).[35]

Direct thiofuran lithiation favours the 2-position; however 3-lithiothiofuran my be prepared from the appropriate bromide precursor.[36] The use of thiofuran as a 4-carbon fragment (*via* exhaustive reduction to the hydrocarbon) is well established. An excellent example of this has recently been described in which the coupling of 2-lithiothiofuran and bromide **27** provides a key step in the synthesis of the C_2 symmetric target (+)-xestospongin A **28**.[37] The thiofuran in this case provides the atoms in the two chains linking the heterocyclic units. Treatment of tetrabromothiofuran may be selectively controlled so that one bromide is predominantly exchanged for lithium, as described in some detail by Iddon.[38]



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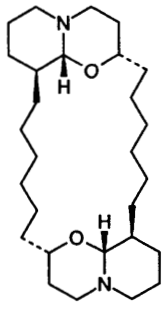

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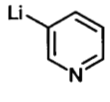

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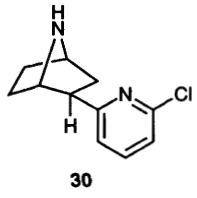
Lithiated pyridines are valuable synthetic intermediates which have been the subject of a good deal of detailed studies recently. A good example is the use of 3-lithiopyridine **29** to provide the heterocyclic ring in a recent short synthesis of epibatidine **30**.[39] Comins[40] has reported further results from his studies on directed lithiations of pyridines using lithiated hemiaminals, which may be introduced *via* reaction of the lithiated pyridine with a formamide (**Scheme 5**). In the sequence illustrated, which is part of a camptothecin total synthesis, further lithiation is achieved directly,



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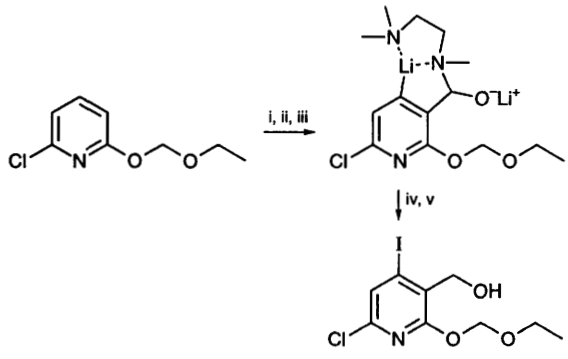


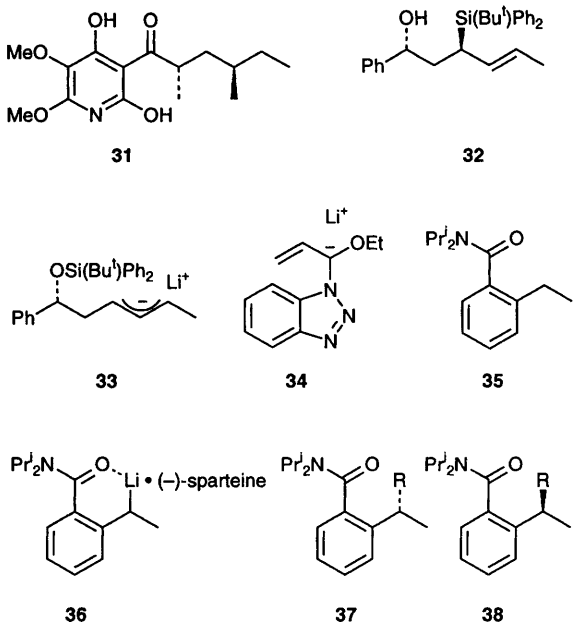
Reagents: i, Bu^{n}Li; ii, $Me_2NCH_2CH_2N(Me)CHO$; iii, Bu^{n}Li; iv, I_2; v, $NaBH_4$, H_2O

Scheme 5

followed by iodination and then reduction of the intermediate aldehyde. In a related sequence, the synthesis of parvifoline has been achieved, although not on a pyridine ring in this case.[41] Finally in this section, the synthesis of atpenin B, **31**, *via* a sequence of four sequential lithiations of 2-chloropyridine, working clockwise around the ring as drawn, is highlighted.[42]

2.1.4 Benzylic and allylic lithium anions

Alkylations of unsymmetric allyllithium compounds can occur with low regioselectivity if the steric differentiation between the 1- and 3-positions is not great. A useful solution to this problem is to perform the alkylation in an intramolecular sense. This idea is illustrated by the formation of allylsilanes **32** *via* a [1,4]-Brook rearrangement of the silyloxy precursor anion **33**, which may be formed by either reduction of an allylic thioether, as in this example,[43] or tin–lithium exchange.[44] In either case the *anti* product dominates (>90% this isomer) and the resultant double bond is invariably

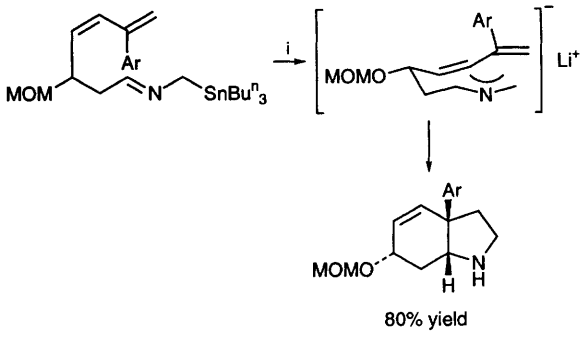


31 32 33 34 35 36 37 38

trans irrespective of the geometry of the starting material. Katritzky has reported further examples of the applications of allylic anions based on benzotriazoles **34**. Such reagents are highly versatile and may be used to prepare cyclopropanes or unsaturated ketone derivatives depending on the exact conditions employed.[45]

The reaction of a strong base such as LDA with a chloromethyl substituted aromatic or heteroaromatic compound generally results in deprotonation to form a benzylic anion. Such anions may subsequently be employed in the formation of epoxides upon reaction with ketones or aldehydes.[46] The reduction of chloromethyl ketones with lithium metal and a polyaromatic, on the other hand, provides an excellent method for the formation of non-stabilised benzylic anions, which are often otherwise difficult to prepare.[47] When there are activating or directing groups on the aromatic ring, such as a phosphate[48] or an amide,[49] direct benzylic deprotonation can be achieved under relatively mild conditions. When (−)-sparteine was used in collaboration with an alkyllithium base for the deprotonation of **35**, an asymmetric complex **36** was formed. The enantioselectivity of alkylation of **36** shows a remarkable dependence on the nature of the alkylating agent; **37** (up to 97% ee) is the product when alkyl tosylates are used whereas the enantiomer **38** (up to 92% ee) is the product when alkyl halides are employed.[49]

Heteroallylic anions featuring a central nitrogen atom have been developed into valuable synthetic reagents in recent years.[50] Pearson has reported a number of inter- and intra-molecular cyclisation reactions directed at the synthesis of alkaloids which feature these reagents (**Scheme 6**).[50a] Trialkyltin–lithium exchange appears to be the method of choice for their generation. A related series of reagents featuring an additional stabilisation by an enolate has also been reported.[51]

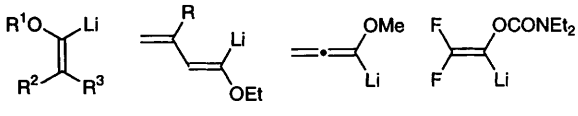


Reagent; i, 2.1 eq. Bu^nLi, THF, −78 °C, 1 h.

Scheme 6

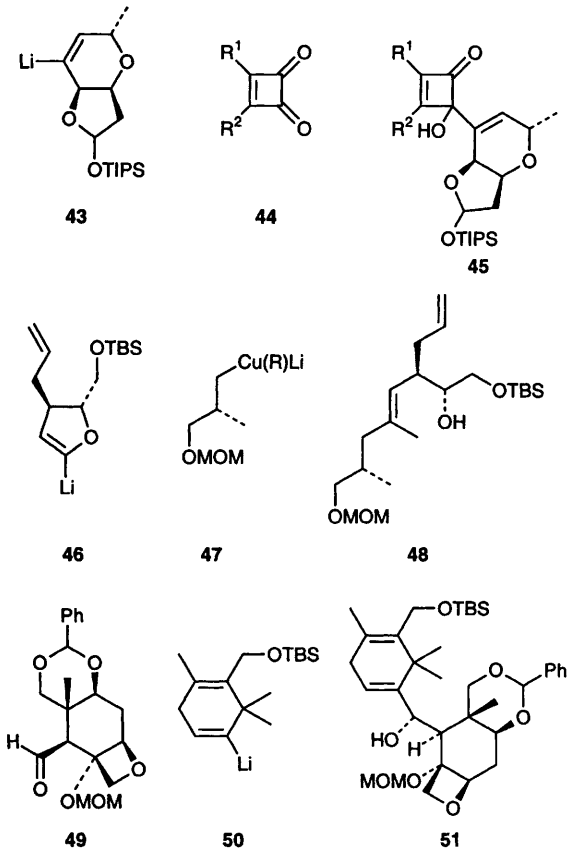
2.1.5 Alkenyl and alkynyl anions

The formation of alkenyllithiums by direct deprotonation is only efficient if a suitable activating[52] or directing group is available to assist the reaction; if not then a reductive method (vinyl chloride, lithium powder, catalytic polyaromatic compound)[53] or a trialkyltin–lithium exchange method[54] may be used. Of all the possible activating groups, α-alkoxy functions are especially effective at promoting deprotonation at vinylic carbon atoms.[52] Several examples of the lithiation of enol ethers and related materials have been reported recently. Applications of diverse alkyllithium species thus formed, represented by **39**,[51a,b] **40**[51c] and **41**[51d] have also been described. The difluoro substituted reagent **42** has been the subject of considerable recent interest. In a recent paper the tandem reaction of **42** with two carbonyl compounds, reacting first as a vinyl anion equivalent and then as an enolate anion, has featured.[55]



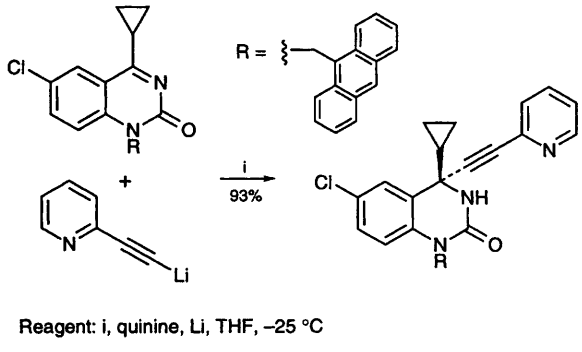
39 40 41 42

Vinylic anions have seen many applications in organic synthesis. The reaction of 1 equiv. of **43** with cyclobutenedione **44** is a key step in the synthesis of isochromaquinones; a ring expansion of product **45** gives the required quinone unit.[56a] A similar addition–rearrangement sequence was used by Paquette in the synthesis of a tricyclic natural product.[56b] Lithiated dihydrofurans, *e.g.* **46**, provide useful building blocks for complex synthetic targets.[57] Upon reaction with cuprate **47** and a subsequent ring opening reaction and methylation, the C(16)–C(23) region of FK506 **48** is prepared.[57a] Perhaps one of the most exciting applications of vinyl anions however has been in the area of Taxol® synthesis.[58,59] A key step in the Nicolaou synthesis was the reaction between **49** and **50** (the latter formed by a Shapiro reaction of the sulfonated hydrazone precursor) to give, in 85% yield, adduct



51.[58] In another synthetic approach, a vinyllithium was employed to set up an intramolecular Diels–Alder reaction in a very concise sequence leading to the Taxol® ABC ring structure.[59b]

Alkynyl anions have also found many applications in synthesis, one of which has been as a building block in the spiroketal subunit of milbemycins.[60] An impressive enantioselectivity (up to 97%) was achieved in the addition of a lithiated 2-acetylenic pyridine to a heterocyclic electrophile using a lithiated quinine to provide the directing effect (**Scheme 7**).[61]

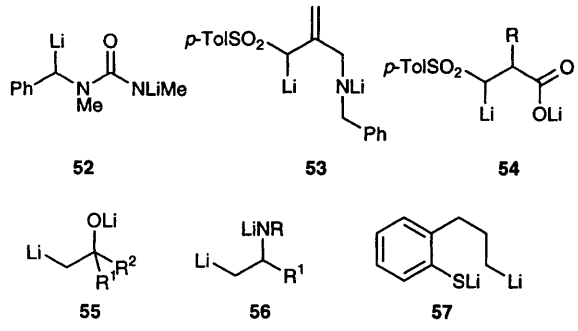


Reagent: i, quinine, Li, THF, –25 °C

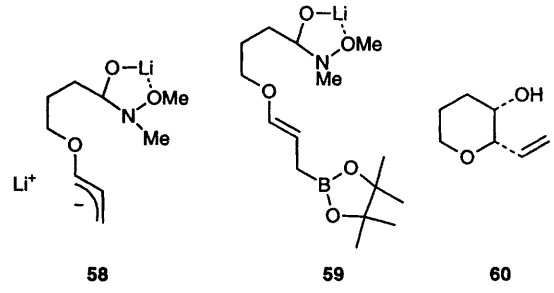
Scheme 7

2.1.6 Di- and tri-lithiated anions

In the presence of a suitable directing group, dilithiated dianions such as **52** may be prepared by direct deprotonation. Whilst it has always been assumed that the directing group was in some way responsible for directing the base to the benzylic position, it is only recently that direct evidence for this has been obtained.[62] Related compounds **53**[63] and **54**[64] featuring further additional stabilisation from a sulfone group have also been reported. In particular these reagents have been employed in the synthesis of nitrogen heterocycles and lactones respectively. Without the additional stabilisation or directing effects, preparation of dianions such as **55**[65] and **56**[66] generally requires an alternative approach. In most cases a variation upon the reductive method is favoured, chlorinated precursors may be employed as the starting materials[65,66a] or, for compounds of type **56**, aziridines.[66b] The reductive cleavage of a sulfide in an intramolecular sense was employed to create the dianion **57**.[67]

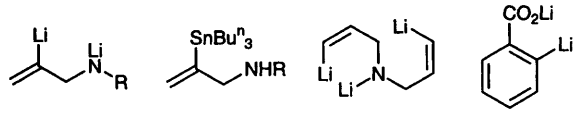


The lithium salt formed by the reaction of lithium methyl(methoxy)amide with an aldehyde serves to protect the sensitive functional group from attack by nucleophiles. In one recent example of the use of this strategy a further deprotonation was undertaken to give dianion **58** which was then converted to the allyl borane **59**. After work-up of the reaction and regeneration of the aldehyde an intramolecular addition reaction completed the synthesis of target molecule **60**.[68] Noteworthy in this sequence is the fact that all the transformations, from the precursor to **58** to target **60**, were carried out as part of a one pot process.



Dianions in which one or more of the anions is located on an sp^2 carbon atom may be created most readily by exchange reactions, and in particular the exchange of trialkyltin groups for lithium using an alkyllithium base has proved to be the most effective method. Allylamine derivatives of general structure **61** may be prepared by such a strategy.[69] Presumably

the trialkyltin precursor **62** has a finely balanced reactivity so that the exchange does not precede deprotonation at nitrogen, as is often a problem in bromine–lithium exchange reactions. A number of related trianionic compounds such as **63**, prepared by similar methods, have been reported.[70]



61 R = alkyl, TMS **62** R = alkyl, TMS **63** **64**

Dilithiations of aromatic compounds are generally less troublesome, and may usually be achieved with direct reaction with a healthy excess of alkyllithium base.[71,72] Whilst directing groups such as carbamates are well known to promote this type of lithiation[71] carboxylic acid salts, traditionally themselves rather prone to nucleophilic attack, can under certain conditions promote *ortho*-lithiation reactions to give, for example, **64**.[72]

2.2 Anions stabilised by sulfur, silicon and other heteroatoms

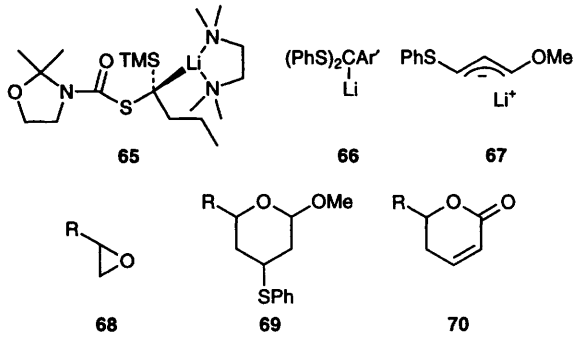
The configurational stability of anions adjacent to sulfur in dibenzyl sulfide has been investigated by Hoffman, who has found that racemisation begins to occur at very low temperatures.[73] Whilst this rather limits applications of such compounds to asymmetric synthesis, there is sufficient stability to permit very low temperature (-100 °C) intramolecular reactions to take place in a stereoselective manner (**Scheme 8**).[74]

Reagent: i, Bu^nLi, −100 °C, 1 h

Scheme 8

In the example shown the reaction is believed to proceed with essentially 100% inversion of configuration. The rather more configurationally stable anion **65**, flanked by both sulfur and silicon, may be formed directly from the enantiomerically pure precursor using *sec*-butyllithium activated by TMEDA ; both the deprotonation and subsequent reaction of this anion with MeOD proceed with retention of configuration.[75]

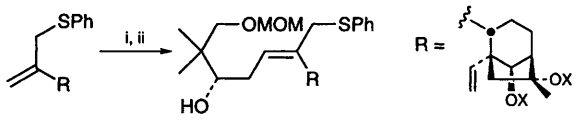
Anions stabilised by two sulfur atoms are very important in synthetic chemistry due to their value as reverse-polarity reagents.[76] A lithiated dithiane has been employed in the total synthesis of FK506.[76a] Further examples of lignan syntheses facilitated by the stereoselective additions of anions such as **66** to α,β-unsaturated-δ-lactones have been reported.[77] Allylic anions stabilised by sulfur such as **67** react cleanly and regioselectively with epoxides **68** to give adducts which cyclise (to **69**). A short



65 **66** **67** **68** **69** **70**

series of transformations completes the synthesis of α,β-unsaturated-δ-lactones **70** for which they were required.[78a]

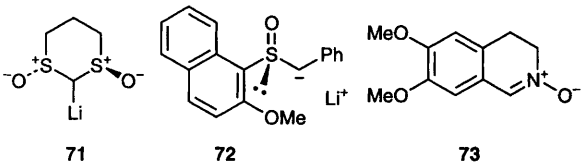
Allylic anions stabilised by sulfones rather than sulfides may be employed for the synthesis of enones in related processes.[78b,c] Whilst the reaction of **67** with **68** was regioselective due in part to the effect of the methoxy group, addition α- to the sulfur atom is often observed. If this is not the required isomer then it is possible to rearrange the adduct *via* a 1,3-shift promoted by heating to 160 °C in xylene in the presence of diphenyl disulfide (**Scheme 9**).[79]



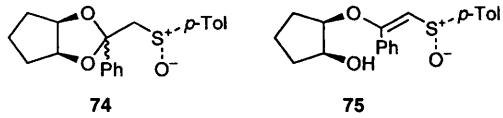
Reagents: i, Bu^nLi, TMEDA, HMPA, THF, −78 °C→ 0 °C; ii, $(PhS)_2$, xylene, 160 °C

Scheme 9

Lithium anions adjacent to sulfoxides are important reagents for asymmetric synthesis because the sulfoxide group may in principle be resolved into enantiomers. Several applications of such anions have been reported recently, and a full paper on the synthesis and reactivity of homochiral 1,3-dithiane-1,3-dioxide **71** has appeared. Anions of **71** react with high diastereoselectivity with aldehydes (>95:5) and may be cleaved to α-alkoxy esters using a short sequence of reactions featuring a Pummerer reaction at a key point.[80] Addition of the anion **72** to the cyclic nitrone **73** proceeds with a



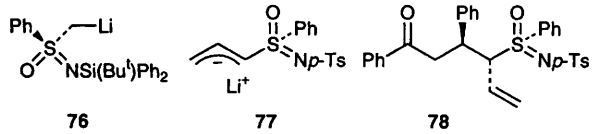
71 **72** **73**



74 **75**

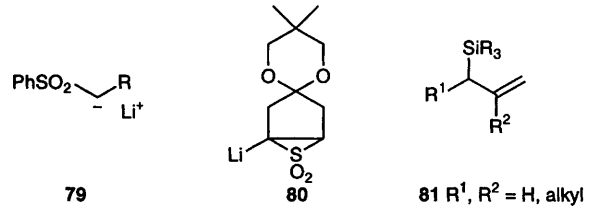
face selectivity of 96:4, the highest yet achieved in this type of reaction. The use of other sulfoxides, such as lithiated methyl *p*-tolyl sulfoxide, has already been reported to give selectivities of up to 92:8.[81] A more unusual application is the ring opening of either diastereoisomer of ketal **74**, to give **75** as the major product, upon treatment with LDA.

This strategy, the stereochemistry of which is controlled entirely by the sulfoxide, provides an alternative to enzymatic differentiation of meso-diols.[82] Sulfoximines such as **76** also feature robust stereochemical centres and have found many applications in asymmetric synthesis. A full paper has appeared on the synthesis and uses of **76** itself,[83] whilst conjugate addition reactions of the related compound **77** to enones have also been described. In the latter example the highly diastereoselective reaction gives **78** as the major product isomer.[84]

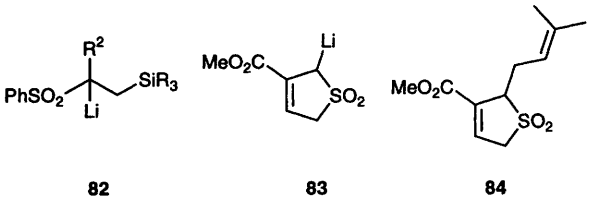


76 **77** **78**

Anions adjacent to sulfones **79** are generally prepared by direct deprotonation but can in some cases be formed by reductive methods.[85] Such anions have been widely employed in synthesis and appear particularly compatible with synthetic approaches to large complex target molecules. Recent applications include key carbon–carbon bond forming steps in the synthesis of rapamycin, which features epoxide opening by a sulfone anion[86] and aplyronine A.[87] In the latter example three important bonds are formed between large fragments of the target, one by a Julia olefination process, the others by displacement of a triflate and an iodide respectively by sulfone anions. Lithiated sulfones which form part of a three membered ring, *e.g.* **80**, have been substituted by a range of electrophiles and then employed to form alkenes by extrusion of sulfur dioxide.[88] A one pot process permits the synthesis of allylic alcohols **81** from lithiated *β*-silyl sulfones **82**, which therefore acts as a vinyl–isoprenyl anion equivalent.[89]

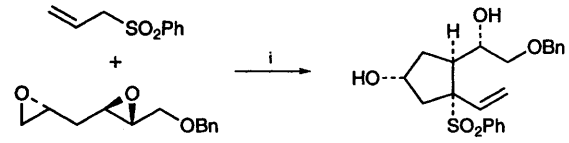


79 **80** **81** R^1, R^2 = H, alkyl



82 **83** **84**

Allylic sulfones may be prepared very readily by deprotonation and display a versatile reactivity pattern. Alkylation of **83** with isoprenyl bromide furnishes **84**, a convenient precursor of a Diels–Alder reagent for apoyohimbine synthesis.[90] In another application a sequence of epoxide opening reactions was employed to form a key building block of brefeldin A in an impressive one pot process (**Scheme 10**).[91]

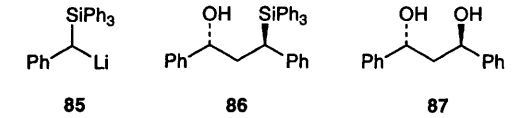


Reagent: i, BuLi, THF, –78 °C to r.t.

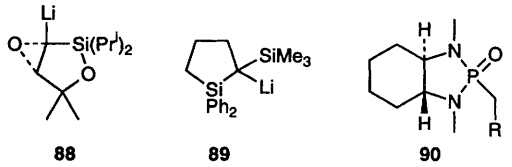
Scheme 10

Silicon stabilised anions have not been as extensively investigated as the sulfur analogues; however some very valuable processes have been developed. The reaction of **85** (formed by lithium metal–polyaromatic reduction of the α-sulfide) with addition to give **86**. Oxidation by a conventional method then completes a very effective synthesis of enantiomerically pure *cis*-diol **87**.[92] Other silyl stabilised building blocks include the heterocycle **88**[93] which was used for the synthesis of epoxy diols and the silacyclopentane **89**, a starting material for the synthesis of *γ*-hydroxy ketones.[94]

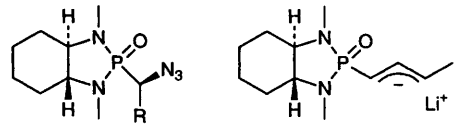
Numerous phosphorus derivatives stabilise adjacent anions and applications to alkene formation methodology are rather too numerous to comprehensively feature in an article of this type. Attention should be drawn however to the recent studies of the reactions of homochiral derivatives of this type such as **90**, lithiation of which, followed by reaction with an aryl sulfonyl azide, gives **91** in high stereoselectivity. Azides of general structure **91** may be converted *via* a short sequence to the corresponding enantiomerically enriched α-amino



85 **86** **87**

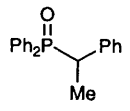


88 **89** **90**



91 **92**

phosphonic acids.[95] Related allylic anions **92** have also been reported, and display remarkably high selectivities in addition reactions to α,β-unsaturated esters.[96] Finally, in this section, an intriguing report has appeared describing the deprotonation of racemic phosphine oxide **93**, followed by asymmetric reprotonation of the anion **94**. Use of the chiral amine **95** to supply the proton returns enantiomerically enriched **93** in up to 83% ee, which can be increased to over 100% by recrystallisation.[97] Very few examples of deracemisation methodology of this type have been reported.



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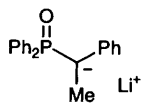

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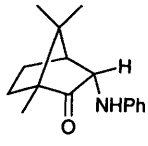


95

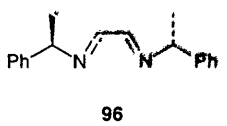
3 Group 2

3.1 Magnesium

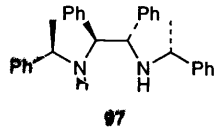
Reviews have appeared recently describing the reactions of alkylmagnesium compounds in general,[98] and also the effects of alkylzirconium species on Grignard reagents in particular.[99]

Any review of organomagnesium chemistry will necessarily be dominated by the enormously versatile Grignard reagents, and this article is no exception to this. One feature that makes such reagents attractive to synthetic chemists is their applicability to stereoselective addition reactions. The reaction of phenylmagnesium bromide with dimine **96**, for example, results in highly selective formation of the useful protected diamine **97**.[100]

Additions of Grignard reagents to pyridinium salts bearing chiral directing groups are highly stereoselective provided the correct substitution pattern is present on the heterocyclic ring, *i.e.* 3-trialkylsilyl-4-methoxy.[101] Such reactions have been employed extensively by Comins for the asymmetric synthesis of alkaloids; the representative example



96



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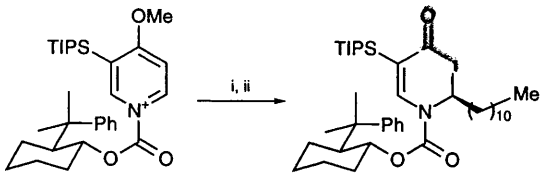
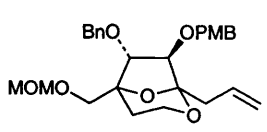


Reagents: i, $Me(CH_2)_{10}MgBr$; ii, H_3O^+

Scheme 11

shown in **Scheme 11** features the key step in the synthesis of (−)-solenopsin A.[101a] An allyl Grignard addition fulfils a key role in a reported synthesis of the zaragozic acid–squalestatin core model structure **98** from lactol **99**.[102] Following the addition of the allylic anion (to the hydroxy aldehyde), the resulting alcohol is oxidised to the ketone level and a careful acid catalysed cyclisation reaction leads to **98**.



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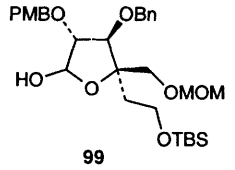
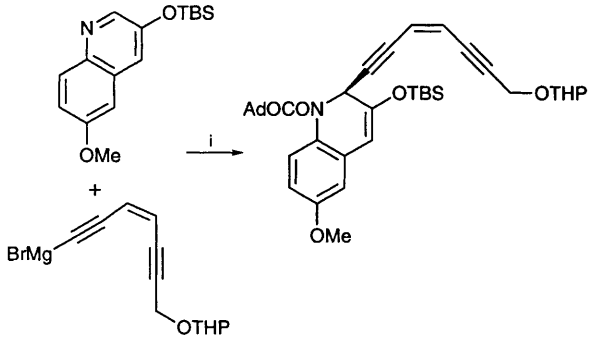


99

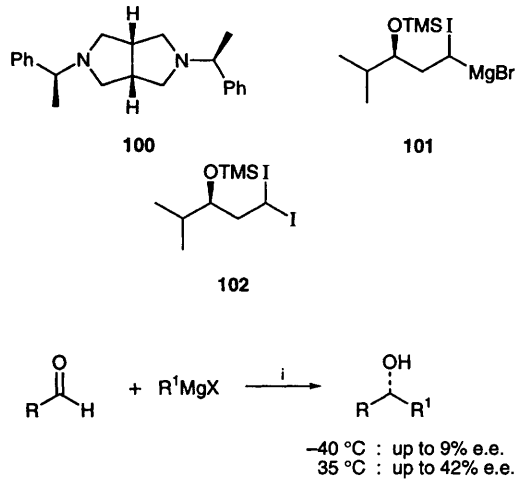
Another target molecule which has excited a great deal of recent interest is that class based on the dynemicin structure. Alkynyl Grignard reagents have played an important role in establishing the enediyne structure in these compounds.[103] In the example shown in **Scheme 12** the introduction of the unsaturated bridge is completed by an acid catalysed cyclisation of the dicobalt hexacarbonyl derivative,[103a] a strategy also successfully applied to the synthesis of the related calcheamicins.



Reagent: i, AdOCOCl

Scheme 12

The use of chiral ligand **100** to modify the reactivity of Grignard reagents with aldehydes gives only modest enantioselectivities.[104] Rather more interesting however is the remarkable observation that the ee induced increases with temperature (**Scheme 13**), a rare but not unknown phenomenon. Modest to good ee's (65–80%) were also obtained in the titanium–chiral diol mediated reaction of certain Grignard reagents with esters, a process which gives chiral cyclopropanes as products.[105] The nickel catalysed reaction of cyclopropyl Grignard reagents with dithianes results in the formation of 1-substituted buta-1,3-dienes.[106] Whilst Grignard reagents are usually formed from alkyl halides and magnesium metal, transmetallation can sometimes be a viable alternative. Hoffman has examined the stereoselectivity of the formation of derivatives **101**

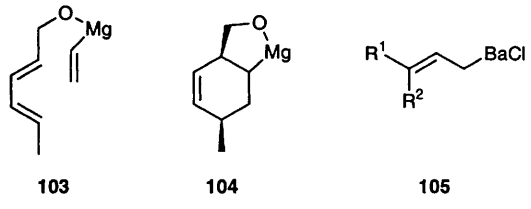


Reagent: i, **100**

Scheme 13

of *gem*-diiodides **102** formed upon reaction with isopropylmagnesium bromide.[107]

The conjugate addition reaction of chiral amines with unsaturated esters has been extensively studied by Davies, who has concentrated on the use of lithium amide nucleophiles. It appears that excellent results may also be obtained when the corresponding magnesium reagents are employed.[108] Intramolecular cycloaddition reactions often proceed with excellent diastereoselectivity, an advantage over intermolecular reactions which are often less selective. This disparity can be rectified by connecting the two reagents in the latter reaction using a temporary 'tether' group. Stork has reported that an alkenyl alkoxy magnesium tether can be used effectively in this capacity: **103**, formed *in situ* by the reaction of an alkoxide with vinyl magnesium bromide, cyclised readily to **104**.[109]



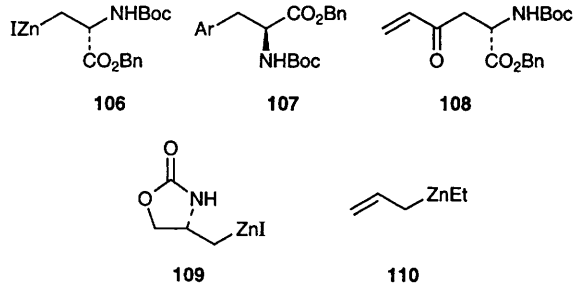
3.2 Barium

Allyl barium reagents **105** have benefitted from a considerable level of recent research activity due to their high regioselectivity in addition reactions to electrophiles.[110] Such compounds are generally prepared by the reaction between an activated form of barium metal and the allyl chloride. A very comprehensive full paper has recently described their use in addition reactions to aldehydes and in conjugate addition reactions to enones. Of particular note are: (i) the consistent observation of addition to the least hindered terminus of the allyl group, (ii) the full conservation of double bond geometry and (iii) high selectivity for 1,4- over 1,2-addition (>99:1).

3.3 Zinc and mercury

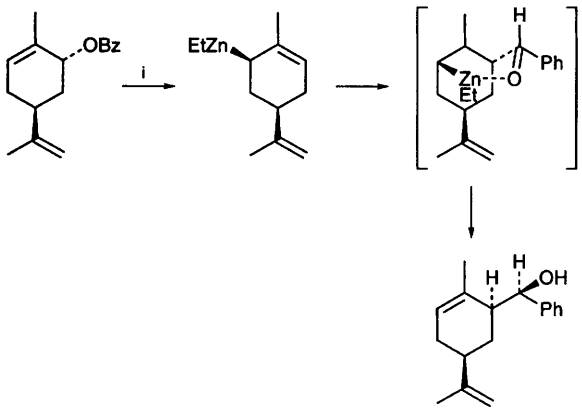
Tremendous recent progress has been made in organozinc chemistry, thanks mainly to the efforts of the Knochel group, who have developed methods for the preparation of several classes of functionalised zinc reagents.[111] Recently reported methods include the reactions of alkyl bromides with either diethylzinc[112] activated by copper(I)–manganese(II) or zinc metal activated on titanium dioxide.[113] Benzylic zinc reagents, which are somewhat more difficult to prepare than alkylzincs, have been made in good yields from the bromides using an electrochemical method.[114]

Organozinc derivatives of α-amino acids such as **106** have been the subject of particular attention in recent years. Of particular note, in addition to versatility in reactions, is the compatibility of the zinc reagent to the usual protecting groups associated with amino acid chemistry. The reagents are configurationally stable and the nitrogen atom remains protonated throughout the sequence of reagent formation and during nucleophilic reactions. Jackson[115] and others have reported full details of much of his communicated research in this area as well as new applications including palladium catalysed coupling reactions with aryl iodides[116] and α,β-unsaturated acid chlorides[117] to give **107** and **108** respectively. Further examples of palladium catalysed coupling reactions will feature throughout this section. The preparation and reactions of closely related, configurationally stable organozinc reagents of type **109** have been reported by Knochel.[118]



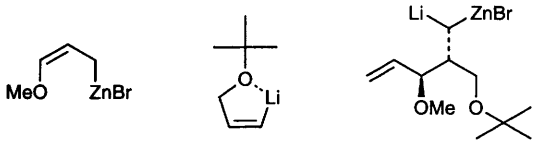
Allylzinc reagents may be prepared by the reaction between diethylzinc and either an allyl palladium complex[119] or a benzoyl protected allyl alcohol.[120] In the former example, reported by Julia, an allyl sulfone was employed together with an appropriate source of palladium(0) to supply the allylic complex which then formed the allylzinc **110** in an *in situ* process. Reactions of **110** with carbonyl compounds were described. In the latter process (**Scheme 14**), which also featured stereoselective reactions with carbonyl compounds, a formal polarity reversal of the π-allyl group was achieved.[120]

A further development of allylzincs such as **111** is for the diastereoselective carbometallation of



Reagents: i, Et_2Zn; ii, PhCHO

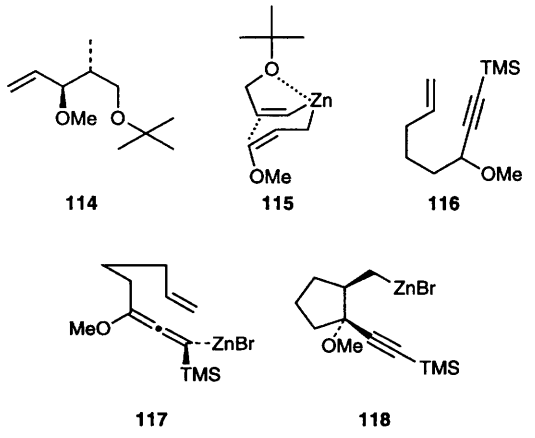
Scheme 14



111 **112** **113**

vinyllithums. For example; reaction of **111** with **112** gives the *gem* dimetallated adduct **113** and subsequently the aliphatic derivative **114** upon quenching with aqueous acid.[121] Several examples have recently been reported by Normant, who has proposed that the stereochemical control is the result of reaction *via* a transition structure such as **115**. In certain cases intermediate **113** can be converted effectively to cyclopropane derivatives, again with control of stereochemistry.[122]

Organozinc compounds also make excellent substrates for intramolecular cyclisation reactions. Building on the work described in the previous section, Normant has examined cyclisations of trialkylsilylalkynes such as **116**; deprotonation with an alkyllithium and zinc–lithium exchange results in formation of the metallated allenic species **117** which then undergoes the intramolecular reaction

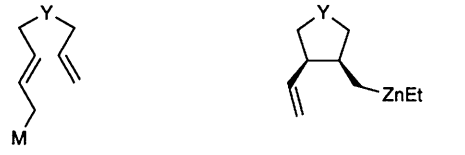


114 **115** **116**

117 **118**

leading to **118**.[123] The resulting alkylzinc may then be quenched upon acidic work-up or employed in further reactions with electrophiles. Since its first report this reaction has proved to be very versatile and may be applied to cyclisations with triple bonds[124] and to the stereoselective formation of *cis*-disubstituted tetrahydrofurans.[125]

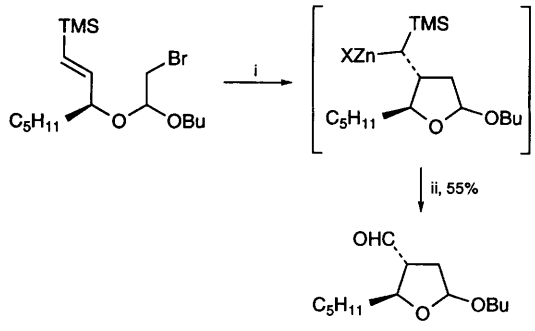
A related cyclisation has been investigated by Oppolzer, who has successfully employed a palladium catalysed process to assist *in situ* formation of precursors **119** to intramolecular zinc–ene reactions from allylic acetates **120**. Cyclisation again favours the *cis*-products **121**, which may again be quenched by acid or further reacted with electrophiles.[126]



119 Y = $C(SO_2Ph)_2$, NTs, M = ZnEt
120 Y = $C(SO_2Ph)_2$, NTs, M = OAc

121 Y = $C(SO_2Ph)_2$, NTs

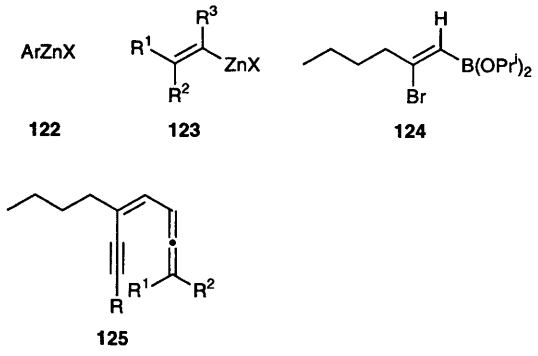
The approach taken by Knochel to intramolecular cyclisations of alkylzinc reagents onto double bonds requires the use of a nickel(II) catalyst.[127] In the representative example selected (**Scheme 15**), the stereoselective formation of a tetrahydrofuran ring results from a concise sequence of reactions.[127a] It is also noteworthy that the enantiomerically enriched starting material in **Scheme 15** was itself formed by an asymmetric addition of a dipentylzinc to an α,β-unsaturated aldehyde.



Reagents: i, Et_2Zn, LiI, cat. $Ni(acac)_2$, THF, 40 °C; ii, O_2, TMSCl, THF, –5 °C

Scheme 15

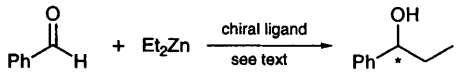
One example of a catalysed (usually by palladium) coupling reaction of an organozinc has already been described in this section.[116] However the literature is replete with further examples of this valuable class of reaction. In general arylzinc derivatives **122** are most commonly prepared by exchange with aryllithium reagents, which in turn originate from directed aromatic metallation[128] or a halide exchange process.[129] Reaction partners in



122 **123** **124** **125**

such processes are commonly aryl halides, vinyl halides, acyl chlorides and allylic halides.[129,130] In some cases the use of arylzincate reagents is favoured, one advantage being their ease of formation directly from the aryl iodides upon reaction with Me_3ZnLi.[131] Vinylzinc reagents **123** react in an analogous fashion but benefit from the additional benefit of ease of formation from the alkyne precursors.[132] The reactions of vinylzincs with allylic bromides, with or without palladium catalysis, have been described in detail.[133] The combined use of palladium catalysed couplings of unsaturated organozinc reagents has generated some powerful methodology. For example sequential reaction of an alkynylzinc and then an allenylzinc with **124** provide a means for the effective synthesis of the complex unsaturated product **125**.[134]

The number of examples of ligands for asymmetric catalytic dialkylzinc addition reactions to aldehydes (**Scheme 16**) has continued to grow unabated. Noyori, who first reported the rate enhancing effect of an amino alcohol derivative on this reaction less than a decade ago, has reported an *ab initio* study of the reaction[135] and a very detailed account of the remarkable non-linear chirality transfer effects which are observed.[136] A comprehensive account of all the new ligands reported within the date range of this account will not be attempted; however representative examples and novel applications will be highlighted.



Scheme 16

Starting first with new catalysts, the results of which are summarised in **Figure 1**, amino alcohols **126**[137] and **127**[138] are reported to give ee's of up to 68 and 96% respectively for the prototype reaction shown in **Scheme 16**. Whilst this suggests that pyridylamines are rather poor catalysts, rather better results have been obtained using the slightly more complex alcohols **128**[139] and **129**,[140] which furnish ee's of up to 93 and 88% respectively. The exact contributions of each of the chiral components in **129** to the overall selectivity is not fully delineated; however the current enthusiasm of researchers for

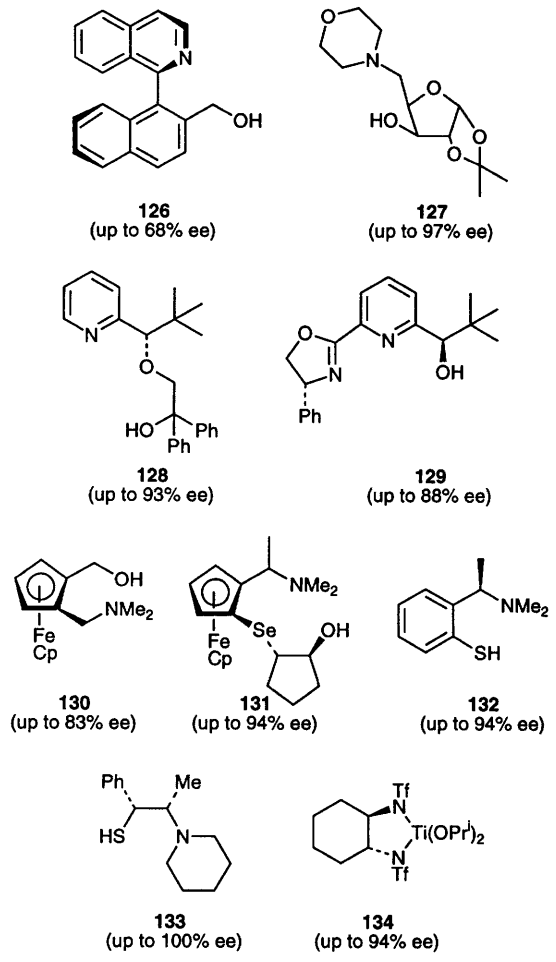


Figure 1 Maximum enantioselectivity for the reaction shown in Scheme 16

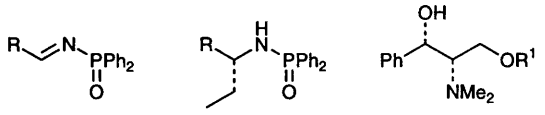
catalysis by chiral oxazolines essentially ensures their inclusion in most applications. The use of amino alcohol **128** to control the addition of alkynylzinc reagents to aldehydes gives slightly better results than with dialkylzincs: up to 95% ee.[141] Further reports have appeared on the use of polymer supported chiral amino alcohols in this application, some of which give results which are almost competitive with the homogeneous reactions.[142] Organometallic reagents containing π-complexed metals can introduce an extra steric or stereochemical element to a ligand which can improve their catalytic properties. Referring again to the prototype reaction of Scheme 16, the chiral ferrocene derivative **130** generates inductions of up to 83% ee.[143] Certain chromium tricarbonyl derivatives of chiral amino alcohols have also been examined and found to be slightly better than the uncomplexed reagents.[144] However perhaps the most interesting new reagent in this class is the selenium derivative **131** of ferrocene, which can give ee's of up to 94% for the prototype reaction.[145] Whilst rather more complex than the simple ligands with which this work is normally associated, results of this type help to expand the horizons of this important asymmetric process.

Replacement of the oxygen atom in the asymmetric ligands with sulfur has been the subject of some attention. Whilst the change is a logical one given the need to coordinate to zinc, slight but important improvements to ee's have only been observed for a limited number of cases. Van Koten's reagent **132** gives up to 94% ee[146] whilst the simple thioamino ligand **133** is reported to give up to 110% ee![147] Knochel has chosen to concentrate his asymmetric alkylzinc addition studies on the use of titanium derived complexes such as **134** as catalysts (formed *in situ* from the reaction between the ditriflated diamines and titanium tetraisopropoxide). Such catalysts, which are believed to be rather better than aminoalcohols for reactions of functionalised organozincs, give ee's in the region of 90–99% for the prototype reaction of **Scheme 16** and related transformations.[148] The Knochel system is particularly applicable to addition reactions to α,β-unsaturated aldehydes, several examples of which have been reported recently.[149] Some impressive ee's (up to 90%) have also been obtained when **134** was used to mediate reactions of dialkylzincs with aliphatic aldehydes, a traditionally difficult process with all currently available chiral ligands.[150]

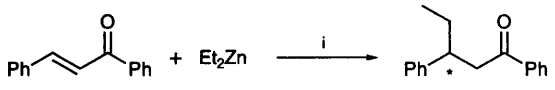
Other researchers have chosen to examine the versatility of ligand-accelerated alkylzinc addition reactions. Conditions have been found for control of the addition of diisopropylzinc to aldehydes, a hindered reagent which is normally ineffective in additions due to competing hydride transfer processes.[151] In a detailed study of mixed dialkylzincs it has been found that methyl and *tert*-butyl are remarkably inactive to transfer to the carbonyl compared to other alkyl groups, and therefore have potential value as non-transferable ligands in more complex reagents.[152] In some cases the products of addition can themselves act as catalysts, thus permitting autocatalytic processes to take place.[153] This can be useful provided that all catalytic species favour formation of the same enantiomer of product. A study of the catalysed reaction of dialkylzincs with chiral aldehydes revealed that the ligand effect greatly dominates that of the chiral substrate, even when it bears an α-chiral centre.[154] In terms of applications to total synthesis, perhaps the most impressive is the cyclisation of **135** to **136** in 91% de ('matched' directing effects operate) using only 1 mol% of the chiral aminoalcohol **137**.[155] Product **136** was taken on to complete an impressive synthesis of (+)-aspicillin.

Asymmetric additions of diethylzinc to C=N double bonds are rather rare. One excellent example is provided by the phosphorus protected imine **138**, which gives enantiomerically enriched phosphinamides **139** (up to 85% ee) upon reaction in the presence of a polymer bound chiral amino alcohol.[156] Free amines may be generated from **139** upon exposure to relatively mild acid.

Whilst by no means as widely exploited as cuprates, organozinc reagents have been employed in conjugate addition reactions to enone and related reagents.[157] Together with an appropriate nickel(II) catalyst and a suitable chiral ligand such as **140**, such addition reactions have been reported to be capable of proceeding with very high ee (**Scheme 17**).[158] An example of a related 'one-off' asymmetric reaction is the combination of diethylzinc with (+)-diisopropyltartrate to give a reagent capable of promoting the asymmetric ring opening of symmetrical aziridines by thiols in up to 88% ee.[159]



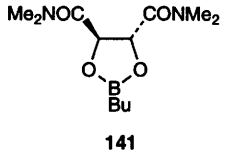
138 R = Ph, 2-Np **139** R = Ph, 2-Np **140**



Reagent: i, $Ni(acac)_2$, ligand **140**

Scheme 17

To complete this section on zinc attention is drawn to the remarkable cyclopropanation reactions of allylic alcohols by bis(iodomethyl)zinc when used in the presence of borate esters such as **141** (**Scheme 18**). This methodology, first reported by



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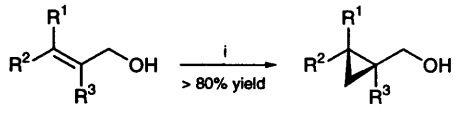
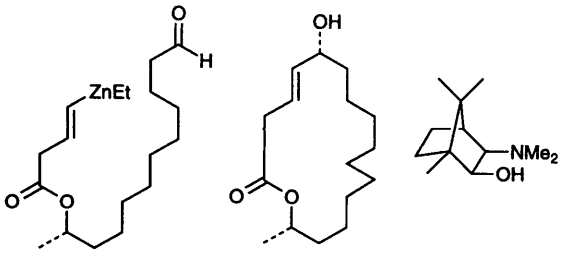


91–94% ee

Reagent: i, 2.2 eq. $Zn(CH_2I)_2$, 25 °C, CH_2Cl_2, 2 h, ligand **141**

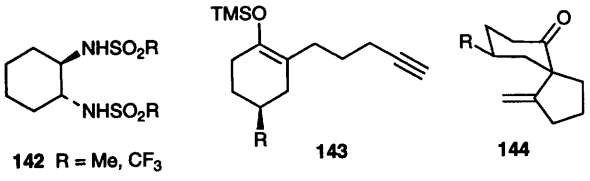
Scheme 18



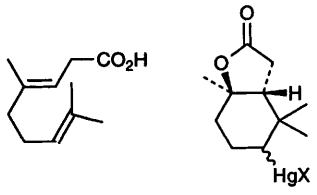
135 **136** (–)-DIAB **137**

Charette, has since been further developed by this author[160] and others.[161] In independent work, Denmark[162] and Kobayashi[163] have discovered that the complex formed between protected amine **142**, diethylzinc and diiodomethane is also an effective material for asymmetric allylic alcohol cyclopropanation, although it is not quite as effective as the Charette method.

Organomercury reagents are most remarkable for their ability to promote cyclisation reactions onto triple[164,165] and double[166] bonds. Spirocyclisations may be carried out using silyl enol ethers as the nucleophilic components as in the conversion of **143** to **144** after demercuration (N.B. the epimer is also formed).[165a] A good example of the value of this methodology is provided by the biscyclisation of **145** to **146** upon treatment with mercury(II) triflate.[166]



142 R = Me, CF_3 **143** **144**



145 **146**

4 Group 13

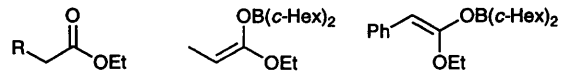
4.1 Boron

In view of the marginal nature of boron as a 'metallic' compound, this section will be somewhat shorter than in previous reviews and will highlight important aspects of organoborane reactivity.

4.1.1 Boron enol ethers, borane catalysts and alkylboranes

Boron enol ethers continue to be of great synthetic significance due to their remarkable versatility and ability to introduce several stereogenic centres in one process. Their application however does require the control of two aspects; enolate geometry and diastereoselectivity of additions to aldehydes. The first has been studied in detail by Brown, who has published a series of articles on enolboration.[167] Above all, these reveal the remarkable sensitivity of the process to substrate structure and reaction conditions; treatment of **147** with dicyclohexylboron iodide and triethylamine in carbon tetrachloride gives the isomer **148** when R = Me but **149** when R = Ph.[167a] In each case the selectivity in each direction is in the region of >97:<3.

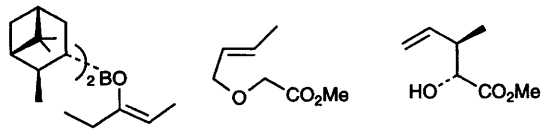
Of those who have studied aldol reactions of chiral boron enol ethers **150**, it is perhaps the group



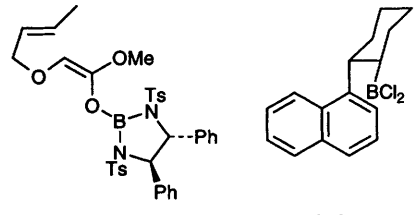
147 **148** **149**

of Paterson who have made the greatest use of these remarkable reagents.[168] The majority of the factors controlling the selectivity of these reagents has largely now been delineated by this group, who have turned their attention to synthetic applications. Whilst a comprehensive review of the achievements of this group is not possible in an article of this type, attention is drawn to the syntheses of target molecules as diverse as oleandomycin,[169] swinholide A[170] and ebelactone A and B,[171] all of which have been reported recently.

Whilst the diisopinocampheylborane group is perhaps the most widely studied directing group, other chiral modifications of boron enol ethers may be made. For example the moderately enantioselective [2,3] Wittig rearrangement of **151** to **152** (83:17 in favour of this isomer) takes place *via* the diamine-derived enol **153**.[172] Menthyl-derived dichloroborane **154** has previously been shown to be a remarkable catalyst for the asymmetric Diels–Alder reaction, giving ee's of up to 99.5%! For the first time an X-ray crystal structure of a complex of this catalyst with a ketone has provided evidence to support the speculation that this stereocontrol is the result of a two point binding effect, rather than simply complexation of a lone pair on the ketone.[173]



150 **151** **152**

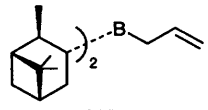


153 **154**

Alkylboranes have numerous applications in synthesis, although alkyl transfers to electrophilic reagents are not so common. One interesting recent example has been reported of such a transfer to a cyclic nitrone, a process which is promoted by initial association of a trialkylborane with the nitrone oxygen atom.[174] Chloromethylborate esters are also valuable synthetic reagents which have application in homologation reactions. The results of a detailed study of this class of reaction employing *in situ* generated alkyllithiums have been reported this year by Brown.[175]

4.1.2 Allyl-, allenic and alkenylboranes

Allylboranes are remarkable synthetic reagents, capable of the generation of high regio- and diastereo-selectivities in addition reactions to carbonyl compounds. Asymmetric modification of these reagents renders valuable chiral reagents such as **155**, a reagent which adds to acyl silanes to give products of up to 92% ee.[176] These reagents may alternatively be of a complex structure, for example **156**, which supplies an α-aminoallyl group in additions to aldehydes to give the product **157** with both de's and ee's in excess of 90%.[177] The related allylboronic esters **158** and **159** have probably received even further attention, Hoffman having recently examined the reactions of diol derived **158**



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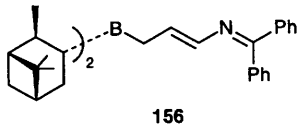

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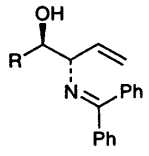

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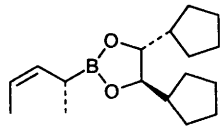
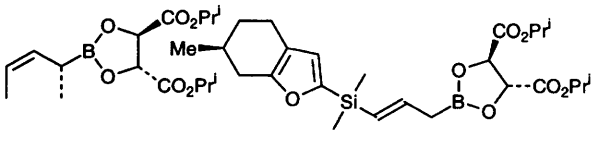
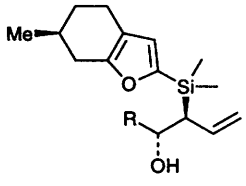


158

with chiral aldehydes[178] and Roush[179] and others[180] the reactions of the tartrate derived versions **159**. A versatile derivative is the menthofuran derived compound **160**, which adds to aldehydes RCHO to give the trans products **161** and subsequently diols **162** upon oxidation.[179b] The brominated allylic reagent **163** adds to aldehydes to give products with ee's of up to 90%.[180] Recently Roush has reported that improved results can in some cases be achieved using a related reagent containing an ethylene bridged tartramide in place of the ester groups in **159**.[181]



159 **160**



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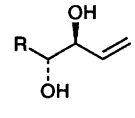

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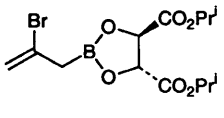

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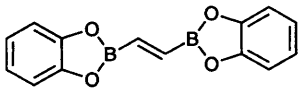

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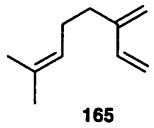
B-Allenyl-9-BBN, a useful reagent for regio- and chemo-selective formation of homopropargylic alcohols upon reaction with aldehydes, has recently been described in a detailed publication by Brown.[182] Related vinylic boron reagents, excellent substrates for palladium catalysed coupling reactions with aryl and vinyl halides,[183] may themselves be formed by coupling reactions of boronic halides with trialkyltin alkenes.[184] The 1,2-diborated alkene **164** is a suitable partner for cycloaddition reactions with unactivated dienes such as **165**; oxidation of the primary cycloadduct then yields 1,2-*trans* diols **166**.[184] Alkenylboranes bearing halides at the α-position react with allylic nucleophiles to give substitution products and subsequently ketones after oxidation.[185]



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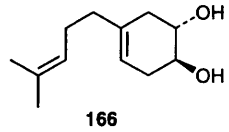
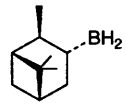


166

4.1.3 Hydroboration and carbonyl reduction by boranes

Hydroboration is a pivotal transformation in boron chemistry. Few monoalkyl boranes are available to the synthetic chemist, however, the hindered thexylborane being the most widely used derivative. Another hindered compound, 2,4,6-trimethylphenylborane, has been reported to be a viable alternative, and benefits from relative ease of preparation and handling.[186] In terms of chiral alkylboranes, monoisopinocampheylborane **167** is well established. However minor modifications to the structure, as in the case of **168**, have been reported to give reagents with dramatically improved selectivities in hydroboration reactions of representative alkenes.[187] A potential problem with such reagents, however, is their non-availability in consistently enantiomerically pure form. To solve this problem a number of upgrading methods have been developed, one based on the formation of a 2:1 complex with a diamine (as used to upgrade **167**)[188] and the other based on the temporary formation of a trialkylborane.[189] Further examples of transition metal complex mediated hydroboration reactions have been reported.[190]



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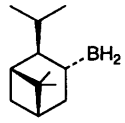

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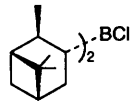

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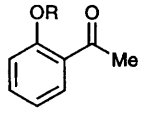
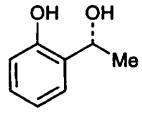


170 R = H
171 R = Me



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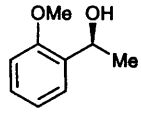


173

Bis(isopinocampheyl)chloroborane **169** is an outstanding reagent for the asymmetric reduction of ketones. Recent reports have appeared on the reductions of fluorinated ketones, which in some cases show improved or even inverted absolute asymmetric induction.[191] The reagent is extremely well suited to the reduction of β-amino ketones, which may be reduced in up to 99% ee in some cases.[192] A remarkable reversal of selectivity was observed in the reduction of the closely related ketones **170** and **171** with **169**.[193] The former gives the *R*-enantiomer **172** in 90% ee while the latter gives the *S*-enantiomer **173** in 92% ee, suggestive of an important coordination effect involving the hydroxy group. Highly selective asymmetric intramolecular reductions by chiral boranes have also been described.[194]

4.2 Aluminium, gallium and thallium

Carboalumination of terminal alkynes by trimethylaluminium may be catalysed by organozirconium complexes, the resultant vinylaluminium reagents **174** then being effective substrates for palladium catalysed coupling reactions with α-amino acetates **175** to give amino ester derivatives **176**.[195] The combination of trimethylaluminium with dimethylamine gives a reagent which is highly effective for the formation of amides from esters[196] whilst the use of trimethylsilyl triflate effectively activates trimethylaluminium towards *gem*-dimethylation of ketones.[197] Although not as well established as the boron complexes described above, aluminium complexes **177** of diamines are effective catalysts of allylic acid cyclopropanation by diethylzinc and diiodomethane.[198] Highly hindered alkoxyalkylaluminium complexes are effective Lewis acids for the promotion of several classes of transformations including hetero Diels–Alder reactions. However, most remarkable is their exquisite chemoselectivity; in certain cases straight chain aldehydes can benefit from the Lewis acid activation in the presence of more hindered derivatives due to the high level of steric hindrance around the aluminium centre.[199] In a similar way, 1,2-addition to cyclic enones can be suppressed compared to 1,4-addition by the steric hindrance in the complex.[199]

Gallium reagents have seen a handful of important applications. The reducing agent formed by the combination of gallium trihydride with a tertiary amine or phosphine is selective for reduction of the carbonyl group of bromoacetophenone.[200] In contrast many aluminium hydride reagents would have cleaved the C–Br bond. Tetraalkylgalate complexes, formed by the reaction of an alkyllithium with a trialkylgallium, transfer a single alkyl group to acid chlorides to give ketones, a process which invariably results in formation of tertiary alcohol when other organometallics are used.[201] Prop-2-ynylic and allylic organogallium compounds **178** and **179** may be prepared from the appropriate bromide precursors and react cleanly with carbonyl compounds.[202]

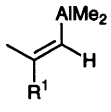
Organothallium reagents have always been somewhat underexploited in synthesis due to their toxicity. An interesting recent application of a trimethylthallium–methyllithium combination for nucleophilic additions to ketones revealed an interesting chemoselectivity; enones were considerably more reactive than the corresponding saturated compounds towards methylation, the reverse of the expected reactivity.[203]

5 Group 4

5.1 Silicon

5.1.1 Silyl enol ethers

The full range of applications of silyl enol ethers in any review period is far too vast to detail comprehensively, and therefore attention here will merely be focused on a small number of interesting studies of the stereochemistry of the reactions of these compounds with aldehydes. The great difficulty in the study of such reactions has always been in delineating all of the various effects – solvent, temperature, counterions, *etc.* – which contribute to a given result. Denmark has devised and studied an ingenious model based on the structure **180** which reduces the problem to that of an intramolecular reaction within a very well defined steric framework. The results of cyclisation studies of **180** have painted a complex picture however: there appears to be an inherent modest preference for an open, *anti*-periplanar reaction



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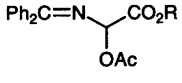

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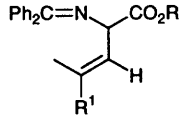

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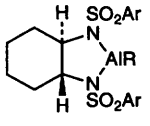

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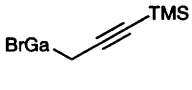

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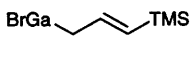

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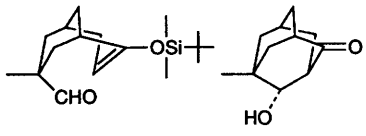
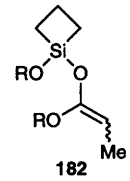


180 **181**



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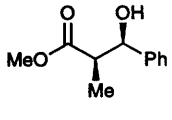
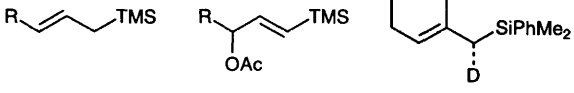


183

mode (to give **181**) in the presence of a range of Lewis acids and fluoride sources.[204] In other cases the selectivity can be reversed, suggesting a chelation between the reaction partners. Denmark has also reported recently on the use of silacyclobutane derived enol ethers **182**, which give predominantly (93:7–99:1) the *syn* aldol products **183** upon reaction with aldehydes.[205] The incorporation of a chiral alkoxy group on silicon also results in asymmetric inductions of up to 97% in the case of (−)-*trans*-2-cumylcyclohexanol.[205]

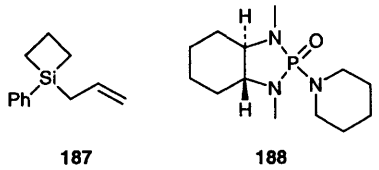
5.1.2 Allyl-, benzy- and alkenylsilanes and their derivatives

Allylsilanes **184** may be made efficiently by the palladium catalysed reduction of allylic acetates **185** by sodium formate; regioselective hydride transfer to the terminal position of the intermediate complex is observed.[206] Another method which allows full control of regio- and stereo-selectivity is the nickel catalysed coupling reaction of vinylselenides with α-trimethylsilylmethyl Grignard reagents.[207] In a series of systematic studies on a stereochemically well-defined substrate **186**, which follow on from previous work, Denmark has examined the intramolecular Lewis acid catalysed cyclisations of allylsilanes and stannanes with aldehydes.[208] These studies suggest that an *anti* electrophilic substitution process operates, *i.e.* the trialkylsilyl group is *anti* to the face of the allyl group which reacts with the aldehyde.

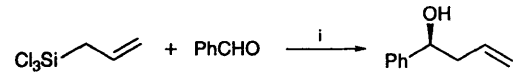


184 **185** **186**

Unlike allylboranes, allylsilanes generally require assistance from a Lewis acid to react with aldehydes. Allylsilacyclobutanes **187** appear to be rather more reactive than average and undergo non-catalysed additions at 130 °C.[209] A rare example of Lewis base catalysed addition of allyltrichlorosilane to aldehydes has also been reported; phosphinamides act as the Lewis bases of choice in this process.[210] This process also benefits from the fact that a homochiral phosphinamide may be employed to induce asymmetry in the reaction. In practice **188** was found to be the best reagent: 1 equivalent of **188** gave an ee of 63% for the reaction shown in **Scheme 19**. It is noteworthy that the two studies



187 **188**

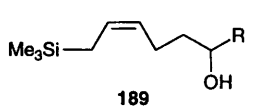


Reagent: i, 1 eq. **188**, −78 °C, CH_2Cl_2

Scheme 19

above also came from Denmark's laboratory, which underlines his very important contributions to this area.

In contrast to aldehydes, oxonium cations react rapidly with allylsilanes, a process which can be used to advantage in intramolecular cyclisation reactions.[211] In the acid catalysed reaction between **189** and acetal **190**, the intermediate **191** cyclised *via* the corresponding oxonium cation to give **192** with a high degree of diastereocontrol.[212] Addition reactions, in the presence of a suitable Lewis acid, of allylsilanes to carbon–nitrogen double bonds have been reported.[213] A related intramolecular cyclisation process featured an allylsilane cyclisation onto the cationic intermediate in a Beckmann reaction.[214] Epoxide opening reactions can promote intramolecular allylsilane-terminated processes, an excellent example of which is the conversion of **193** to **194** upon activation by dichloromethylaluminium at −78 °C.[215] The silyl group is essential for the success of this transformation.



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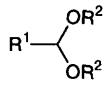

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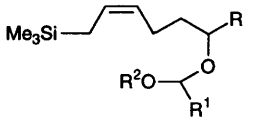

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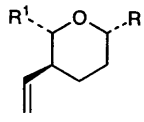

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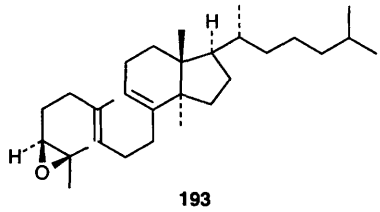

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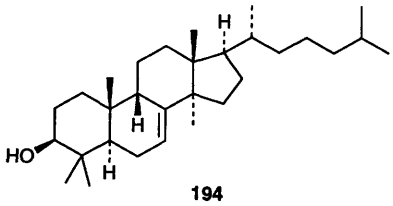
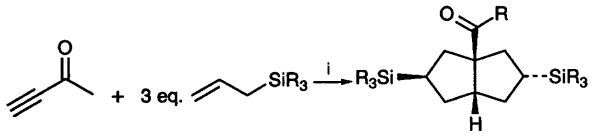


194

In some cases Lewis acid catalysed allylsilane additions to electrophiles can give rearrangement products. The use of niobium pentachloride, for example, results in the formation of a product containing a cyclopropane ring.[216] Reactions with

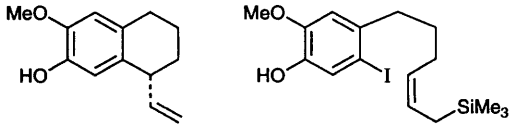
alkynes bearing electron withdrawing groups may give products of overall [3+2]-cycloaddition.[217] **Scheme 20** features a remarkable example in which two sequential reactions of this type take place.[217a] A similar process can on occasions take place in additions to ketones;[218] however in some cases [2+2]-cycloaddition reactions can compete.[219]



Reagent: i, $TiCl_4$, CH_2Cl_2, –78–20 °C

Scheme 20

Palladium(0) complexes can assist the reactions of allylsilanes with allylic acetates[220] and aryl triflates.[221] The incorporation of a chiral diphosphine can render this process asymmetric. An example is the formation of **195** in 91% yield and 92% ee from **196** when *R*-BINAP is employed as the ligand in the catalyst.[222] Coupling of allylsilanes with benzylsilanes may be achieved by oxidative methods.[223]



195 **196**

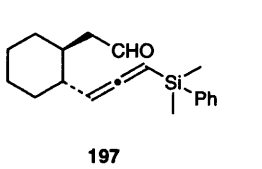
Prop-2-ynylic[224] and allenic silanes[225] may participate in intramolecular cyclisation reactions. The reaction of **197** with benzylamine in the presence of tin tetrachloride gives **198** with a high degree of stereocontrol *via* cycloaddition onto the intermediate imine.[225] Compound **198** is an advanced intermediate in the synthesis of the C2 symmetric compound papuamine. An alkynylsilane, **199**, is an advanced intermediate employed in the key step of the synthesis of a cyclic enediyne compound **200**; dry caesium fluoride is employed to promote the reaction.[226]

A silicon atom has been used as part of a temporary 'tether' to mediate the intramolecular [2+2]-cycloaddition between an alkenylsilyl group and the carbon–carbon double bond of an enone. Following the reaction the silicon was removed in an oxidative process to give a diol.[227] Stereoselective epoxidation of an allylsilyane followed by a concerted intramolecular cyclisation, silyl migration and epoxide opening provided a means for the stereoselective formation of γ-lactones, precursors of building blocks for nonactin.[228]

5.1.3 Other classes of silicon reagent

Trialkylsilanes are ubiquitous reagents for the protection of alcohols. Whilst it is not possible to present a comprehensive review, the ability to selectively remove a *tert*-butyldimethylsilyl group from either an aliphatic or phenolic position, depending on the exact conditions used, is noteworthy.[229]

Hydrosilylation reactions of carbon–carbon double bonds may be employed to promote intramolecular cyclisations of 1,5-dienes, provided an ytterbium catalyst is used.[230] Intramolecular asymmetric hydrosilylation of **201**, using a combination of rhodium(I) with *S*-BINAP gives the siloxacycle **202** in up to 96% ee.[231] Rhodium catalysed hydrosilylation of *N*-acyl enamines results in introduction of the silyl group α- to the nitrogen atom, as in **203**.[232] Asymmetric ketone hydrosilylation may also be achieved by the use of appropriate complexes of rhodium(I)[233] and a similar asymmetric reduction process of nitrones by the use of a ruthenium–BINAP combination (ee's up to 91%).[234] This hydrosilylation process can also be used to prepare silanes which are chiralat silicon; reaction of 1-naphthylphenylsilane with symmetrical ketones, catalysed by a rhodium(I) BINAP catalyst, is reported to give products **204** of up to 99% ee. Subsequent reaction of **204** with methylmagnesium bromide results in conversion to the corresponding chiral silane **205** in equally high ee.[235] The insertion reaction of carbenes into silicon–hydrogen bonds has been shown to be an effective method for the preparation of alkylsilanes.[236]



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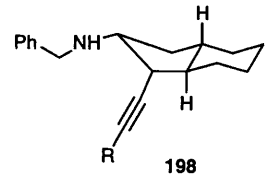

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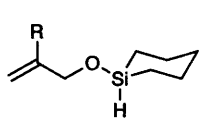

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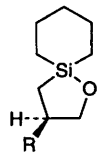

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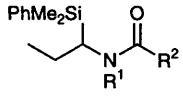

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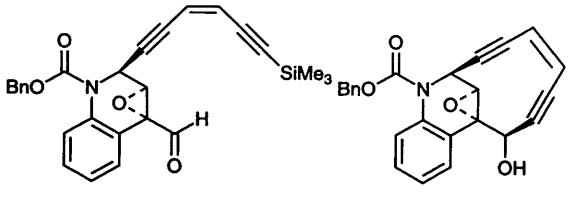

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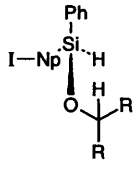

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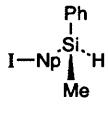

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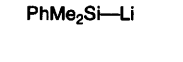

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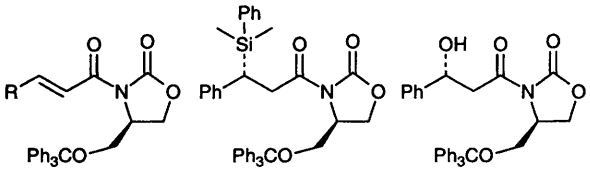
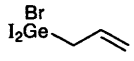
Acylsilanes may be prepared by the ring opening of silylated epoxides, followed by oxidation of the α-hydroxy silane product.[237] The addition of carbanionic nucleophiles to chiral acylsilanes can in some cases be a diastereoselective process.[238] although in some cases a synthetically useful silyl migration from carbon to oxygen takes place.[239] Lithiated silanes **206** may be formed from the chlorides[240] and participate in stereocontrolled conjugate addition reactions to chiral electrophiles such as **207**.[241] Oxidation of the intermediate adduct **208** gives the enantiomerically enriched β-hydroxy product **209**.



207 **208** **209**

5.2 Germanium

The germanium equivalent of the Peterson reaction has been known for some time. Recently however the X-ray crystal structure of the ketone addition intermediate has been solved.[242] Allyl germanium reagents, formed *in situ* from allyl bromides, react efficiently with aldehydes *via* the tetra-coordinated intermediate **210**.[243] Alkenylgermaniums have been prepared from terminal alkynylsilanes.[244]



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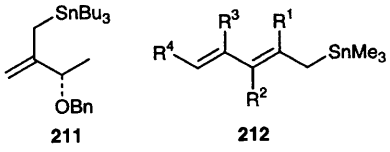
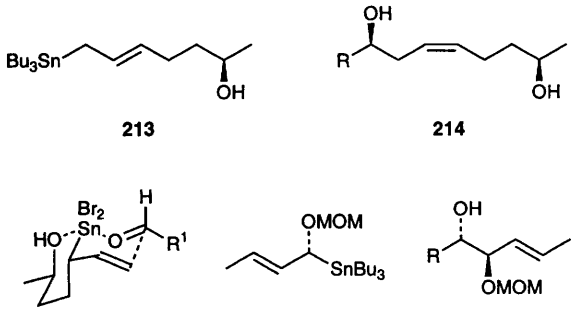
5.3 Tin

Asymmetric aldol reactions may be mediated by the combination of a tin(II) complex with an appropriate chiral diamine, a process which has now been refined for a wide range of substrates.[245] The asymmetric addition of tributyltin to aldehydes may be catalysed by chiral quaternary amine salts, although in rather modest ee (up to 24%).[246] The intramolecular cyclisation of a vinyl iodide with an aldehyde may be mediated by tributyltin anion generated *in situ* by the reaction between trimethylsilyltributyl tin and caesium fluoride.[247]

The Barbier coupling reaction of allyltins (generated *in situ* from the bromides) with aldehydes may be catalysed effectively by copper(I) salts.[248] In most cases, however, allyltin compounds may be prepared by a variety of methods, and isolated before use. The most common application of allyltins is in reactions with aldehydes, in which high stereoselectivities are invariably achieved. In some cases palladium salts provide a conveniently mild form of catalysis.[249] Studies of the functionalised reagents **211**[250] and **212**[251] have been reported. Remote functional groups can have a dramatic stereodirecting effect,[252] an example of which is 1,7-asymmetric induction in the addition reaction of **213** to aldehydes RCHO, upon



211 **212**



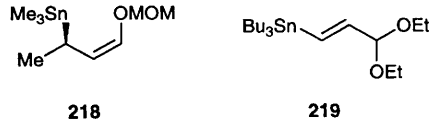
213 **214**

215 **216** **217**

treatment with tin tetrabromide, to give **214** in high de.[252a] In this reaction the tin tetrabromide exchanges with the organometallic to give a terminal alkene which then adds to the aldehyde *via* a chelated transition state **215**. A similar chelating effect operates in a very attractive example of an allylation of an unprotected α-hydroxy ketone.[253]

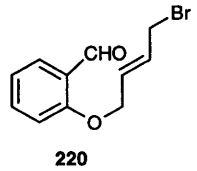
α-Alkoxyallylstannanes such as **216** can be prepared by the insertion of carbenes into tin–hydrogen bonds[254] or by the asymmetric reduction of acyltin reagents.[255] The reactions of these compounds with aldehydes to give products **217** are highly selective, although rearrangement to γ-alkoxyallyltin compounds **218** usually precedes the addition reaction. In the case of **216** indium trichloride catalysis was employed to give products with ee's in excess of 95%.[256] Full details of the additions of this class of reagent to numerous classes of aldehyde have been reported by Marshall.[255,257] Allyltin reagents such as **218** may be made by the S_N2' reaction of cuprates with vinyltin reagents such as **219**.[258] A word of caution regarding the catalysis of the addition reactions – the use of a fluoride source along with boron trifluoride has been reported to effect conversion of the enol ether unit of **218** to the corresponding aldehyde, an unexpected observation.[259] An asymmetric version, containing a carbohydrate derived directing group, has been reported by Roush.[260]

Intramolecular reactions of allyltin reagents onto aldehydes[261] and oxonium cations,[262] have been



218 **219**

reported. Typical is the stereoselective conversion of bromide **220** to **221** upon reaction with excess activated tin(0).[261a] Allyltin compounds also react with alkyl iodides (a radical process)[263] and in cycloaddition reactions with singlet oxygen.[264] Allenyltin compounds **222** undergo stereoselective additions to aldehydes, the selectivity of which depends on the method of catalysis; using boron trifluoride, **223** is formed whilst the isomer **224** results from the same reaction in the presence of tin tetrachloride.[265]



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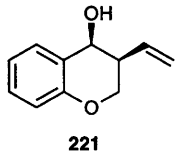

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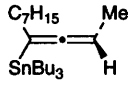

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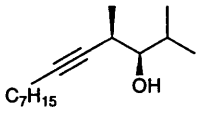

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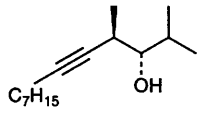

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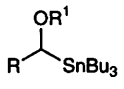
α-Alkoxymethyltin derivatives **225** may be prepared by a number of methods, and in enantiomerically pure form by the reduction of acyltin compounds or the corresponding acetals.[266] Oxidation of these reagents by ozone provides a means for the synthesis of esters[267] although they are most synthetically powerful when used as α-alkoxymethyl anion equivalents, a process which can in some cases be assisted by palladium(0) catalysis.[268] Such compounds also participate in intramolecular cyclisation reactions onto bromonium cations[269] and couple to allyltrimethylsilanes under anodic oxidation conditions.[270] Transmetallation of trialkyltin substituted epoxides has been reported,[271] as have a series of studies on the 2-trialkyltin substituted tetrahydrofurans **226**.[272] A synthesis of α-aminotributyltin compounds **227** has been reported.[273]



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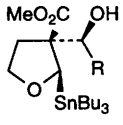

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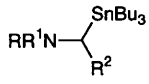
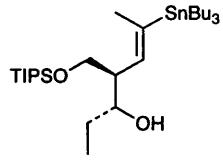


227

Although vinyltin reagents may be prepared from alkynes using palladium catalysed additions of various tin sources,[274] the regiochemistry of this process can often be difficult to control.[275] One example of a regioselective reaction, however, is the exclusive formation of the useful building block **228** from **229**.[275a] The preceding example was reported by the Kocienski group, who have also described a regio- and stereo-selective formation of vinylstannane **230** by treatment of the lithiated dihydrofuran **231** with a tributylstannane cuprate

228 X = O, S; R^1, R^2 = alkyl

229 X = O, S; R^1, R^2 = alkyl



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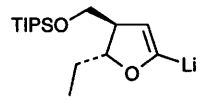
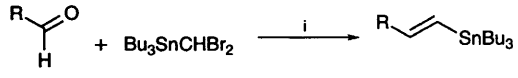


231

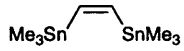
reagent.[276] Another versatile approach to the synthesis of *trans*-vinylstannanes, in this case from aldehydes, has been described by Hodgson (**Scheme 21**).[277]



Reagent: i, 4 eq. $CrCl_2$, LiI, DMF, THF, 25 °C

Scheme 21

Vinylstannanes are most commonly employed in palladium catalysed coupling reactions with a range of reaction partners including acid chlorides,[278] aryl halides[279] or each other.[280] In the field of natural product synthesis *cis*-1,2-bis(trimethyltin) **232** is an excellent reagent for the late-stage formation of enediyne units in the synthesis of the dynemicin antitumour antibiotics.[281] In a synthesis by Danishefsky the two alkynyl iodides in **233** were connected, to give **234**, using this reagent. In his synthesis of strychnine, Overman employed a palladium catalysed carboarylation reaction between a vinyltin, an aromatic iodide and carbon monoxide as a key step.[282]



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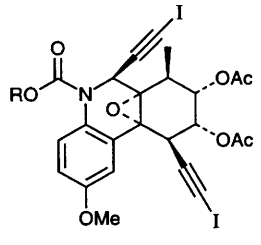

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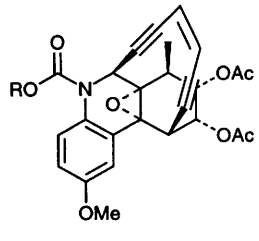

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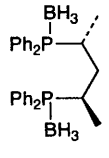
6 Group 15

6.1 Phosphorus

The area of ligands which are chiral at phosphorus has been reviewed recently.[283] The protection of phosphines with borane, which may then simply be removed by treatment with excess amine, is an idea which has received increased attention recently.[284] Such ligands, for example **235**, may be prepared directly by the reaction of borane-coordinated phosphorus anions **236** with appropriate electrophiles, in this case **237**.[284a] Knochel has described the preparation of functionalised phosphines *via* the reaction between functionalised organozincs and chlorophosphines.[285] Once again the borane-protected phsophines are actually isolated.



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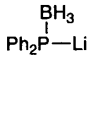

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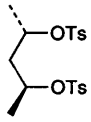


237

6.2 Arsenic, antimony and bismuth

Together with a palladium source, salts of all three of the metals in this section have been shown to be capable of catalysis of the conjugate addition reaction of sodium tetraphenylborate with enones.[286] Arsenic ylides have been employed for the synthesis of α-phenylselenyl acrylates[287] and for the synthesis of 3-hydroxy leukotrienes from lactol precursors.[288] In the latter case, the olefination reaction proceeded with a high degree of *trans*-selectivity.

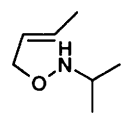
Triarylantimony reagents may be employed as sources of aryl groups in conjugate addition reactions to enones[289] or in carboxylation reactions[290] in the presence of an appropriate palladium catalyst. Allenylantimony reagents have been used in addition reactions to aldehydes.[291]

Triaryldibromobismuth compounds have been used effectively as reagents for the dehydration of secondary and tertiary alcohols.[292] Bismuth ylides give epoxides upon reaction with aldehydes.[293] Triarylbismuth reagents can be activated towards *N*-arylation of cyclic amines.[294]

7 Group 16

7.1 Selenium

Phenylselenium halides are excellent reagents for the promotion of intramolecular cyclisation reactions.[295] A 6-*exo-trig* cyclisation of *O*-allyl oximes provides an efficient entry to the quinolizidine alkaloids;[296] however most of the reported cyclisations proceed through the 5-*endo* mode,[297,298] as in the representative conversions of oxime **238** to **239**[297] and tryptophan derivative **240** to **241**.[298] The tin tetrachloride catalysed reaction of *trans*-



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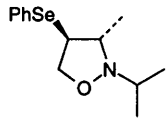

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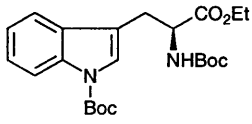

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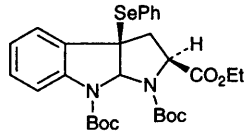

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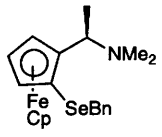
1-phenylselenyl-2-trimethylsilylethene with enones gives a cyclopropane as the product *via* a selenium assisted 1,2-silyl shift.[299]

Homochiral selenium reagents can give enantiomerically enriched alkene addition products.[300] The reaction of styrene with **242** results in the formation of **243** and subsequently **244** in 98% ee after reductive cleavage of the carbon–selenium bond.[300a] A similar directing group was employed for the synthesis of allyl amines from chiral selenium compounds in ee's of 77 to 87%.[301]



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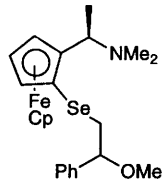

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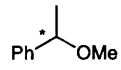

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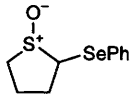
Alkylselenium reagents may be employed in radical reactions; several recent examples of intramolecular cyclisations onto double and triple bonds have been reported. These reactions may be terminated by tributyltin hydride,[302] resulting in a reductive cyclisation, or by the alkylselenyl radical, to give the product of addition across the unsaturated bond.[303] In the case of enol ethers the radical addition invariably takes place at the β-position (hence the alkylselenium is incorporated adjacent to the alkoxy group),[304,305] and good diastereoselectivity may be obtained if the substrate is chiral.[305] The radical generated from sulfoxide **245** may be trapped with allyltin compounds to give **246** as a mixture of isomers.[306] A Pauson–Khand



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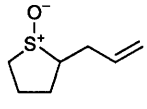

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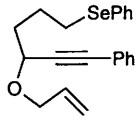

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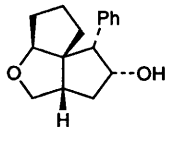

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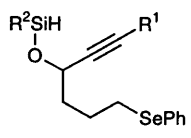

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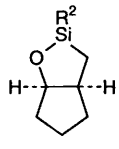
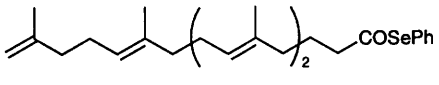


250

reaction followed by a radical cyclisation transforms **247** into tricyclic product **248** in two steps – a powerful reaction combination.[307] A sequence involving radical addition across a triple bond, hydride abstraction from silicon and further cyclisation converts **249** into the silacycle product **250** in one remarkable step.[308]

Acylselenium compounds, which may be prepared by the oxidative reaction of an alkylselenyl-aluminium complex with aldehydes,[309] also participate in radical cyclisation reactions.[310] An outstanding example is the conversion of **251** to the tetracycle **252** (a 1:1 mixture, 53%) in one step with a combination of tributyltin hydride and AIBN.[310a]



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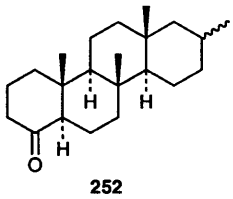

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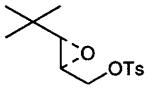
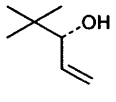
The preparation and use of selenoglycosides as reagents for the synthesis of polysaccharides has been described in some detail. These reagents provide an excellent balance between stability and reactivity and are excellent synthetic reagents.[311] Intramolecular cyclisations onto α-seleno carbenium ions formed from selenium–oxygen heteroacetals have been described.[312]

7.2 Tellurium

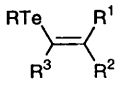
Sodium hydrogen telluride, and close derivatives thereof, are powerful reducing agents for double and triple bonds[313] and are particularly efficient at the conversion of epoxides such as **253** into the corresponding allylic alcohols **254**.[314] Other leaving groups may be used in place of tosylate in this sequence which permits the asymmetric synthesis of allylic alcohols from readily available Sharpless epoxidation products. Vinyl tellurides **255** may be prepared from alkynes *via* zirconium chemistry[315] or by Wadsworth–Emmons reaction of α-phenyltellurides with aldehydes.[316] These compounds represent excellent precursors of vinyllithium compounds, which may be formed *via* the reaction with n-butyllithium[317] (the corresponding alkyltellurides are equally effective at this process[318]). In most cases the most effective method for alkylselenyl substitution is by reaction with a cuprate, a process which has been described



253



254



255

in some depth.[317b,319] Methods for the formation of acyl tellurides,[320] and their applications to enolate chemistry[321] and photoinduced free radical chemistry[322] have been reported.

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