# Main group organometallics in synthesis

MARTIN WILLS

*School of Chemistry, University of Bath, Claverton Down, Bath, BA 2 7AY, UK*

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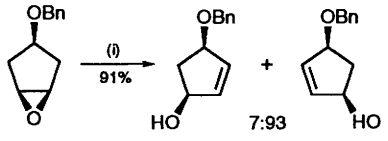
Due to the extensive scope of the subject area this review will concentrate on synthetic aspects rather than mechanistic and structural properties of organometallic compounds and complexes. Whilst every effort has been made to be comprehensive, the emphasis of the review will be on novel methodology rather than applications of widely accepted methods. Furthermore, in some cases the number of references have been necessarily minimized by the exclusion of papers which contain closely related work to that specifically discussed in the review.

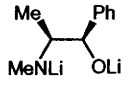
## 1 Group 1

### 1.1 Lithium

#### 1.1.1 Lithium amides and enolates

The study of chiral, non-racemic, lithium amide bases for the asymmetric deprotonation of prochiral ketones and in kinetic resolution reactions continues to be a productive research area.[1] Additives, such as lithium chloride, can have a dramatic and beneficial effect on the enantioselectivity of asymmetric deprotonations of several classes of ketone, for reasons that are yet to be fully explained.[1] A recent development in the field has been the use of *dilithiated* derivatives of amino alcohols, such as **1**, for the enantioselective ring-opening of epoxides (**Scheme 1**).[2] The advantage of these reagents is that the reaction takes place at much lower temperatures than those traditionally required for monolithiated amide bases.



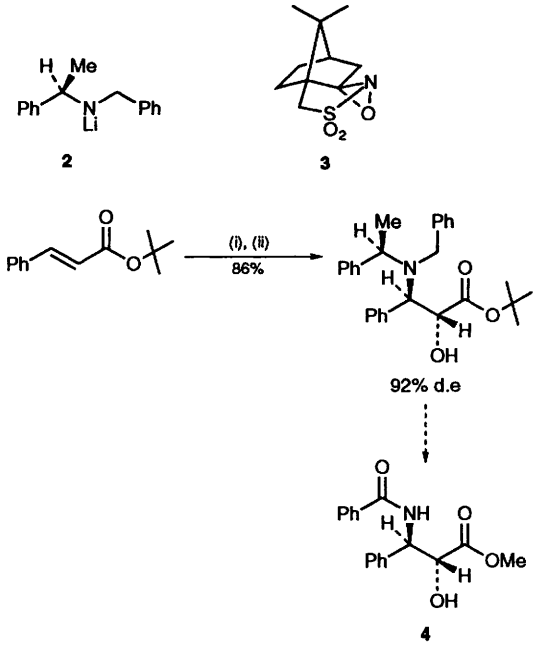

Reagents (i) **1**, THF, –78 °C to r.t., 16h

**1**

**Scheme 1**

The remarkably diastereoselective addition of chiral lithium amides **2** derived from $\alpha$-methylbenzylamine to $\alpha,\beta$-unsaturated esters[3] has been employed in a concise synthesis of the side-chain **4** of the anti-tumour drug taxol, *via* oxidation of the intermediate enolate with the chiral oxaziridine **3** (**Scheme 2**).[3(a)] A diastereoselective cyclization of lithium amides onto non-activated double bonds has been employed for the synthesis of pyrrolidine alkaloids.[4]

The nickel-catalysed isomerization of lithiated allylic alcohols to enolates has been optimized by refinement of the catalyst to the point where essentially a single regioisomer of enolate can be formed and alkylated in the one pot.[5] The extremely hindered lithiated amide derived from diadamantylamine has




Reagents (i) 2; (ii) 3.

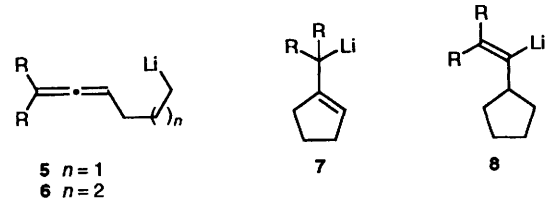
**Scheme 2**

been shown to exist as a monomeric species even in the presence of donor solvents and is capable of generating *E*-enolates of greater than 50:1 diastereoisomeric purity.[6] An excellent review has been published describing the use of chiral diamines to control the asymmetric reactions of enolates with aldehydes and $\alpha,\beta$-unsaturated ketones.[7]

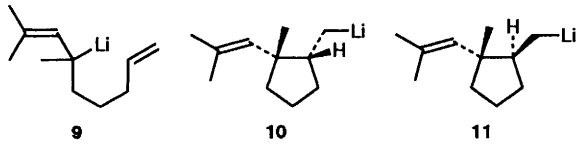
### 1.1.2 Non-stabilized organolithium reagents

The reaction of alkyl lithium reagents with carbon dioxide is known to give *gem*-dialkoxides, and subsequently ketones upon hydrolysis. A report has appeared describing a synthesis of unsymmetric ketones from two different alkyl lithiums in a one-pot reaction, thereby considerably increasing the scope of the process.[8] Substrate controlled stereoselective synthesis is by no means a novel concept. This year, however, a detailed investigation has been reported on 'Cram' selective additions of alkyl lithium reagents to chiral ketones, in which optimization of solvent, temperature, and addition rate serves to produce higher diastereoselectivities than have previously been achieved for this class of reaction.[9]

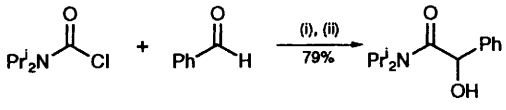
Following an initial breakthrough some years ago, intramolecular cycloaddition reactions of non-stabilized alkyl lithiums have continued to be a productive area of research. Full papers have appeared on tandem cyclizations, which have been featured in previous reviews,[10] and new applications have been reported, such as the cyclization of allenyl organo-lithiums as illustrated by the conversion of **5** into **7** and of **6** into **8**.[11] In each case there is strong preference for the formation of a five-membered ring, providing an 'allowed' cyclization pathway is available.




Dramatic solvent-effects in such reactions are not unusual. Cyclization of **9** (generated from the phenylselenyl reagent using n-butyllithium) in THF at −110°C gives a 54% yield of the cyclized products **10** and **11** in a 1:9 ratio. The same reaction in ether at −30°C gives exclusively **10**.[12] Similar cyclization reactions have been employed for the synthesis of tetrahydrofurans.[13] In each of the cases discussed above, the alkyl-lithium reagents were generated by an exchange reaction with n-butyllithium. However, it is noteworthy that the recent development of polyaryl-*catalysed* reductive lithiations of halides, ethers, and sulfides present attractive alternative methods,[14] several more of which will be featured in this review.



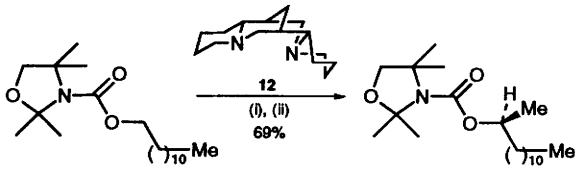

Acyl anions are probably the most widely employed class of 'umpolung' reagents. Whilst several equivalents of such species, *e.g.* dithianes and cyanide anion, are known, true acyl anions have not been widely exploited due primarily to their high reactivity. However, two recent reports have described the *in situ* preparation of such reagents by low-temperature (−110°C) addition of alkyl lithiums to carbon monoxide[15] and by direct reduction of *N,N*-di-isopropylcarbamoyl chlorides using lithium powder and a catalytic amount of naphthalene (3 mol%). In the latter case the acyl lithium reagents are immediately trapped by a carbonyl compound (**Scheme 3**).[16]




Reagents (i) Li, $C_{10}H_8$(3 mol%), THF, −78 °C → 20 °C; (ii) $H_2O$

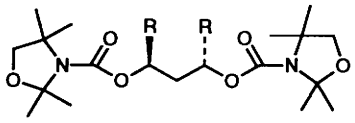
**Scheme 3**

Lithiation adjacent to an oxygen atom may be achieved by direct deprotonation with the aid of a carbamate directing group, which serves to simultaneously activate the protons and to direct deprotonation. In the presence of the chiral diamine (−)-sparteine **12**, one of a pair of prochiral protons can be removed with high selectivity (**Scheme 4**).[17] This is a remarkable transformation as much for its versatility as well as selectivity. The symmetrical substrate **13** has been converted in a two stage process into the C2-symmetric adduct **14**[18] and the

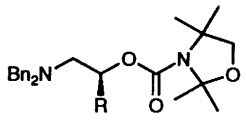



Reagents (i) Bu$^s$Li; **12**, $Et_2O$, –78 °C, 16h; (ii) $CH_3I$, –78 °C, 4h

**Scheme 4**



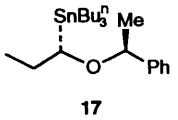
**13** R = H
**14** R = Me



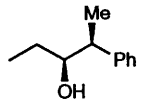
**15** R = H
**16** R = $CO_2Me$

amine-substituted **15** has been converted into a series of enantiomerically enriched derivatives such as **16**.[19] In the latter case it is essential that the dibenzyl derivative is employed, since the less hindered dimethylamino compound competes with the carbamate for chelation sites and gives products of low enantiomeric excess. Apart from the enantio-directing effect, a chiral diamine also serves to maintain configurational stability in the anion. Without this, such anions have been demonstrated to be reasonably stable at low temperatures ( − 78°C) but rapidly epimerize if they are warmed ( − 20°C).[20]

Whilst all the alkylations of carbamate stabilized anions discussed above are postulated to proceed with retention of configuration, there is conflicting evidence from the results of certain Wittig reactions.[21,22] Treatment of **17** with n-butyllithium gives the rearrangement product **18** with 88% stereoselectivity, whilst the diastereoisomer of **17** gives the opposite diastereoisomer as the major product.[21(a)]



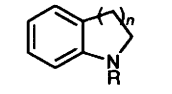
**17**



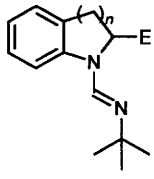
**18**

Assuming that the trialkyltin/lithium exchange proceeds with retention the only explanation is predominant inversion of configuration at the lithiated carbon atom. In fact the energy difference between the retention and inversion pathways is small, and highly dependent on the nature of the electrophile; examples of such sensitivity have featured in previous reviews and an example is given in a following section. The related [2,3]-Wittig rearrangement[22] has been successfully employed in a number of total syntheses of natural products such as rapamycin.[23]

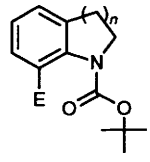
Carbamates also make excellent directing groups for deprotonations adjacent to nitrogen[24] and, together with formamidines,[25] dominate the chemistry of such transformations. The two directing groups appear to be in many respects complementary in terms of directing effect and stereochemical control.[26] For example, lithiation of formamidine **19** ($n = 1$ or 2, Bu$^t$Li, − 20°C, ether) gives predominantly the 2-substituted product **21** after addition of an electrophile whilst the same transformation on carbamate **20** ($n = 1$ or 2, Bu$^s$Li, TMEDA, − 78°C, ether, followed by addition of an electrophile) gives the aromatic substitution product **22**.[26(a)]



**19** R = CH=NBu$^t$
**20** R = $CO_2$Bu$^t$



**21**

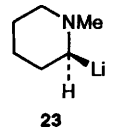


**22**

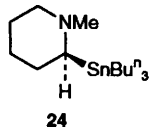
Trialkyltin/lithium exchange has also been used extensively to generate lithio-anions adjacent to nitrogen.[27] The enantiomerically enriched species **23**, generated from **24**, has been shown to be configurationally stable for at least 45 minutes at − 40°C.[27(a)] A preparation of lithiated aziridines **25** *via* trialkyltin/lithium exchange has been reported.[28]

### 1.1.3 Lithiated aromatic and heteroaromatic groups

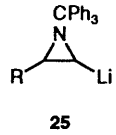
Amides and carbamates are two of the most effective directors of *ortho* lithiation of aromatic rings when a butyllithium is employed as the base. Whilst the directing ability of amides is largely due to the combination of a strong directing effect and the ability to increase the acidity of the aromatic protons, the ability of the amide to achieve a coplanar geometry is also essential. This factor is clearly demonstrated by the comparative ease of lithiation of the series of compounds **26**–**28**, in which the increasingly large *ortho*-substituent hinders the achievement of coplanarity (**Figure 1**).[29]



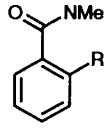
**23**



**24**



**25**

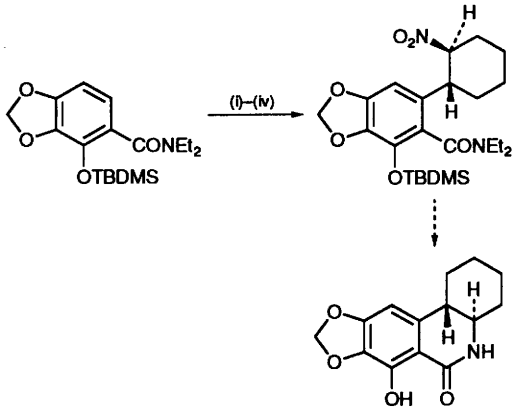


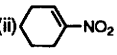
| Compound | Relative Rate |
|---|---|
| **26** (R = H) | 200 |
| **27** (R = Pr$^i$) | 17 |
| **28** (R = Bu$^t$) | 9 |

**Figure 1** Relative rate of *o*-lithiation

An additional advantage of the amide group is that it may be subsequently employed for the creation of further functionality in the molecule, or for intramolecular cyclizations.[30,31] An excellent example

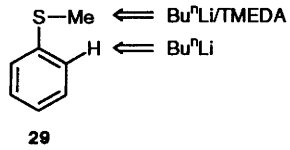
is provided by a very concise synthesis of a pancratistatin model compound *via* addition of a functionalized aryl lithium to an unsaturated nitro-compound (**Scheme 5**).[30] Amides bearing homochiral groups have been shown to be capable of generating moderate diastereomeric excesses in addition reactions to aldehydes.[31]




Reagents (i) Bu$^s$Li, TMEDA, THF, –78 °C, (ii)  (iii) AcOH, (iv) $Et_3N$, EtOH, reflux

**Scheme 5**

Recently, lithiated amides have emerged as suitable bases for aromatic lithiations of suitably activated compounds. Remarkably, competition studies have shown that fluorine is one of the best directing groups in this situation. In contrast it is inferior to many other groups when an alkyl lithium base is employed to create the aryl anion.[32] The effect of an apparently small change in the nature of the base employed for *ortho*-lithiation can be dramatic. Reaction of **29** with Bu$^n$Li alone results in aromatic lithiation whilst, in contrast, deprotonation using Bu$^n$Li with Bu$^t$OK (*i.e.* a 'superbase') gives a benzylically-lithiated anion (**Figure 2**).[33] This result serves to underline the contention that such a combination of alkyl lithium and a metal alkoxide gives a base which is of fundamentally different reactivity to either component and not simply a highly reactive derivative.

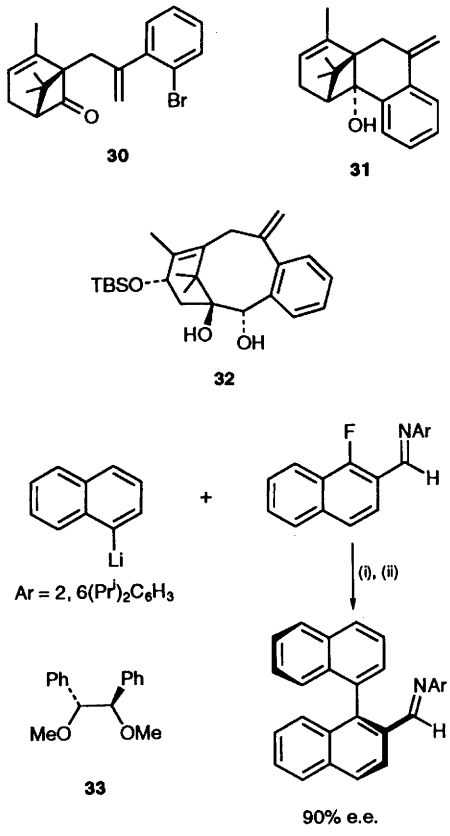



**29**

**Figure 2**, Position of lithiation in a thioether.

Intramolecular cyclization reactions of aryl lithiums generated by *in situ* exchange of a halide for lithium can be powerful synthetic tools.[34] This is amply illustrated by the conversion of **30** into **31** (Bu$^t$Li, TMEDA, THF, −78°C, 67%) and subsequently into **32**, a potential precursor of the anti-tumour compound taxol and its derivatives.[34(a)]

The asymmetric addition of 1-lithio naphthyl derivatives to appropriately substituted naphthyl acceptors, mediated by the chiral diether **33**, has been demonstrated to be capable of giving binaphthyl products with enantiomeric purities of up to 90% e.e. when 1.1 equivalents of **33** are employed (**Scheme 6**).[35] Rather more impressive is the observation that when only 2.5 mol% of diether **33** is used an e.e. of 82% is still generated.

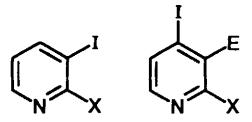



Reagents: (i) 1.1eq **33**; (ii) $H^+$, $H_2O$, toluene, –45 °C

**Scheme 6**

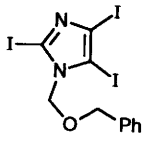
Lithiation of *N*-phenyl pyrrolidine occurs selectively at the 2-position, as expected. Rather less expected is the observation that the lithiation process involves an initial kinetic preference for formation of a dilithiated intermediate (also lithiated on the phenyl group) followed by a slow equilibrium.[36] Such a process in which one lithiated group directs a second rapid lithiation is not unusual, and an example of a detailed study of a related system will be described in the section on dilithiated anions. The reaction of alkyl lithium bases with aromatic or heterocyclic iodides invariably results in iodine/lithium exchange. If lithium diisopropylamide is used as the base, however, it is possible to lithiate adjacent to iodine. In the case of **34**, lithiation is followed by iodine migration to give a more stabilized heteroaryl lithium which subsequently reacts with an electrophile to give substitution products **35**.[37]

Lithium/halide exchange is an effective method for the generation of heteroaryl lithium compounds, but the rate of the reactions is generally very high, and



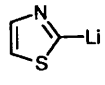
**34** (X = F, Cl) **35** (X = F, Cl)

selective bromide exchanges can be difficult to control. An ingenious example where control is possible is in the lithiation of **36** (a purine building block), the substitution pattern of which permits the three iodines to be distinguished in sequential lithium/iodine exchange processes. The first exchange is of the iodine between the nitrogen atoms and the second involves the iodine proximal to the directing ether group.[38] A similar sequence has been reported for a tribromo analogue.[39]



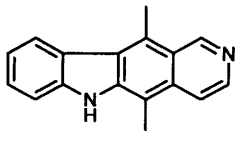
**36**

One of the most versatile lithiated heterocyclic compounds, and certainly one of the most prolific in terms of applications, is the lithiated thiazole anion **37**.[40,41] This is a valuable formyl anion equivalent and it has been employed in the synthesis of numerous classes of target compound, including $\alpha$-amino aldehydes, which may be accessed *via* addition of **37** to nitrones.[41]



**37**

Finally, in this section, a very short synthesis of the important anti-tumour compound ellipticine **38** has been reported in which the key step is the addition of lithiated indole **39** to the anhydride **40**. The addition product **41** is formed in 92% yield and the remaining mass balance is accounted for by the unwanted regioisomer. From **41**, the synthesis of **38** requires only five further steps.[42]



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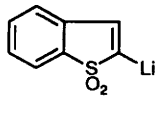
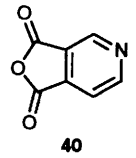
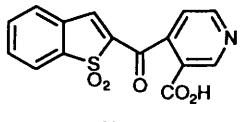


**39**



**40**

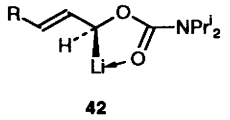


**41**

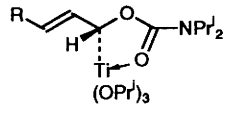
### 1.1.4 Benzylic and allylic lithium anions

An excellent review has been published on the preparation and regio- and stereo-control of reactions of polar allylic organometallic compounds.[43] Cyclopropane synthesis *via* intramolecular cyclizations of tributyltin-derived benzylically stabilized anions with displacement of a *p*-toluenesulfonate group has been reported, but the pattern of stereochemical control in such reactions is highly sensitive to the reaction conditions.[44]

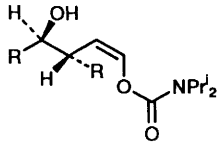
Although the carbamate-stabilized anions based on the structure **42** are formally allylic reagents, they react in many ways as localized anions. As for the related structures previously discussed, such anions may be created in enantiomerically pure form using a combination of the chiral diamine base (−)-sparteine and an alkyl lithium (see **Scheme 4**).[45] One of the most valuable applications of allylic anions **42** are in additions to aldehydes, which are generally most selective after exchange of lithium for a titanium(IV) derivative.[46] If titanium tetrachloride is used, the transmetallation proceeds to give the inversion product **43** and subsequently **44** in 80–90% e.e. after reaction with an aldehyde. An inversion of configuration is also observed in the reaction of homochiral anion **45** with methyl chloroformate (or carbon dioxide then diazomethane) to give **46**.[47] (Note that the sparteine ligand has been omitted from all illustrations of chiral anions for reasons of clarity.)



**42**



**43**



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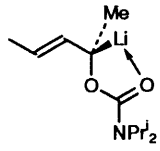

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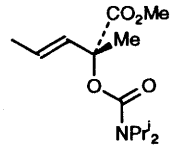
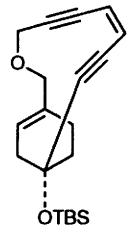
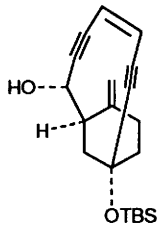


**46**

Several examples of the synthetic application of Wittig rearrangements of allylic anions have been reported.[48] Perhaps the most impressive of these is the contraction of enediyne **47** into **48** following treatment with lithium tetramethylpyrolidine for five minutes at −25°C.[48]

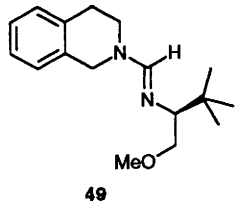


**47**



**48**

Asymmetric benzylic lithiations adjacent to tetrahydroisoquinolines may be achieved if a chiral formamidine is employed as the directing group, as in **49**.[49] Meyers has demonstrated that initial lithiation of **49** removes the $\alpha$-proton to give **50** which is subsequently alkylated ($E^1$ is the electrophile) from the top face (as illustrated) to give **51**. The second



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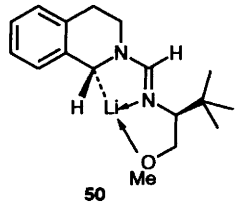

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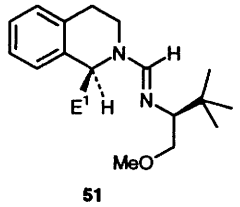

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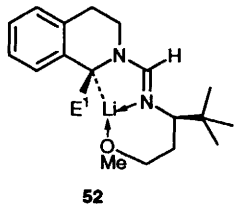

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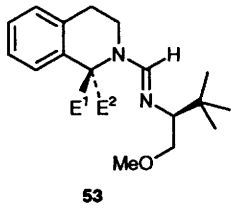
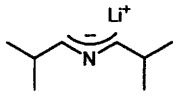


53

lithiation process gives **52** with the lithium on the lower face again, but alkylation ($E^2$ is the electrophile) of this anion occurs from the lower face to give **53**, with retention of configuration.[49(a)] Although the lithiated species are illustrated with tetrahedral geometry the anion has a significant amount of $sp^2$ character due to benzylic overlap, with the lithium atom predominantly lying on one side due to stabilization by donation from oxygen and nitrogen atoms of the side chain. The sense of alkylation is in each case controlled by steric effects from the chiral formamidine group.

Allylic organo-lithium compounds **54** in which the central atom is nitrogen have been generated by trialkyltin/lithium exchange and by direct deprotonation and give pyrrolidines **55** upon reaction with appropriately substituted alkenes.[50]



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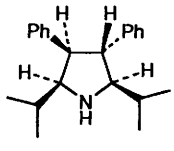
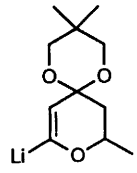


55

### 1.1.5 Alkenyl and alkynyl anions

Lithiation of the position adjacent to the oxygen atom of enol ethers is a relatively facile process which has been employed extensively in synthetic applications. For example, the vinyl lithium **56** (generated using $Bu^tLi$, THF/HMPA, −78°C) is a key component in a total synthesis of breynolide reported this year by A. B. Smith.[51] The potential for asymmetric synthesis in the addition of such reagents to aldehydes has been realised by the incorporation of a homochiral group as in **57**, which reacts with the ketone **58** to give a 4.5 : 1 ratio of diastereoisomeric adducts in which **59** predominates. The nature of the aromatic ring on the ether is critical—reaction of the corresponding anion in which a phenyl has replaced the 2,4,6-trimethylphenyl group with the same ketone gives a 1 : 1 mixture of adducts.[52] Both prolinol and diacetone glucose groups have been employed as chiral auxiliaries in related addition reactions of lithiated allenyl ethers.[53]



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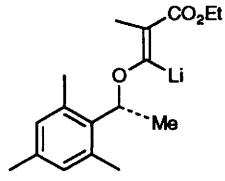

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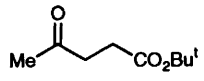

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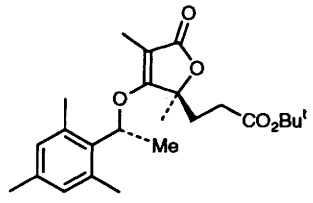
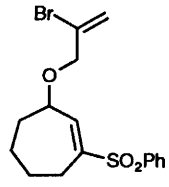


59

Lithium/bromine[54] or tributyltin/lithium[55] exchange are reactive processes which allow reactive organometallic reagents to be created in the presence of functional groups that may become subsequently involved in, for example, intramolecular cyclization reactions. Two examples of such applications are provided by the conversion of **60** into **61** (86%)[54] and **62** into **63** (81%)[55] *via* intramolecular reactions of $\alpha,\beta$-unsaturated sulfones and ketones respectively.



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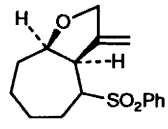

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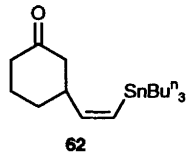

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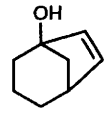
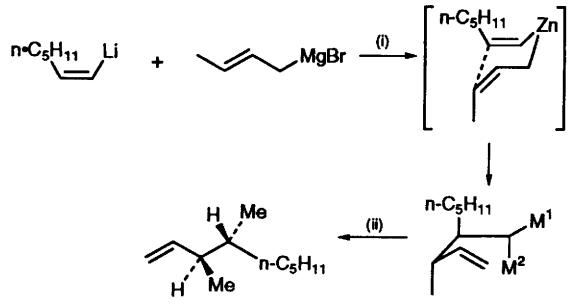


63

The combination of alkenyl lithium compounds with an allyl magnesium bromide in the presence of zinc(II) bromide results in zinc(II)-mediated allylation of the vinylic compound. As illustrated in **Scheme 7**, this is achieved by initially generating, through a chair-like transition state, a dimetallic intermediate which upon quenching with a source of protons gives

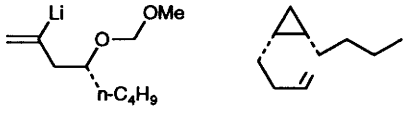


Reagents (i) $ZnBr_2$, THF; (ii) $H_3O^+$

**Scheme 7**

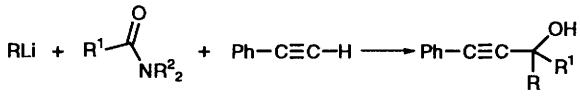
the hydrocarbon product ($M^1$ and $M^2$ represent two non-identical metal counter-ions which may be zinc, lithium, or magnesium).[56]

This 'mixed-organometallic' chemistry has recently been extended to a synthetic approach to cyclopropane rings.[57] In this case the starting material, the vinyl lithium reagent **64**, contains a methoxymethylether function which acts as a leaving group for cyclopropane formation following the allylation process. The final product, after quenching of the reaction, is the *cis*-cyclopropane **65**.



**64** **65**

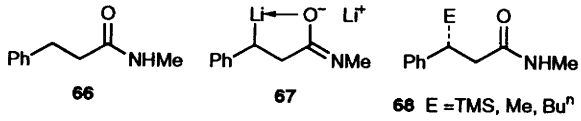
The combination of an alkyl lithium, a tertiary amide, and a terminal alkyne results in the formation of propargylic alcohols in a one-pot process (**Scheme 8**).[58] In this process the reaction of the alkyl lithium with the amide gives a ketone and a lithium amide. The latter deprotonates the terminal alkyne, which subsequently adds to the newly formed ketone.



**Scheme 8**

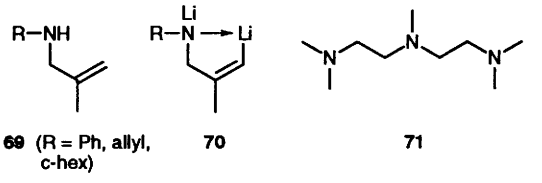
### 1.1.6 Di- and tri-lithiated anions

Treatment of amide **66** with two equivalents of Bu$^s$Li in the presence of (−)-sparteine **12** (−78°C, THF/methyl-t-butyl ether solvent) results in enantioselective benzylic lithiation to give **67**. Such a mode of lithiation, in a situation where enolate formation is also possible, is very unusual and underlines the importance of the amide group as a director of lithiation.[59] Reaction of **67** with an electrophile gives enantiomerically enriched products **68** (80–94% e.e.) in high yield (77–86%).

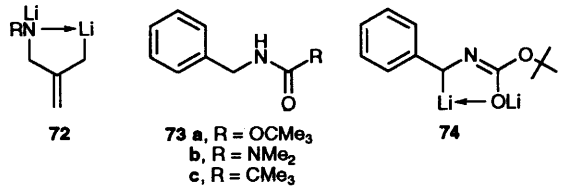


**66** **67** **68** E = TMS, Me, Bu$^n$, Bn, $Ph_2C(OH)$

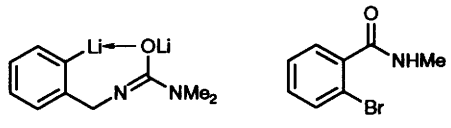
Dilithiation of allylic secondary amines has been shown to be an effective method for the generation of alkenyl lithiums.[60] However, like many similar reactions this is very sensitive to the exact solvent conditions. Treatment of **69** with Bu$^n$Li in ether at −50 to −30°C followed by Bu$^t$Li at −30 to 20°C gives the expected dilithium **70**. Should the same reaction be carried out in the presence of a coordinating di- or tri-amine, such as pentamethyldiethylenetriamine (PMTEDA, **71**), then allylically dilithiated anion **72** is formed.[60(a)] The nature of the directing group is critical in lithiations of compounds based on the structure **73**. Dilithiation (Bu$^s$Li) of carbamate **73a** gives exclusively the benzylically substituted **74** (79% yield after reaction with carbon dioxide) whilst the same transformation of urea **73b** gives exclusively the aryl lithium **75** (82% yield after reaction with carbon dioxide). The *N*-pivaloyl compound gives a mixture of lithiation at both positions.[61] Several other reports have appeared describing aromatic lithiations directed by carbamate groups,[62] including a very valuable one detailing the relative stabilities of Bu$^n$Li and Bu$^t$Li in ether and THF solutions.



**69** (R = Ph, allyl, c-hex) **70** **71**

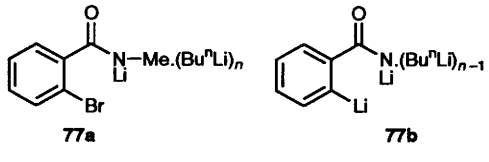


**72** **73** a, R = $OCMe_3$; b, R = $NMe_2$; c, R = $CMe_3$ **74**



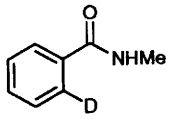
**75** **76**

The reaction of **76** with Bu$^n$Li has been investigated in great detail by Beak *et al.* since there is some controversy over the relative rates of lithium/bromine exchange compared to amine deprotonation.[63] It has been concluded that amide deprotonation is the faster reaction and that this initially gives a complex with several molecules of Bu$^n$Li, *i.e.* **77a**. This has the effect of producing a very high local concentration of Bu$^n$Li in the region of the deprotonated amide, and bromine/lithium exchange takes place (to give **77b**) within the complex at a rate *faster* than mixing of the



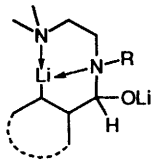
**77a** **77b**

$Bu^nLi$ within the reactive solution. The result then is that (theoretically) 50% of the substrate is rapidly dilithiated, whilst the other 50% is not lithiated at all. Some of the species **77** acts to deprotonate unchanged **76**. This can be proved by deuterium labelling studies—the use of *N*-deuterio-**77** results in formation of a quantity of **78** in the final reaction mixture.[63]



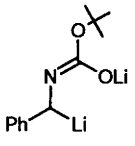
**78**

Aldehydes normally react rapidly with alkyl lithium reagents, but prior treatment with a monolithiated diamine results in the formation of $\alpha$-amino alkoxides, which are themselves good directing groups for further lithiation. The resulting dianions **79** may be alkylated with a number of electrophiles and are converted back into the parent aldehyde upon workup.[64] This methodology appears to be excellent for alkylation reactions of heterocyclic compounds such as pyridines and furans.[64]



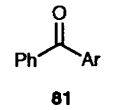
**79**

Dianions localized on adjacent atoms are difficult to make by deprotonation, for obvious reasons. One solution is to stabilize the charge at each location as in **80**, which may be prepared by direct deprotonation of the benzylically substituted amide precursor ($Bu^sLi$, THF, TMEDA)—note that aryl lithiation is not favoured.[65]

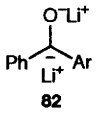


**80**

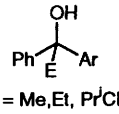
An attractive, alternative method is the direct reduction of a double bond using lithium metal in the presence of a catalytic amount of a polyaromatic such as naphthalene. In this way aromatic ketones such as **81** can be reduced (lithium, 8mol% naphthalene) to dianions **82** which subsequently react with a variety of electrophiles to give adducts **83**.[66] Addition of such dianions to imines gives $\alpha$-amino alcohols in good yields.[67] The literature coverage suggests, predictably, that at least one aromatic substituent on the ketone is essential for a clean reaction. Providing this is the case, ketals may also be used as substrates for this reduction process.[68]



**81**

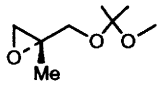


**82**

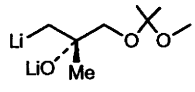


**83** E = Me,Et, $Pr^iCH(OH)$, PhCH(OH)

A similar reductive dilithiation may be achieved using strained oxygen-containing rings as substrates (three- or four-membered).[69] In this case a carbon–oxygen bond is cleaved, as illustrated by the conversion of epoxide **84** into dianion **85** (a side chain component in a total synthesis) using lithium 4,4′-di(t-butyl)dibenzene (LDDB).[69(a)] Reactions of similar dianions with chromium-arene complexes have been used for the synthesis of lactones.[69(b,c)] Analogous reductions of aziridines, such as **86**, lead to dilithiated species **87**, which are useful building blocks for alkaloid synthesis.[70]



**84**

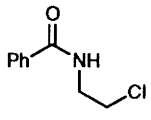


**85**

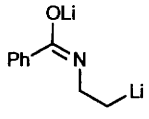
**86**

**87**

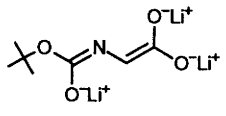
The combination of lithium metal with a catalytic amount of naphthalene may also be used for the reductive conversion of chlorides such as **88** into alkyl lithiums **89** (the amide is first deprotonated using n-butyllithium).[71,72] The lithio-anions thus formed may be alkylated with a variety of electrophiles or, as in recent reports, coupled with aryl or vinyl halides.[72] Finally, in this section, is the report that mono-*N*-protected amino acids may be *tri*-lithiated with excess LDA to give highly reactive species such as **90**, which have been used as intermediates for the synthesis of a number of functionalized amino acid derivatives.[73]



**88**



**89**



**90**

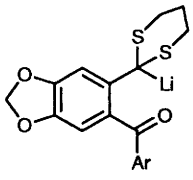
### 1.2 Sodium and potassium

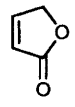
The use of a combination of alkyl lithium and potassium alkoxide, or 'superbase' can lead to the formation of highly reactive alkyl potassium reagents. Such reagents have been employed recently in the synthesis of $\alpha$-santalol, using a displacement of a bromide by an allyl potassium as the key step[74] and, *via* an epoxide opening by a benzyl potassium reagent, a chiral auxiliary.[75] The reductive generation of a benzyl potassium reagent, by treatment of a cyclic aminal with potassium metal, has also been reported (see previous section).[76]

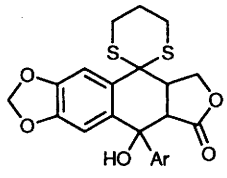
### 1.3 Anions stabilized by sulfur, silicon, and other heteroatoms

The synthesis of natural products *via* the addition of sulfur-stabilized anions to $\alpha,\beta$-unsaturated carbonyl reagents has been investigated in some depth. A novel

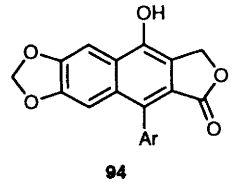
variation on this is in the 'cascade' reaction of anion **91** with **92** to give adduct **93** in one step. Subsequent transformations yield the natural product analogue **94**.[77]

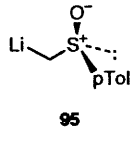

**91**

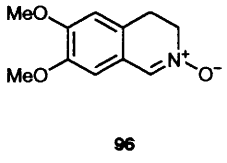

**92**

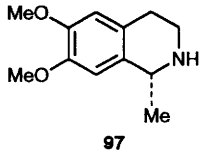

**93**

An excellent and comprehensive review has been published describing the scope of carbon–carbon bond forming reactions using lithiated sulfoxides such as **95**.[78] Such anions have potential for asymmetric synthesis if enantiomerically pure sulfoxides are used and many applications have been reported in previous reviews. Additions to nitrones, in which diastereoisomeric ratios of up to 92:8 (in the case of **96**) may be realized, have been reported this year.[79] Reductive removal of the sulfoxide from the major adduct (after separation) derived from **96**, using Raney nickel, furnishes the enantiomerically pure tetrahydroisoquinoline **97**.[79]

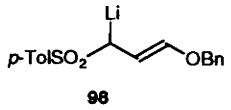

**94**

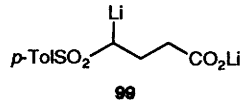

**95**

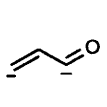

**96**

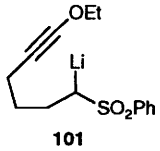

**97**

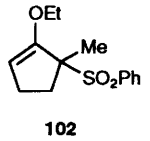
Lithiated sulfones are very versatile reagents for synthesis, and several examples of their application have been reported this year.[80,81] They appear to be particularly useful as $\beta$-lithio enone equivalents, since the sulfone can be removed by elimination to give the double bond. Reagents **98**[80(a)] and **99**[80(b)] are both equivalents of the synthon **100**, and have been used to prepare $\alpha,\beta$-unsaturated-$\gamma$-lactones *via* reactions with aldehydes. Funk[82] has reported a novel method for intramolecular cyclization which relies on a lithiated sulfone. It was found that **101**, generated by deprotonation (Bu$^n$Li, THF, 0°C) gave the cyclized compound **102** upon quenching with iodomethane.


**98**

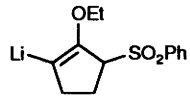

**99**

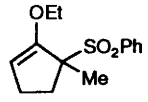

**100**


**101**

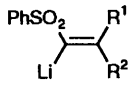

**102**

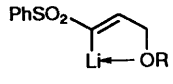
The proposed mechanism for this transformation involves the initial formation of anion **103** followed by translithiation to the more stabilized anion **104**.[82] The process also works for other anion stabilizing groups such as esters and phosphonium salts.


**103**

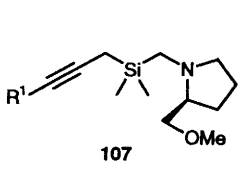

**104**

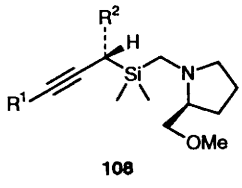
Synthetic applications of $\alpha$-lithiated-$\alpha,\beta$-unsaturated sulfones **105** have also been extensively reported this year. Such reagents often contain a donating group on the $\beta$-substituent, as in **106**, to improve the configurational stability of the anion.[83]

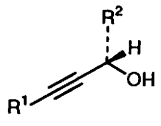

**105**


**106**

$\alpha$-Lithiated organosilanes may be employed as tools for asymmetric synthesis if an appropriate chiral directing group is incorporated into the substrate.[84,85] Lithiation of **107** (2eq. Bu$^s$Li) followed by the addition of excess alkyl halide ($R^2X$ = MeI, EtI, allyl bromide) results in formation of the alkylated derivatives **108** in diastereoisomeric ratios of up to 98:2. Subsequent oxidative desilylation (20% $H_2O_2$, MeOH, THF, KF, $KHCO_3$) then gives propargylic alcohols **109** in up to 97% enantiomeric excess.[84] Studies of the configurational stability of such compounds have been reported.[85] Synthetic applications of trialkyl-stabilized allylic reagents have been reported, including additions to ketones[86] and to activated naphthyl systems.[87]


**107**

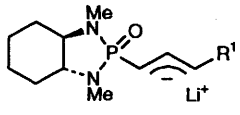

**108**


**109**

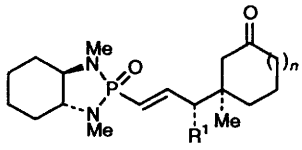
Arylselenyl-stabilized organo-lithium compounds have been employed in a small number of transformations and are generally prepared by reaction of the *gem*-diselenated precursors with an n-butyl-lithium.[88] Configurational stability studies have been reported.[88(c)]

Allyl lithiums substituted by chiral phosphorus groups may be employed in asymmetric Wittig reactions of 4-monosubstituted cyclohexanones[89] and in asymmetric Michael addition reactions.[90] The

addition reaction of **110** with cyclic β-methyl enones gives adducts of up to 90% diastereoisomeric excess ($n = 1$ or 2; only two out of a possible four products are formed) in which **111** predominates.[90]



**110**



**111**

Lithiated trialkylboranes are relatively rare in synthesis. Recently, however, a large number of papers have been published by Pelter's group describing the synthesis, structural properties, and reactivity of the lithiated boranes of general structure **112**.[91]

$(Mes)_2BCH_2Li$

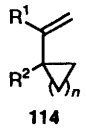
**112**

## 2 Group 2

### 2.1 Magnesium

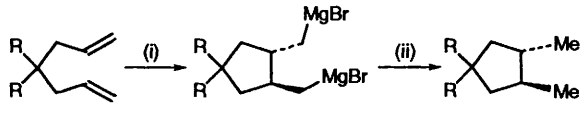
Magnesium activated by association with aromatic compounds has been used to good effect in the preparation of other finely divided metals.[92] The reaction of activated magnesium ('Reike' magnesium) with 1,3-dienes results in cycloaddition to magnesium-containing five-membered organometallics (**113**). Subsequent reaction with a n-$C_x$-alkyl ($x = 3$, 4, or 5) dibromide gives spirocyclic products **114**.[93]

**113**



**114**

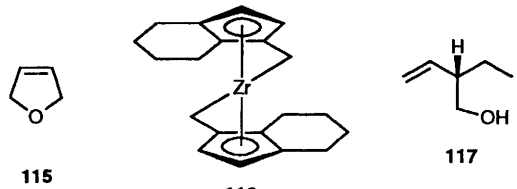
A related transformation is the conversion of 1,6-dienes into *trans*-di-Grignard reagents using a combination of butylmagnesium bromide and catalysis by a zirconium complex (**Scheme 9**).[94] This is only one example of a large number of zirconium-catalysed transformations of Grignard reagents reported in recent years.



Reagents: (i) 3–4eq. $Bu^nMgBr$, $Cp_2ZrCl_2$(5–10 mol%); (ii) $H_3O^+$

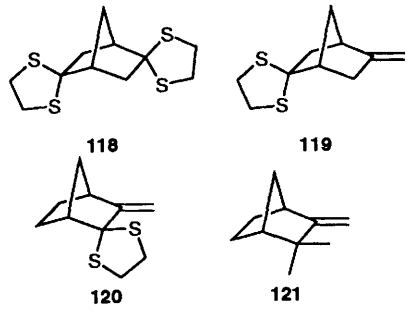
**Scheme 9**

The reaction of 2,5-dihydrofuran **115** with ethyl magnesium bromide mediated by 10 mol% of homochiral zirconium complex **116** gives the ring-opened adduct **117** in 65% yield and > 97% e.e.[95]



**115** **116** **117**

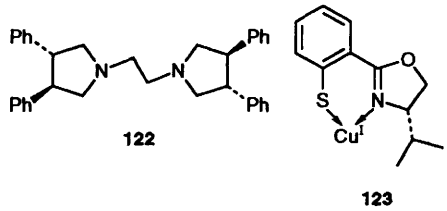
The nickel-catalysed reaction of methyl magnesium bromide with dithianes such as **118** results in the formation of the alkene **119**.[96] Conversely, the same reaction with a substrate bearing a double bond adjacent to the dithiane, such as **120**, results in formation of the *gem*-dimethyl adduct **121**.[97(a)] Transmetallation to the zinc reagent has been reported to give a cleaner reaction in a similar process.[97(a)]



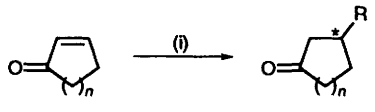
**118** **119**

**120** **121**

Asymmetric catalysis of the addition of Grignard reagents to aldehydes, to give products of up to 75% e.e., has been achieved with the use of the chiral diamine ligand **122**.[98] Slightly higher e.e.s have been obtained in the asymmetric catalysis of the Michael addition of Grignard reagents to cyclic enones mediated by the chiral catalyst **123** (**Scheme 10**).[99]



**122** **123**



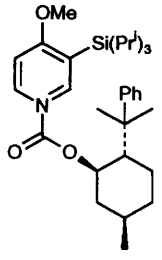
$n = 1$ 16 – 37% e.e.
$n = 2$ 60 – 72% e.e.
$n = 3$ 53 – 87% e.e.

Reagents: (i) RMgBr, 5 mol% **123**, –78 °C

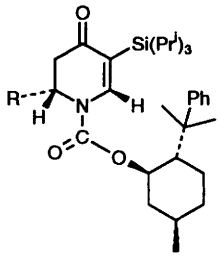
**Scheme 10**

Mixed sulfur/nitrogen donor ligands based on the chiral oxazole system are ideal for this application because of the combination of an excellent copper ligand (sulfur) and a stereochemically well-defined asymmetric environment. More applications of such ligands in asymmetric Michael additions are certain to be reported in the near future.

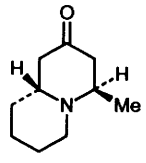
The addition of Grignard reagents to pyridinium salts **124** bearing a chiral group on the carbamate has proved to be a highly versatile and valuable synthetic process for the asymmetric synthesis of alkaloids.[100] The bulky trialkylsilyl group in **124** assists in the control of the regioselectivity of the addition and high diastereoselectivities have been observed in the addition products.[100] Adduct **125** has been converted into (−)-pumiliotoxin C,[100(a)] adduct **126** into (+)-myrtine **128**,[100(b)] and adduct **127** has been elaborated to the intramolecular Diels–Alder precursor **129** and subsequently the lycopodine alkaloid skeletal molecule **130**.[100(c)]



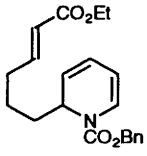

**124**



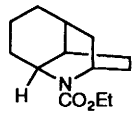

**125** R = $CH_2CH_2CH_2CH{:}CH_2$
**126** R = $CH_2CH_2CH_2CH_2Cl$
**127** R = $(CH_2)_4OCHCH_3OCH_2Me$




**128**

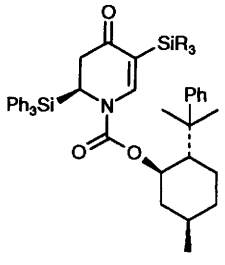



**129**




**130**

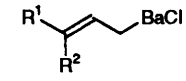
Whilst the majority of Grignard reagents add to **124** to give adducts of the absolute configuration shown in **125**. A triphenylsilyl Grignard reagent gives the product of opposite configuration **131**, for reasons that are not fully understood.[100(d)]




**131**

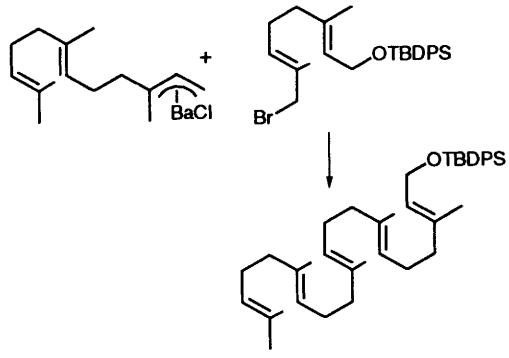
## 2.2 Barium

Allyl barium reagents **132** are presently the subject of significant interest from the synthetic community.[101,102] Prepared by the reaction of barium metal with allyl chloride, these reagents show a high selectivity for alkylation at the less substituted terminus. This is in contrast to the reactivity of most other allyl metals, such as magnesium reagents. Compatible electrophiles include carbon dioxide[101] and allylic bromides.[102]




**132**

Corey has used allyl bariums to good effect in the synthesis of open chain precursors for cyclization to steroids (**Scheme 11**).[103]




**Scheme 11**

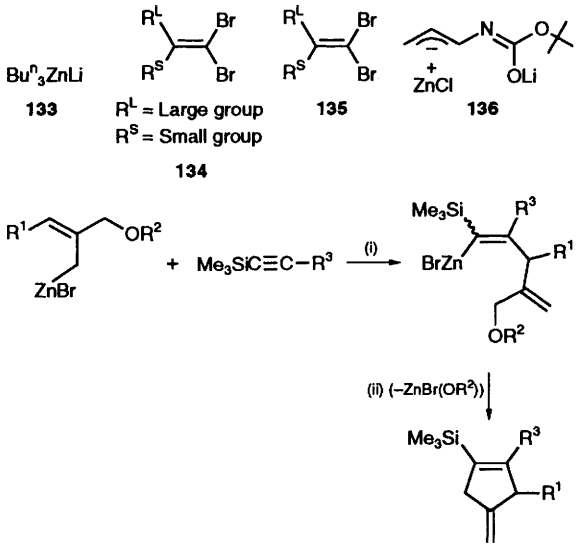
## 2.3 Zinc, cadmium, and mercury

The chemistry of the versatile reducing agent zinc borohydride has been reviewed.[104] Intramolecular cycloadditions of non-stabilized alkyl zinc reagents onto unactivated double bonds have been found to proceed in a manner analogous to the alkyl lithium compounds **5**, **7**, and **9** described at the start of this review, with a preference for the 5-*endo-tet* mode of cyclization.[105]

The mixed lithium/zinc reagent **133** has proved to be a useful reagent for certain transformations.[106] In the selective lithium/bromine exchange of the 1,1-dibromoalkenes **134**, for example, **133** exhibits a much higher selectivity for exchange of the halide *cis*-to the larger group, to give **135**, than n-butyl-lithium alone. This may be due to the higher level of relief of steric interactions in lengthening and breaking of this C–Br bond than that *cis*-to the small group.

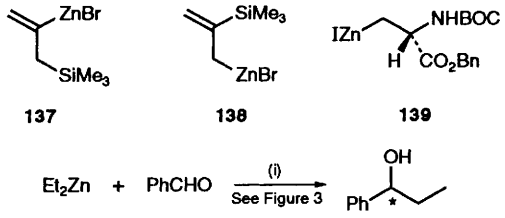
Allyl zincs may be prepared by alkyl lithium deprotonation followed by transmetallation with a source of $Zn^{II}$, as in the case of **136**.[107] Subsequent reactions of **136** with aldehydes are rather more selective than the parent allyl lithium reagents. The direct reduction of allyl bromides or allyl ethers with an activated source of zinc also provides an attractive method for allyl zinc synthesis.[108] Reactions of thus derived allyl zinc reagents with aldehydes and ketones are valuable reactions, which have been used extensively in synthesis.[108] Rather more interesting is the reported cycloaddition of this class of organometallic with trialkylsilyl substituted acetylenes. In this sequence the synthesis of a five-membered carbocycle is completed by a palladium-catalysed cyclization of the initially formed alkenyl zinc (**Scheme 12**).[109]

Alkenyl zinc reagents have been used extensively in palladium-catalysed coupling reactions with aryl- and



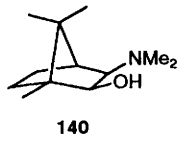

Reagents: (i) THF, 100 °C, 30h; (ii) $Pd(PPh_3)_4$ (5–10%) 24h 65 °C

**Scheme 12**




Reagents: (i) Ligand

**Scheme 13**




**140**

vinyl-halides.[110] However, a note of caution was expressed in a recent report that the *in situ* rearrangement of **137** to the allyl zinc **138** occurred in the presence of a Lewis acid catalyst.[111] Although this rearrangement was not observed in a nickel(II)-catalysed coupling process, it may be a source of unwanted side-products in some cases. Palladium-catalysed coupling reactions of the $\alpha$-amino-acid derived organozinc reagents **139** with $\beta$-bromoenones,[112] acyl chlorides,[113] and heteroaromatic iodides have been reported recently.[114] It is a remarkable feature of zinc organometallics that reagents which contain both a reactive carbon–metal bond and a source of reasonably acidic protons may be prepared and manipulated with such ease, and this underlines their synthetic importance. The Knochel group has reported extensively the results of its studies on the synthesis and applications of organozinc reagents functionalized with esters, amides, ethers, sulfides, and halides.[115,116] Most of the work has been summarized in an excellent review.[115] The majority of applications developed by Knochel have involved the prior conversion of the zinc reagent to a mixed copper/zinc species, thus providing an entry to functionalized cuprate compounds.[117] A detailed comparison of analogous zinc and copper reagents has been reported.[118]

Few would argue, if the number of related publications is taken as a measure of the level of interest, that the single most important development in organozinc chemistry has been the asymmetric catalysis of their addition to carbonyl groups (**Scheme 13**).[119]

Although most commonly reported for the case of diethylzinc, more functionalized organozincs have been employed, some of which will be discussed later in this section. The breakthrough in terms of asymmetric induction in this reaction was achieved using the conformationally restricted amino alcohol DAIB (**140**) and was reported some years ago by Noyori. Since this report, several new amino alcohols have been screened as catalysts. The structures and maximum asymmetric inductions for the reaction in **Scheme 13**, for these and other catalysts, are shown in **Figure 3**, along with the appropriate reference source.

Many of the compounds are obvious structures which derive from (−)-DAIB. Organometallic reagents such as **142** and **143** have been very successful in terms of asymmetric induction, and some effective nitrogen heterocycle derivatives, such as **144–146**, have been investigated. Sulfoxide and sulfoximine catalysts **148** and **149** have not proved to be as effective as might have been expected. The *N*-protected ephedrine derivatives **150** and **151** appear to be promising reagents, since they are readily available and give high e.e.s in the addition reaction. Most recently a class of C2-symmetric titanium(IV) complexes, represented by **152** and **153**, have emerged and are rapidly gaining momentum in terms of their level of synthetic application.

Extension of the asymmetric addition methodology beyond the use of simple dialkyl zincs has lagged somewhat behind the rate at which new ligands have been screened. A study of the use of *N,N*-diallyl-(−)-ephedrine as a catalyst for the addition of a zinc(II) enolate to acetophenone failed to give an e.e. in excess of 74%.[133] On the other hand an induction of 99% e.e. was achieved for the addition of a simple dialkyl zinc to ferrocenal using (*S*)-**154** as the ligand.[134]

For the addition of functionalized (remote ethers and esters) zinc reagents to aldehydes, Knochel has found that best results are obtained with the newer titanium(IV)-based complexes based on **152**.[135] In contrast, Oppolzer has found that the original aminoalcohol DAIB (**140**) was the catalyst of choice for the impressive intramolecular cyclization of **155** to **156**, a precursor of the perfume ingredient (*R*)-muscone.[136] This inconsistency serves to underscore the need for studies of the mechanism of this important asymmetric reaction, rather than continued empirical studies.

The related addition reaction to imines, to give chiral amines, has been achieved *via* addition to the

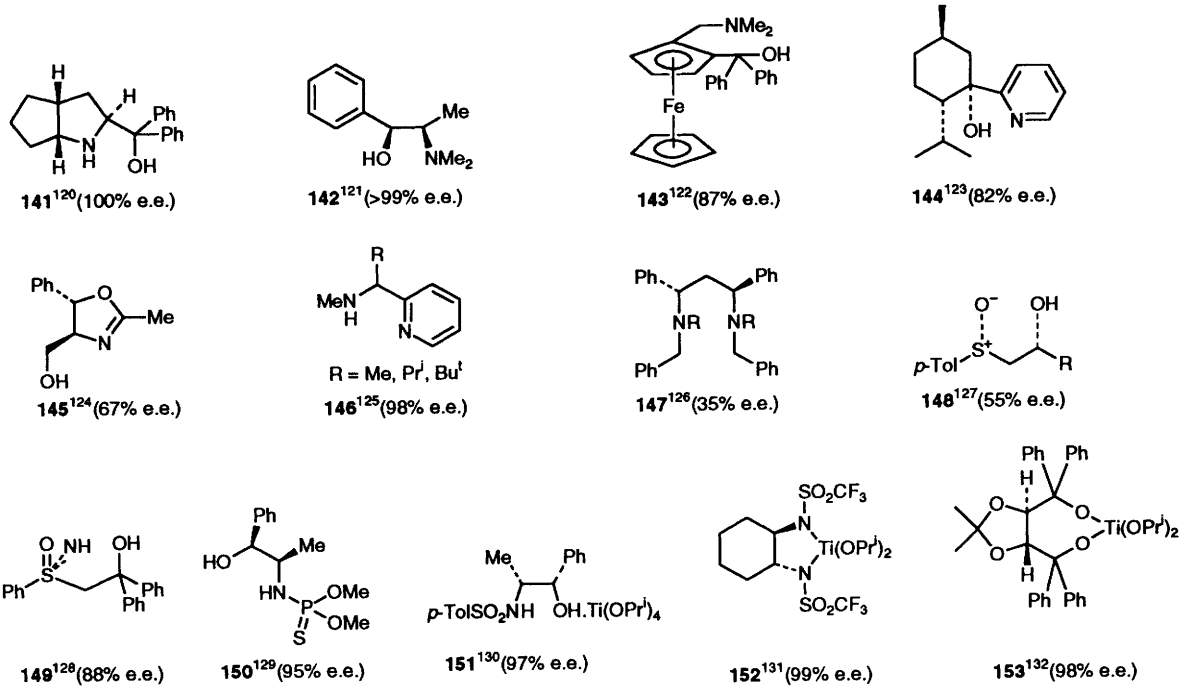


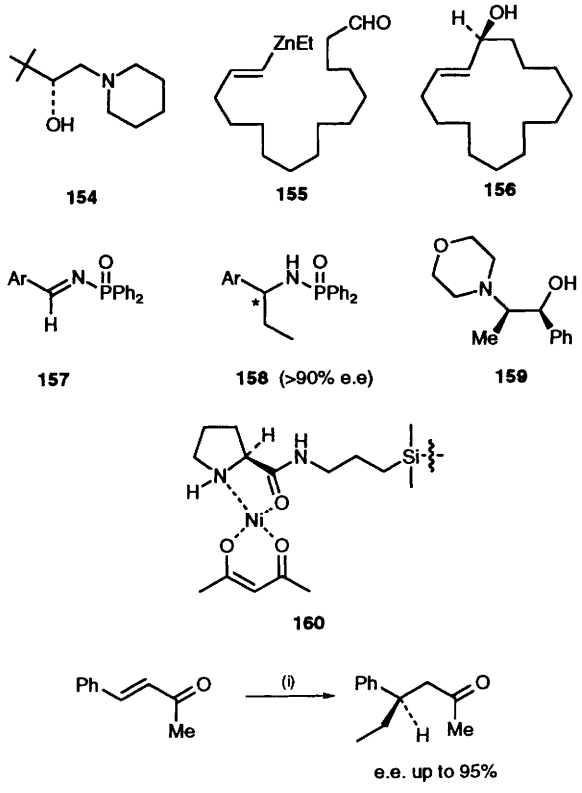

**Figure 3** Catalysts for diethyl zinc addition to benzaldehyde with e.e. obtained and reference

diphenylphosphonyl protected imine **157**. Here asymmetric inductions in excess of 90% have been obtained in the product **158** using the ephedrine-derived catalyst **159**.[137] The protecting group can be removed after the reaction by treatment with mild aqueous acid.

On a slightly different subject, the reaction of diethylzinc with enones gave products of e.e.s greater than 95% when the polymer supported nickel catalyst **160** was employed (**Scheme 14**).[138] Given the level of recent activity in carbonyl addition chemistry, it is likely that this preliminary observation will be followed in the near future by the screening of various chiral nickel(acac) complexes for improved asymmetric induction, versatility, and reactivity.

A Barbier-type procedure for the synthesis of allyl cadmium reagents has been reported. Additions of these reagents to aldehydes were also described.[139]

Phenylmercuric chloride mediated stereoselective intramolecular cyclization reactions have been employed in the synthesis of functionalized tetrahydrofurans,[140] pyrrolidine rings,[141] and cyclic peroxides.[142] In certain cases, mercuration can lead to ring expansion if no cyclization pathway is available.[143] Organomercury(II) compounds have been employed in palladium-catalysed coupling reactions with allylic substrates[144] and allyl mercury compounds have been employed in substitution reactions with acyl chlorides.[145]




Reagents (i) **160** (5–10 mol%), $Et_2Zn$, hexane.

**Scheme 14**

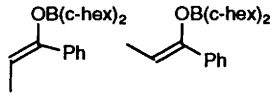
## 3 Group 13

### 3.1 Boron

#### 3.1.1 Alkyl boranes

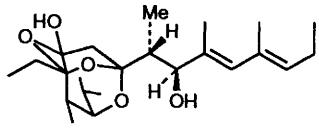
The steroechemistry of enol boration of ketones is remarkably sensitive to the nature of the borating agent. In a series of in-depth studies, Brown has found that in the case of formation of the di(cyclohexyl)boron enolate of propiophenone the combination of dialkylboron chloride and triethylamine gives predominantly the *E*-enolate **161**, whilst the use of the

dialkyl iodide or triflate favours formation of the *Z*-enolate **162**.[146] In many cases the selectivity can exceed 97:3. An attempt has been made to rationalize this effect with the aid of molecular modelling.[147]



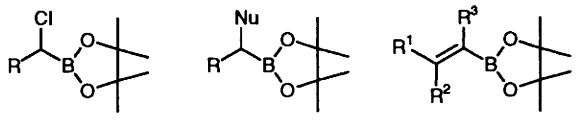

**161** **162**

The importance of boron enolates as tools for stereoselective synthesis has been underlined by the publication of a number of total and partial synthesis such as that of bafilomycin A, reported by Evans,[148] and rapamicin[149] and (+)-muamvatin[150] (**163**) reported by Paterson. The synthesis of **163**, a marine polypropionate, involved several aldol reactions of chiral boron enolates and was completed by an impressive cyclization from the open-chain precursor under conditions of mild catalysis.[150] A series of molecular modelling studies on such aldol reactions have been reported.[151]




**163**

Chloromethylboranes **164** are useful intermediates for synthesis because nucleophilic substitutions may be achieved using a variety of nucleophiles to give the derivatives **165**. Such reactions take place *via* initial addition of the nucleophile to boron, followed by a migration.[152] The order of addition may be reversed; addition of chloromethyllithium to **166** gives the allyl borane **167**, and subsequently **168** upon oxidative hydrolysis.[153] Related methodology has been applied to the synthesis of $\alpha,\beta$-unsaturated esters,[154] $\alpha$-aminoboronic acids, and the beetle pheromone stegobiol, in which all of the four chiral centres were created *via* chloromethylborane intermediates.[155]



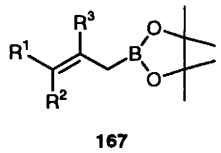

**164**



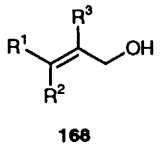

**165**




**166**



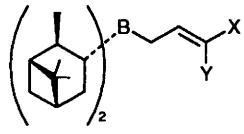

**167**



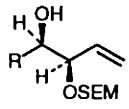

**168**

### 3.1.2 Allyl, allenic, and alkenyl boranes

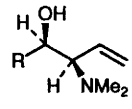
Like boron enolates, allylic boranes are well established reagents for asymmetric and stereoselective synthesis, offering almost unparalleled control over relative and absolute steroechemistry in the creation of at least two new chiral centres in addition reactions to aldehydes. Probably the most commonly used chiral allyl boranes are derivatives of the diisopinocampheylborane, $(Ipc)_2B$, system, as typified by **169**.[156-158] The reactions of two classes of heteroatom substituted derivatives serve to illustrate the synthetic scope and sense of the selectivity in additions to aldehydes. Addition of **169a** to an aldehyde gives the product **170**, of *syn*-stereochemistry,[157] whilst the same reaction of **169b** gives the *anti*-product **171**.[158]




**169 a**, X = H, Y = OSEM
**b**, X = $NMe_2$, Y = H

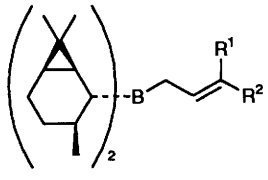



**170**

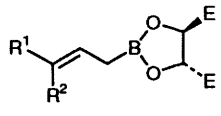



**171**

Additions to propargylic aldehydes are generally less selective than most other aldehydes or ketones. This situation can be remedied, however, by complexation of the alkyne to dicobalt-hexacarbonyl prior to the addition reaction.[159] The alternative chiral allyl boranes of choice are *B*-allylbis(2-isocaranyl)-boranes **172**, which have been applied in a small number of papers.[160] In some cases these reagents give improved stereochemical control compared to the $(Ipc)_2B$ reagents. Another class of promising reagents are boronic esters derived from C2 symmetric alcohols, generally tartrate derivatives, based on the structure **173**.[161,162] In terms of relative stereochemistry these compounds add to aldehydes to give analogous products to those derived from dialkyl boranes, but additionally generate asymmetric inductions routinely in excess of 90%, in a predictable sense. Of particular note is the application of **173b** to a key step in the synthesis of an erythronolide analogue.[162]



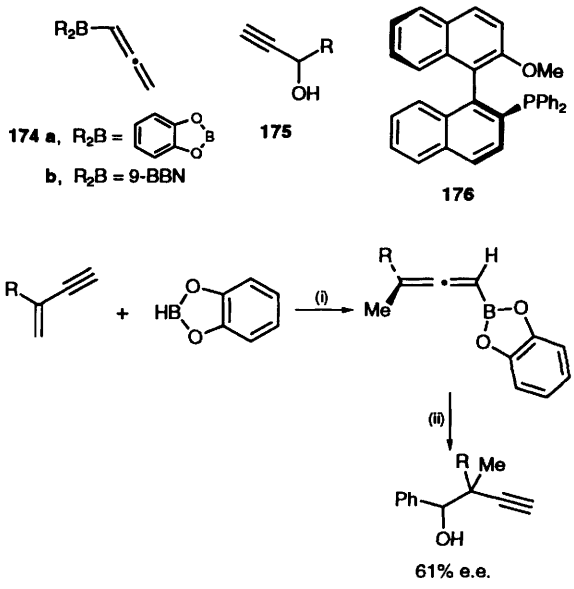

**172**




**173 a**, E = $CO_2Pr^i$[161]
**b**, E = c-hex[162]

Related reagents are the allenyl boranes **174**, which act as propargylic anion donors, furnishing products **175** upon reaction with an aldehyde.[163,164] The palladium-catalysed asymmetric synthesis of allenyl boranes may be achieved using the mixed phosphorus/oxygen donor ligand **176** to mediate the reaction of catecholborane with an enyne substrate. Addition of the resultant enantiomerically enriched boranes to ketones gives addition products in up to 61% e.e. (**Scheme 15**).[164]

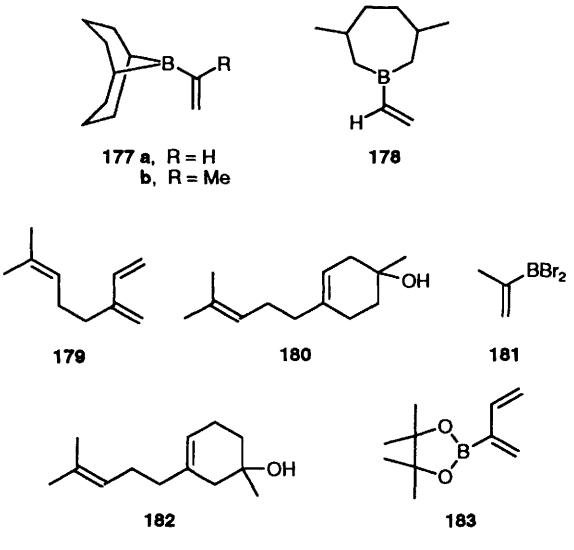
Cycloadditions of alkenyl boranes with dienes gives 4-borated cyclohexenes. In a detailed comparative study of the structural requirements of the borane component it was found that whilst trivinylborane was the most reactive, borane **177a** was the most




Reagents (i) Cat. **176**, $Pd(dba)_2$, $CH_2Cl_2$; (ii)PhCHO

**Scheme 15**

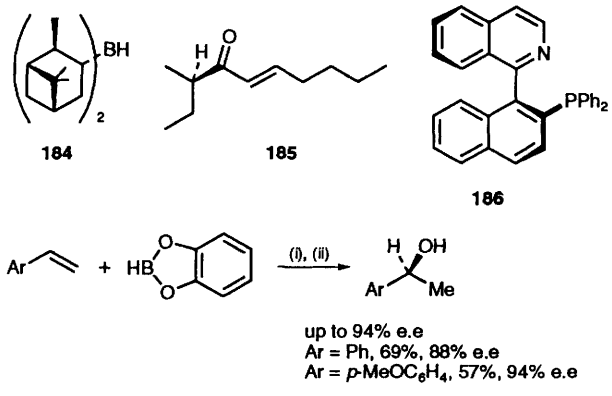
regioselective and **178** was the most stable and *endo*-selective in reactions with cyclopentadiene.[165] A sterically-driven regioselectivity can be overriden in some cases by electronic factors. Cycloaddition of **177b** with **179** gives mainly **180** after oxidation, whilst the bromo-substituted borane **181** reacts to give exclusively the opposite regioisomer **182** in the same sequence.[166] Similar cycloadditions of alkynyl silanes with dienes have been reported,[167] as have the reactions between 1,3-dienes substituted at the 2-position with a boronic ester (**183**) and electron-poor alkenes.[168]




Vinyl- and aryl-boranes and boronic acids make excellent substrates for palladium-catalysed coupling reactions with aryl-(vinyl)triflates or halides.[169] Recently this process has been applied to a very concise synthesis of ibuprofen.[170] However, a note of caution—the nature of the triarylphosphine ligand used in the catalyst is critical. Triphenylphosphine can in some cases transfer a phenyl group, in which event the use of tri(2-methoxyphenyl)phosphine, which has less tendency to do this, is recommended.[171]

### 3.1.3 Hydroboration and carbon reduction by boranes

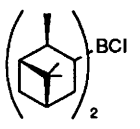
Asymmetric hydroboration of alkenes by $(Ipc)_2BH$ **184** continues to find synthetic applications. Recent examples include the asymmetric synthesis of $\alpha$-amino alcohols by the reaction of **184** with enamines[172] and the preparation of enantiomerically pure enones **185** by hydroboration of but-2-ene followed by a sequence of reactions featuring a combined carbonylation/alkylation elimination sequence from a borane complex.[173] Alkene hydroboration can be catalysed by rhodium and ruthenium complexes, which provides an obvious potential for asymmetric catalysis.[174] Although many of the popular diphosphines have been screened they only give moderate results, but this potential has been realized by the use of the mixed nitrogen/phosphorus donor ligand **186**, which is capable of generating enantiomeric excesses of up to 94% in the reaction of styrene with catecholborane (**Scheme 16**).[175]




Reagents: (i) Rh complex, **195**, (ii) $H_2O_2/HO^-$

**Scheme 16**

For the asymmetric reduction of carbonyl groups, *B*-chlorodiisopinocampheyl borane (DIP-Cl) **187** is a superior reagent to the more established hydride analogue in terms of reactivity and selectivity. Asymmetric inductions of > 98% may be routinely obtained with this reagent.[176] Chiral boronic esters are capable of directing the asymmetric reductions of carbonyl groups three[177] or four[178] carbon atoms distant, using borane as the reducing agent. Reduction of **188** gives **189**, a precursor of chiral tetrahydrofurans, in 93% e.e. and 97% yield after oxidation.[178] The combination of a stereoselective carbonyl reduction followed by an intramolecular hydroboration of the intermediate boronic ester provides a means for the creation of two new chiral alcohols in a single synthetic step.[179]



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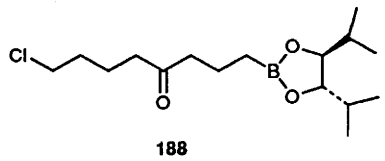

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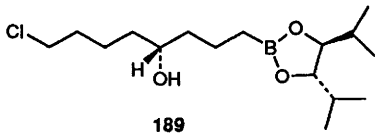

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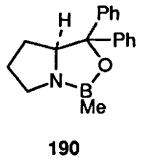
Chiral oxazaborolidines have proved to be excellent catalysts for the asymmetric reductions of ketones, and two excellent reviews have been published recently on the subject which serve to summarize much of the recent research.[180] A number of reports have appeared describing new methods for the proline-derived catalyst **190**, which has been developed and used extensively by Corey.[181] Corey himself has reported a method for the *in situ* formation of this compound from the amino alcohol precursor and alkylbis-(2,2,2-trifluoroethoxy)borane which allows ketone reductions to be undertaken directly and with equal asymmetric inductions, as are obtained when isolated **190** is employed.[182] A group of Merck chemists have also invested a great deal of effort in this area and have found that whilst **190** is a rather labile material, the borane complex **191** is a relatively stable, free-flowing material for which an *X*-ray crystal structure determination has been obtained.[183] The Merck team have also employed **190** in a range of synthetic applications and have investigated the means by which enantioselectivity is generated.[184] One intriguing observation is that the addition of triethylamine to the reduction medium results in an increase in the enantioselectivity of the reductions.[185] Although these studies concentrated on the *stoichiometric* reduction (using **191**), in the case of acetophenone the enantioselectivity improved from 96% to 99.2% e.e.



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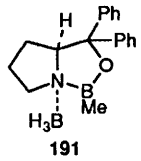

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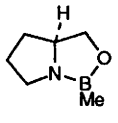
Perhaps the most remarkable development in this area is contained in the report that, at elevated temperature (110°C), catalytic quantities of prolinol are capable of generation of e.e.s in excess of 95% for acetophenone reduction by borane, presumably *via* intermediacy of the oxazaborolidine **192**.[186] At low temperatures the enantioselectivity is much lower (8–59% e.e.), in contrast to **190**.



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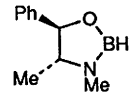
A possible explanation is provided by the observation that at low temperature **193** dimerizes to the non-catalytic species **194**, a process that is reversed at high temperatures.[187] If this is the case with **192** then this may help to explain the temperature dependence. This is a very important observation, since the two phenyl groups in **190** are considered to be important contributors to the enantioselectivity of the reduction—it may be that they simply increase the bulk of the oxazaborolidine and prevent an unproductive dimerization.

Ketones which contain heterocycles with donor groups are generally good substrates for asymmetric reduction, although an excess of borane may be required in certain cases due to complexation with the heteroatoms.[188] Reduction of trichloromethyl ketones gives products of high enantiopurity which may be subsequently converted into α-hydroxy or α-amino acids.[189] Novel classes of catalysts for asymmetric borane reduction of ketones include the amino alcohols **195**[190] and **196**,[191] which are capable of generating e.e.s of 94% and > 99% respectively, the sulfoximine **197**[192] and the phosphinamide **198**.[193]



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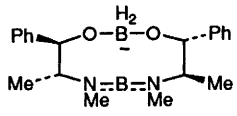

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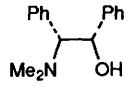

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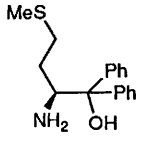

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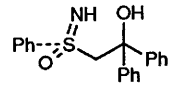

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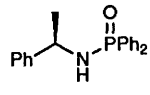

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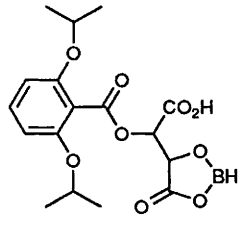
### 3.1.4 Borane catalysts

The borane complex **199**, formed between a tartrate derivative and borane, has been used for the asymmetric catalysis of Diels–Alder reactions,[194] the reactions of trialkyltin allyl reagents with aldehydes,[195] and aldol reactions of trimethylsilyl enol ethers.[196] The enantiomerically pure BINOL-derived reagent **200** has been used for asymmetric catalysis of hetero Diels–Alder reactions[197] and the additions of trimethylsilyl enol ethers to imines.[198] The tryptophan derived borane complex **201**, and related reagents, have been used for the catalysis of Diels–Alder[199] and aldol reactions.[200]



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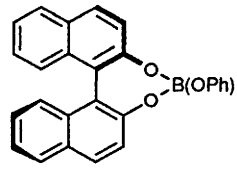

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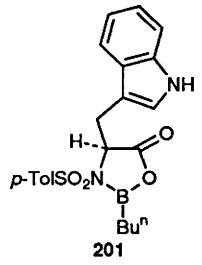
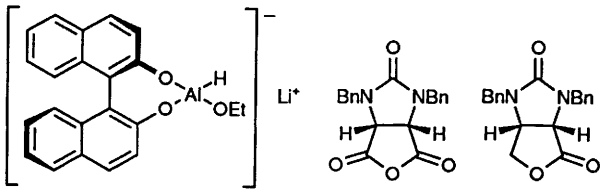


201

### 3.2 Aluminium and thallium

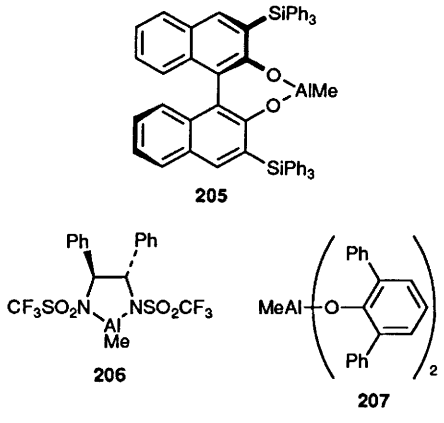
The use of chiral ligands for the modification of lithium aluminium hydride can lead to the generation of highly selective carbonyl reduction catalysts.[201] Whilst this is by no means a new concept, a novel application of the R-BINAL hydride reagent **202** is in the selective reduction of one carbonyl group of the C2-symmetric anhydride **203** into **204** (up to 90% e.e.), a precursor of biotin analogues.[202]



202 203 204

Stereoselective cleavage of chiral cyclic acetals by alkyl aluminium reagents has been the subject of a considerable amount of synthetic interest. Recently, the use of perfluoroalkoxy substituted aluminium reagents for this process has been shown to be capable of generating higher levels of stereoselectivity than the simple trialkylaluminium compounds.[203] The zirconium-catalysed addition of trimethylaluminium to terminal alkynes, to give terminal alkenes, proceeds at a much faster rate, and at lower temperatures, in the presence of an equivalent of water than under dry conditions.[204]

The chiral aluminium complexes **205**[205] and **206**[206] have been employed to good effect in the asymmetric catalysis of Diels–Alder reactions. The reaction of one equivalent of a nucleophile to one equivalent of a straight-chain and a branched-chain aldehyde in the presence of the aluminium alkoxide complex **207** results in predominant addition to the latter.[207] This is believed to be due to the preferential complexation of the smaller aldehyde to the aluminium complex, which serves to sterically 'protect' the carbonyl group as illustrated in **Figure 4**. Synthetic applications of the related aluminium (III) complex **208**, mainly for the catalysis of cycloaddition reactions, have also been described.[208]



205 206 207

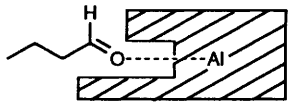
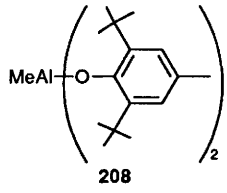


**Figure 4**



208

The level of synthetic interest in thallium reagents is declining, possibly as a consequence of their known high toxicity, and recent reported applications of these organometals are as catalysts. Grigg has reported that the intramolecular cyclization of aryl palladiums onto double bonds gives much higher yields in the presence of thallium acetate (86% compared to 15% under a typical set of reaction conditions).[209]

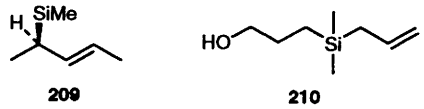
## 4 Group 14

### 4.1 Silicon

The importance of the cation-stabilizing effect (the '$\beta$-effect') of chloroalkylsilyl groups compared to trialkylsilyl groups has been reviewed,[210] as have the synthetic applications of trialkylsilyl substituted dienes[211] and the use of silyl protecting groups for alcohols.[212]

#### 4.1.1 Allyl, benzyl, and alkenyl silanes and their derivatives

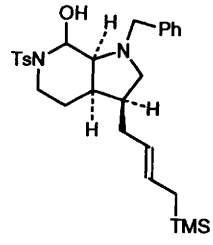
A method for the synthesis of enantiomerically enriched (90–98% e.e.) allyl silanes *via* a Wittig reaction of $\alpha$-trialkylsilylaldehydes of similar enantiomeric purity has been reported.[213] Fleming has reported the synthesis of allyl silanes **209** of greater than 99.9% e.e. and greater than 99.95% geometric purity using a chiral auxiliary directed approach.[214] Trichloroallylsilanes have been reported to be as good, if not superior, sources of anionic allyl groups to trialkylallyl silanes in terms of yields and addition stereoselectivity.[215] The alkoxide formed by deprotonation of the hydroxy group in **210** can form a



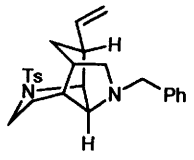
209 210

bond to the silyl group, giving a hypervalent reagent which is activated towards allyl transfer to electrophiles under mild conditions.[216]

The intramolecular cyclization of allylic silanes with iminium cations has been used to great effect in the total synthesis of alkaloids.[217-219] Treatment of **211** with iron(III) chloride results in cyclization to **212**, a key step in the synthesis of sarain A in 61% yield.[217]

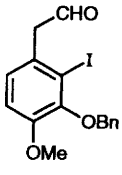



**211**

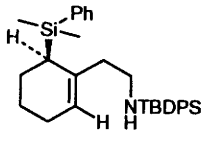



**212**

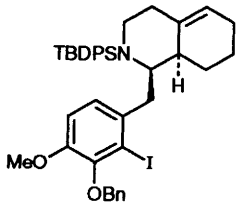
Even more remarkable is the reaction between **213** and **214** to give the major cyclized product **215**, a precursor of (−)-morphine, in 82% yield (a 20:1 mixture of diastereoisomers is formed).




**213**

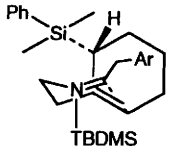



**214**

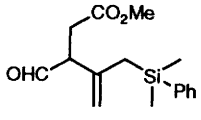



**215**

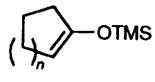
The cyclization presumably takes place *via* a transition state similar to **216**.[218] A remarkable series of cyclization reactions converts a mixture of the allyl silane **217** and silyl enol ether **218** into **219** ($n = 1, 2$) under conditions of mild Lewis acid catalysis.[220]



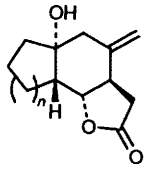

**216**




**217**

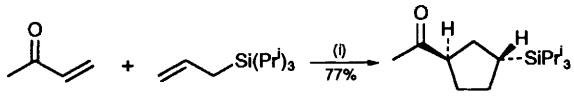



**218**




**219**

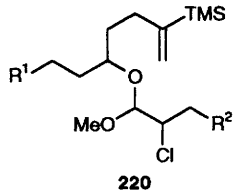
Remaining with the theme of cyclization reactions, there have been a number of reports of the addition of allyl silanes to enones, which involves subsequent silyl migration and ring closure (**Scheme 17**).[221] Reactions appear to be quite wide in scope and stereoselective, with a preference for formation of the *trans*- product. A related transformation of propargylic silanes has been reported.[222]



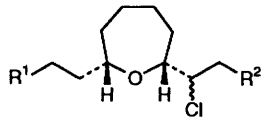

Reagents: (i) $TiCl_4$, $CH_2Cl_2$, −78 °C

**Scheme 17**

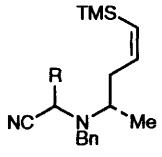
Alkenyl silanes may be prepared by the reaction of terminal acetylenes with triethylsilane.[223] This reaction is remarkably sensitive to the reaction conditions. Using $[Rh(cod)Cl_2]$ as the catalyst in ethanol/DMF solvent the major product is the *Z*-isomer whilst use of the same catalyst in the presence of added triphenylphosphine in acetonitrile favours formation of the *E*-isomer. Intramolecular reactions of alkenylsilanes are very valuable in synthesis.[224-226] Treatment of **220** with ethylaluminium dichloride gives the seven-membered ether **221**,[224] whilst treatment of **222** with a source of acid results in cyclization to the alkaloid precursor **223**.[225] Lewis acid catalysed additions of allenyl silanes to aldehydes have been described,[227] as have subsitution reactions of alkynyl silanes with glycosides.[228]



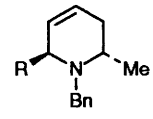

**220**




**221**



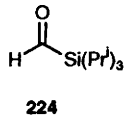

**222**



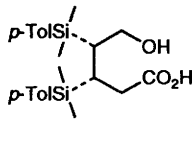

**223**

### 4.1.2 Other classes of organosilyl reagent

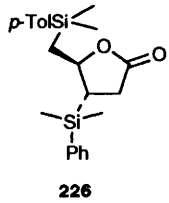
The synthesis and addition chemistry of the unusual but remarkably stable formylsilane **224** has been described.[229] In the previous section the example of a trialkylsilyl-migration mediated cycloaddition was described. Similar processes operate in the conversion of **225** into **226** (DEAD, $PPh_3$)[230] and the reaction of α,β-unsaturated acyl-silane **227** with an enolate (of $RCOCH_3$) to give **228**.[231,232]



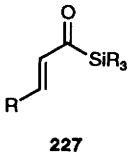

**224**



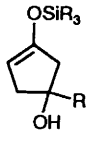

**225**




**226**



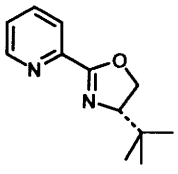

**227**



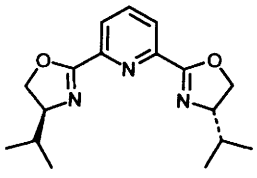

**228**

Silicon-based groups make excellent tethering groups for intramolecular Diels–Alder reactions[233] and intramolecular radical cyclizations[234] due to their ease of removal or potential for conversion into other functional groups after use. Several examples of applications have been reported recently.

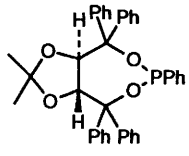
Asymmetric catalysis of hydrosilylation reactions is an area which has lagged behind the related subject of asymmetric hydrogenations, for reasons that are not readily obvious, since both reactions have a similar range of potential applications. Polydentate oxazoline ligands such as **229**[235] and **230**[236] have proved to be valuable ligands for the reduction of carbonyl groups (**Scheme 18**), and have been reported in previous reviews; a novel ligand for this application, however, is the C2 symmetric phosphorus donor **231**, reported by Seebach.[237] The homochiral titanium complex **116**



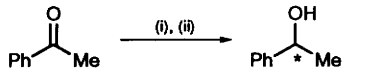
**229**



**230**



**231**



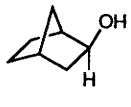
**229** (90% e.e.)
**230** (94% e.e.)
**231** (97% e.e.)

Reagents: (i) catalyst **229**, **230**, or **231**; (ii) $H_3O^+$, $Ph_2SiH_2$

**Scheme 18**

(see section on magnesium chemistry) is an excellent catalyst for the asymmetric hydrosilylation of imines, although the best results are obtained using cyclic imine substrates.[238] The mixed oxygen/phosphorus ligand **176**, which has already been described, has been employed in the asymmetric hydrosilylation of alkenes such as **232** (silyl trichloride, palladium catalyst) to give **233** in 96% e.e. after oxidation.[239] Intramolecular hydrosilylation reactions of carbon–carbon double bonds have been used in the stereoselective synthesis of diols.[240]

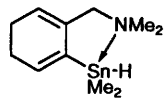
**232**



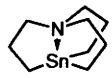
**233**

## 4.2 Tin

Tributyltin compounds can act as nucleophiles in reactions with powerful electrophiles. This property has been employed for the phenylselenyl cation promoted intramolecular cyclization reactions[241] and for stereoselective opening of chiral cyclic aminals.[242] Appropriately-located donor groups can activate nucleophilic transfers from the resultant hypervalent tin complex. The tin hydride **234** shows an improved reducing ability[243] and **235** is highly activated towards transfer of an alkyl group in palladium-catalysed coupling reactions with aryl bromides[244] as a result of such effects.

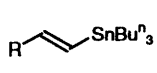


**234**

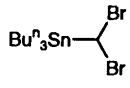


**235**

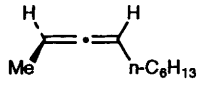
Alkenyl stannanes are important synthetic reagents which may be prepared by hydrostannylation of alkynes in a reaction which may be catalysed by zirconium (for *Z*-vinyl stannanes) or palladium complexes.[245] *E*-Alkenyl stannanes **236** may be prepared by the chromium dichloride mediated reaction of **237** with aldehydes.[246] $\alpha,\beta$-Unsaturated $\gamma$-lactones substituted at the $\alpha$- or $\beta$-position by tributyltin groups have been prepared by a regiospecific exchange reaction with thiophenyl precursors.[247] Vinyl tributyltin compounds formed in this way have been applied to an asymmetric synthesis of allenes **238**, *via* elimination from the homochiral alcohol **239**.[248] Alkenyl tin compounds are more widely employed in palladium-catalysed coupling reactions than any other single process.[249] The



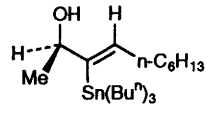
**236**



**237**



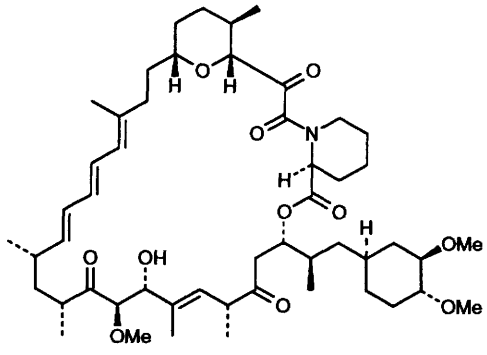
**238**



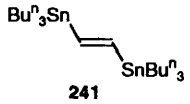
**239**

intramolecular variant of this process has been employed to good effect in the synthesis of macrocyclic natural products[250] of which perhaps the most impressive is the concluding sequence of a synthesis of rapamycin **240**.[251] Cyclization is achieved using 1,2-distannane **241**, which provides the central double bond in the triene, *via* coupling to the corresponding bis-vinyl iodide.

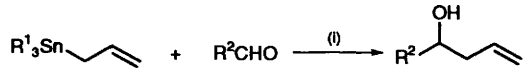
The role of Lewis acids in the reactions of allyl tin compounds with electrophiles such as aldehydes and ketones (**Scheme 19**) has been reviewed.[252] Using lanthanide catalysts or acid catalysis these reactions can be performed in aqueous media.[253]



240



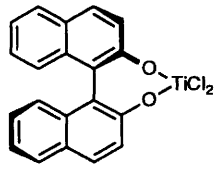
241



Reagents: (i) Lewis acid

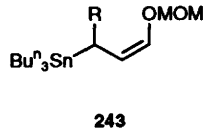
**Scheme 19**

An investigation of perchlorate salts has revealed that the cations (Li, Mg, Ca, *etc.*) often do not act as Lewis acids but assist the reaction by mediating development of the six-membered transition states.[254] High pressures (up to 800 kbar!) are reported to be capable of accelerating this class of reaction.[255] A chiral titanium(IV) catalyst **242** derived from enantiomerically pure BINOL has been employed for the asymmetric catalysis of the reaction, giving products with e.e.s of up to 99%.[256] Rather unexpectedly it was found that the addition of a trace of triflic or trifluoroacetic acid improves the enantioselectivity sharply.

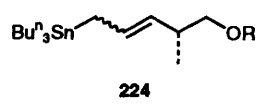


242

γ-Alkoxyallylstannanes **243**, the *Z*-isomers of which may be simply prepared by isomerization of the α-alkoxyallyl precursors, have been employed in the total syntheses of complex target molecules such as the alkaloid diepicastanospermine (using **243**, R = H)[257] and the marine sponge metabolite bergamide E (using **243**, R = iso-propyl).[258] Reaction of allyl stannanes **244** with aldehydes using tin tetrachloride as catalyst essentially gives exclusively the adduct **245**, presumably a result of tin(IV) exchange to intermediate **246**, which is stabilized by the donation from the adjacent alkoxy group.[259]



243



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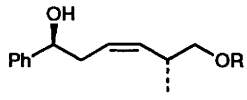
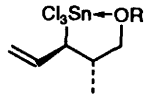


245



246

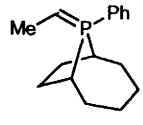
Under conditions of titanium tetrachloride catalysis, trialkyl lead reagents will transfer alkyl groups to aldehydes.[260] Aryl lead triacetates have been employed as aryl transfer reagents in reactions with nucleophiles.[261]

## 5 Group 15

### 5.1 Phosphorus

The use of borane as a protecting group to prevent oxidation of phosphines is an established method.[262] A recent paper has described the *in situ* removal of the borane from a chiral diphosphine ligand which circumvents the need to isolate the phosphine.[263] A new method for the synthesis of mixed phosphorus/heteroatom donor ligands involves the reaction of potassium diphenylphosphide with *o*-substituted aryl fluorides.[264] Cycloaddition reactions mediated by diphenylphosphinyl radicals have been described.[265]

Wittig reactions of non-stabilized phosphorus ylids generally give *Z*-alkenes. In contrast, ylids derived from the reagent 9-phenylphosphabicyclo [4.2.1] nonane **247** show a strong preference for the formation of *E*-alkenes.[266] Better *Z*-selectivity is achieved in the reaction of the stabilized ylid **248** with aldehydes than is obtained using the triphenyl-phosphine analogues.[267]



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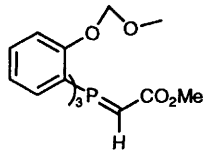
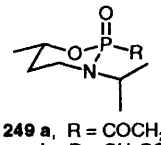


248

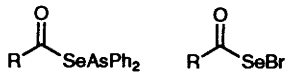
Enantiomerically pure phosphorus reagents based on the structure **249** have been used as chiral auxiliaries for the stereoselective alkylation of attached enolates (**249a**)[268] and the reduction of attached β-carbonyl groups (**249b**).[269] The alcohols derived from the latter reaction have been converted into stereochemically pure alkenes *via* a phosphonate elimination.



**249 a**, R = $COCH_2Me$
**b**, R = $CH_2COR$

### 5.2 Arsenic, antimony, and bismuth

The addition of triphenyl-arsenic, -antimony, or -bismuth to the titanium tetrachloride catalysed reaction of cyclopentadiene with a chiral acrylate (dichloromethane, −78°C) reduces the level of polymerized diene which is formed as a side product. These additives also have a mediating effect on the reaction of allyl tin compounds with aldehydes.[270] The arsenic reagent **250** acts as a precursor for the formation of **251**, a powerful electrophile for additions to alkenes under mild conditions (NBS, dichloromethane, −78°C).[271]



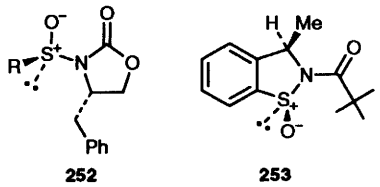

**250** **251**

A triaryl-bismuth diazide has been reported to react, under photochemical conditions, with alkynes to give 1,2,3-triazides[272] whilst in another application triphenylbismuth has been used as a leaving group in α-keto derivatives.[273] The *in situ* formation of alkyl bismuth compounds, from metallic bismuth and an alkyl halide, and their addition reactions with imines have been reported.[274]

## 6 Group 16

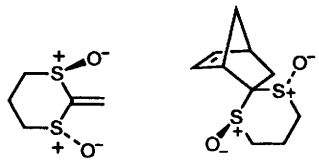
### 6.1 Sulfur

The asymmetric synthesis of sulfoxides by sulfide oxidation gives products of up to 95% e.e. using a combination of enantiomerically pure BINOL, titanium isopropoxide and t-butyl hydrogen peroxide[275] and up to 47% e.e. using a manganese-salen complex with sodium hypochlorite.[276] The stereoselective synthesis of sulfoxides proximal to epoxides, and their subsequent intramolecular reactions, have been described.[277] Enantiomerically pure sulfoxides may also be prepared by displacement of a chiral leaving group from a diastereoisomerically pure sulfinate ester with a Grignard reagent. Although this is generally thought to involve inversion of configuration at sulfur, recent evidence has revealed that in some cases retention of configuration is observed.[278] The displacement of homochiral oxazolidinones from the diastereoisomerically pure sulfinamides such as **252**, which must be purified by flash chromatography, represents an attractive alternative to the use of sulfinate esters.[279] The related homochiral cyclic sulfinamide **253** reacts with a range of nucleophiles with inversion of configuration at sulfur to give intermediates which may be subsequently converted into enantiomerically enriched alcohols and amines.[280]



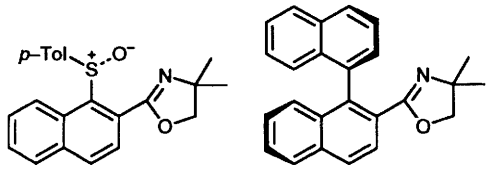

**252** **253**

Sulfoxides have been shown to be excellent directing groups for cycloaddition reactions[281-283] as illustrated by the reaction of **254** with cyclopentadiene under conditions of boron trifluoride catalysis, to give a 25:1 mixture of cycloadducts, in which **255** predominates.[281]




**254** **255**

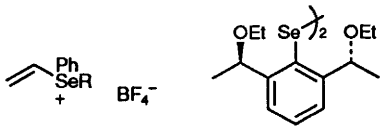
The known ability of zinc(II) bromide to invert the selectivity of sulfoxide-directed reductions has been extended to the reduction of imines[284] and carbonyl groups proximal to cyclic sulfoxides.[285] Chiral sulfoxides have been used as leaving groups; the Grignard reagent derived from 1-bromonaphthalene adds to **256** to give the biaryl product **257** in up to 60% e.e.[286]




**256** **257**

### 6.2 Selenium and tellurium

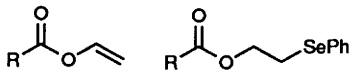
Triphenylselenium(IV) chloride has proved to be an excellent catalyst for phase-transfer cyclopropanation of alkenes by dichlorocarbene. Five mol% of this additive gives a 92% yield of product in one reaction with cyclohexene, 10 mol% gives a 99% yield.[287] Cyclopropanes are also the products of the reactions of cations **258** with active methylene compounds.[288] Homochiral α-phenylselenyl ketones have been prepared using 'Evans' enolates with phenylselenyl chloride.[289] Asymmetric addition of phenylselenyl chlorides across double bonds may be achieved using a chiral auxiliary[290] or a homochiral selenating reagent, such as **259**, to give addition products in diastereoisomeric ratios of up to 66:1 (methanol is used to trap the intermediate selenium cation).[291]




**258** **259**

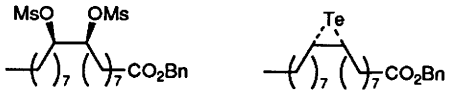
Oxidation of selenium(II) compounds to the selenoxides followed by elimination provides double bonds under mild conditions. A valuable application of this reaction is the synthesis of vinyl esters **260** (which are used extensively in esterification reactions) from

the ester **261**, itself prepared from a carboxylic acid and β-phenylselenylethanol.[292] Holmes has reported further examples of the use of a mild selenoxide elimination for the preparation of enol ethers, precursors of medium ring amides and esters, which are formed *via* intramolecular [3, 3] sigmatropic rearrangements.[293]

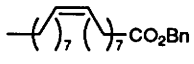


**260** **261**

The reaction of dilithium tellurolate ($Li_2Te$) with 1,2-ditosylates such as **262** results in formation of a three-membered selenium-containing ring (**263**) from which metallic tellurium is readily extruded to give the alkene **264**. This reaction is stereospecific;—the *cis*-dimesylate gives the *cis*-alkene.[294]

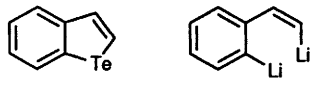


**262** **263**



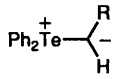
**264**

A similar reductive transformation of epoxy alcohols[295] and stereospecific debromination/cyclopropyl ring-opening[296] has been reported. The reaction of α-bromo esters with lithium benzene tellurate in the presence of cerium trichloride cleanly generates the cerium enolate, which goes on to react with carbonyl compounds.[297] *Z*-Alkenyl tellurides, generated from acetylenes, have been used as precursors for stereochemically pure cuprates[298] whilst cyclic tellurides, such as **265**, have been converted into the dilithium reagents **266** upon reaction with two equivalents of n-butyl-lithium.[299]



**265** **266**

Tellurium ylids **267a** and **b**, formed by deprotonation of the salt by a lithium amide, react with ketones to give epoxides[300] and with α,β-unsaturated esters to give cyclopropanes.[301] Attempts to form the tellurium ylids using n-butyl-lithium, however, results in tellurium/lithium exchange.[301(a)] The stabilized tellurium ylid **267c** gives alkenes upon reaction with ketones.[302] Chiral aryltellurolates containing binaphthyl groups have been reported to react with α,β-unsaturated esters in a 1,4-fashion to give adducts in up to 70% d.e.[303]



**267 a**, R = CH=CHR[1]
**b**, R = C≡CR[1]
**c**, R = $CO_2R^1$

Phenyl-selenium and -tellurium compounds are excellent substrates for radical cyclization reactions.[304,305] In this respect they are especially effective as sources of acyl radicals.[304]

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