REVIEW

Recent developments in lanthanide mediated organic synthesis

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Covering the literature to December 2000.

1 Introduction

Over the past decade lanthanide reagents have found an ever increasing role in organic synthesis. This has been recognized by a number of excellent review articles covering various aspects of lanthanide mediated synthetic organic chemistry.[1–6] This account will therefore attempt to focus on the more recent developments referring to earlier work when necessary to put developments into context. The review will be organised following the nature of the lanthanide reagent, low oxidation state (0, II) to high oxidation state (III, IV) and will cover the literature to the end of 2000. The subsections within the text describe broad areas. However, in many cases the boundaries are blurred and consequently there is frequent overlap between sections. Where possible, to minimise duplication of material, this has been indicated in the text. Although there have been considerable efforts to use these reagents in polymer synthesis,[7] space precludes a detailed study of these processes and this article is limited to 'small molecule' organic synthesis.

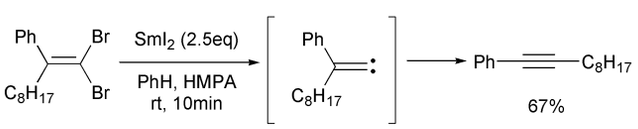
2 Low valent lanthanide mediated transformations

2.1 Introduction

Whilst the lanthanide metals are all electropositive elements which can be employed in many dissolving metal transformations, the more novel chemistry of low valent lanthanides is dominated by samarium(II) compounds and analogous species of ytterbium. More recently there has been an emphasis on the use of these lanthanide metals directly since the M^{3+}/M^{0} redox potential is larger than the M^{3+}/M^{2+} potential.

2.2 Generation and reactivity of the reagents

Of the low valent lanthanide compounds, samarium [normally in the form of samarium(II) iodide, SmI_2] has found the most widespread application. Although the use of other metal salts (Yb, Eu, Tm, Dy) has been reported, the balance between activity and ease of preparation has tended to limit their utilisation. In general SmI_2 is most conveniently prepared as a 0.1 M solution in THF from the reaction between Sm(0) and diiodomethane. However, there are a number of problems with the use of THF, notably the instability of the intermediate organosamarium leading to radical abstraction of the THF α-hydrogen and ring opening reactions when acid chlorides are employed. Furthermore, attempted reaction of allylic and benzylic halides with SmI_2 in THF is complicated by competing Wurtz coupling reactions.[8] Benzene has been proposed as an alternative solvent although the preparation requires HMPA and is non-trivial.[9,10] With this system, generation of vinyl- and alkynylsamarium species is possible,[11] whilst 1,1-dihaloalkenes react to provide vinyl carbenoids (Scheme 1).[12,13] Alkynylsamariums can also be accessed *via* transmetallation with tetrahydrofurylsamarium, itself generated *in situ* from SmI_2 and iodobenzene in THF, or *via* metal–metal exchange using an alkynyllithium and SmI_3.[14]



Scheme 1

In contrast, the use of tetrahydropyran (THP) allows the direct preparation of SmI_2 from diiodoethane. More importantly, the organosamariums derived from acid chlorides,[8] allyl, benzyl and alkyl halides (requires HMPA)[15] and α-aminoalkyl halides[16] are relatively stable non-basic species which can be combined with a range of electrophiles including β-ketoesters (Scheme 2). The only limitation appears to be the low solubility of SmI_2 in THP ($\sim 10^{-2}$ M). The generation of acylsamarium species has also been reported in acetonitrile[17] although some doubt has been cast on this protocol. A more reliable alternative to this problem is realised using pivalonitrile (^{t}BuCN), although not all transformations are enhanced in this solvent.[18] For example, Barbier reactions with alkyl iodides do not proceed and whilst benzyl bromides and allylic halides react, they do so only slowly, albeit with higher regioselectivity than with SmI_2–THP.

A number of alternative Sm(II) compounds have been developed including Cp_2Sm, $SmBr_2$ and $Sm(OTf)_2$. The first of these, previously employed in Barbier reactions and coupling of acid chlorides, provides routes to stable benzylic and allylic organosamarium compounds.[19–21] The second has been much less widely used but appears to exhibit enhanced reactivity in pinacol coupling reactions and the deoxygenation of sulfoxides.[22,23] Whereas both these two compounds are relatively insoluble and are generated as suspensions in THF, the corresponding samarium(II) triflate is soluble and can be prepared at considerably higher concentrations than is possible for SmI_2 (≤0.1 M). This reagent can be generated by a number of methods including direct reaction between Sm metal and triflic acid,[24] reaction of $Sm(OTf)_3$ with organometallics[24,25] or

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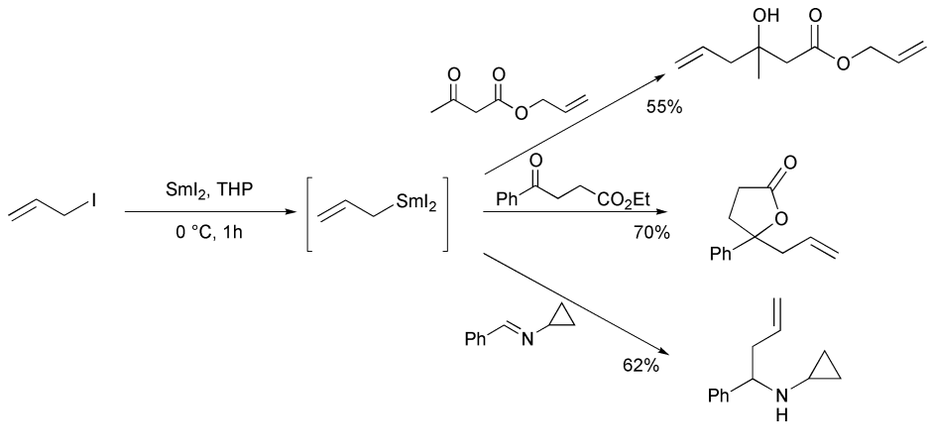


Scheme 2

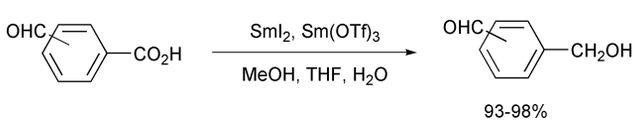
samarium metal in DME,[26] and the reduction of 1,5-dithioniabicyclo[3.3.0]octane bistriflate with samarium.[27] The last two methods produce salt free reagents and these exhibit markedly different reactivity to those prepared from organometallic reagents. For example, $[Sm(OTf)_2{\cdot}OMe_2]$ promotes Barbier type products, whereas the complex containing lithium salts leads to an enhancement of pinacol coupling and simple reduction.[26] In general, the reactivity of $Sm(OTf)_2$ with aldehydes and ketones can be ranked between that of SmI_2 and $SmBr_2$. As seen with SmI_2 the nature of the solvent can influence the reactivity—for example, the 'salt free' version of $Sm(OTf)_2$ is more effective for the pinacol reaction in nitrile solvents as opposed to THF.

Highly reactive species are generated from the combination of diarylmetals with diaryl ketones or the related imines.[28] In addition these can function as effective catalysts for a variety of alkene transformations similar to those promoted by lanthanocenes (see section 3.2).[29]

As first noted by Inanaga, the presence of additives can dramatically influence the reactivity of Sm(II) reagents and this is true of all these variants.[30] In general, such additives can be divided into two classes: proton donors such as water and low molecular weight alcohols which are believed to protonate basic organometallic intermediates and electron donors such as HMPA, DMPU and various aqueous inorganic bases and metal salts.[31]

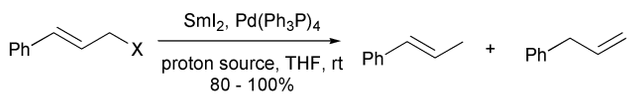
Flowers and co-workers have explored the effect of various co-solvents on the M^{3+}/M^{2+} redox potential in THF.[32] Although DMPU produces the maximum increase, the concentration of DMPU required causes precipitation of the complex. Consequently, optimal enhancement is observed with HMPA which leads to an increase of 0.72 V with only 4 ligating molecules. This is consistent with a number of structural studies of HMPA complexes, which show that in solution $Sm(HMPA)_4I_2$ is monomeric and active,[33] and also with the determination of the rate constants for generation of an organosamarium from an alkyl halide.[34] Although the highest rate of reaction is achieved with 4–5 equivalents of HMPA, if a slower reduction is required, *e.g.* to facilitate a slower radical reaction, then lower SmI_2 concentrations and only 2 equivalents of HMPA per Sm may offer a solution.[35]

Although it appears that HMPA provides the most effective enhancement of reactivity this is not always true for every substrate and a large number of alternative 'non-toxic' additives have been proposed.[30,36] Interestingly, the choice of optimal co-solvent can depend on the particular solvent used; *e.g.* DMPU is more effective in MeCN than THF whilst water has a beneficial effect in THF but is not a useful additive in MeCN.[31] Indicative of the non-basic nature of these reactions, water has been employed in a variety of processes to enhance Sm(II) mediated transformations. For example, it minimises β-elimination in the reduction of α-substituted carbonyl compounds, *vide infra*.[37] Water may be replaced by a number of other protic species including acetic acid, pivalic acid and other carboxylic acids.[38,39] The use of these acid promoters has been widely studied by Komochi and Kudo who have demonstrated that aqueous base additives are also effective.[40,41] These latter additives have been exploited in a lanthanide(III)/(II) mediated selective reduction of carboxylic acids in the presence of aldehydes *via in situ* acetal formation (Scheme 3).[42]



Scheme 3

Proton sources have also been shown to exert an influence on the stereochemical and regiochemical outcome of Sm(II) reductions.[43] For example, the reduction of allyl esters affords predominantly the γ-product with water but the α-product with ^{t}BuOH (Scheme 4).[44,45] In a related fashion, the intramolecular conjugate addition of ω-iodoenolates proceeds efficiently in the presence of ^{t}BuOH but not in HMPA where preferential 1,4- reduction occurs.[46]

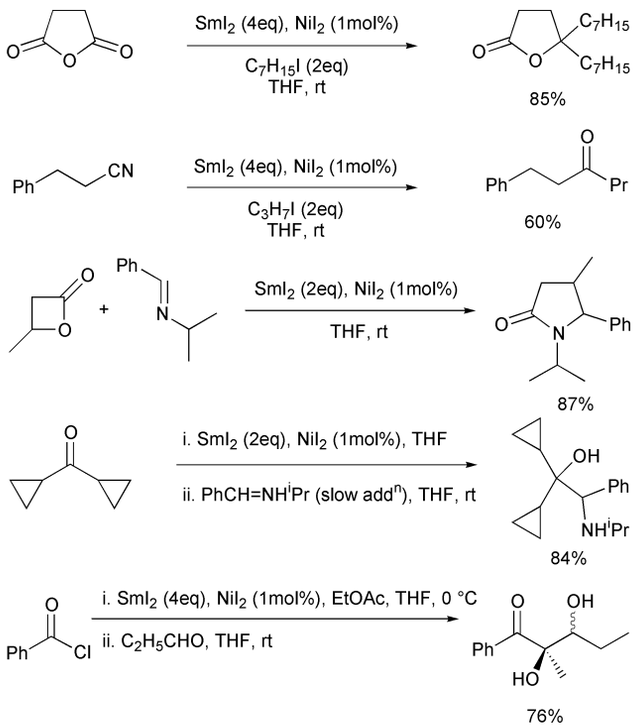


X	Proton source	α	γ
OAc	^{t}BuOH	81	19
OAc	H_2O	5	95
$OP(OEt)_2$	^{t}BuOH	81	19
$OP(OEt)_2$	H_2O	7	93

Scheme 4

A great variety of inorganic promoters for SmI_2 mediated reductions have been proposed including FeX_3[47] and NiI_2. The latter appears to be the most effective requiring ≤1 mol% to promote a wide range of reactions (Scheme 5).[48–54] The rationale for this enhanced reactivity is still unclear although Flowers *et al.* have shown that the beneficial effects of large excesses (≤12) of lithium salts on pinacol couplings are due to an enhancement of the Sm^{3+}/Sm^{2+} reduction potential.[55,56]

$E°$ for Sm^{3+}/Sm^{2+} has been estimated at ~−1.33 V whereas the Sm^{3+}/Sm potential has a value of −2.41 V. Consequently, there have been a number of reports extolling the advantages of using metallic samarium rather than preformed SmI_2.[57] Promoters are still required for these transformations and a number have been reported including $HgCl_2$ and Cp_2TiCl_2, and ammonium chloride.[58–61] The use of substoichiometric amounts of iodine is also effective and this presumably generates SmI_2 *in situ*.[62–68] Furthermore, the combination of metallic Sm and



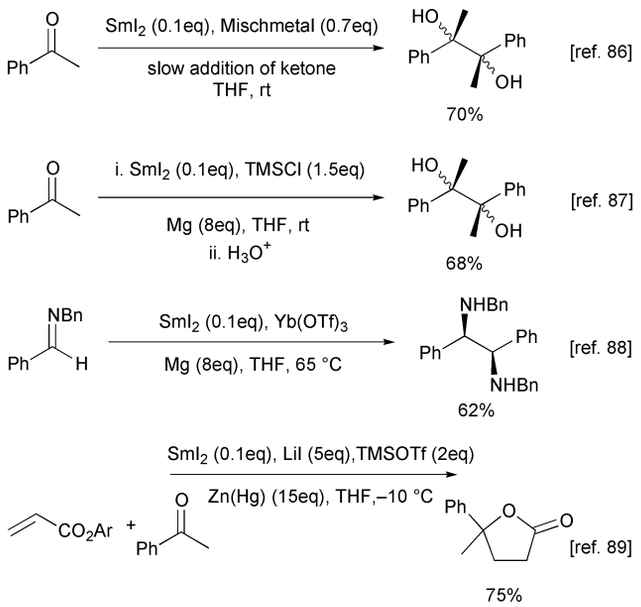
Scheme 5

SmI_2 is reported to be more effective than either reagent alone.[69] A similar effect has been noted using a Yb–YbI_2 combination.[70] Similarly active [Ln(II)] reagents can be generated from metallic lanthanide and allyl bromide,[71] Et_2AlI[72] or Me_3SiX (X = I or Br).[73–75] In each case the reactivity is described as being similar to that of the preformed reagent.

In addition to acting as an initiator, Me_3SiCl has been shown to have a beneficial effect on SmI_2 mediated pinacol couplings and copper catalysed conjugate additions.[76,77] In the absence of the copper salts a rapid 1,2-addition (Sm Barbier–Grignard) addition is observed. The precise mechanisms involved in these processes are still far from clear and there is a continuing debate over the role of free radical and/or organosamarium intermediates.[78] In general, if the intermediate 'organosamarium' reagent is unstable the Barbier procedure is superior. However, if electrophiles such as aryl alkyl ketones, aldehydes and disulfides are required then a Grignard type protocol is required to prevent prior reduction by SmI_2.[79–81] The addition of copper salts can modulate the reactivity of the intermediate organosamarium and allow the efficient cross coupling with alkyl halides.[82]

A similar ongoing debate concerns the nature of the initial electron transfer process—inner or outer sphere. The prevailing opinion is that this is highly substrate dependent with the reduction of alkyl halides proceeding *via* an outer sphere pathway whilst carbonyl compounds are reduced by an inner sphere pathway.[56,83–85] The presence of additives such as HMPA complicates this picture since most substrates are not sufficiently basic to displace these ligands from the coordination sphere, thus requiring the initial electron transfer to be outer sphere.[32] However, following the second electron transfer, the resultant carbanion is normally more basic than the initial ligands and coordination of the samarium ion can occur which has implications for the generation of asymmetric protocols.

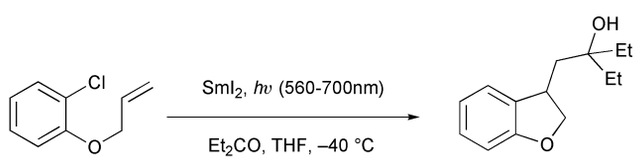
The other limitation of these low valent samarium based processes is the requirement for stoichiometric quantities of the lanthanide. There have been several methods to overcome this hurdle. Helion and Namy have introduced the use of Mischmetal, a cheap lanthanide alloy for the Barbier reaction.[86] Endo and Annunziata have exploited Mg to regenerate active SmI_2 whilst Corey has advocated the use of Zn(Hg) amalgam for a similar process (Scheme 6).[87–89] In most cases a large excess



Scheme 6

of the stoichiometric reductant is required, as is the use of TMSX reagents, to ensure a rapid recycling of the Sm^{III} species. Although no reaction was observed in the absence of samarium, both stoichiometric reductants are known to promote similar reactions.

Alternative modes for lanthanide(II) regeneration include electrochemical and photochemical reduction.[90,91] The former, as developed by Dunach and co-workers, can also suffer from competing pathways. Whilst photochemical recycling has not been reported, irradiation with light of wavelength 560–700 nm has been shown to enhance electron transfer from SmI_2 to halides with a similar magnitude to HMPA.[92] For example, reduction of alkyl chlorides is normally difficult but can be achieved under photochemically enhanced conditions (Scheme 7).[93,94] A number of related tranformations involving selenides, tosylates and tellurides have also been reported.[95] Similar photochemically enhanced transformations are also possible using YbI_2.[96]



Scheme 7

Higher reduction potentials are observed for thulium diiodide ($E°$ $Tm^{3+}/Tm^{2+} \approx -2.3$ V) and dysprosium diiodide ($E°$ $Dy^{3+}/Dy^{2+} \approx -2.5$ V). Although these can be used to carry out similar Grignard–Barbier type chemistry and in the case of the latter reagent, Birch type reductions, the applications are likely to be limited by the low stability and difficulties in the preparation of these reagents.[97,98]

Finally, the use of Rochelle's salt can greatly simplify the work-up of SmI_2 reactions as this can generate homogeneous solutions without the need for acidic conditions to dissolve Sm(III) salts.[99]

2.3 Functional group reduction

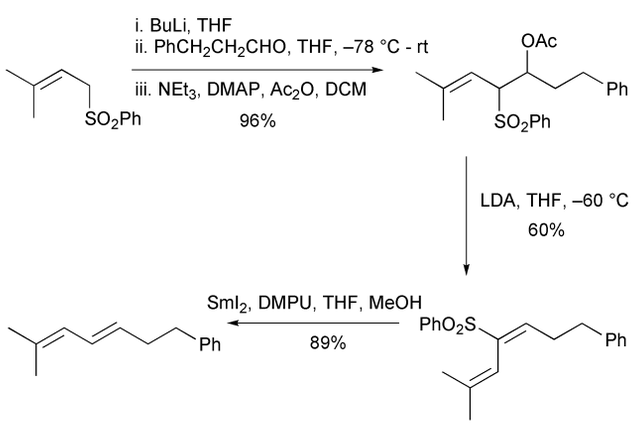
Much of the early work with SmI_2 focused on its ability to effect selective reduction of various functional groups. A comprehensive account of this area appeared in 1994[100] and only some of the more recent developments are described below. In many cases the reduction of one functional group has been used

to generate a carbon-based radical/organolanthanide species which has subsequently been employed to generate a new C–C bond and these transformations will be covered in later sections.

The reductive cleavage of phenyl sulfones requires the presence of an additive, *e.g.* HMPA, to achieve viable rates and yields.[101] In one solution to this problem Kende and Mendoza have reported that reduction of the corresponding *N*-methylimidazol-2-yl sulfones can be efficiently achieved, at room temperature, without the need for any additives.[102] Similar enhancements in reactivity are observed with the corresponding 2-pyridyl sulfones and this is attributed to a lower lying LUMO for these heteroaryl sulfones.[103] In contrast to the corresponding phenyl sulfones, where complete reaction necessitates the use of large excesses of the lanthanide reagent, with these latter substrates only two equivalents of SmI_2 are required. This can be rationalised by the fact that the phenyl sulfinate probably undergoes competitive deoxygenation reactions.

The related reduction of arenesulfonamides ($R^1R^2NSO_2Ar$) shows a similar profile[104] with, in general, reactivity increasing in the order Ar = Tol < Ph < 2-Pyr. Whilst reduction of arenesulfonamides requires elevated temperatures and the use of DMPU as a promoter,[105] the pyridyl derivatives are cleaved at room temperature. However, problems of competitive aziridine cleavage, enone reduction and partial racemisation of amino acid derived substrates can sometimes be observed with all these methods. The corresponding acylsulfonamides undergo a very rapid room temperature cleavage in the absence of additives.[106,107]

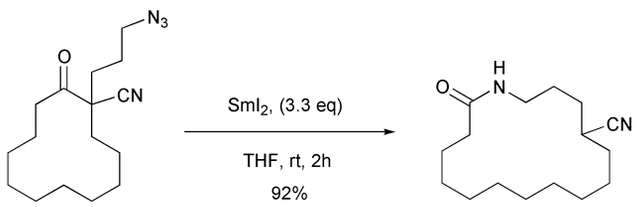
Applications of these observations have been made in the samarium modified Julia olefination and related fragmentation processes where the use of SmI_2 can be advantageous compared to Na(Hg) amalgams.[102,108–111] In general, reduction of β-hydroxy or acetoxyphenyl sulfones in the presence of HMPA occurs in good yields but modest selectivities. The latter problem can be avoided by base promoted elimination to the vinyl sulfone and subsequent SmI_2 mediated reduction.[112] In the absence of additives the reaction was slow (five days at room temperature) but the selectivity excellent (25 : 1). Significant acceleration to the rate with no loss of stereochemical control can be realised through the use of DMPU and MeOH as co-additives (Scheme 8). Related 1,2-eliminations of dihaloalkanes can be achieved using SmI_2–Sm, Sm and a catalytic amount of acid or Sm in methanolic medium.[113,114] The last of these appears to provide the most general solution although reduction of α,β-unsaturated carboxylic acid derivatives to the corresponding saturated system is also possible with this reducing system.[115]



Scheme 8

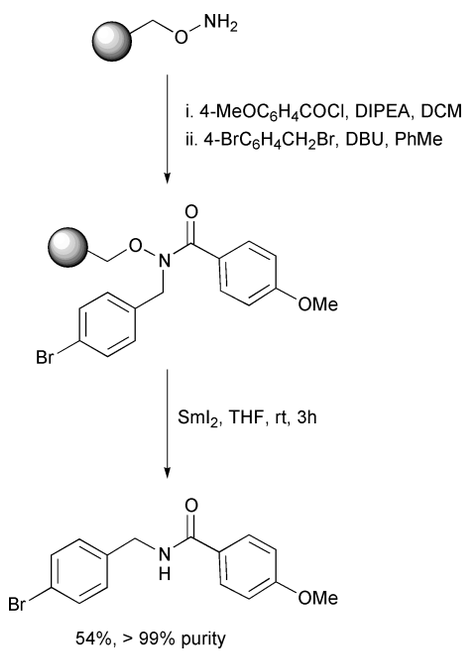
Other C–S bonds are also cleaved by low valent lanthanide reagents. Ketene dithioacetals are reduced to the corresponding vinyl sulfides whilst the dithioacetals afford the corresponding sulfide on treatment with SmI_2 in the presence of ^{t}BuOH or AcOH in benzene–HMPA.[116,117] In both cases evidence is found from trapping experiments to implicate the involvement of α-sulfenyl anions. Chalcogen anions are generated by reductive cleavage of C–S, S–S, Se–Se, Te–Te, Si–S and Si–Te bonds using a variety of low valent samarium systems.[118]

Developments in lanthanide mediated reduction of nitrogen containing functionality focus on the generation of simplified procedures. Although nitro groups can be efficiently reduced to either amine (6–8 eq.) or hydroxylamine (4 eq.) through the use of SmI_2 in the appropriate stoichiometry it is simpler to use Sm metal promoted by a catalytic amount of iodine[63,66] or ultrasound.[119] A similar reducing system is also suitable for the reduction of aromatic imines to secondary amines.[67] Under the same conditions alkyl imines afford the corresponding diamine in a pinacol type coupling process. Both aromatic and aliphatic amines can be obtained efficiently and selectively from the reduction of azides with SmI_2.[120,121] Carbonyl groups are stable to this latter transformation and this can be exploited in a simple ring expansion strategy (Scheme 9).[122]



Scheme 9

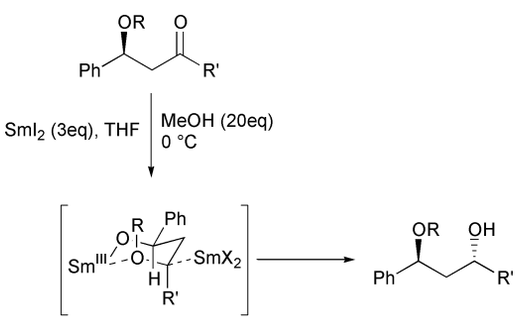
Reductive cleavage of the N–O bond in hydroxylamines and hydroxamic acids with SmI_2 is facile. The process can be combined with a direct acylation using TFAA or Ac_2O to provide the corresponding amide in good yields.[123–126] This protocol has seen widespread application including the development of a traceless linker strategy for solid phase organic synthesis (Scheme 10).[127]



Scheme 10

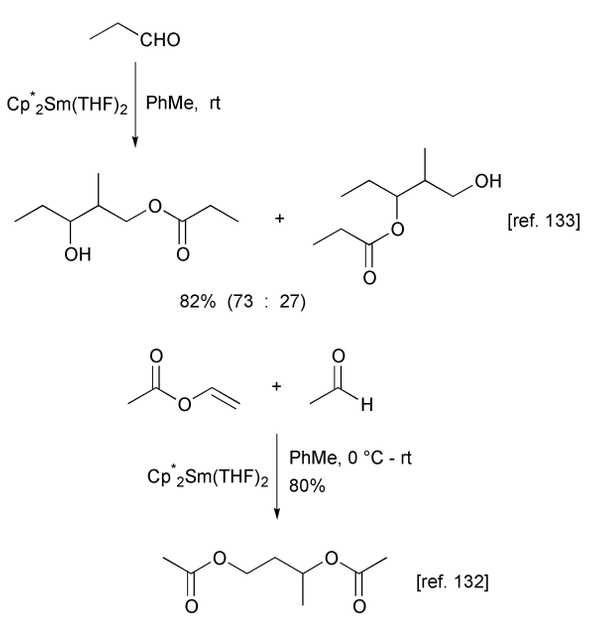
Although carbonyl reduction is facile with low valent lanthanide reagents only in certain cases is it competitive with the multitude of hydride based methods. For example, the non-basic conditions allow the reduction of acylsilanes to occur with no evidence of products arising from a Brook rearrangement.[128] Other advantages include the possibility of trapping the intermediate ketyl with a range of electrophiles, *vide infra*. In a related context, whilst chemoselectivity in the

order RCHO > RCOR′ > RCO_2Me is good, simple diastereoselectivity frequently is only moderate. However, in substrates containing proximal hydroxy groups a very rapid, highly *anti*-selective reduction is observed. This selectivity is attributed to the formation of a chelated Sm(III) complex in which the Sm carbanion occupies the less hindered equatorial position (Scheme 11).[129] Replacement of the hydroxy group by MeO or MOM has minimal effect on the selectivity but the use of larger alkoxy substituents hinders the reaction and diminishes the selectivity.[130] Consistent with this model, which requires the axial orientation of the α′ ketone substituent (R′), reduction of the corresponding *tert*-butyl ketone is non-selective. In general, this provides an alternative strategy for the generation of *anti*-diols to the modified Tishchenko reduction developed by Evans and Hoveyda.[131] Enhancements to this latter transformation have largely been conducted with Sm(III) reagents generated *in situ* (*vide infra*). However, in a related process Ishii and co-workers have developed aldehyde trimerisation and 1 : 2 vinyl ester–aldehyde cross-coupling sequences to functionalised 1,3-diols catalysed by $Cp^*_2Sm(THF)_2$ (Scheme 12).[132,133]



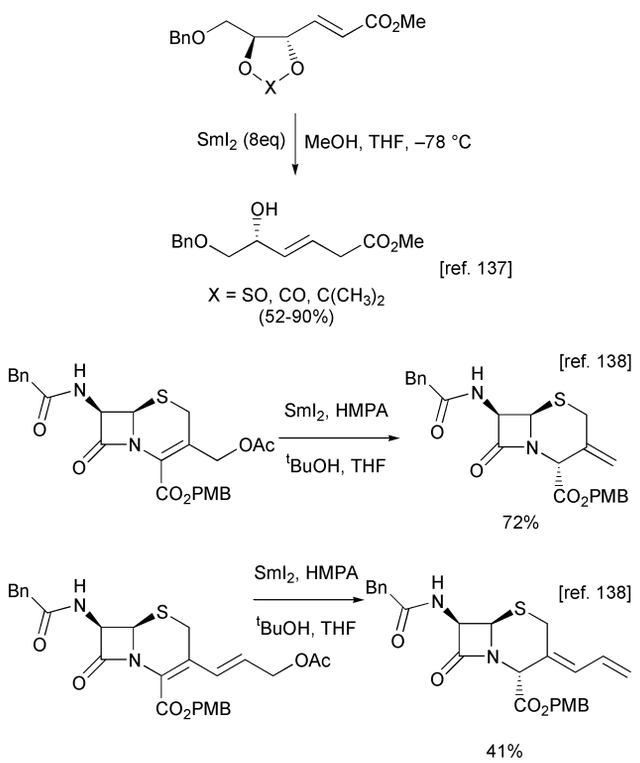
R	R'	Time	Yield	*anti:syn*
H	Me	1h	95%	99 : 1
Me	Me	1h	99%	99 : 1
Et	Me	18h	30%	87 : 13
Bn	Me	12h	nr	–
H	^{t}Bu	–	96%	50 : 50

Scheme 11



Scheme 12

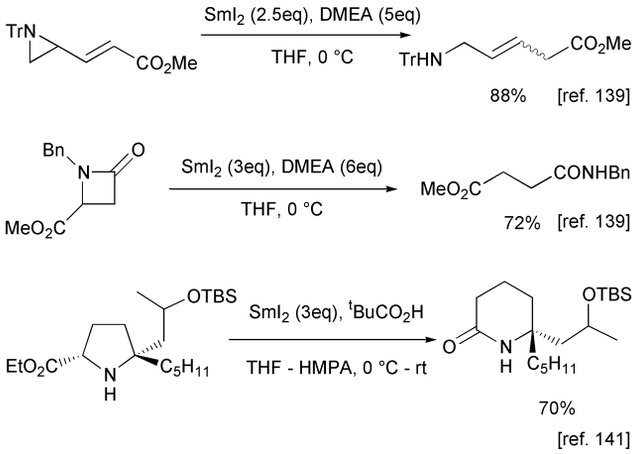
A wide range of α-heterosubstituted carbonyl compounds can be reduced to the parent compound on treatment with SmI_2. A recent report by Simpkins and co-workers has shown that tertiary amides and α-bromo but not α-oxy secondary amides behave similarly.[134,135] The reaction is considerably slower than that observed for ketones and esters and requires the presence of LiCl to ensure efficient reaction. Conjugation has been previously exploited in the reductive cleavage of α,β-unsubstituted γ,δ-epoxy esters,[136] and these observations have been extended to the corresponding cyclic sulfites, carbonates and acetonides.[137] Reduction of more extended conjugated systems is also possible, albeit with diminished efficiency, as seen in Scheme 13.[138]



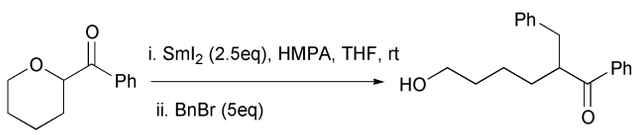
Scheme 13

Reductive cleavage of α-amino functionality is less common. Molander and Stengel have shown that acylaziridines and azetidinones undergo facile ring fragmentation in the presence of *N*,*N*-dimethylethanolamine [DMEA, 2-(*N*,*N*-dimethylamino)-ethanol] (Scheme 14), although attempts to trap the presumed Sm enolate were not efficient.[139] Whilst, with these strained systems, the use of HMPA as an additive leads to complex mixtures, this is essential in fragmentation of proline derivatives and related acyclic amides as is the presence of a proton source (MeOH, pivalic acid or DMEA).[140,141] The equivalent fragmentation of α-acyl cyclic ethers is much more facile and the resulting samarium enolate can be alkylated (Scheme 15).[142] Interestingly, good yields require two equivalents of SmI_2 presumably owing to the relatively low reactivity of the intermediate samarium ketyl. Given a choice, there is preferential cleavage of an exocyclic acetal rather than the fragmentation of the ring ether. This also reflects the high reactivity of anomeric leaving groups to SmI_2 (*vide infra*).[37,143]

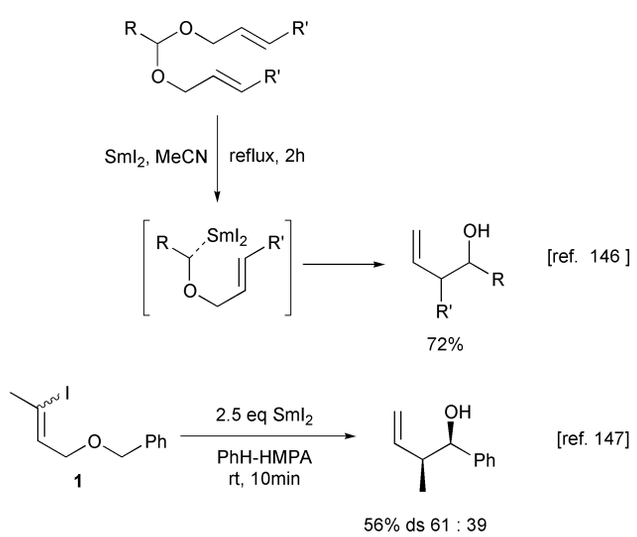
Simple acetals are normally stable to SmI_2, however Studer and Curran have reported that, in the presence of TFA or water, dimethyl acetals are converted to the corresponding ether.[144] Aromatic acetals react in a similar fashion with SmI_2 in the presence of $AlCl_3$. In the absence of additives, diallyl ethers undergo reduction to give an alkoxysamarium species which then undergoes a [2,3] Wittig rearrangement to produce homoallylic alcohols (Scheme 16).[145,146] Similar intermediates can be generated *via* 1,5-radical translocation of the vinyl radical generated in the SmI_2 mediated reduction of vinyl halide **1**.[147]



Scheme 14



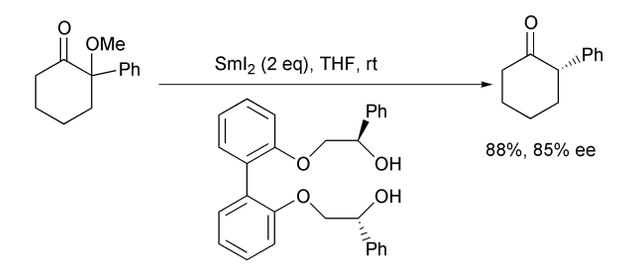
Scheme 15



Scheme 16

α-Deoxygenation of α-hydroxylactones is possible using SmI_2 in aqueous THF with no activation of either leaving group or protection of the other alcohols.[37] Interestingly, reflecting the fact that alcohols can enhance the reactivity of SmI_2, protected substrates require additives such as HMPA or ethylene glycol.[148,149]

The intermediate samarium enolate is prochiral and building on Takeuchi's pioneering work,[150] the asymmetric protonation of samarium enolates has been the subject of a number of studies. Good levels of enantioselectivity are now possible (Scheme 17).[151,152] Since the products are frequently labile with respect to racemisation, the use of fluorous tagged proton sources with fluorous extraction techniques can help to give enhanced levels of optical purity.[153]

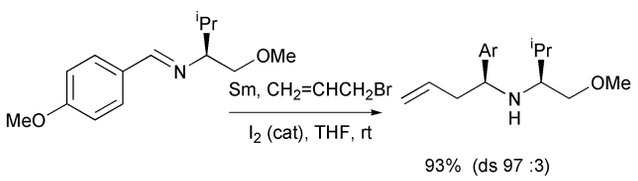


Scheme 17

2.4 Carbon–carbon bond forming processes

2.4.1 Barbier–Grignard processes

The reaction of organic halides with carbonyl compounds, the samarium Barbier–Grignard reaction, has been comprehensively reviewed[4] and only selected aspects of this very useful transformation will be considered. Imines also react readily with organosamariums under both Barbier and Grignard type conditions and if the imine carries a suitable chelating chiral auxiliary very high levels of diastereoselectivity can be observed (Scheme 18).[68]



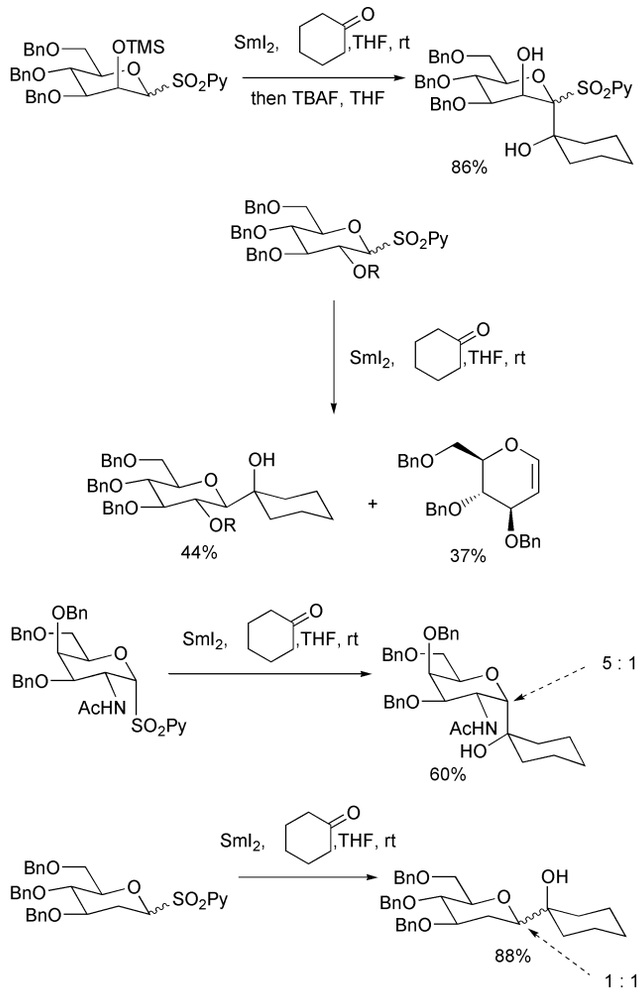
Scheme 18

As indicated above, α-deoxygenation reactions generate an Sm enolate which may be trapped with a variety of electrophiles. Carbonyl compounds have been widely used in this regard and a wide variety of examples have been reported, notably those using carbohydrate derived precursors.[154–156]

Reductive generation of anomeric radicals is well precedented[109] and may be manipulated to afford either the reduced sugar, the glycal, or if carried out in the presence of an electrophile (Barbier type reaction), a C-glycoside.[157] The construction of such carbohydrate analogues *via* reductive anomeric samariation has been an area of much activity particularly by the groups of Sinay, Beau and Skrydstrup.[109,158,159] The critical features of these processes are the nature of the anomeric group and the C-2 functionality. For example, C-2 acylated substrates yield the glycal exclusively, whilst the use of less reactive leaving groups such as ethers allows efficient generation and trapping of the resultant organosamarium. The stereochemistry of the newly formed glycosidic centre is also a function of substrate structure with glucosyl, mannosyl and galactosyl derivatives affording the 1,2-*trans*-glycoside whereas the corresponding α-galactos- and glucosamines preferentially yield the α-glycoside (Scheme 19).[103,160–164] The anomeric substituent is also important: glycal formation is favoured by glycosyl phenyl sulfones, which undergo a relatively slow first electron transfer, whereas pyridyl sulfones undergo a relatively much faster initial electron transfer leading to high concentration of anomeric radical and efficient cyclisation or dimerisation in the absence of an electrophile (Scheme 20).[165,166] The addition of NiI_2 to the reaction leads to enhanced levels of coupling regardless of the initial sugar stereochemistry.[53] Similar enhancements to the synthesis of C-glycosides *via* reductive samariation are observed using the corresponding glycosyl iodides which can be conveniently generated *in situ*.[167]

The pyridyl sulfone group has also proved to be more effective than the corresponding halide for alkoxymethylation of carbonyl compounds with few problems of competing pinacol reactions.[168] Similar transformations have been reported for the arylselenyl and benzotriazolyl analogues although the former is limited to reactions with ketones.[169,170]

The reaction of α-halocarbonyl compounds with SmI_2 can generate either a samarium enolate or a Reformatsky type reagent. Evidence for the latter arises from the self-condensation to generate γ-samario-β-oxobutanoates **2** which can subsequently combine with a range of electrophilic species (Scheme 21).[171,172] At higher temperatures the Reformatsky reagent **2** rearranges to generate a samarium enolate. These samarium acetylacetonates are too unreactive to continue the process, and this can provide a non-basic pathway to provide β-ketoesters. In the presence of excess SmI_2, these can undergo further reduction to afford the corresponding β-hydroxyester.[173]



Scheme 19

In a similar fashion, the corresponding β-diketones can be accessed by the SmI_2 mediated reaction of α-haloketones with a variety of acylating agents.[174–177] The use of acylnitriles has been proposed as the optimal choice leading to minimal side reactions. However, the order of addition is important, as Baruah *et al.* have reported the SmI_2 promoted dimerisation of acyl nitriles to α-diketones.[178]

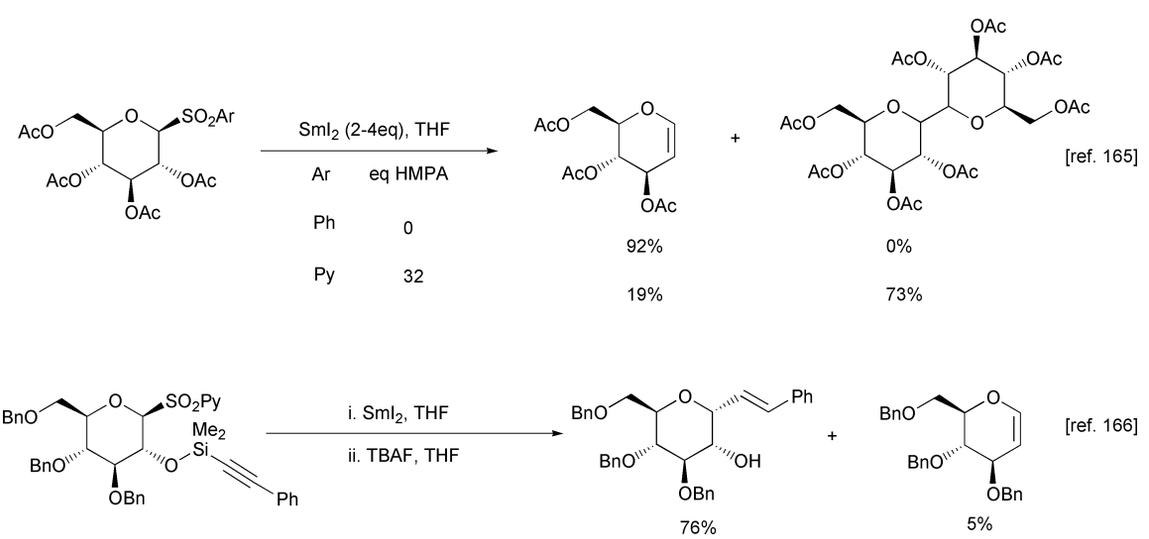
The intermolecular samarium Reformatsky reaction has continued to be developed; α-haloketones, α-haloamides and α-halonitriles can be used.[179–183] In many cases various additives are required to give good yields. In addition, these additives can also influence the stereochemical course of these reactions as observed in the reaction of phenacyl bromide with cyclohexanones where TMEDA favoured production of the equatorial alcohol whilst Et_2AlCl led to predominant formation of the axial alcohol.[180] A particular advantage of these processes is the low basicity of the various organosamarium intermediates as reflected in the efficient and selective functionalisation of bromoglycine containing peptides with no need to protect the other amide bonds.[184] Absolute stereocontrol is also possible in these processes using a variety of chiral auxiliaries (Scheme 22).[185–187]

Similar organosamarium intermediates can be generated through the reductive cleavage of a nitrile group and, in the presence of HMPA, efficient alkylation and carbonyl condensations can be observed.[188] On treatment with one equivalent of SmI_2 the corresponding isonitriles rearrange to the nitrile which can be further reduced with excess reagent.[189]

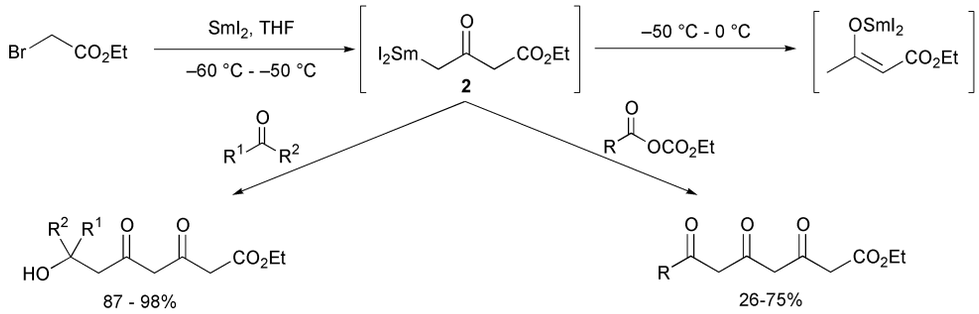
Barbier type processes with dichloroacetates are also feasible, giving good yields of the chlorohydrin.[190] Similar transformations are also possible with halodifluoroacetates.[191] In general there are significant advantages (lower temperatures and faster reactions) to these processes compared to conventional Zn based Reformatsky methods.

Diiodoalkanes and triiodoalkanes undergo an efficient Barbier reaction with aldehydes to give iodohydrins and 2-hydroxydiiodoalkanes respectively (Scheme 23).[192] The former occurs with good diastereoselectivity favouring the *syn* isomer and in the case of chiral aldehydes high levels of asymmetric induction are observed. Similar transformations commencing from the analogous α-chlorosulfides have been reported[193] as has the use of 1,1-dibromides in the presence of a catalytic amount of a cobalt salt.[192,194] The use of triiodoalkanes provides convenient access to α-hydroxyacids and α-iodoaldehydes. The oxidant in the former transformation is presumably air, although this is not explicitly stated. Alternatively, treatment of the 2-hydroxydiiodoalkanes with further SmI_2 gives an efficient route to (*Z*)-iodoalkenes.[195,196] Related SmI_2 mediated reduction processes provide efficient entry to (*Z*)-vinylsilanes[197] and (*E*)-enoates.[198]

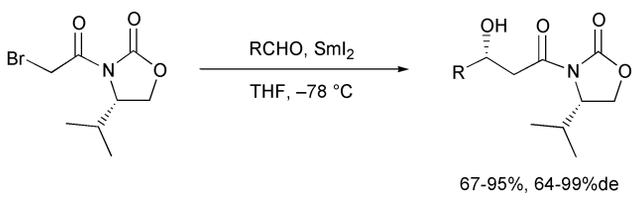
Allylic organosamariums can be generated *in situ via* the SmI_2 reduction of allylic sulfones.[199] As with the equivalent Barbier processes using halides and phosphates, unsymmetrical substrates give regioisomeric products. Inanaga has previously shown that enhanced control of the regiochemistry and stereochemistry is realised using a Pd(0) catalyst in the presence of HMPA.[200] Palladium catalysis is also required for the reduction of propargylic (prop-2-ynyl) esters and phosphates. In a similar fashion to the related reduction of allylic esters described above, mixtures of allenyl and alkynyl products are observed



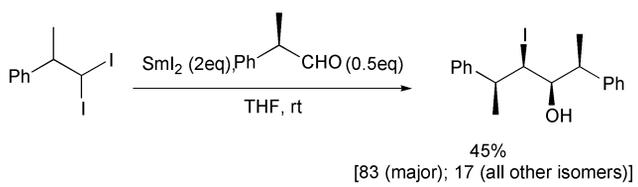
Scheme 20

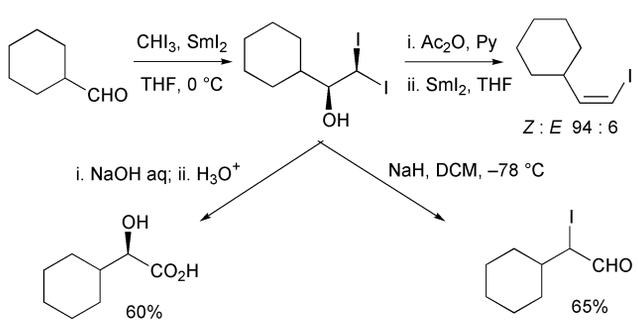


Scheme 21



Scheme 22





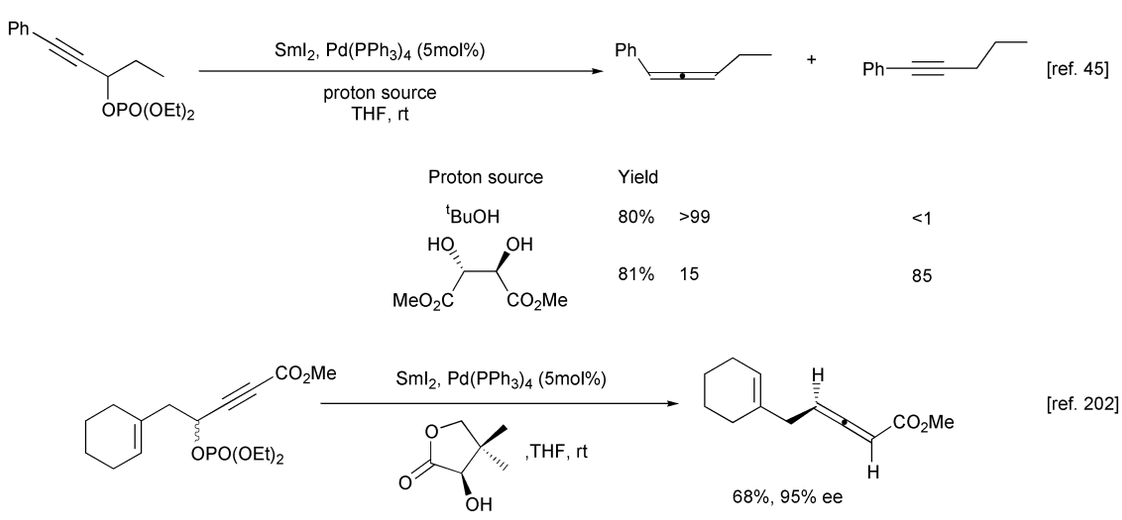
Scheme 23

depending on the co-solvent and substrate structure (Scheme 24).[44,45,201,202] Unsurprisingly, the intramolecular version of this reaction leads to exclusive formation of the homopropargylic alcohol.[203] Related processes are observed with vinyl and alkynyloxiranes (Scheme 25).[204–206] The former produce the *E* alkene selectively whilst the latter forms allenic products exclusively. These variants may also be carried out in a palladium-catalysed fashion, although giving different diastereoselectivities indicative of a change in mechanism. The uncatalysed processes are believed to proceed *via* a samarium ketyl whilst the palladium catalysed reactions involve an organosamarium generated by reduction of an intermediate π-allyl palladium complex. Allyl-, allenyl- and vinylsamarium complexes are generated on treatment of allylic, propargylic and vinylic ethers with $Cp^*_2Sm(THF)_n$.[207–209] These undergo highly regioselective reactions with a range of electrophiles, often with complementary selectivity to that exhibited by the SmI_2 strategy (Scheme 26). However the practical use of these reagents appears to be limited by the sensitive nature of the initial samarium complex.

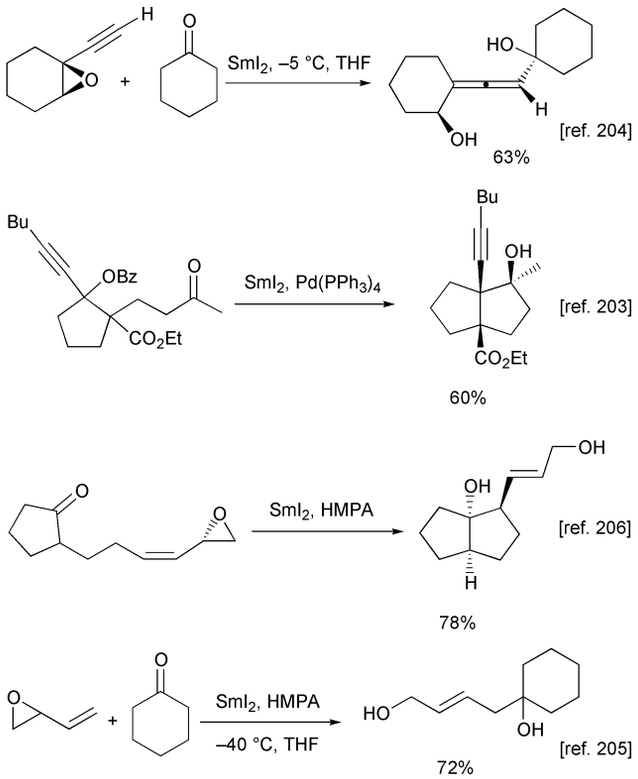
Alkynylsamarium species have been proposed in Grignard–Barbier type processes with alkynyl iodides and carbonyl compounds.[210] The alternative pathway involving addition of a ketyl radical to an Sm-complexed alkyne is also possible and this is the suggested pathway for the coupling of alkyl iodides and terminal acetylenes in the presence of an Sm–SmI_2 combination.[211]

2.4.2 Radical alkene addition reactions

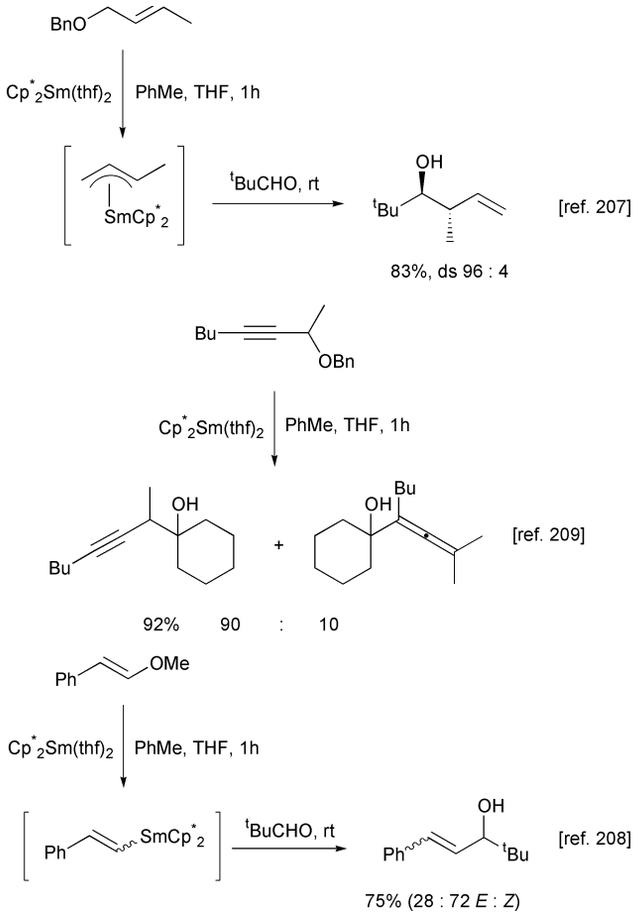
The involvement of vinyl radicals generated by the addition of a samarium radical has been demonstrated in the cyclisation of ω-iodoalkynes[212] and the glycosyl sulfones discussed above, Scheme 20.[166] Such species undergo efficient cyclisation only if the concentration of the initial radical is sufficiently high; *e.g.* alkynyl esters are reduced significantly faster than the C–I bond and thus do not represent viable substrates for these cyclisations. The direct generation of vinyl radicals through Sm(II) reduction has been studied and whilst simple radical cyclisation can be efficient, hydrogen atom abstraction and subsequent reduction of the alkyl radical is frequently competitive.[213] Consequently, in these and related radical cyclisations, the precise conditions and particular substrate structure are crucial. For



Scheme 24



Scheme 25



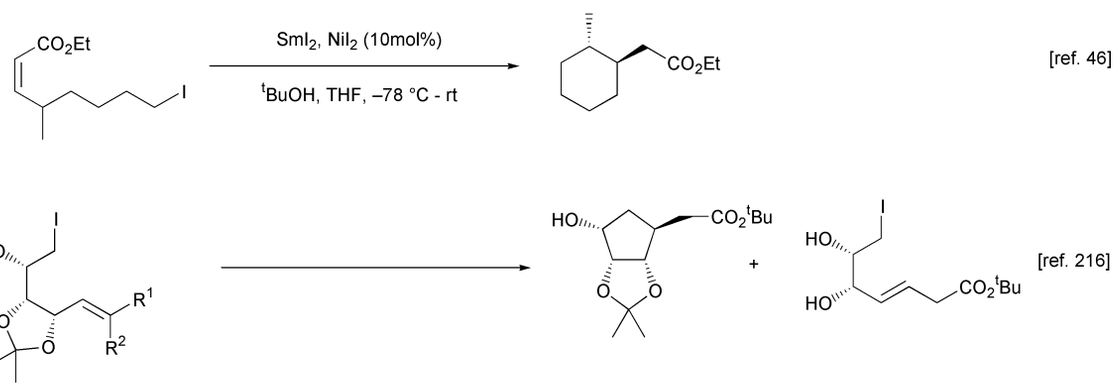
Scheme 26

example, in the cyclisation of alkyl substituted iodo acrylates the use of HMPA was deleterious, leading to extensive double bond reduction, whilst the presence of NiI_2 or FeX_3 salts was beneficial, albeit not essential.[46] In contrast, sugar derived substrates required both HMPA and a proton source to allow cyclisation to compete against 1,4-reduction and deoxygenation (Scheme 27).[214–216] However, regardless of which method is ultimately employed the process seems to be significantly more versatile than related anionic methods using lithium–halogen exchange and has found widespread application including in solid phase organic synthesis.[217]

Smaller strained rings can also be prepared by this method and it is suggested that the cyclisation is rendered irreversible by rapid reduction and protonation of the intermediate α-acyl radical.[218] Similarly, the presence of a proton source appears to be essential for the efficient *anti*-selective 4-*exo*-*trig* cyclisation of samarium ketyls to acrylates (Scheme 28).[219,220] In this latter case a geminal substitution pattern is required for efficient cyclisation.

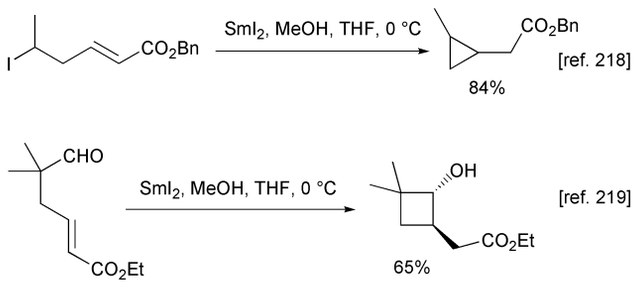
2.4.3 Ketyl radical alkene addition reactions

Samarium ketyl olefin additions have continued to be used widely. As with samarium mediated radical additions, cyclisation is highly facile for five-membered rings and occurs with good diastereoselectivity that can be rationalised on the basis of a six-membered chair-like transition state.[221] When the tether is substituted, moderate to good levels of asymmetric induction are observed although this is critically dependent on the nature of the substituents and additives.[222] (Similar observations have



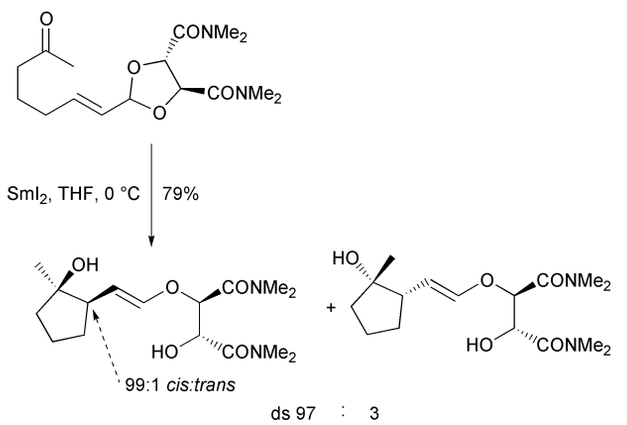
$R^1 = CO_2{}^tBu$, $R^2 = H$	SmI_2, MeOH, HMPA, THF, –78-0 °C	91% (78:1)	–	
	SmI_2, MeOH, THF, rt	18%	–	56%sm
$R^1 = H$, $R^2 = CO_2{}^tBu$	SmI_2, MeOH, HMPA, THF, –78-0 °C	86% (99:1)	–	
	SmI_2, MeOH, THF, rt	–	44%	14%sm

Scheme 27

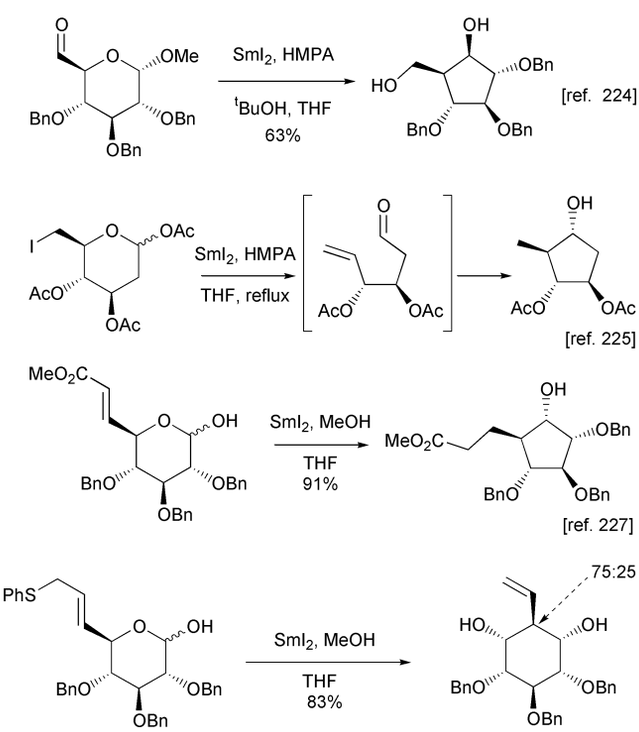


Scheme 28

also been made in related pinacol type cyclisation processes—*vide infra*.) More remote control of the stereochemistry is possible when chelation of the ketyl radical, alkene and controlling chiral centre is possible (Scheme 29).[223] Many of these substrates can be simply accessed *via* SmI_2 mediated fragmentation of carbohydrate derivatives (Scheme 30).[154,222,224–227] A further degree of complexity can be achieved by further reduction of the exocyclic radical and trapping of the resultant anion with an electrophile.[228]

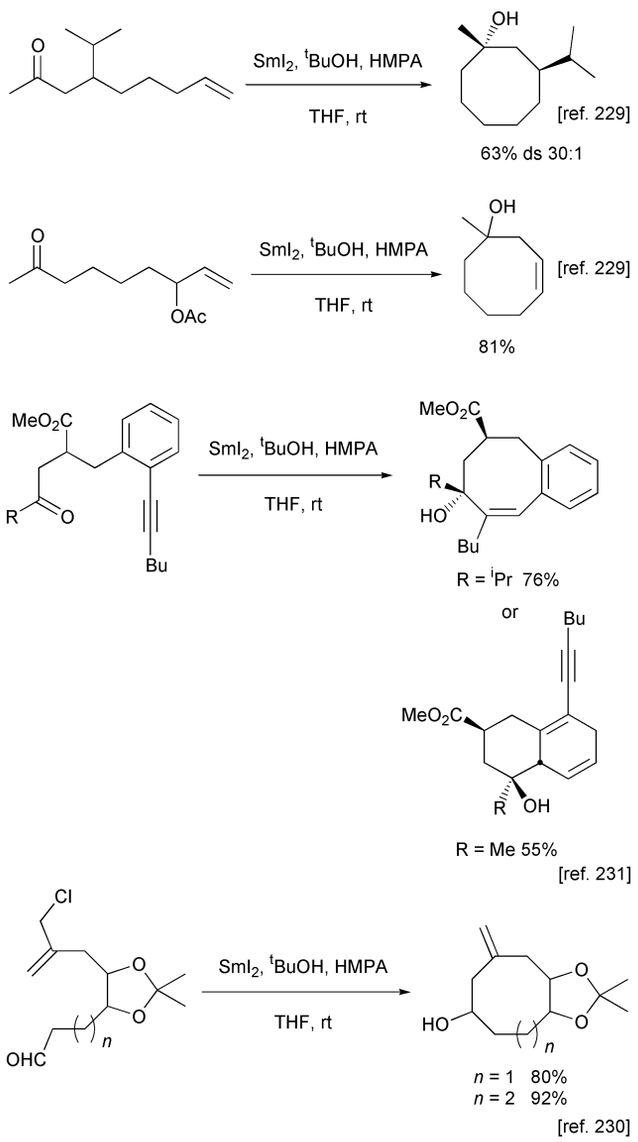


Scheme 29



Scheme 30

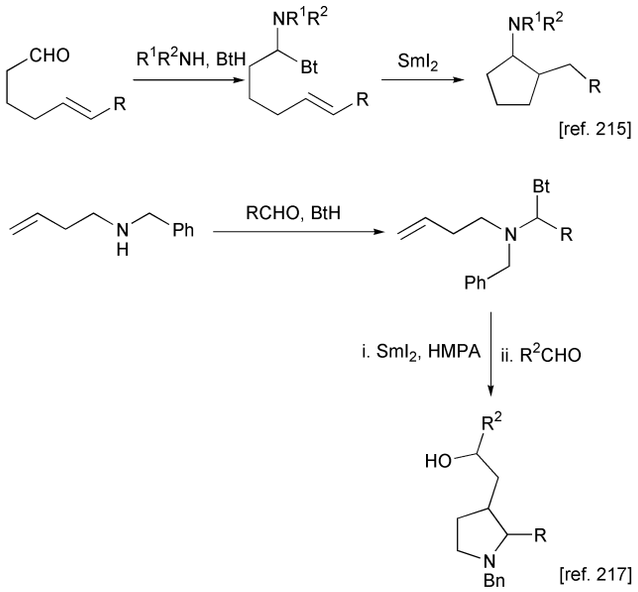
Such sequential reactions (*vide infra*) require rapid radical cyclisation and whilst this is normal for 5-*exo* cyclisation the corresponding 6-*exo*-*trig* processes are slower and subject to steric limitations at the ketyl centre. However, larger ring systems are also accessible *via* this strategy (Scheme 31).[229–231] As with all these Sm(II) mediated cyclisations, the position and nature of substituents and additives appear to be crucial to both stereoselectivity and efficiency.[221,231–234] Whilst the efficiency of these radical cyclisations can be enhanced through the use of enoate acceptors, the level of diastereoselectivity is not always ideal and higher selectivity can be obtained employing allyl sulfides and sulfones as the accepting group.[235]



Scheme 31

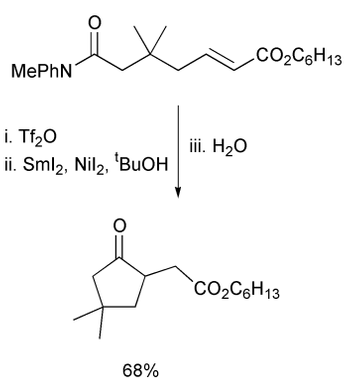
Alternatives to both the 'ketyl' radical source and acceptor alkene have been employed. For example, quinomethanes and arenes, both free and complexed with transition metals, can function as the acceptor;[236–240] whilst α-amino radicals can be generated through the SmI_2 mediated reduction of hydrazones, oximes and imines.[241] A particularly versatile method for the latter involves the treatment of an α-benzotriazolylamine with SmI_2 (Scheme 32). These substrates, easily prepared from an amine, aldehydes and benzotriazole, provide an entry to cyclic amines, *via* cyclisation onto a pendant alkene, amino alcohols and diamines, *via* coupling with carbonyl compounds or imines (dimerisation) respectively, *vide infra*.[242–245]

Owing to their lower reactivity, amides have received relatively little attention as the radical source. In an elegant approach to this area McDonald *et al.* have shown that treatment of an amide with triflic anhydride followed by SmI_2



Scheme 32

generates an α-amino-α-alkoxy radical (acyl radical equivalent) which can add to an appropriately substituted alkene to produce cyclic ketones in moderate yields (Scheme 33).[246]

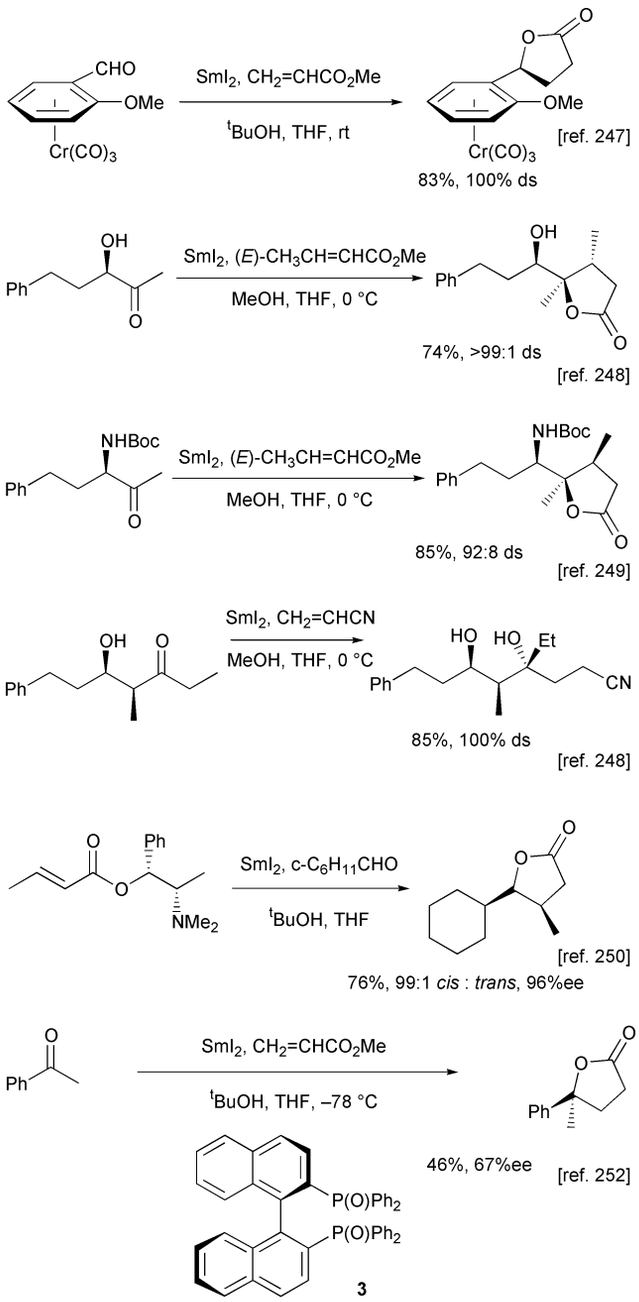


Scheme 33

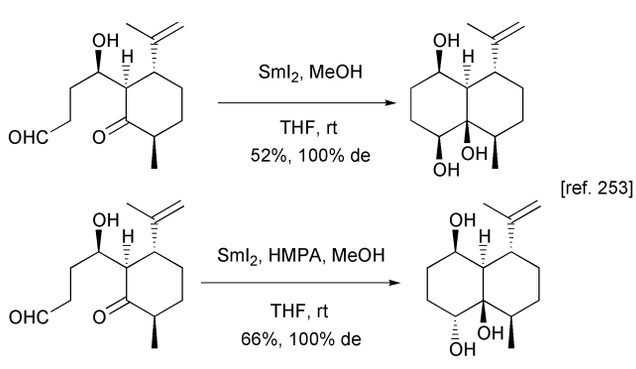
Whilst diastereoselectivity is a common feature of the intramolecular ketyl olefin cyclisation, the same is not intrinsically true of the intermolecular version and efforts have been made in this regard.[247–249] Selectivity can be attained either through stereoelectronic effects or *via* chelation to control the conformation of the ketyl radical (Scheme 34). In this latter case, chelation has the dual effect of controlling the stereochemistry and enhancing the reaction rate. Consequently, the addition of HMPA destroys the selectivity, whilst alternative substrates for which chelation is not feasible do not react. In a similar fashion, chelation is required to achieve diastereoselectivity in the addition to acrylate esters containing chiral auxiliaries.[250,251] Asymmetric induction through the use of external chirality has been achieved in this process through the use of chiral proton sources to trap the intermediate samarium enolate, *vide supra*, or, in the case of non-symmetrical ketones, through the use of the chiral promoter, BINAPO **3**.[252] This latter transformation remains the only really successful method for intermolecular asymmetric induction in an Sm(II) mediated C–C bond forming process.

2.4.4 Pinacol coupling processes

As with ketyl olefin coupling the pinacol reaction produces mixtures of diastereoisomers. Substrates containing free hydroxy groups have long been known to give enhanced selectivity. Disruption of chelation by the addition of HMPA can therefore lead to alternative stereoselection (Scheme 35).[253]



Scheme 34



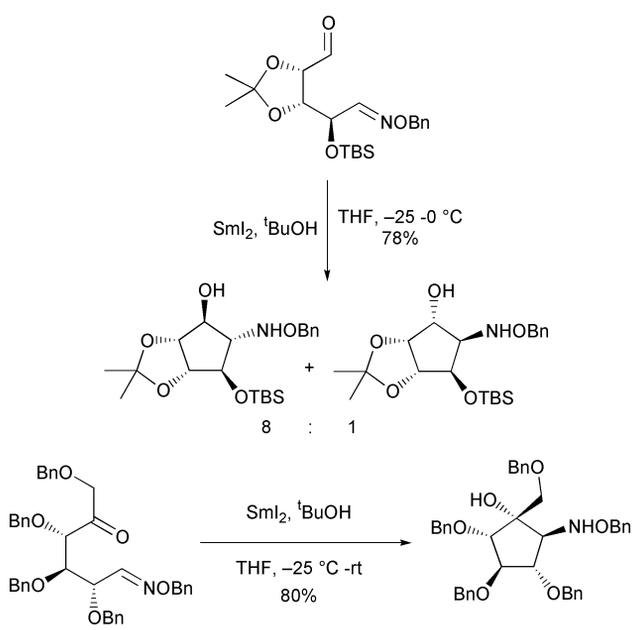
Scheme 35

A similar effect has been noted in the intermolecular pinacol coupling reactions of transition metal complexed benzaldehydes which can exhibit very high levels of selectivity.[254,255] The addition of polyethers to the reaction mixture can exert a similar influence on the diastereoselectivity.[256] Interestingly, there is a changeover in selectivity from aryl aldehydes (*meso*-diols) to alkyl aldehydes (*rac*-diols) and this could reflect a

mechanistic switch from ketyl dimerisation to alkoxyanion ketyl addition to a carbonyl group.[257] α-Ketocarboxamides and esters undergo a highly diastereoselective pinacol coupling and if a chiral auxiliary is employed, very high levels of asymmetric induction are observed.[187,258,259]

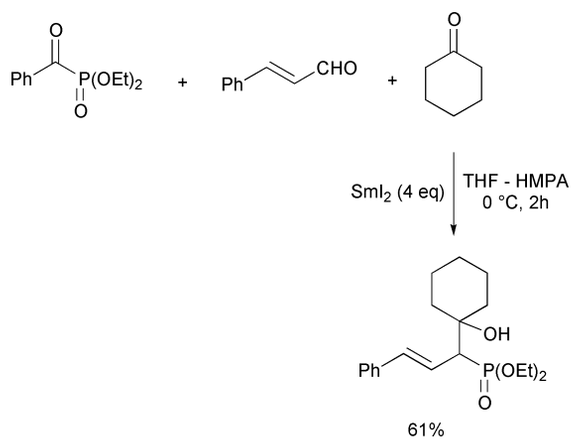
A variety of Lewis acidic additives have been screened for enhancements to selectivity and although high selectivity can be attained in certain cases no clear cut trends have been observed.[27,260,261] *In situ* generated Ce(II) reagents have been postulated to be involved in a highly diastereoselective pinacol coupling of both aliphatic and aromatic aldehydes using either manganese metal or diethylzinc as the stoichiometric reductant.[262,263] Although samarium salts are sufficiently Lewis acidic to promote the generation and subsequent dimerisation of imines from α-benzotriazolylamines,[264] the use of strong Lewis acids in conjunction with SmI_2 is required to achieve the reductive dimerisation of acetals.[144] Since it was first reported,[265] the SmI_2 mediated dimerisation of imines to diamines has been achieved with various forms of low valent samarium including Sm^0 and catalytic iodine,[67] $SmBr_2$,[22] salt free $Sm(OTf)_2$[26] and SmI_2/NiI_2.[52] Since this last system does not promote the pinacol coupling of non-aromatic ketones, cross coupling reactions between aromatic aldimines and non-aromatic ketones are possible. As with Barbier allylation reactions, imines bearing chiral auxiliaries can dimerise to give diamines with high levels of asymmetric induction.[266]

Amino alcohol functionality can also be generated through the coupling of carbonyl compounds and other C=N functionality including hydrazones[267] and oximes.[241,268–271] Both inter- and intramolecular versions are known with the latter proceeding with very good diastereoselectivity (Scheme 36). With oximes, concomitant reduction of the N–O bond occurs if water is present as a co-additive. In a related reaction, alkyl ketones combine with phenanthroline although not with pyridine or isoquinoline.[240] Nitriles are generally too unreactive to couple efficiently with ketyl radicals unless the reactivity of the SmI_2 is enhanced photochemically.[272] Even then efficient cyclisation is limited to five-membered rings. However, more recently, Zhang and co-workers have reported that both inter- and intramolecular ketyl nitrile couplings can be achieved using SmI_2 in refluxing THF.[273]



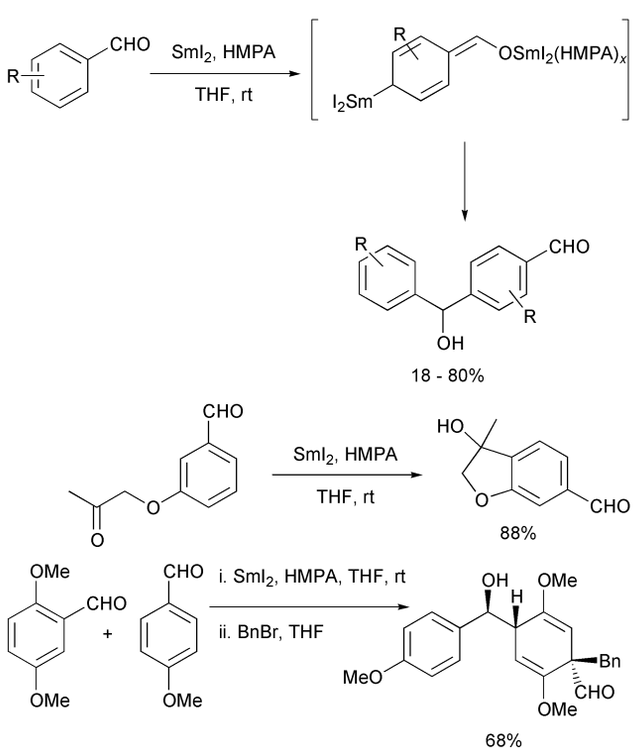
Scheme 36

Whilst intramolecular cross pinacol coupling reactions are facile, even for strained systems, intermolecular examples are more challenging.[274] In general, aldehydes and aromatic ketones react preferentially to give the homocoupled products. However, α-diketones and aldehydes cross couple efficiently[275,276] as do *N*-alkylphthalimides[277] or *N*-acyllactams[278] with both aldehydes and ketones. Further deoxygenation of pinacol products to give the alkene is rare although examples are known.[70,279] In general, other low valent coupling methods directed towards alkene synthesis are more efficient.[280] In this context, Takaki *et al.* have reported an interesting 'one pot' three component coupling, between acylphosphonates and two carbonyl compounds, to give β-hydroxyphosphonates with no evidence for alkene formation in the absence of additional base (Scheme 37).[281]



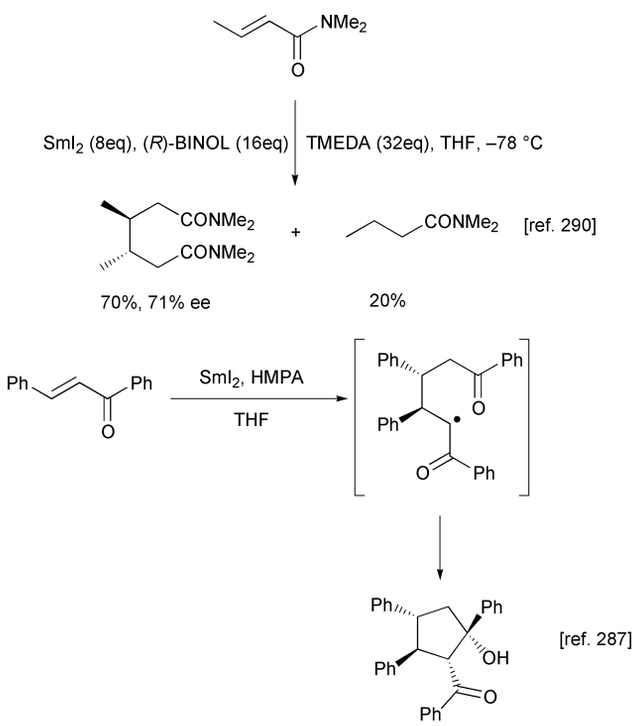
Scheme 37

In the presence of HMPA simple dimerisation of the ketyl radical is inhibited and alternative coupling pathways have been recorded for aromatic carbonyl compounds (Scheme 38).[282] These transformations proceed *via* a samarium dianion which can couple in both an inter- and intramolecular fashion to yield a varied array of skeletons. Alternatively the anionic intermediates can be trapped with a variety of other electrophiles. Related products derived by different mechanisms are formed from the intramolecular addition of ketyl radicals to arenes to afford hexahydronaphthalene products and the reaction of acylphosphonium salts to give biaryl ketones or diketones.[233,283] Similar transformations have subsequently been observed with a number of heteroaromatic substrates.[284–286]



Scheme 38

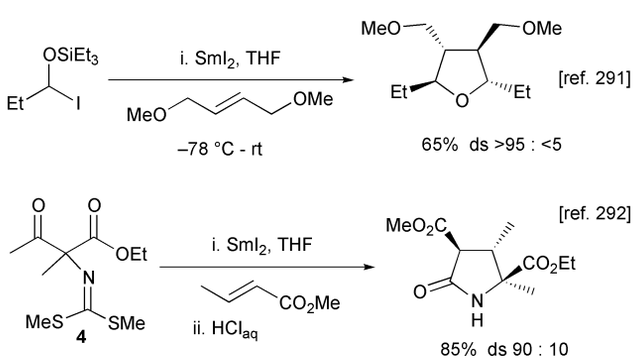
In a process closely akin to pinacol coupling, α,β-unsaturated carbonyl compounds can undergo hydro-dimerisation through conjugate addition of the β-radical to a second molecule of the starting material.[287–289] This process can be rendered enantioselective through the use of a large excess of BINOL as a chiral additive,[290] whilst, in the absence of a proton source, reduction of the α-keto radical then generates an enolate and cyclisation to the observed cyclopentane products occurs (Scheme 39).



Scheme 39

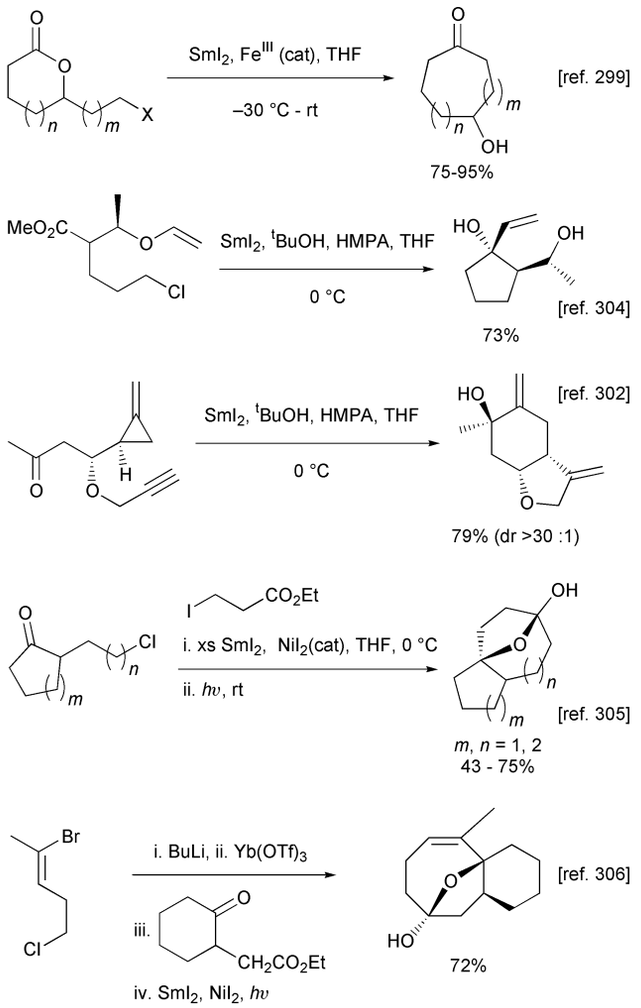
2.4.5 Miscellaneous C–C bond forming transformations

Reduction of iodohydrins with SmI_2 leads to the unusual generation of non-stabilised carbonyl ylides which can react with a range of dipolarophiles.[291] Samarioazomethine ylides are produced in the one electron reduction of β-ketoester **4** and can be trapped to provide efficient access to pyroglutamate derivatives (Scheme 40).[292]



Scheme 40

Radical mediated fragmentation of small rings initiated by one electron transfer from low valent lanthanide is a facile process. Cyclopropanes,[293–297] cyclobutanes,[298] epoxides[299] and β-lactones[51] are all cleaved by this process. Unstrained systems may also undergo similar fragmentation provided that the correct alignment of radical and acceptor orbitals is possible.[300,301] This has been widely exploited in the ring contraction of carbohydrates to carbocycles, *vide supra*. Ring expansions are also possible (Scheme 41) and these represent simple examples where the resulting radical (or anion if reduction is faster) may be employed as part of a cascade sequence.[302,303] These sequenced reactions can occur in various orders involving radical–anionic, anionic–radical or anionic–anionic processes. This area of Sm(II) chemistry has been recently reviewed by Molander and Harris[3] and more recent work in this area has considered even more complex compilations of lanthanide mediated processes (Scheme 41).[304–306]



Scheme 41

3 Lanthanide(III) mediated transformations

First finding use as NMR shift reagents, lanthanide(III) salts have become reagents of choice for many Lewis acid catalysed processes providing high levels of activity combined with broad solvent tolerance, including water, and the scope for asymmetric catalysis. There have been a number of reviews in this area.[307–309]

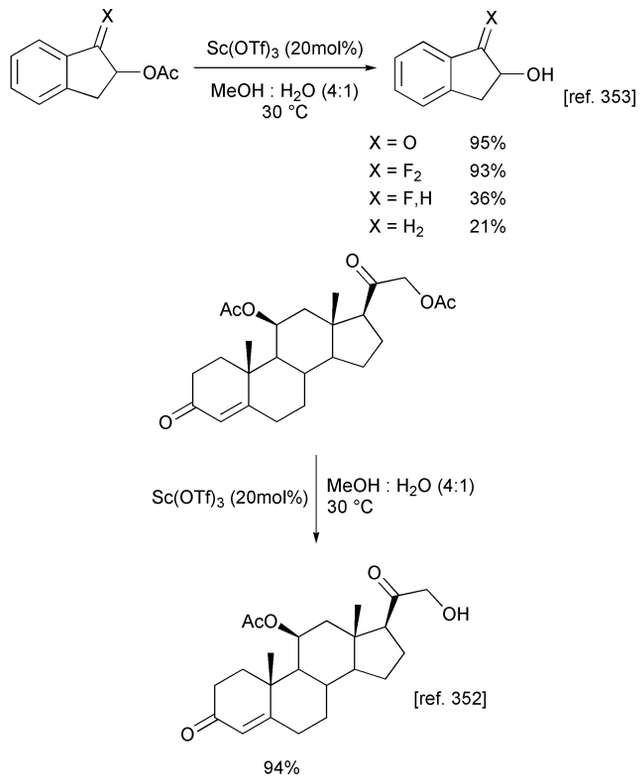
Although not strictly a lanthanide, scandium salts have similar reactivity profiles and, in general, owing to its smaller ionic radius it exhibits higher activity.[310] The reactivity can be tuned by suitable choice of lanthanide and counter ion. For example, a study of the effectiveness of rare earth trihalides as catalysts for the MPV (Meerwein–Ponndorf–Verley) reduction has shown that activity increases with ionic size and that, of the common salts, the triflate provided greater tolerance to water.[311] Similarly, in the hetero Diels–Alder reaction of Danishefsky's diene with salicylaldehyde derivatives the stereochemistry varied as a function of ionic radius.[312] One problem with scandium salts is that since there is no common source and there are difficulties with isolation and separation from the ores they are somewhat expensive. $YbCl_3$ is considerably cheaper, more readily available and can catalyse a similar array of reactions including aldehyde allylation and the Diels–Alder reaction of

unactivated dienes.[313,314] The drawback is that anhydrous conditions are required, although more water tolerant triflate salts are known. Since drying hydrated salts is not efficient, simple preparations of these anhydrous lanthanide salts have been developed.[315–318]

Various strategies have been introduced to enhance the activity and facilitate recovery of these rare earth catalysts.[319] For example, immobilisation of lanthanide salts onto a mesoporous silicate provides an efficient heterogeneous catalysts for heteroatom Diels–Alder reactions with no leaching being observed, even after 6 cycles.[320] Other immobilisation strategies have been reported, including those based on silica gel,[321] Nafion and poly(acrylonitrile),[322–325] although these seem not to exhibit the same levels of activity as the monomeric species. Solutions to this problem have been proposed through the use of microencapsulated scandium triflate.[326] A limitation of all these polymeric supports is the poor performance in water. This can be circumvented through the use of a colloidal system generated from the combination of the lanthanide Lewis acid and a surfactant, sodium dodecyl sulfate.[327] Alternatively, modified water compatible polymers (and dendrimers) have been developed which exhibit enhanced handling profiles relative to the colloidal particles.[328,329] Whilst PEG solubilised $Ln(OTf)_3$ complexes have been developed, at the time of writing,[316] the soluble polymer approach to supported Ln(III) catalysts does not yet appear to have been explored.

Higher activity in Ln^{3+} catalysis is achieved though the application of high pressures,[330] ionic liquids as solvents,[331] or more simply by using the salts of superacids. In general, these are fluorinated acids as they have the low pK_a required for catalytic activity.[332–334] More recently Waller and Barrett have introduced triflide salts $[C(SO_2CF_3)_3]$ and corresponding perfluorinated derivatives $C(SO_2R_f)_3^-$ as even more powerful Lewis acid catalysts for Friedel–Crafts acylation reactions,[335] the nitration of deactivated arenes using a stoichiometric amount of nitric acid[336–338] and the debenzylation of benzyl ethers, esters and amides.[339] Mechanistic studies have indicated that the lanthanide ion enhances the Brønsted activity of the nitric acid through binding of the nitrate conjugate base.[340,341] An additional benefit to the use of these perfluorinated acids is the increased solubility in a fluorous phase solvent and supercritical carbon dioxide which facilitates recycling of the catalyst.[342,343]

The direct acylation of alcohols can be achieved using acetic acid and a catalytic amount of $Ln(OTf)_3$.[344] In a related fashion, the use of $Sc(OTf)_3$ alone can promote a very efficient acylation of alcohols with anhydrides. Interestingly, a mixed anhydride can be generated *in situ* through the use of a *p*-nitrobenzoic acid and this method can be extended to give macrocyclic lactones in high yields.[345] A modification of this approach using a $Sc(OTf)_3$–DMAP combination permits the efficient esterification of tertiary alcohols without the need for generation of an active acylating agent.[346] Both amines and alcohols are efficiently acylated using a range of vinyl esters.[347] In a related process ketones can be directly converted to the corresponding ester by means of a tandem MPV reduction–acylation protocol catalysed by $Ln(OTf)_3$ in the presence of isopropenyl acetate.[348] Very low loadings of a complex yttrium alkoxide provide an efficient and selective acylation of amino alcohols,[349] whilst diols can be selectively monoacylated in the presence of $LnCl_3$.[350] The selectivity depends on the lanthanide ion and with chiral acylating agents a moderately successful desymmetrisation may be realised. In contrast, in the presence of water, $Sc(OTf)_3$ promotes the selective hydrolysis of esters possessing a proximal binding group (Scheme 42).[351,352] This promotion of reactivity is attributed to a strong chelating effect with the scandium ion. A similar enhancement of activity is observed for esters which have proximal CF_2 or CF_3 groups[353] and related Ln–F coordination is believed to be involved in the Ln(III) activation of glycosyl fluorides.[354–356] Lanthanide salts,

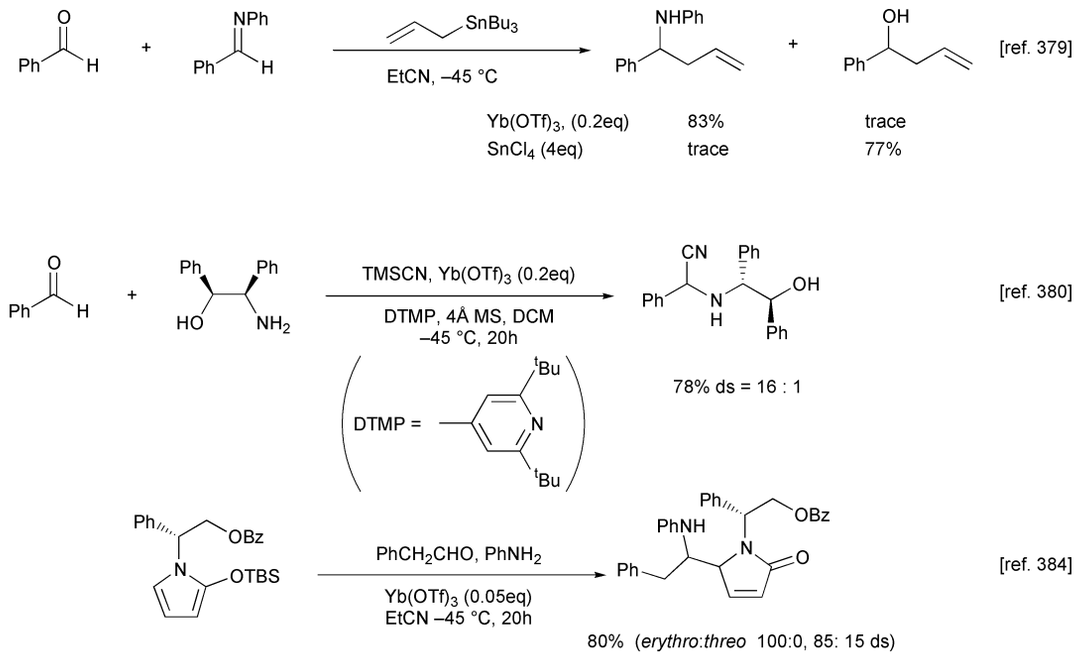


Scheme 42

most commonly the triflates, have also been shown to be effective promoters of other glycosylation protocols,[357] trityl ether hydrolysis,[358] various Friedel–Craft protocols,[359,360] the silylation of alcohols with methallylsilane,[361] the decarbonylation of electron-rich aldehydes,[362] and the diazoalkane insertion reactions of OH, SH and carbamate NH bonds.[363]

Allylation of aldehydes with allylsilanes[313,364] and stannanes[316] is promoted by lanthanide salts. With the stannanes, the addition of one equivalent of benzoic acid has been shown to dramatically enhance the reaction rate by sequestering the tin salts and regenerating the active lanthanide triflate.[365] Only substoichiometric amounts of lanthanide triflates are required for the propargylation of aldehydes with allenylstannanes[366] whilst an efficient Prins cyclisation is noted in the reaction of aryl aldehydes with but-3-enol.[367] Catalytic Lewis acid activation of the carbonyl group by lanthanide salts has been used to effectively promote, amongst others, glyoxalate ene reactions,[368] oxazoline formation from esters,[369] Michael reactions,[370] Tishchenko reductions of β-hydroxy ketones,[371] and Baeyer–Villiger oxidations.[372] In the last of these, related to Barrett's observations, TfOH is also capable of the same acceleration but, in contrast to the use of $Sc(OTf)_3$, rigorously anhydrous conditions are required.[373]

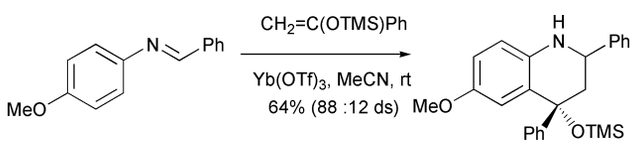
The aldol reaction continues to be an active area for lanthanide catalysis. Owing to the highly oxophilic nature of the ion, lanthanide chloride complexed enolates can give very high levels of selectivity under kinetic conditions.[374] In contrast the more active triflates, notably $Yb(OTf)_3$, can provide access to the thermodynamic aldol products.[375] These catalysts have been widely exploited to enhance Mukaiyama type aldol reactions between acetals and silyl enol ethers. In many cases the prior formation of the acetal is not required and the parent carbonyl compound may be used directly. Importantly, and in contrast to more classical Lewis acids, in the presence of $Ln(OTf)_3$, aldimines react in preference to aldehydes with a range of nucleophiles including silyl enol ethers (and ynolates), allylstannanes,[376] phosphites[377] and cyanide.[378–382] This reactivity profile can be exploited to allow the generation of the imine *in situ*, *i.e.* a one pot multicomponent coupling reaction[383,384] (Scheme 43). Further extension of this strategy to allow the



Scheme 43

generation of the imine from an acetal using *in situ* lanthanide triflate catalysis is also possible.[385] Other C=N functionality can be employed in these aza-aldol reactions including cyclic imines,[386] hydrazones[376] and nitrones.[387]

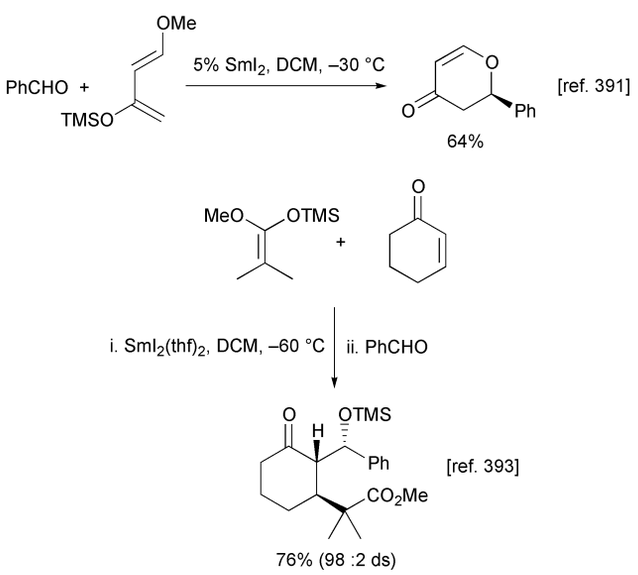
In related processes, ketene acetals give simple imino aldol products whilst styrenes, in the presence of $Yb(OTf)_3$, and TMSX (X = Cl or OTf) give good yields of the homoallyl amine.[388] In contrast, the reaction of arylimines with enol ethers is promoted by $Yb(OTf)_3$ to give aza-Diels–Alder adducts (Scheme 44).[389]



Scheme 44

Other lanthanide catalysts for these and related transformations have been reported. Notably, the use of alkoxy samarium diiodides, generated *in situ*, have proved to be excellent promoters for a range of transformations including aldol condensations, Michael additions, Diels–Alder cycloadditions, ene reactions, epoxide opening reactions *etc.* (Scheme 45).[390–393]

Despite the use of SmI_2 in the catalyst preparation these are believed to be Lewis acid catalysts as, in the non-coordinating solvents employed, the reduction potential of Sm(II) is significantly lower whilst the Lewis acidity is enhanced. Further evidence for this viewpoint is obtained from the observations that (i) as the reactions are initiated, the blue colour of SmI_2 is immediately dissipated to give the characteristic yellow colour associated with Sm(III) salts; and (ii) no difference in rate between these processes and those using preformed Sm(III) complexes can be detected. Of more practical relevance, the iodide salts are significantly more effective than other counterions. Similar observations have been recorded for the imino-aldol reactions in which SmI_3 functioned more effectively than did $SmCl_3$.[394,395] In contrast, related aldol reactions catalysed by Sm(II) menthoxides are suggested to proceed *via* ketyl addition to the silyl enol ether although an Sm(III) promoted pathway cannot be ruled out.[396] Sm(III) enolates are generated in the reaction of α-haloketones with SmI_3 and may be trapped with a variety of electrophiles.[175–177,397,398] A combination of Sm(II) and Sm(III) Lewis acid catalysis promotes the tandem aldol-

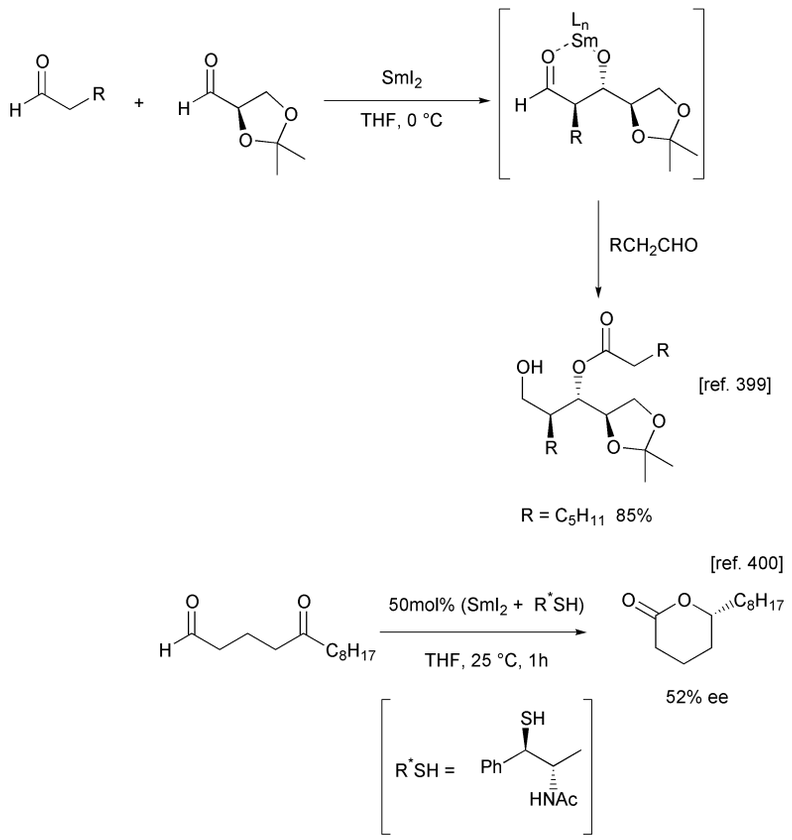


Scheme 45

Tishchenko reaction.[399] Developments of this sequence have included catalytic asymmetric versions using sub-stoichiometric SmI_2 and a chiral thiol (Scheme 46)[400] or a complex yttrium alkoxide in the presence of a salen ligand.[401]

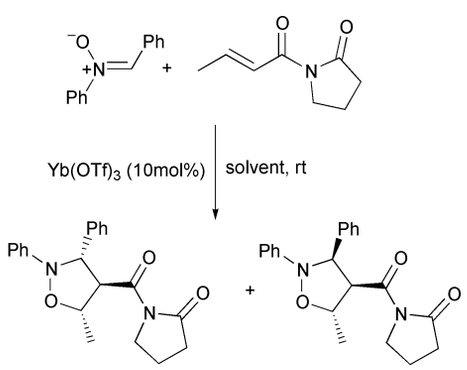
Related transformations of imines, formally catalysed by SmI_2, have also been reported. These include reactions with epoxides to give 1,3-oxazolidines[402] and nitroalkenes providing a one pot multi-component route to pyrroles.[403,404]

Give the tolerance of the catalysts to water many of the lanthanide triflate enhanced processes can be carried out in aqueous media.[405–407] Problems can arise in that many of the nucleophilic species, *e.g.* silyl enol ethers, are not particularly stable to these conditions. One elegant solution is to carry out the process in the presence of sodium dodecyl sulfate. This surfactant promotes the formation of micelles which allows imines to be formed and react with silyl enol ethers with minimal hydrolysis.[408] Further refinements to this strategy have seen the use of scandium trisdodecyl sulfate as the surfactant and this produces a heterogeneous but highly active colloidal suspension.[327,409] In a similar fashion to that described above, multiple component condensation processes can be conducted under aqueous conditions.[410]



Scheme 46

As described above, lanthanide triflates are excellent promoters of various cycloadditions. The reactions are generally very tolerant and can be carried out in a range of solvents, both organic and aqueous, as well as on a solid phase support.[411,412] Very low loadings are needed and there is no need for rigorously anhydrous conditions, although in some cases the nature of the solvent can influence the selectivity (Scheme 47).[413] In a similar fashion to the imino aldol condensations, these aza-cycloaddition processes can be carried out in a multi component fashion,[411,414] and this concept has also been applied to lanthanide promoted reactions of imines with diazoesters,[414] and nitrones[415] (Scheme 48).



solvent			
MeCN	65%	21	79
PhMe	70%	91	9

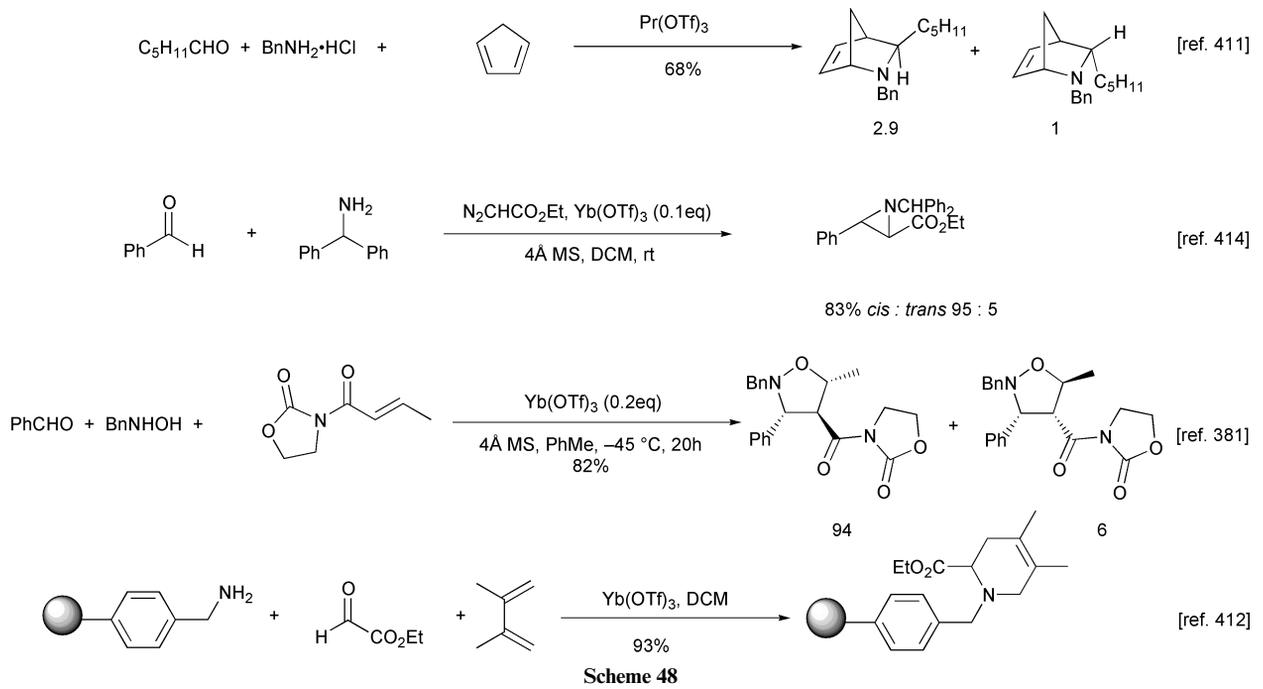
Scheme 47

In all these processes very high levels of absolute stereochemical control have been reported using a variety of chiral ligands. Foremost amongst these are the binaphthyl complexes developed by Kobayashi which also efficiently catalyse a large range of other transformations.[309] In a related approach the heterobimetallic complexes pioneered by Shibasaki and co-workers have been utilised to catalyse asymmetric numerous C–C, C–O and C–P bond forming processes.[416–421] An improved, simplified preparation of these La–BINOL catalysts has been published.[422] More recently, Shibasaki and co-workers have shown that such lanthanide heterobimetallic complexes, which normally function as combined Brønsted base–Lewis acid catalysts, operate solely as Lewis acids in non-polar solvents, catalysing simple Diels–Alder reactions with up to 86% ee.[423] As with $Ln(OTf)_3$, these multifunctional catalysts can be immobilised onto polymer supports, although the use of simple polymer bound BINOL ligands is not ideal and specifically designed 'linked BINOL' ligands are considerably more effective.[424]

Various other modified lanthanide binaphthyl systems have been studied.[425–430] Interestingly the mixed iodo binaphthyl Sm(III) complexes produce different enantiomers of a cyclopentadiene acrylate Diels–Alder adduct depending upon the reaction temperature (Scheme 49).[431]

In some cases the simple binaphthyl system is not sufficient. For example, Shibasaki reported that the Mannich reaction catalysed by a mixed Al–Li–BINOL complex in the presence of $La(OTf)_3$ was more effective than the La–BINOL system.[432] In a different approach Kobayashi and Kawamura have shown that 1,3-dipolar cycloadditions require not only binaphthyl but also a chiral amine to achieve high ee (79–96%).[433] Non-binaphthyl chiral ligands have been explored although, in general, these seem not to provide such efficient asymmetric catalysts.[43,372,434] Notable exceptions to this include the MPV reduction of aryl methyl ketones using an iodoaminoalkoxide Sm(III) complex reported by Evans *et al.*,[435] and the asymmetric cyanohydrin formation promoted by an $SmCl_3$-chiral bis(phosphoramidate) complex[436] or lanthanide Pybox catalysts.[437]

In contrast to the lanthanide salts of strong acids, lanthanide alkoxides are basic and can promote a variety of carbonyl transformations including aldol reactions, Michael reactions, cyanohydrin formation and carboxylation.[438–440] In many cases MPV reductions promoted by metal alkoxides can compete and in general the smaller lanthanides provide the greater aldol activity. Unlike the triflate salts, activity is compromised by



Scheme 48

T/°C	ee(*endo*)	Absolute configuration (major isomer)
20	18	1*S* 4*S* 5*S*
0	64	"
–28	81	"
–50	26	"
–60	30	1*R* 4*R* 5*R*
–78	34	"

Scheme 49

water and to overcome this the use of molecular sieves or higher coordination numbers is advocated. The latter is effectively achieved using polydentate ligands such as $PEG_{200}OH$.[425]

The related lanthanide amide complexes are more basic and are effective catalysts for carbonyl condensations, cyanohydrin synthesis and the Tishchenko reaction.[441,442] Attempts to generate asymmetric versions were not successful and, in general, reports of asymmetric $Ln(OR)_3$ or $Ln(NR_2)_3$ catalysis seem to be surprisingly few in number and modest in selectivity.[443,444]

The transmetallation of alkali metal of organometallic compounds of Group 1 and 2 with lanthanide salts, notably $CeCl_3$, has long been noted to provide more effective nucleophiles of particular use in reactions with more acidic substrates.[445,446] The synthetic applications of organocerium reagents has been recently reviewed.[5] Whilst $CeCl_3$ remains the reagent of choice for this function similar observations have been made for other lanthanide salts—for example, the combination of $Yb(OTf)_3$ and an organolithium can lead to much enhanced diastereoselectivities in additions to α-alkoxycarbonyl compounds.[447] Modified organocerium reagents have also been an area of some activity. Although somewhat substrate dependent it has been shown that the sterically more demanding ate complex $LiRCe(OR)_3$ gives the highest selectivities, albeit at the cost of lower reactivity. In many cases, to balance these two objectives, the optimal reagent is $RLi–ClCe(OR)_2$.[448] The corresponding amino complexes are too basic to provide effective nucleophiles.

The use of chiral alkoxides has been widely studied by Greeves *et al.* and the optimum ligands to date are those based on a TADDOL (α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol) structure.[449–451] There does not appear to be a single generic catalyst with selectivity depending on a number of inter-related factors including substrate, organolithium and TADDOL structure and the metal–ligand ratio.

These processes all require at least stoichiometric $CeCl_3$. However, the first examples of the catalytic use of $CeCl_3$ have been reported.[452] In this the nature and method of preparation of anhydrous $CeCl_3$ and the generation of "$RCeCl_2$" are crucial. Enhancements to both these areas have been reported.[450,453–455]

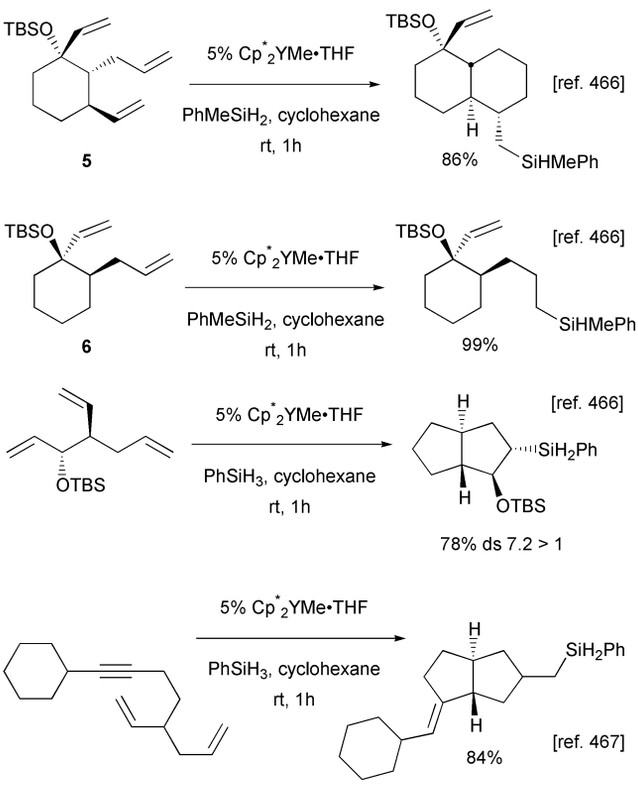
A specific method for the efficient generation of "$MeCeCl_2$" has been published. This reagent combines efficiently with cyclic dialkylamides to give high yields of the corresponding ketone with no evidence for overaddition even in the presence of excess $MeCeCl_2$.[456] An excess of $MeLi–CeCl_3$ is required for optimal yields of addition to hydrazones[457,458] whilst in the addition to cinnamaldehyde imines good selectivity for 1,2-addition is observed with all the early lanthanides (La > Ce > Gd).[459] In this latter case, chiral imines give reasonable diastereoselectivity. Similar observations have previously been reported for the double addition to nitriles.[460] $CeCl_3$ promotes the nitrile-aldol reaction and related carbonyl condensation processes. In these, the intermediacy of a cerium enolate has been postulated although the possibility of simple Lewis acid activation cannot be excluded. In this context, there have been a number of reports detailing the use of $CeCl_3$ as a mild but effective Lewis acid, particularly in conjunction with sodium iodide.[461]

4 Lanthanocene complexes in synthesis

Over the past decade, a major synthetic application of lanthanide reagents has been the use of lanthanide based metallocene catalysis. These complexes catalyse a plethora of alkene (and alkyne) transformations including hydrogenation, hydrosilylation, hydroboration, hydroamination, isomerisations, oligomerisation and polymerisation.[462] A number of these processes may be carried out in an intramolecular fashion and if dienes

are employed these can be used to provide a wide range of carbocyclic and heterocyclic targets with high efficiency. There have been a number of review articles published on the structural, synthetic and mechanistic aspects of this area[463–465] and this section will simply consider some of the more recent developments.

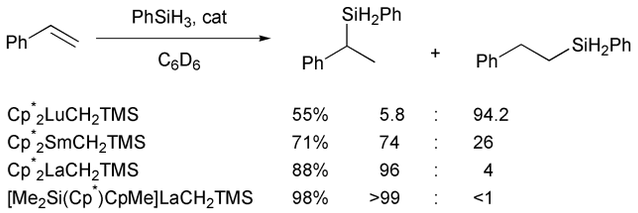
The reactivity in these hydrometallations of alkenes and alkynes is generally determined by the steric effects within the substrate, although alkynes and conjugated alkenes exhibit an electronic enhancement of rate. In general, these processes follow a predictable pathway with insertion occurring preferentially at the least hindered alkene. For example, cyclisation of the cyclohexane triene **5** proceeds *via* initial addition to the allyl group and subsequent addition to the relatively unhindered vinyl group. Consistent with this, a similar substrate **6** lacking this latter group does not undergo cyclisation and the simple hydrosilylated material is the only isolated product. In a similar fashion, more complex substrates containing multiple unsaturated linkages can be cyclised in a controlled manner to give polycyclic products in good yield (Scheme 50).[466,467] In general, for a given substrate the regioselectivity is a function of catalyst structure, *vide infra*. Enhanced control is realised in functional substrates where protic groups are metallated and the resultant complex undergoing intramolecular alkene insertion is dictated by the shape and length of the tether.[468–470]



Scheme 50

Whilst the normal olefin selectivity mirrors that of classical hydroboration and hydrosilylation, with attack occurring on the least hindered alkene with the lanthanide complex being sited at the terminal position, aryl substituents can lead to selective benzylic functionalisation.[471] This is attributed to the aromatic nuclei functioning as a Lewis base interacting with a proximal Lewis acidic lanthanide complex. In order for this interaction to occur the lanthanocene complex must be coordinatively unsaturated and in agreement with this theory high levels of benzylic substitution are observed with more open complexes (Scheme 51).

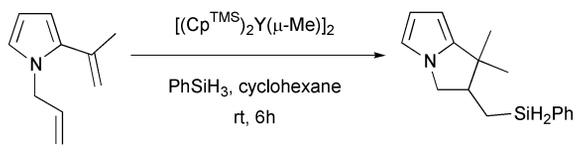
Similar results are seen in the cyclisation of substituted heteroaromatic dienes. Using $[(Cp^{TMS})_2Y(\mu\text{-Me})]_2$ as the catalyst precursor affords good yields of the cyclised products



$Cp^*_2LuCH_2TMS$	55%	5.8	:	94.2
$Cp^*_2SmCH_2TMS$	71%	74	:	26
$Cp^*_2LaCH_2TMS$	88%	96	:	4
$[Me_2Si(Cp^*)CpMe]LaCH_2TMS$	98%	>99	:	<1

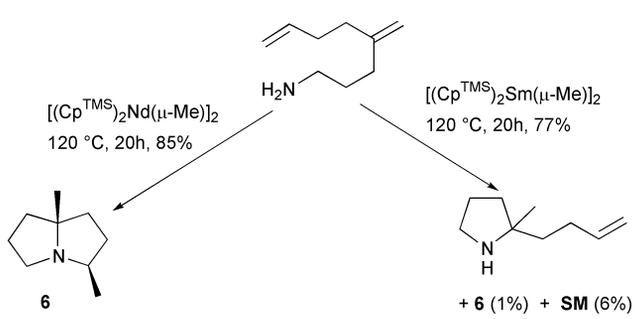
Scheme 51

even when a tertiary organometallic is a required intermediate (Scheme 52).[472] Similarly, in alkene hydrosilylation, larger more accessible lanthanide complexes tend to produce greater amounts of the secondary silane although not normally to the extent of providing synthetically useful selectivities.[473]



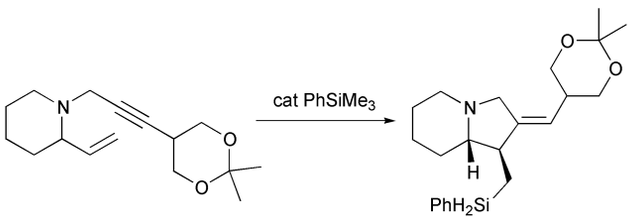
Scheme 52

Detailed studies on these hydrometallation processes have indicated that modulation of catalytic activity can be achieved through variation of lanthanide metal and ligand set. For example, one limitation has been that the cyclisation onto hindered alkenes can be slow relative to trapping of the intermediate hydrocarbyl. Modification of the ligand structure can be exploited to control reactivity with reduced substitution on the Cp ligand leading to efficient hydrosilylation of hindered olefins, albeit at the cost of reduced regioselectivity for monosubstituted alkenes.[471,474] This second insertion can be accelerated using larger lanthanide metals for which the co-ordination sphere is slightly more open (Scheme 53).[475] Alternatively, Marks and co-workers have reported that significantly higher activity in intramolecular hydroamination can be obtained with less sterically saturated ligand sets, $\{[Me_2Si(C_5Me_4)^tBuN]LnE(SiMe_3)_2$ $(E = N, CH)\}$.[476] Although the silicon bridged complexes, pioneered by Marks, exhibit excellent reactivity and selectivity profiles, practical applications of these are limited by the extreme air sensitivity of these complexes. Schumann and Molander have developed the chemistry of the bridged methyl complex $[(Cp^{TMS})_2LnMe]_2$ which shows moderate air stability and excellent reactivity. Consistent with other complexes, stability increases with decreasing ionic size reflecting the reduced accessibility to the metal centre.[477]



Scheme 53

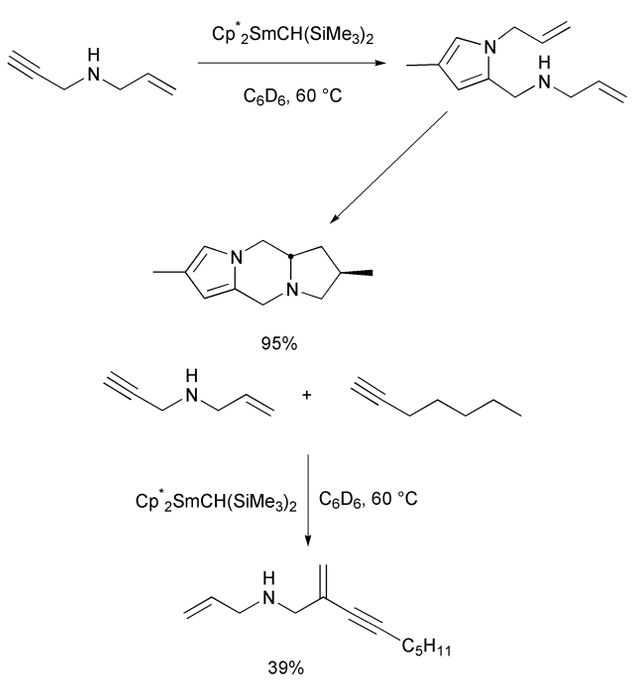
In a related fashion, the cyclisation–silylation of nitrogen containing enynes can be compromised by the formation of a relatively stable chelate between the lanthanide metal and nitrogen atom. Switching from Cp*YMe·THF to the smaller, more sterically crowded Lu analogue reduced the ability of the nitrogen to bind to the metal and restored high acitivity (Scheme 54).[478] Similar effects have been noted in the silylation of oxygen containing alkenes. A particularly useful facet of the hydrosilylation–cyclisation sequence is the ability to convert the



Scheme 54

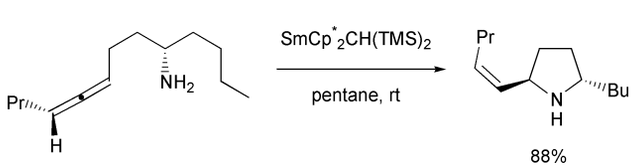
resultant silane into an alcohol. However, in some cases this oxidation can prove problematic. Enhancements of this process can be realised through the use of fluoroalkylsilanes which not only undergo facile oxidation but also provide accelerated insertion into the lanthanide–carbon bond relative to $PhSiH_3$.[479]

In aminoalkyne hydroamination, larger cations lead to lower turnover numbers attributed to a more facile complexation by a second amine and intermolecular protonolysis. Such intermolecular hydroamination has been exploited to provide an intermolecular hydroamination–cyclisation strategy giving access to complex pyrroles (Scheme 55).[480] The presence of an amine in both components is beneficial as attempts to cross couple a propargylic amine with hexyne afforded only poor yields of the desired amine.



Scheme 55

Aminocyclisations have been extended to include aminoallenes (Scheme 56), which permits the preparation of pyrrolidines and piperidines containing unsaturated α-substituents suitable for further elaboration. These substrates appear to possess intermediate reactivity when compared with the analogous aminoalkenes and alkynes.[481–483]



Scheme 56

More recently, Marks has extended this work to allow the hydrophosphinylation–cyclisation of phosphinoalkenes and alkynes.[484] Although significantly slower (5–10 ×) than the corresponding aminocyclisations, both primary and secondary phosphines are suitable substrates and exhibit a similar dependence of rate on catalyst structure. In contrast to hydroamination, $Cp_2Ln(CHTMS)_2$ precatalysts are not suitable giving only slow initiation and effective rates require the more active Cp_2LnH to be used.

Whilst the Marks complexes can be be prepared in enantiomerically pure forms this involves the separation of highly air sensitive diastereoisomers by selective recrystallisation. Advances in this area are complicated by the dependence of the diastereoselectivity of complexation on the lanthanide ion size.[485] Bercaw and co-workers have shown that *ansa*-metallocenes can be prepared directly in a single enantiomeric form using a binaphtholate tether.[486] However, these do not function with comparable asymmetric efficiency to the Marks systems.[487]

Finally, cationic lanthanide complexes have long been known to provide effective promoters of olefin polymerisation. Molander and Rzasa have demonstrated that these highly Lewis acidic reagents can function as catalysts for small molecule organic synthesis efficiently promoting heteroatom Diels–Alder reactions.[488]

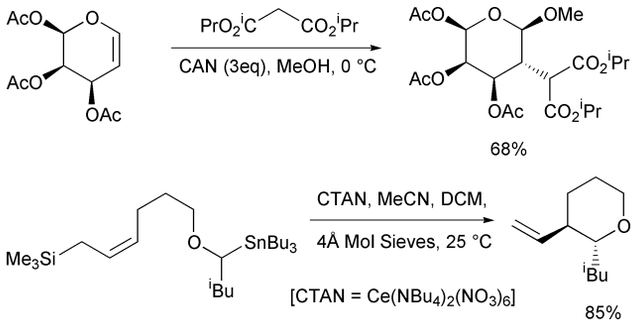
5 Lanthanide(IV) reagents

Oxidative processes mediated by lanthanide reagents continue to be dominated by CAN. Owing to its mild and relatively non-acidic nature, this reagent continues to find widespread application in functional group manipulations. For example, acyl hydrazides may be converted directly to the corresponding ester on reaction with CAN in the presence of an alcohol;[489] whilst the selective monodebenzylation of *N*,*N*-dibenzylamines,[490] hydrolysis of 1,1-diacetates[491] and the cleavage of trityl ethers,[492] TBS ethers,[493] cyclic acetals and ketals,[494] Boc carbamates and *tert*-butyl esters[495] also occur efficiently. The addition of azide to cinnamic esters, acids and α,β-unsaturated ketones to give azidocinnamates, β-azidostyrenes and α-azido-α,β-unsaturated ketones, respectively, is enhanced by the presence of CAN.[496] With simple styrenes the addition of iodine to the reaction mixtures provides an efficient access to azidoiodides.[497]

The application of CAN to benzylic oxidation has long been recognised and recent advances in this area have produced methods for the oxidation of electron-rich dimethylbenzylamines[498] and alkylpyrroles to the corresponding formyl derivatives.[499–501] More powerful chemoselective oxidants than CAN, notably $Ce(OTf)_4$ and $Ce(OMs)_4$ have been introduced. The former is now commercially available and a number of applications have been reported.[502]

Oxidation of acidic C–H bonds to generate synthetically useful radical cations is relatively facile using Ce(IV) reagents. Malonates and acetoacetamides undergo simple air oxidation to give tartronic acids and oxamates respectively.[503,504] The former are postulated as intermediates in the dimerisation of malonates[505] and other β-dicarbonyl compounds mediated by CAN.[506,507] The cation generated in these processes may be utilised in a wide variety of C–C bond forming reactions with nucleophilic alkenes and this has been employed to provide entry to a wide variety of carbocyclic and heterocyclic products. Whilst many of these radical transformations can be mediated by other transition metal salts, notably $Mn(OAc)_3$, CAN offers several advantages in view of its lower acidity and higher reactivity at lower temperatures. For example, this has been exploited in the addition of malonates to glycals, with minimal competing Ferrier processes, and in the oxidative cyclisation of α-stannyl ethers (Scheme 57).[508,509]

Many of these transformations require large quantities of CAN and efforts to circumvent this have been investigated. The oxidative dimerisation of β-dicarbonyl compounds can be



Scheme 57

realised using sub-stoichiometric quantities of $Ce(NO_3)_3$ in an electrochemically assisted process, although problems can arise with high levels of competing oxidation.[510] Other approaches to the use of catalytic Ce(IV) have been explored. For example, 10 mol% of CAN in the presence of bromate salts as the stoichiometric oxidant provides similar results to the use of a full equivalent of CAN.[511] CeO_2 has been proposed as a cheaper alternative to CAN and may be used as a catalyst in the presence of $NaBrO_3$ or Ru–O_2.[512,513] Both systems are heterogeneous and therefore offer considerable practical advantages. Other immobilised versions of CAN have been developed for a variety of oxidative transformations.[491,514,515]

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