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# Synthetic methods

## Part (ii): Oxidation and reduction methods

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5 This Report highlights advances in some of the most commonly used oxidation and reduction reactions, focusing on the literature from 2009. The review is subdivided in a similar fashion to the author's previous review in this area.<sup>1</sup> In the field of oxidation, salen complexes, oxaziridinium salts and carbohydrate-derived dioxiranes continue to attract much attention in  
10 the context of alkene epoxidation. Elsewhere, a significant disclosure from Que is the first system able to catalyse the dearomatising dihydroxylation of an arene<sup>59</sup> and Katsuki has reported the use of a dimeric Fe "salan" (reduced salen) complex to catalyse oxidative dimerisation of naphthols, affording BINOLs that are themselves ligands for asymmetric synthesis.<sup>132</sup>  
15 In the field of reduction, the development of novel chiral phosphine ligands remains a prominent subject of research for alkene hydrogenation. There is sustained interest in oxazaborolidines as catalysts for ketone reduction and several methods for direct asymmetric reductive alkylation are reported. A general trend seen is increased activity in the area of green chemistry and  
20 there have been many reports on the use of nanoparticles as catalysts.

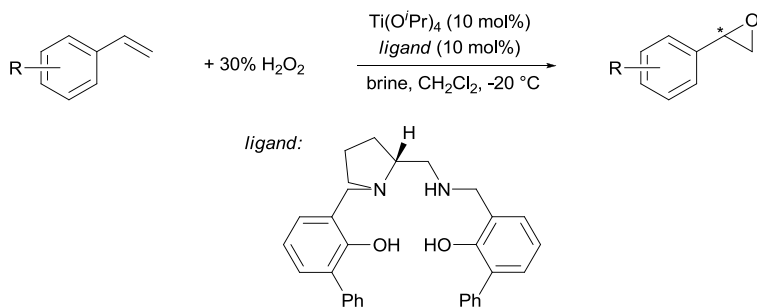
### 1 Oxidation reactions

#### 1.1 Alkene epoxidation

2009 has seen the publication of several reviews pertaining to alkene epoxidation, including those from Lattanzi (on electron-poor alkenes with aminoalcohol  
25 organocatalysts<sup>2</sup> and on diarylprolinol catalysts<sup>3</sup>) and from Colonna (on use of polyileucine catalysts<sup>4</sup>). Beller has also written a book chapter on iron-catalysed epoxidation with hydrogen peroxide.<sup>5</sup>

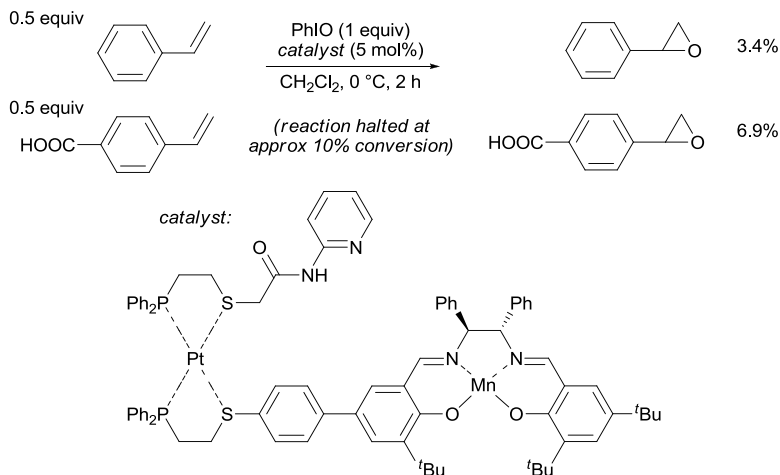
Sustained activity in the area of salen complexes for asymmetric epoxidation led to numerous publications in 2009. Corey and co-workers have studied the origin of  
30 enantioselectivity in the Jacobsen–Katsuki epoxidation and propose a two-step mechanism proceeding *via* a carbocation intermediate.<sup>6</sup> Two reports from Katsuki concerning the use of reduced salen ligands were published; in the first,<sup>7</sup> a partially reduced "salalen" titanium complex (reported previously) is shown to catalyse effectively the epoxidation of  $\beta$ -arylalkenylsilanes, with *e.e.* values of >99%  
35 observed for every substrate examined. In the second,<sup>8</sup> Katsuki introduces new "salan" (reduced salen) ligands derived from proline (Scheme 1). Titanium complexes of these have been shown to epoxidise substituted styrenes and 2-vinylnaphthalene with *e.e.* values of 96–98%.

Other modified salen ligands have also been reported. Schatz, Mirkin and co-  
40 workers have detailed their preparation of a bimetallic Pt<sup>II</sup>–P,S tweezer complex that combines a Mn<sup>III</sup>–salen epoxidation catalyst with an amidopyridine receptor.<sup>9</sup> The emphasis of the work is on the ability of the catalyst to epoxidise preferentially substrates bearing a carboxylic acid recognition group (Scheme 2).



Scheme 1

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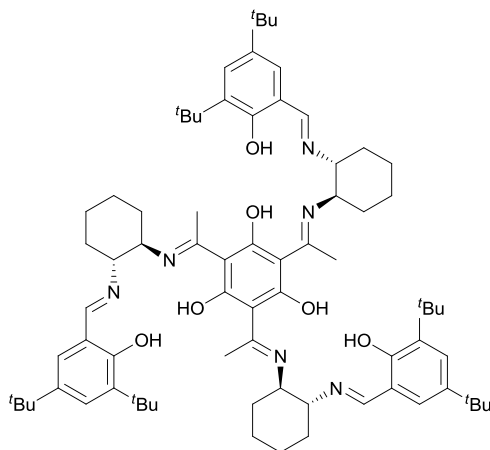


Scheme 2

Elsewhere, Glaser has described<sup>10</sup> the synthesis of a trimeric  $C_3$ -symmetric ligand (Scheme 3), with which only modest *e.e.* values have been obtained, and Zhao has described<sup>11</sup> carbohydrate-derived salen ligands (Scheme 4), with which *e.e.* values up to 87% have been obtained. Plattner has also reported a modification of the Jacobsen–Katsuki epoxidation involving the introduction of pyridine *N*-oxide additives in fluororous solvents.<sup>12</sup>

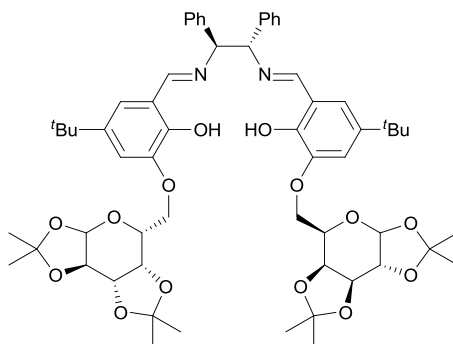
The field of carbohydrate-derived organocatalysts for oxone<sup>®</sup>-mediated asymmetric epoxidation continues to progress. Shi has introduced a new fructose-derived diacetate catalyst (Scheme 5a)<sup>13</sup> that effects the epoxidation of *trans* and trisubstituted olefins including electron-deficient  $\alpha,\beta$ -unsaturated esters and certain *cis* olefins; *e.e.* values up to 98% are obtained and the catalyst is reported to demonstrate enhanced activity and less susceptibility to Baeyer–Villiger decomposition with respect to the previously reported bis(acetonide) catalyst (Scheme 5b). The Shi group subsequently reported<sup>14</sup> an  $\alpha,\alpha$ -dimethylmorpholinone catalyst (Scheme 5e) which combines structural features of their previously reported catalysts (Scheme 5b-d). The catalyst is effective for *trans* and trisubstituted olefins and up to 97% *e.e.* has been achieved. Other substrate classes are addressed in further Shi group publications: epoxidation of nonconjugated *cis* alkenes with oxazolidinone-containing catalysts (Scheme 5c) in up to 92% *e.e.*<sup>15</sup> and a comparison of catalysts (Scheme 5a-c) for epoxidation of fluoroalkenes in up to 93%

*e.e.*<sup>16</sup> Amongst the various uses of Shi's catalysts reported in 2009, noteworthy is a report from Lim, Hill and Myers, describing a method for the preparation of monosilylated *trans*-1,2-diol derivatives from cyclic ketones in an enantio- and diastereocontrolled manner.<sup>17</sup> In addition, McDonald has detailed an enantio- and regioselective synthesis of squalene tetraepoxide, a putative biosynthetic precursor of many triterpenoids.<sup>18</sup>



Scheme 3

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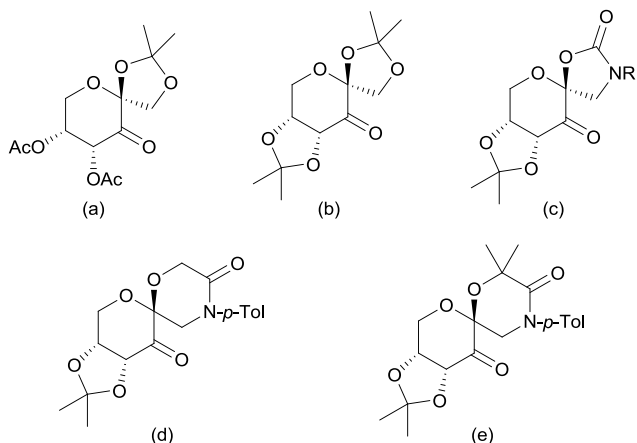
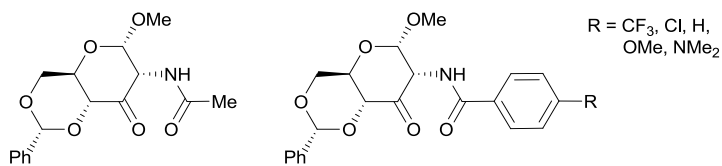
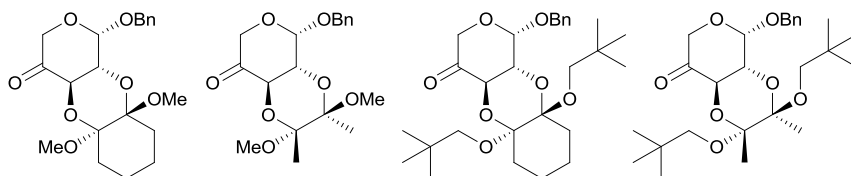


Scheme 4

The Davis group have targeted 1,1-disubstituted olefin substrates, which have typically undergone epoxidation with low *e.e.* values when catalysed with such carbohydrate-derived ketones. They report the synthesis and evaluation of a series of glucosamine ketone catalysts (Scheme 6).<sup>19</sup> In the event, epoxidation of 1,1-disubstituted olefins was effected with up to 42% *e.e.*, although values up to 82% *e.e.* were obtained for other substrate classes.

Elsewhere, the Shing group have disclosed their studies on arabinose-derived catalysts containing a cyclohexane-1,2-diacetal (Scheme 7).<sup>20</sup> Enantioselectivities obtained with these catalysts vary significantly with catalyst and substrate combination; in the best instance, epoxidation of a *trans* stilbene proceeded with 89% *e.e.*

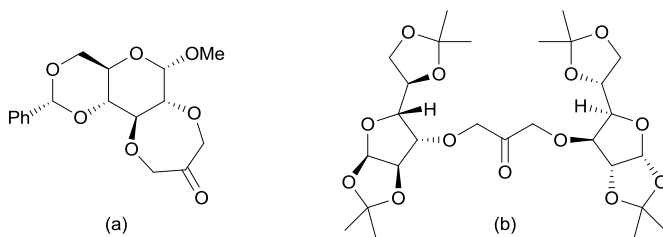
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**Scheme 5**

**Scheme 6**


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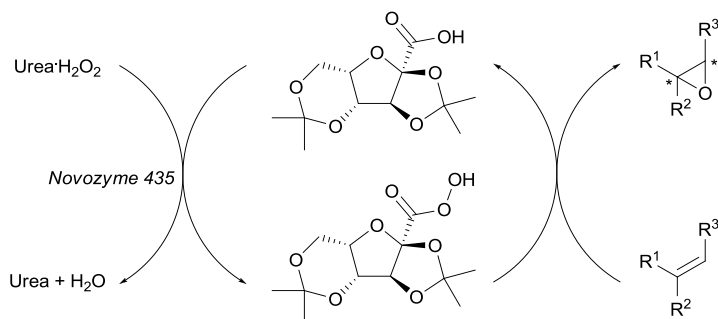
**Scheme 7**

Glucose-derived ketones have been evaluated by Vega-Pérez, Iglesias-Guerra and co-workers,<sup>21</sup> who found that whereas a dioxacycloheptanone catalyst (Scheme 8a) was able to effect epoxidation of aryl alkenes with *e.e.* values up to 74%, a gluco-functionalised acetone derivative (Scheme 8b) imparted no enantiomeric excess in the corresponding transformations, which they ascribe to the acyclic nature of this ketone, in contrast to all ketones discussed above.


**Scheme 8**

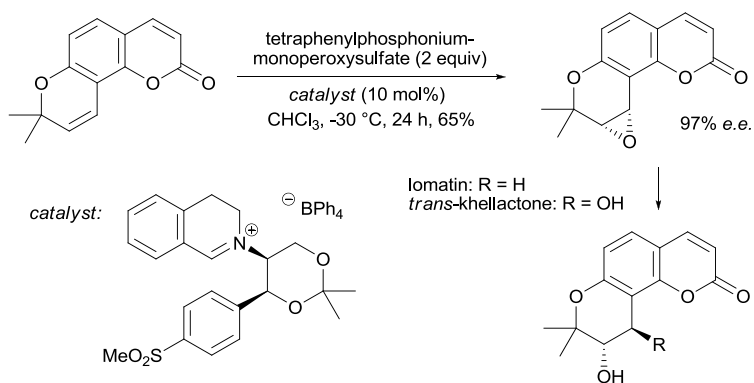
105 Goswami *et al.* have reported a carbohydrate-derived organocatalyst for alkene epoxidation that differs from those above in that it employs urea–hydrogen peroxide

complex as terminal oxidant instead of oxone<sup>®</sup>. Generation of the active oxidant, a peracid, is itself catalysed by a lipase; *e.e.* values of 35–71% are reported for various alkenyl substrates (Scheme 9).<sup>22</sup> Similarly, the Li group have reported in-situ peracid formation with a lipase and urea–hydrogen peroxide complex; in this instance, the peracid precursor is an achiral lactone, affording racemic epoxide products.<sup>23</sup>



Scheme 9

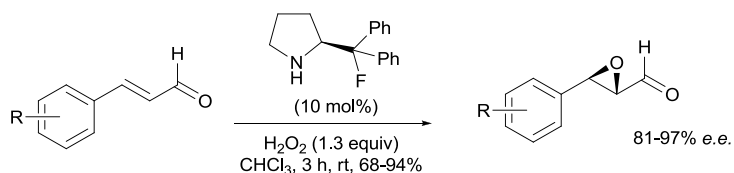
Other modes of organocatalytic alkene epoxidation have also seen fruitful developments in 2009. In the area of oxaziridinium-mediated epoxidation, the Page group have published a full account of their development of binaphthalene-derived iminium ion catalysts.<sup>24</sup> They have also employed a related iminium ion catalyst in concise asymmetric syntheses of lomatin and *trans*-khellactone,<sup>25</sup> (Scheme 10). Thus far, monoperoxsulfates such as oxone<sup>®</sup> have been the terminal oxidants typically employed for oxaziridinium-mediated alkene epoxidation, but a significant disclosure from the Page group is the finding that sodium hypochlorite may be used as an alternative terminal oxidant of lower cost and with greater atom economy.<sup>26</sup> Concurrently, the Lacour group have continued their investigations in this area and have published their findings on the importance of the iminium counteranion and also the influence of *N*(*sp*<sup>2</sup>)-*C*(*sp*<sup>3</sup>) rotamers in determining the *e.e.* values of the products.<sup>27</sup>



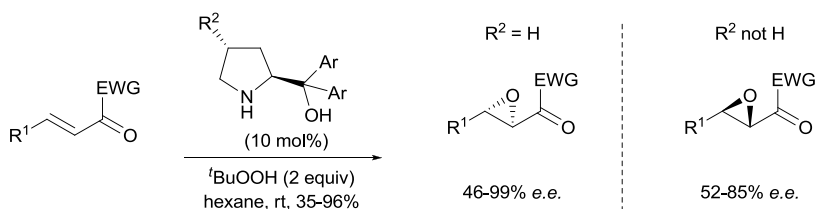
Scheme 10

Several reports concern iminium ion catalysis in a slightly different context: epoxidation of enals and enones by means of nucleophilic peroxide addition. A significant disclosure from Gilmour pertains to the exploitation of the fluorine-

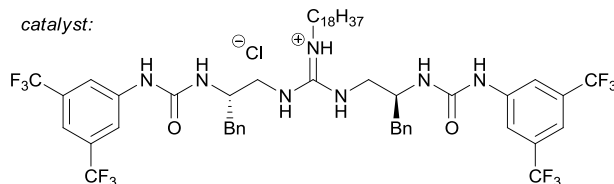
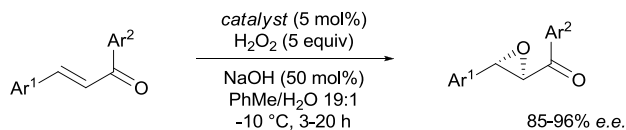
iminium ion *gauche* effect to obtain good enantioselectivities.<sup>28</sup> A pyrrolidine bearing an exocyclic  $\beta$ -fluorine catalyses the epoxidation of cinnamaldehydes, citral and cyclohexen-1-carboxaldehyde in up to 97% *e.e.* due to the strong conformational preference for a *gauche* N-C-C-F torsional angle (Scheme 11). The Zhao group have evaluated the catalytic abilities of several novel diarylprolinols which extend their previous work by incorporating substitution not only on the arenes but also on the pyrrolidine ring.<sup>29</sup> The substrates evaluated were  $\beta,\gamma$ -unsaturated  $\alpha$ -ketoesters; the introduction of a substituent (and hence a stereocentre) on the pyrrolidine ring led to the *opposite* sense of enantioinduction and it was determined that the catalyst which afforded the highest *e.e.* was in fact one in which the pyrrolidine ring remained unsubstituted (Scheme 12). Another report of organocatalytic epoxidation worthy of comment is from Nagasawa, who has reported a bifunctional urea-guanidinium catalyst which is able to effect the epoxidation of chalcones with *e.e.* values up to 96% by means of co-operative substrate and peroxide interactions.<sup>30</sup>



Scheme 11



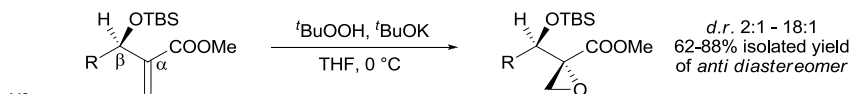
Scheme 12



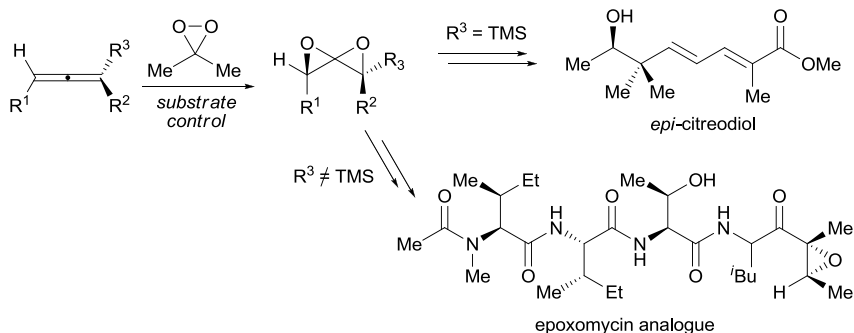
Scheme 13

Several noteworthy reports of diastereoselective epoxidation under substrate control appeared in 2009. Švenda and Myers have published a mechanistic study on the nucleophilic epoxidation of methyl  $\alpha$ -methylene- $\beta$ -*tert*-butyldimethylsilyloxy-carboxylate esters (Scheme 14).<sup>31</sup> They outline the anti-selectivity obtained for structurally diverse substrates and present evidence obtained by isotopic labelling

studies that is suggestive of a concerted mechanism. Elsewhere, the Corey group have communicated evidence that  $\text{Cu}(\text{MnO}_4)_2$  effectively epoxidises trisubstituted steroid olefins by a nonconcerted pathway, demonstrating the applicability of this methodology to both  $\Delta^5$ -sterols and  $\Delta^7$ -sterols.<sup>32</sup> In addition, Williams has studied the DMDO-mediated formation of allene-derived spirodiepoxides, applying the methodology in the context of epoxomycin analogue synthesis.<sup>33</sup> The methodology has also been extended to encompass the stereoselective formation and regioselective opening of silyl-substituted spirodiepoxides (Scheme 15).<sup>34</sup>



Scheme 14



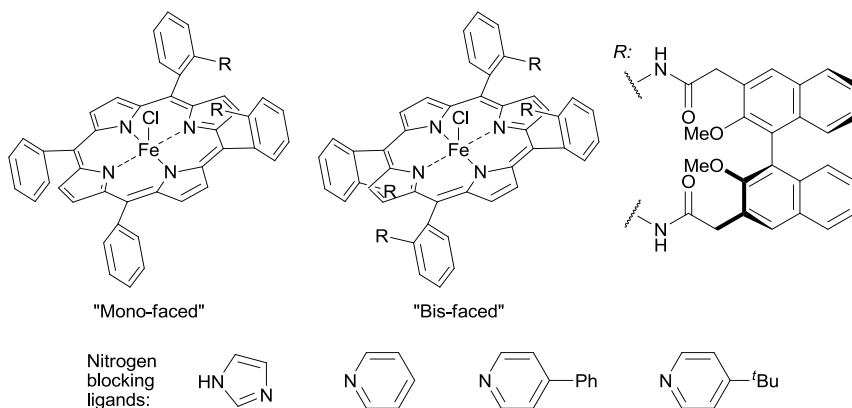
Scheme 15

In the area of biomimetic epoxidation catalysts, the Beller group has published a comprehensive account of the design and mechanistic evaluation of 1-aryl-substituted imidazolyl iron catalysts for hydrogen peroxide-mediated epoxidation.<sup>35</sup> They determined that the free 2-position of the imidazole ligand is essential for good catalytic activity and that both aromatic and aliphatic olefins can be epoxidised with defined and also *in situ* generated catalysts. Que, Costas and co-workers have published a study using  $^{18}\text{O}$  hydrogen peroxide labelling that revealed olefin-dependent discrimination between two  $\text{HO-Fe}^{\text{V}}=\text{O}$  tautomers when alkene oxidation was effected with non-heme iron catalysts they have described previously.<sup>36</sup> Xia, Sun and co-workers have examined a different metal, combining a chiral tetradentate nitrogen ligand with a manganese centre to catalyse hydrogen peroxide-mediated alkene epoxidation in up to 89% *e.e.*<sup>37</sup>

Several groups have reported porphyrin-based systems for alkene epoxidation in 2009. The Ren group have reported studies<sup>38,39</sup> on chiral mono and bis face-strapped porphyrins in conjunction with nitrogen blocking ligands as catalysts for asymmetric alkene epoxidation (Scheme 16). With iodosylbenzene as stoichiometric oxidant, *e.e.* values of up to 94% have been obtained. Separately, Ren, Yan and co-workers have reported phase-transfer of porphyrins by polypeptide-containing hyperbranched polymers and an (achiral) iron<sup>III</sup> porphyrin epoxidation catalyst.<sup>40</sup> Elsewhere, the Ji group report that use of  $\mu$ -oxo-bisiron<sup>III</sup> tetraphenylporphyrin as catalyst for aerobic alkene epoxidation effects an enhancement of TON with respect to mono-porphyrin systems.<sup>41</sup> Brudvig, Crabtree and co-workers have reported<sup>42</sup> a manganese porphyrin complex incorporating a molecular recognition functionality to favour alkene



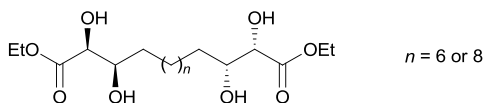
epoxidation over other modes of oxidation, in work that has conceptual parallels to that of Schatz and Mirkin.<sup>9</sup>



**Scheme 16**

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The Knight group have reported a useful modification of the Sharpless asymmetric epoxidation protocol, in which they employ a recoverable tartrate surrogate (Scheme 17).<sup>43</sup> In a model epoxidation of cinnamyl alcohol, the Knight diisopropyl tartrate. The major advantage is that the ligand can be recovered following a relatively simple work-up procedure.



**Scheme 17**

A use of asymmetric epoxidation technology in total synthesis from Deng merits attention.<sup>44</sup> The Deng group have established that catalytic LiOH effectively promotes the enantioselective epoxidation of Knoevenagel adducts using Seebach's TADDOH peroxide as stoichiometric oxidant. They proceeded to showcase this methodology with a synthesis of (–)-plicatic acid (Scheme 18).

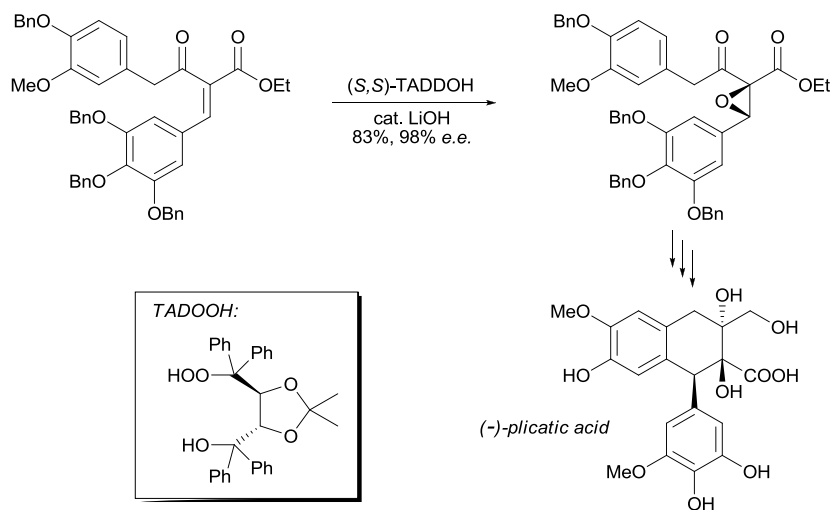
Another approach relying on the use of stoichiometric chiral organoperoxides to effect enantioselective epoxidation is due to Hamann and Liebscher.<sup>45</sup> They employed *gem*-dihydroperoxides to epoxidise 1,4-naphthoquinones with *e.e.* values up to 82% (Scheme 19).

Two additional disclosures from 2009 specifically concern the epoxidation of  $\alpha,\beta$ -unsaturated ketones. The Ding group have examined the use of catalysts derived from  $\text{ZnEt}_2$  and bis(BINOL) ligands (Scheme 20) and have obtained *e.e.* values up to 93% for  $\beta$ -aryl and  $\beta$ -alkyl substrates;<sup>46</sup> such values are comparable to those obtained by the organocatalytic approaches summarised in Schemes 11-13. The Rinaldi group have also reported the (racemic) epoxidation of  $\alpha,\beta$ -unsaturated ketones with  $\text{H}_2\text{O}_2$ , catalysed by simple aluminium salts and propose both ionic and radical mechanisms depending on the substrate employed.<sup>47</sup>

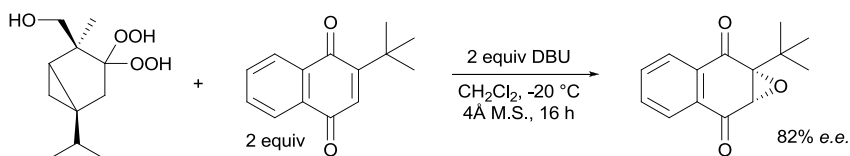
The Malkov group have examined the vanadium-catalysed epoxidation of allyl alcohols using a hydroxamic acid ligand (Scheme 21).<sup>48</sup> Specifically, they report

obtaining high *e.e.* values (up to 94%) employing water as solvent, which overcomes the ligand deceleration effect that hampered this transformation previously.

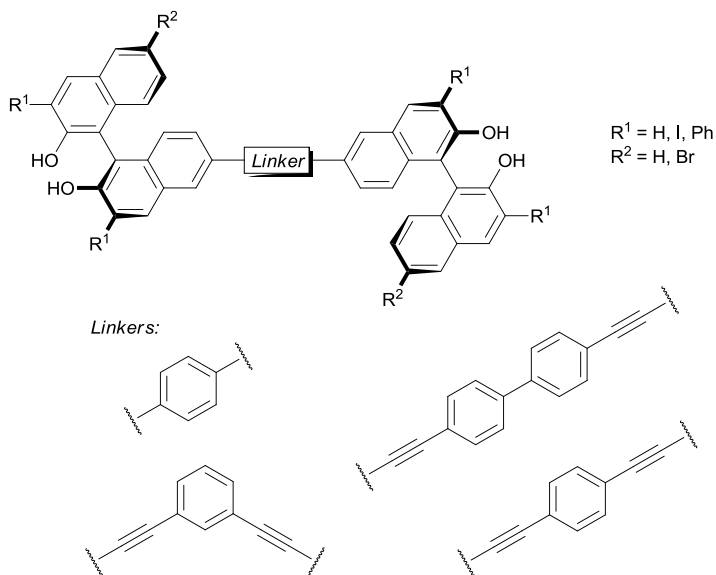
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Scheme 18

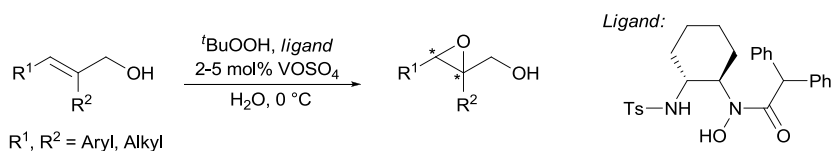


Scheme 19



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Scheme 20



Scheme 21

The Schmid group have reported a practical, scalable asymmetric styrene epoxidation based on improved *electroenzymatic* methodology.<sup>49</sup> The approach uses dioxygen as terminal oxidant and FADH<sub>2</sub> as co-factor. The concept of using electrical power for regenerating the co-factor is highly appealing, as it is certainly the cheapest reductant, but thus far such systems have displayed low reaction stabilities and slow electrochemical cofactor regeneration rates. In the current work, such restrictions have been overcome by careful choice of electrode design to address the rate-limiting mass transfer process. Under these conditions, as much as 20.5% of the utilised current could be channelled into (*S*)-styrene oxide formation.

Several reports on the use of metal clusters in alkene epoxidation appeared last year. The Haruta group have demonstrated epoxidation of propene with dioxygen, catalysed by Au clusters, potentially a process of great industrial significance.<sup>50</sup> Also, the Mizuno group have published a full paper on H-bond assisted epoxidation of allylic (and homoallylic) alcohols with H<sub>2</sub>O<sub>2</sub> and a selenium-containing dinuclear peroxotungstate.<sup>51</sup>

Other noteworthy disclosures last year include Ribas and Costas' report of a manganese complex that catalyses H<sub>2</sub>O<sub>2</sub>-mediated epoxidation of a broad range of alkenes.<sup>52</sup> Of particular interest here is the fact that their system exhibits an unusual preference for epoxidation of *trans*-stilbene over *cis*-stilbene. The Itoh group has reported an environmentally benign metal-free epoxidation of alkenes with oxygen and benzaldehyde under UV irradiation proposed to proceed *via* perbenzoic acid formation.<sup>53</sup> Qian, Shi and co-workers have reported an industrially relevant bioepoxidation, namely the stereoselective epoxidation of *cis*-propenylphosphonic acid by the newly isolated *Bacillus simplex* strain S101, to give the antibiotic fosfomycin.<sup>54</sup>

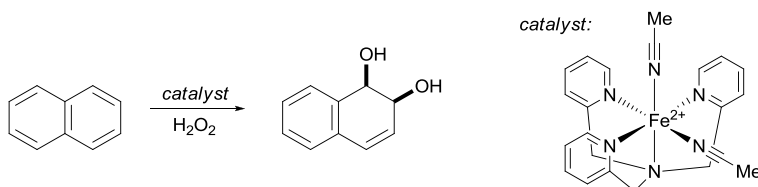
Finally, in the arena of mechanistic and theoretical epoxidation studies, Singleton and co-workers report transition-state geometry measurements from <sup>13</sup>C isotope effects in the context of oxaziridine-mediated alkene epoxidation.<sup>55</sup> Breslow and Friesner have undertaken quantitative DFT modelling of the *e.e.* values of dioxirane-catalysed alkene epoxidations and obtain good correlation with experiment.<sup>56</sup> Comba, Llobet and co-workers contributed a paper to a special edition of *Dalton Transactions* on the synergy between theory and experiment; their work contrasted the stereoselectivity obtained with iron and ruthenium catalysts in alkene epoxidation.<sup>57</sup> Tian *et. al.* have modelled the oxidation of propene with the V<sub>4</sub>O<sub>11</sub><sup>-</sup> cluster and conclude that it is highly selective for epoxidation over other modes of oxidation.<sup>58</sup>

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## 1.2 Alkene dihydroxylation

A highly significant disclosure<sup>59</sup> from the group of Que Jr. is the report of a non-heme iron complex that is able to catalyse the dihydroxylation of naphthalene with H<sub>2</sub>O<sub>2</sub> (Scheme 22). This reaction, which involves permanent disruption of the

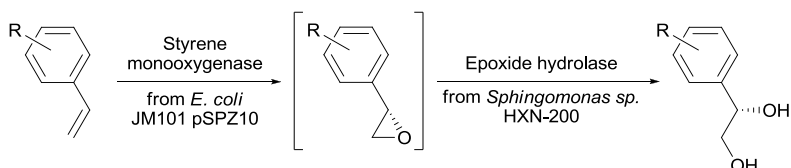
275 substrate's aromaticity, is a synthetic equivalent of the dihydroxylation effected by naphthalene dioxygenase enzymes, expressed by certain soil bacteria for the metabolism of arenes. Whilst such arene dihydrodiols derived by biotransformation have seen many uses in synthesis, the only synthetic equivalent to date has been the photolytic osmylation of arenes.<sup>60,61</sup> Que's selective, non-biocatalytic entry into  
 280 arene dihydrodiols will undoubtedly serve to further popularise these arene dihydrodiol building blocks in synthesis. (In conjunction with Rybak-Akimova, Que has also examined this and related catalysts for the *ortho*- and *ipso*-hydroxylation of benzoic acids.<sup>62</sup>)



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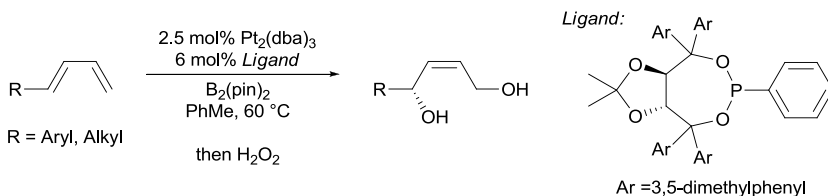
**Scheme 22**

Li and co-workers have reported a tandem dual biocatalytic process for the asymmetric dihydroxylation of aryl olefins.<sup>63</sup> The reaction employs a one-pot transformation of styrenes first into transient styrene oxides and then into the desired dihydroxylation products (Scheme 23). The presence of both an enantioselective  
 290 styrene monooxygenase and also a regioselective epoxide hydrolase in one pot obviates the need to isolate the intermediate epoxides.



**Scheme 23**

The Morcken group have reported an enantioselective 1,4-dihydroxylation of  
 295 dienes by means of Pt-catalysed diboration and subsequent oxidation with H<sub>2</sub>O<sub>2</sub> (Scheme 24).<sup>64</sup> Asymmetry is induced by means of a TADDOL-derived phosphonite ligand. Good yields (up to 92%) and *e.e.* values (up to 96%) are obtained for a variety of 1-substituted 1,3-diene substrates.

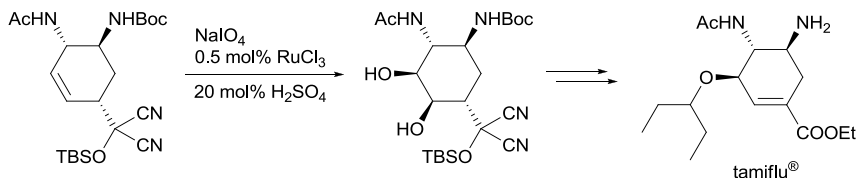


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**Scheme 24**

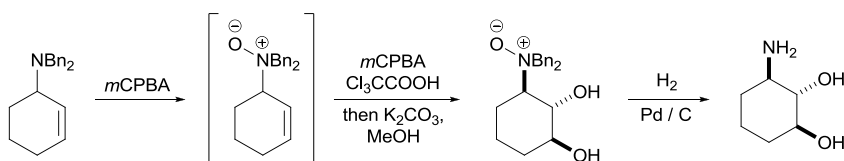
Three reports from 2009 touch on aspects of substrate control of stereochemistry in alkene dihydroxylation. Firstly, the Shibasaki group have published a full account of their synthetic studies towards tamiflu<sup>®</sup>.<sup>65</sup> Key to their attempts to circumvent the

need for a Mitsunobu inversion step (and hence the use of potentially explosive reagents) was a ruthenium-catalysed dihydroxylation under substrate control (Scheme 25).



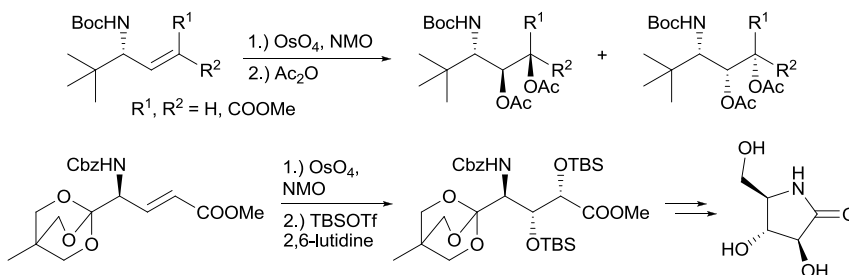
Scheme 25

Secondly, the Davies group have reported further on the use of allylic amines as substrates for directed dihydroxylation, showing that oxidation of 3-*N,N*-dibenzyl aminocyclohex-1-ene *N*-oxide with *m*CPBA in the presence of  $\text{Cl}_3\text{CCO}_2\text{H}$  is highly *anti*-selective.<sup>66</sup> After deprotection, 1,2-*anti*-2,3-*anti*-3-aminocyclohexane-1,2-diol is accessed in good yield (Scheme 26).



Scheme 26

Thirdly, the Kim group have also studied allyl amines, finding diastereoselectivity in such systems to be highly influenced by the position of an ester substituent. They have further elaborated an OBO ester-containing substrate<sup>67</sup> to a polyoxygenated  $\gamma$ -lactam target having glycosidase-inhibitory activity (Scheme 27).<sup>68</sup>



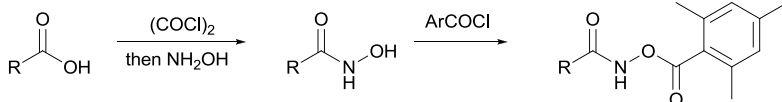
Scheme 27

Other noteworthy reports in the field of alkene dihydroxylation include Hormi's comprehensive study of the role of methanesulfonamide in Sharpless asymmetric dihydroxylation,<sup>69</sup> and Bowden's ingenious use of "thimbles" fabricated from polydimethylsiloxane to separate otherwise-incompatible Grubbs' catalyst and ADMIX.<sup>70</sup> Substrates are able to diffuse across the thimble wall, but the metal catalysts are not; the methodology thus makes possible one-pot tandem ring-closing metathesis followed by asymmetric alkene dihydroxylation.

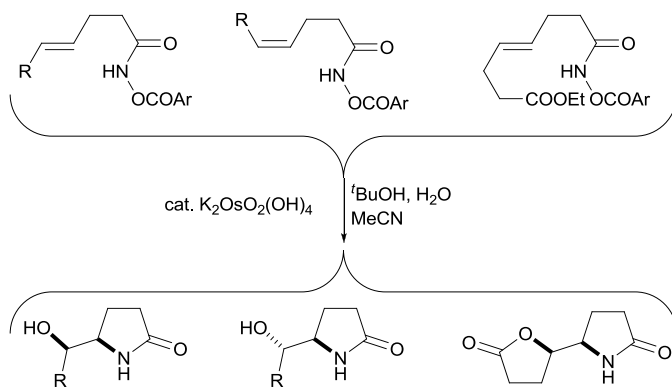
### 1.3 Alkene aminohydroxylation

The Donohoe group have continued to expand the synthetic utility of their tethered aminohydroxylation methodology in 2009. They report a tethered aminohydroxylation of amides, giving rise to lactams bearing an exocyclic hydroxyl group (Scheme 28).<sup>71</sup> The approach benefits from high-yielding preparations of the substrates and high diastereoselectivity in the cyclisation step. It should also be noted that the NOCOAr moiety acts as reoxidant, thus negating the need for an external terminal oxidant. The group has also extended the methodology to allow the synthesis of tetrahydrofurans bearing an adjacent oxazolidinone (Scheme 29).<sup>72</sup> This is achieved by means of two discrete oxidations occurring in one pot – first the tethered aminohydroxylation (catalysed by Os<sup>VIII</sup>), then an oxidative cyclisation to form a tetrahydrofuran (catalysed by Os<sup>VI</sup> formed in the first step).

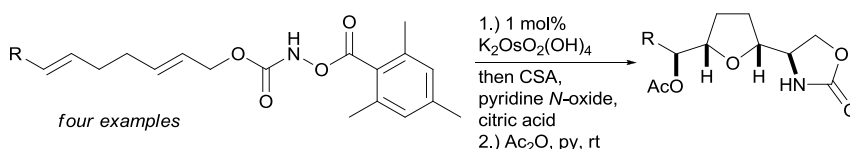
Substrate preparation:



Cyclative alkene aminohydroxylation:



Scheme 28



Scheme 29

Elsewhere, tethered aminohydroxylation methodology has been employed by two groups to access sphingosines: Castillón reports the synthesis of *D/L-erythro*-sphingosine<sup>73</sup> and Kumar reports the synthesis of *L-arabino*- and *L-xylo*-C<sub>18</sub>-phytosphingosines.<sup>74</sup> Two other reports concern the synthesis of non-natural amino acids by means of aminohydroxylation methodology: from McLeod<sup>75</sup> (homoserine derivatives) and from the Taylor group<sup>76</sup> (*erythro*- $\beta$ -hydroxyasparagine).

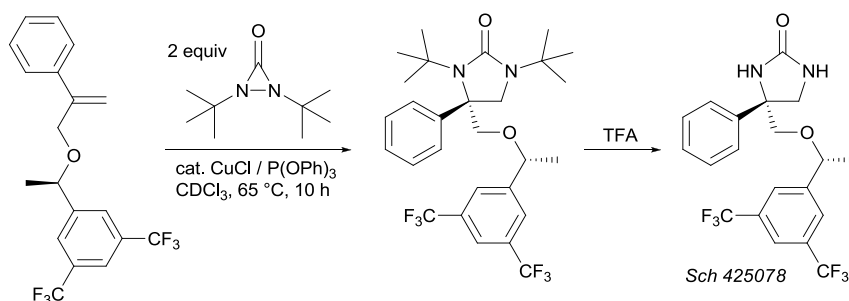
The Yoon group have further developed their methodology that employs oxaziridines for the aminohydroxylation of alkenes. Most recently this methodology

355 has been applied to carry out enantioselective aminohydroxylations of styrenes, catalysed by a homochiral Cu-box catalyst,<sup>77</sup> obtaining moderate to good *e.e.* values. Furthermore, the group disclose the finding that halide additives induce a pronounced increase in reaction rate for oxaziridine-mediated aminohydroxylation.<sup>78</sup> Evidence is presented in support of a radical reaction pathway.

360

#### 1.4 Alkene diamination

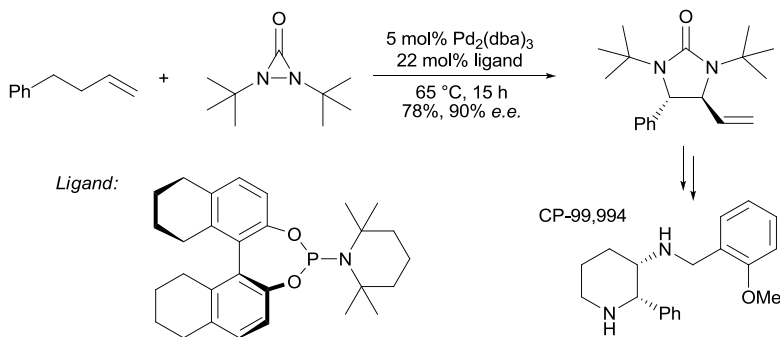
Two reviews concerned with diamination were published in 2009, from Goti<sup>79</sup> and from de Figueiredo,<sup>80</sup> both concerning metal-catalysed 1,2-diamination reactions. The Shi group have published extensively in the field of alkene diamination and in 365 2009 have reported syntheses of medicinally relevant targets by this methodology. They report the Cu<sup>I</sup>-catalysed diamination of 1,1-disubstituted alkenes and showcase this methodology with a synthesis of the potent NK<sub>1</sub> antagonist Sch 425078 (Scheme 30).<sup>81</sup>



370

**Scheme 30**

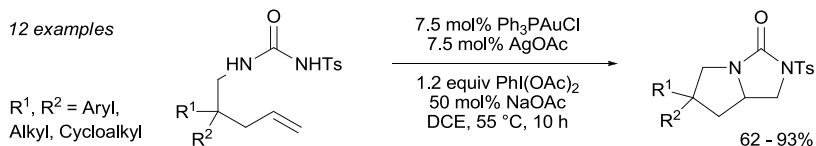
A different mode of oxidative diamination is employed in the Shi group's synthesis of the potent substance P receptor antagonist CP-99,994. In this case, Pd<sup>0</sup>-catalysed diamination with the same nitrogen oxidant (di-*tert*-butyldiaziridinone) gives rise to the regiochemically distinct product in which nitrogen has been 375 introduced at the allylic and homoallylic positions, leaving the alkene unaltered (Scheme 31).<sup>82</sup> The Shi group also report on their preliminary attempts to induce asymmetry in the copper-catalysed diamination of conjugated olefins, achieving up to 61% *e.e.* for this transformation so far.<sup>83</sup>



380

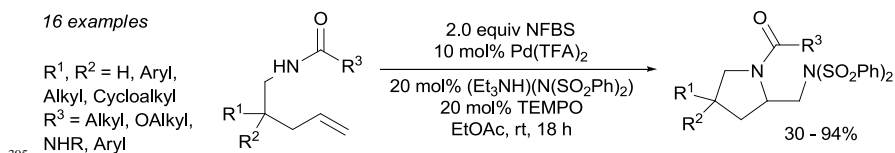
**Scheme 31**

The Muñiz group have expanded their diamination methodology to encompass a gold-catalysed oxidative intramolecular diamination reaction (Scheme 32).<sup>84</sup> To date previous reports from the group have centred on Pd catalysis of this transformation. Indeed, 2009 saw the publication of a theoretical DFT investigation into such Pd-catalysed intramolecular diaminations.<sup>85</sup>



Scheme 32

The Michael group have reported a related intra/intermolecular alkene diamination in which *N*-fluorobenzenesulfonimide acts as both oxidant and intermolecular nitrogen source (Scheme 33).<sup>86</sup> This was an unexpected mode of reactivity for NFBS, which was instead expected to effect alkene fluoroamination. Later in 2009, the Michael group published a full paper on this transformation,<sup>87</sup> including mechanistic studies (suggesting the intermediacy of a  $\text{Pd}^{\text{IV}}$  species) and extension of the methodology to alkene carboamination.

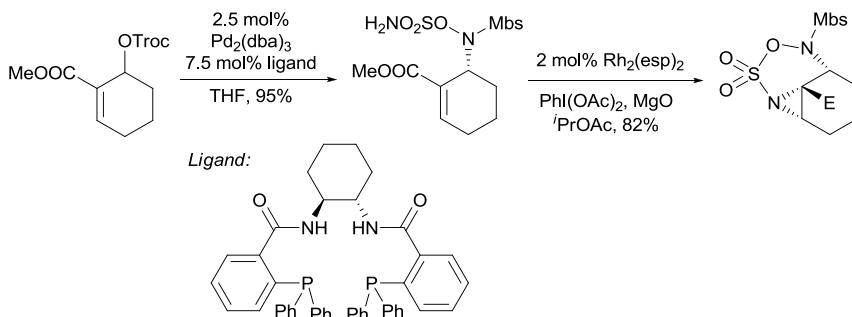


Scheme 33

## 1.5 Alkene aziridination

Reviews published in 2009 concerning aziridination include those from Gallo<sup>88</sup> (nitrene transfer mediated by porphyrin complexes), Minakata<sup>89</sup> (use of *N*-X bonds in aziridination) and De Kimpe<sup>90</sup> (2-methyleneaziridines).

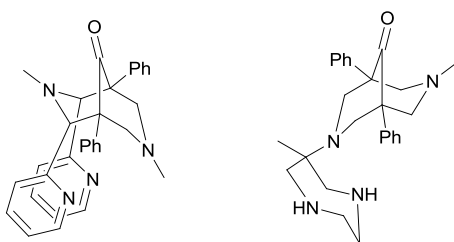
Trost, Du Bois and co-workers have demonstrated an alkene aziridination in which subsequent steps are catalysed by Pd and Rh respectively (Scheme 34).<sup>91</sup> Furthermore, both Du Bois<sup>92</sup> and Trost<sup>93</sup> have separately exploited alkene aziridination (Rh- and Cu-mediated respectively) as a key step in their syntheses of agelastatin A.



Scheme 34

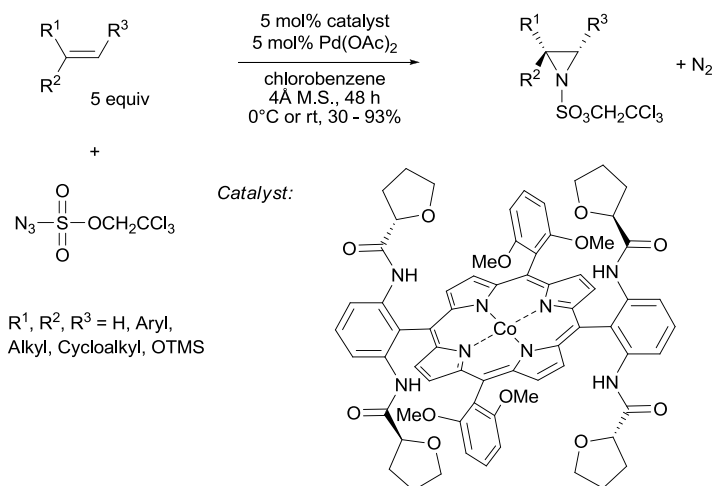


Elsewhere, Cu remains subject to much research in the context of alkene  
 410 aziridination catalysts. Nicasio, P. Pérez and co-workers have reported Cu<sup>I</sup>-catalysed  
 aziridinations with chloramine-T in ionic liquids<sup>94</sup> and the Chan group have reported  
 catalysis with CuI of aziridination of alkenes with iododisylbenzene as oxidant.<sup>95</sup>  
 Comba and co-workers have reported tetraaza-bispidine ligands for Cu-catalysed  
 aziridinations (Scheme 35),<sup>96</sup> Morales, J. Pérez and co-workers report the use of  
 415 various tris(2-pyridyl) ligands<sup>97</sup> and Lovely, Raskia Dias and co-workers report a  
 copper-ethylene triazapentadienyl complex<sup>98</sup> in the same context. As regards  
 enantioselective Cu-catalysed aziridination, the Hajra group report<sup>99</sup> an aziridination  
 / ring opening route to *trans*-2-amino-1-aryltetralins achieving *e.e.* values up to 92%  
 and Van der Eycken and co-workers investigated homochiral imidates as ligands,<sup>100</sup>  
 420 achieving *e.e.* values up to 51%. The decomposition of copper Schiff base  
 complexes used for aziridination has also been studied<sup>101</sup> and DFT modelling of Cu-  
 catalysed aziridination undertaken.<sup>102</sup>



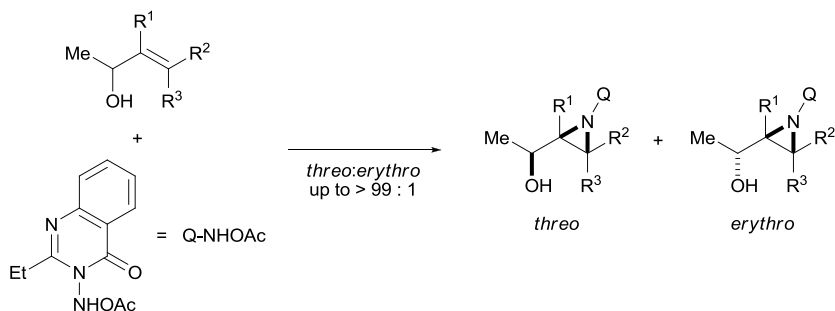
Scheme 35

425 Other metals have also been employed for alkene aziridination in 2009. Phillips,  
 Halfen and co-workers have published a mechanistic study on Fe-catalysed  
 aziridination.<sup>103</sup> The Zhang group reports an aziridination with trichloroethoxy-  
 sulfonyl azide (TcesN<sub>3</sub>), catalysed by homochiral Co-porphyrin complexes,  
 routinely achieving good *e.e.* values (up to 96%) for a wide variety of electron-rich  
 430 and electron-poor substrates (Scheme 36).<sup>104</sup> Yields were best for aryl alkenes.



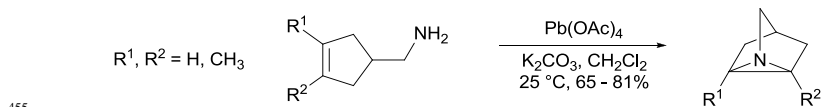
Scheme 36

In the field of substrate control of stereochemistry, Liu and co-workers have reported the Rh-catalysed aziridination of glycols (for which they observe high levels of diastereocontrol) to access aminoglycosides.<sup>105</sup> Pellacani and co-workers also report high stereocontrol in the bis(aziridination) of 2,3-dinitrodiene.<sup>106</sup> Kilic and co-workers have employed acetoxyaminoquinazolinone (“Q-NHOAc”) for the aziridination of allyl alcohols, which they find to be an extremely diastereoselective transformation (Scheme 37).<sup>107</sup> Good stereocontrol has also been achieved by the Hamada group, who report an enantioselective aziridination of  $\alpha,\beta$ -unsaturated aldehydes with a proline-derived organocatalyst, achieving up to 99.4% *e.e.* for  $\beta$ -aryl and  $\beta$ -alkyl substrates.<sup>108</sup>

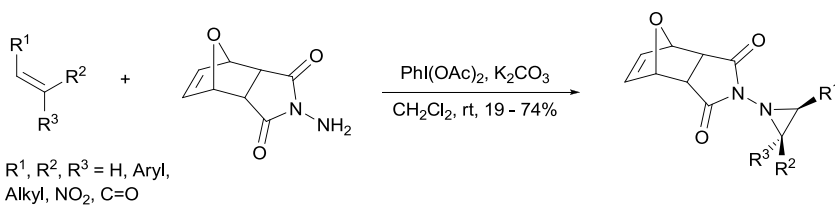


Scheme 37

Elsewhere, Coates has investigated the mechanism of a  $\text{Pb}(\text{OAc})_4$ -mediated intramolecular aziridination<sup>109</sup> (Scheme 38) and found the rate to be highly dependent on the degree of alkene substitution. Kunitzov and co-workers report the use of *N*-amino-*exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalimide as a highly reactive aminoaziridinating agent<sup>110</sup> (Scheme 39), having previously examined *N*-amino-phthalimide in this context.<sup>111</sup> Racioppi and co-workers have described the aziridination of enol ethers by means of photolysis of 2-azido-1,3-thiazoles<sup>112</sup> and the Minakata group have investigated the aziridination of fullerenes.<sup>113</sup> Loreto and co-workers have described a route to spiroaziridine-oxindoles,<sup>114</sup> and the Bottega group have studied the aziridination of unsaturated fatty acids.<sup>115</sup>



Scheme 38

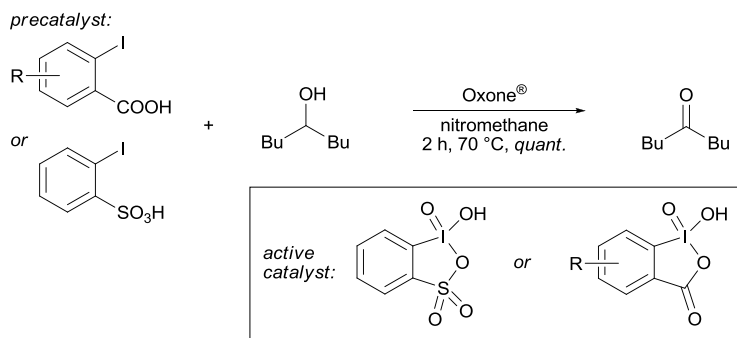


Scheme 39

460

## 1.6 Alcohol oxidation

Ishihara and co-workers disclose a significant advance in the field of hypervalent iodine-mediated oxidation.<sup>116</sup> In nitromethane, oxone<sup>®</sup>-mediated alcohol oxidation is effectively catalysed by iodoxybenzoic acids (IBXs) and it is reported that substituted IBXs are in many instances superior to the parent IBX for this role.<sup>465</sup> Additionally, iodoxybenzenesulfonic acid (IBS) was much more active than modified IBXs (Scheme 40). A great advantage of this approach is that simple readily-available iodoarenes serve as pre-catalysts, being oxidised to the active IBS/IBXs *in situ*. Also in the field of hypervalent iodine, the Zhang group have introduced a new I<sup>III</sup> reagent (1-chloro-1,2-benziodoxol-3(1H)-one) as stoichiometric oxidant in a TEMPO-catalysed oxidation of alcohols.<sup>117</sup><sup>470</sup>



**Scheme 40**

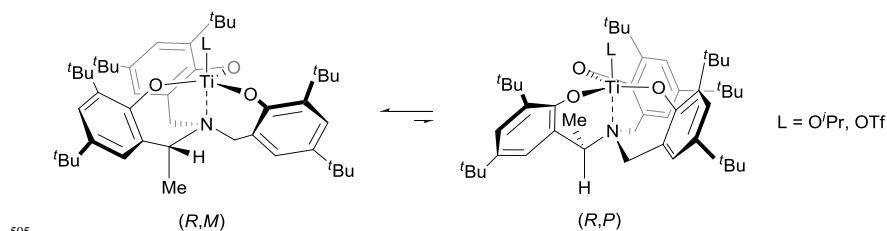
Au-catalysed alcohol oxidation has been the subject of active research in 2009 – reports on the use of Au nanoparticles as catalysts for aerobic alcohol oxidation have been forthcoming from Park and co-workers<sup>118</sup> and from Li, Hensen and co-workers.<sup>119</sup> In addition, the Garcia group report on liposomes formed by polymerisation of an imidazolium ionic liquid and their use as microreactors for Au-catalysed alcohol oxidation.<sup>120</sup> Finally, Chechik and co-workers have reported a detailed mechanistic study of Au-catalysed alcohol oxidation with various catalysts.<sup>121</sup><sup>475</sup><sup>480</sup>

Ru-catalysis is the subject of a report from the Katsuki group, who have optimised the design of a salen complex such that it displays excellent chemoselectivity for the oxidation of primary alcohols in the presence of secondary alcohols.<sup>122</sup> Zen and co-workers also report on a Ru-functionalised nickel hydroxide catalyst for highly efficient aerobic alcohol oxidations<sup>123</sup> and the Peng group have studied the catalytic activity of RuO<sub>2</sub>·xH<sub>2</sub>O / carbon nanotube catalysts for aerobic oxidation of benzyl alcohol.<sup>124</sup> In other developments, the Shimazu group report the activity of a Pd catalyst supported on Ni–Zn for aerobic alcohol oxidation<sup>125</sup> and Privalov has reported theoretical studies on phopshinoborane-mediated<sup>126</sup> and methyltrioxorhenium/H<sub>2</sub>O<sub>2</sub>-mediated<sup>127</sup> alcohol oxidation.<sup>485</sup><sup>490</sup>

## 1.7 Sulfide oxidation

Bull, Davidson and co-workers have reported a conceptually novel pseudo-C<sub>3</sub>-symmetric Ti triflate with propeller-like chirality as a catalyst for asymmetric sulfoxidation with organic hydroperoxides<sup>128</sup> The catalyst relies on point chirality of

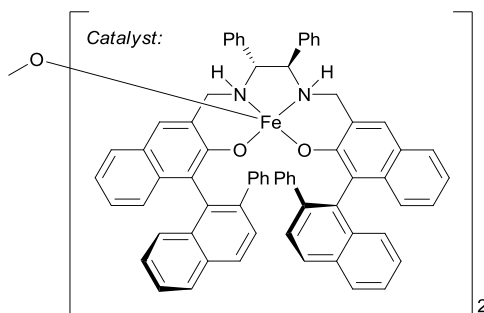
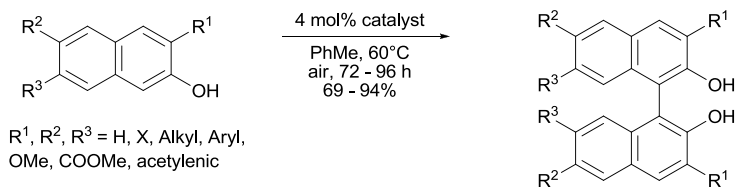
a single stereogenic centre to control the propeller chirality of its aryl rings (Scheme 41) and is able to effect sulfoxide formation from phenyl benzyl thioether in up to 47% *e.e.* Elsewhere, Burrows and co-workers have demonstrated the post-synthetic oxidation of sulfur-tagged metal–organic frameworks with DMDO,<sup>129</sup> and the Lattanzi group have reported a mild and highly chemoselective sulfide oxidation that relies on *N,N'*-bis[3,5-bis(trifluoromethyl)phenyl]thiourea as a hydrogen-bonding catalyst.<sup>130</sup> Additionally, Faber and co-workers have detailed the biooxidation of thioethers mediated by NADH:FMN-dependent oxidoreductases.<sup>131</sup>



Scheme 41

### 1.8 Other oxidations

The Katsuki group report an enantioselective oxidative dimerisation of 2-naphthols (Scheme 42), which will have applications in the synthesis of BINOL-type ligands for further asymmetric transformations.<sup>132</sup> Products having up to 96% *e.e.* have been obtained so far.



Scheme 42

515 Other reported oxidations that merit comment include the Quideau group's disclosure of an asymmetric hydroxylative phenol dearomatization by *in situ* iodine generation from chiral iodoarenes and *m*CPBA,<sup>133</sup> and the Moorthy group's report<sup>134</sup> of an IBX-I<sub>2</sub> redox couple for facile generation of IOH and I<sup>+</sup>.

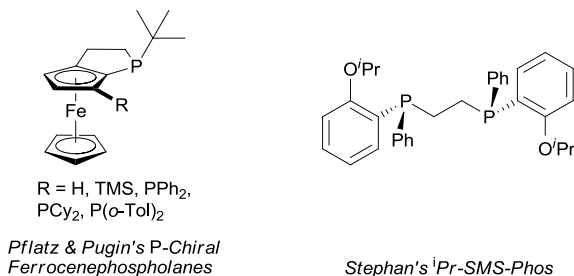
## 520 2. Reduction reactions

### 2.1 Alkene reduction

Reviews published in 2009 which are relevant to alkene hydrogenation include those from Stephan<sup>135</sup> (frustrated Lewis pairs in hydrogenation catalysis) and Nikolaev and co-workers<sup>136</sup> (catalytic hydrogenation of alkyne and diene impurities in alkenes).

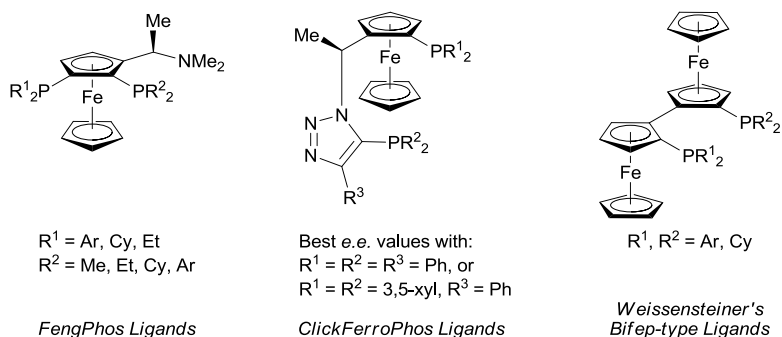
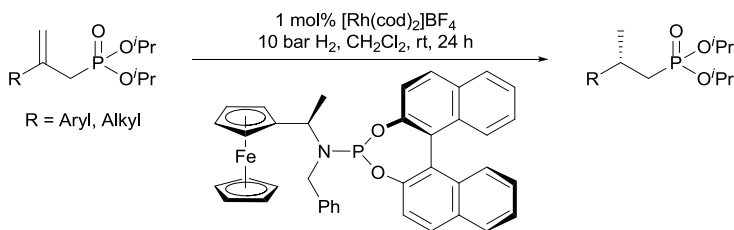
525 Book chapters have been written by Oro<sup>137</sup> (dihydrido iridium triisopropylphosphine complexes) and by Scholten and Dupont<sup>138</sup> (catalytic properties of soluble iridium nanoparticles).

A trend that has continued in 2009 is that Rh-catalysed alkene hydrogenation has been the subject of more papers than any other metal. Many of these publications 530 concern the synthesis and use of novel phosphorus ligands. Within this field, several reports concern *P*-chiral ligands (Scheme 43): The Pfaltz group, in collaboration with Pugin and co-workers at Solvias report the synthesis and catalytic evaluation of ferrocenephospholanes.<sup>139</sup> They obtain up to 93% *e.e.* when using these ligands in Rh-catalysed hydrogenation of dimethyl itaconate (DMI), methyl 2- 535 acetamidoacrylate (MAA) and methyl  $\alpha$ -acetamido-cinnamate (MAC); *P,P*-Ir complexes of the same ligands afforded *e.e.* values up to 77%. The Stephan group, in collaboration with PhosPhoenix, report the synthesis and evaluation of <sup>i</sup>Pr-SMS-Phos,<sup>140</sup> which they term “DiPAMP’s big brother” – they state that the ligand displays enhanced catalytic activity and enantioselectivity in Rh-catalysed 540 hydrogenation of many substrates, e.g. dehydro- $\alpha$ -amido acids, itaconates, acrylates, enamides, enol acetates,  $\alpha,\alpha$ -diarylethylenes, etc. *E.e.s* up to 99.6% are reported.



Scheme 43

Phosphorus ligands not containing *P*-stereogenic centres have also enjoyed 545 sustained use in Rh-catalysis. Amongst these, ferrocene remains a popular structural motif. Pugin and co-workers at Solvias have reported the synthesis of a new family of “Fengphos” ligands (Scheme 44).<sup>141</sup> They achieve an *e.e.* value of 99.4% for the hydrogenation of DMI; other substrates give slightly lower *e.e.* values. The Fukuzawa group report on the effect of substitution on the ClickFerroPhos ligand 550 family (Scheme 44), finding that sterically hindered analogues afford the best *e.e.* values, 97–99% for a range of substituted MACs.<sup>142</sup> Elsewhere, Weissensteiner and co-workers have evaluated various bifep-type ligands,<sup>143</sup> (Scheme 44) achieving 48% *e.e.* for the Rh-catalysed hydrogenation of MAC. (The ligands fared better in the Ru-catalysed hydrogenation of ketones, achieving up to 82% *e.e.*). Hu, Zheng 555 and co-workers report Rh-catalysed hydrogenation of  $\beta,\gamma$ -unsaturated phosphonates using ferrocene-based phosphoramidite ligands (Scheme 45).<sup>144</sup> Quantitative conversions with *e.e.* values of 90–98% were routinely achieved.

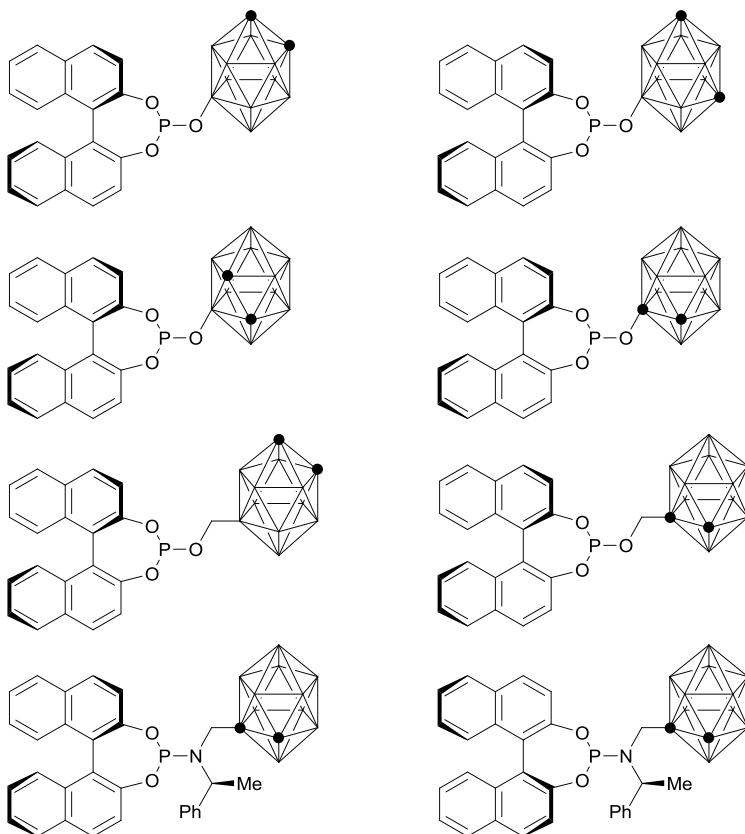

**Scheme 44**

**Scheme 45**

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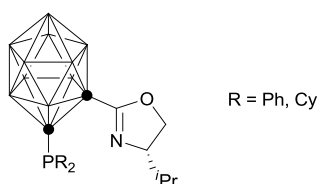
Additional reports have appeared on carborane-containing phosphorus ligands in 2009. Lyubimov has explored BINOL-derived carboranylphosphite and carboranylphosphoramidite ligands (Scheme 46), achieving up to 96% *e.e.* in the Rh-catalysed hydrogenation of MAA.<sup>145</sup> Kim, Kang and co-workers disclose new types of *o*-carborane-based phosphinoxazoline ligands, (“Cab-PHOX”),<sup>146</sup> with which they also achieve up to 96% *e.e.*, this time in the Rh-catalysed hydrogenation of MAC (Scheme 47).

Reek and co-workers describe Rh-catalysed alkene hydrogenation with sulfonamido-phosphoramidite ligands (Scheme 48), which give rise to dinuclear Rh complexes that impart excellent levels of enantioselectivity in the reduction of MAA and cyclic enamide substrates (up to 99% *e.e.*).<sup>147</sup> Reek has also detailed amino acid derived phosphoramidite ligands for Rh catalysed alkene hydrogenation, with which *e.e.* values up to 97% are achievable, although these are variable.<sup>148</sup> The Keay group detail the synthesis and resolution of 3,3'-disubstituted xyBINAP ligands, which they state are superior to BINAP for Rh-catalysed MAC reduction, achieving *e.e.* values of 91% at rt and 99% at -20 °C.<sup>149</sup>

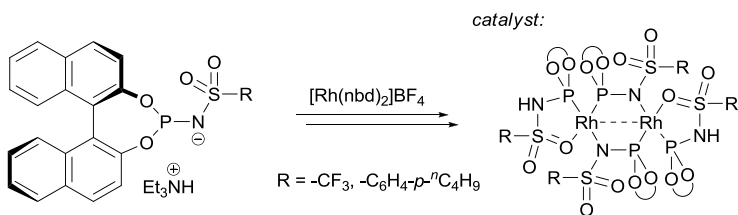
Reports on Rh-catalysed alkene hydrogenation that do not concern novel phosphorus ligands include the Kazlauskas group's report of stereoselective alkene hydrogenation using a Rh-substituted carbonic anhydrase.<sup>150</sup> The group used 2,6-pyridinedicarboxylate as a Zn chelator to remove Zn from the active site of an engineered carbonic anhydrase and then replaced it with Rh. Site-directed mutagenesis to remove surface histidine residues minimised nonspecific Rh incorporation. The resulting reductase catalysed alkene reduction and so constitutes the first cofactor-independent reductase that reduces organic molecules using H<sub>2</sub>. The reductase showed a 20-fold preference for reducing *cis*- over *trans*-stilbene, suggestive of the presence of Rh in a chiral environment, although preliminary experiments on the reduction of prochiral substrates have only given *e.e.s* of <10%.


**Scheme 46**

590



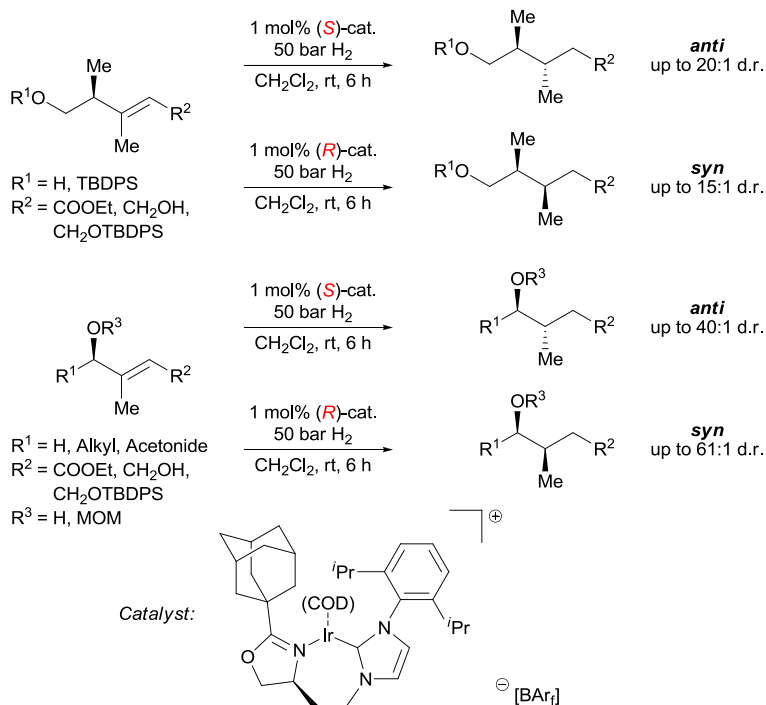
R = Ph, Cy

**Scheme 47**

**Scheme 48**

595 Elsewhere, Lei, Zhang and co-workers disclose the synthesis of  $\beta$ -arylisopropylamines by means of enamide reduction with a Rh-tangphos catalyst, achieving up to 99.3% *e.e.*<sup>151</sup> The Stradiotto group describe phosphoramidite

$P,N$ -ligands derived from BINOL and 7-azaindole, with which Rh and Ir-catalysed MAA reduction proceeded in up to 65% *e.e.*<sup>152</sup> The Brown group have published a full paper on stereoselectivity in the Rh-catalysed reductions of non-conjugated dienes<sup>153</sup> and the Grutzmacher group have reported on [bis(olefin)amine]Rh<sup>I</sup> complexes for transfer hydrogenation, achieving up to 58% *e.e.*<sup>154</sup>

It also remains the focus of sustained research efforts. Two significant papers from Burgess concern the use of a chiral oxazoline-based Ir complex (Scheme 49). Reduction of trisubstituted alkenes that bear a pre-existing allyl stereocentre proceeds under catalyst control, such that opposite enantiomers of the catalyst afford diastereomeric *syn* and *anti* products;<sup>155</sup> the same methodology is applicable to allyl ethers.<sup>156</sup>



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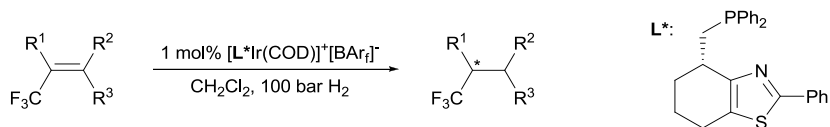
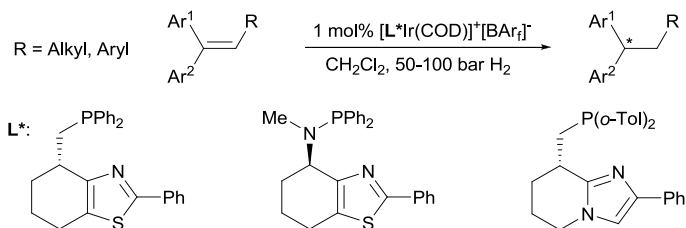
**Scheme 49**

The Andersson group continue to publish extensively on Ir-catalysed alkene reduction. They have recently examined trifluoromethyl-substituted alkenes as substrates<sup>157</sup> and have published a full paper on Ir-catalysed alkene reduction as a route to diarylmethines.<sup>158</sup> In the former case, they find that a thiazole-derived phosphine affords the best *e.e.* values (up to 87%) and find that the reaction is selective for reduction of the *Z* isomer in an *E/Z* substrate mixture (Scheme 50). In the latter case, the optimal ligand varies with substrate, but *e.e.* values above 90% are typical and above 99% are observed in many instances (Scheme 51). Separately, the group has published a full paper in collaboration with Börner and Diéguez on phosphite-oxazoline Ir catalysts for the reduction of 1,1-disubstituted alkenes,<sup>159</sup> in which they report the synthesis of a library of ligands, from which catalysts may be derived to effect asymmetric reduction in up to >99% *e.e.* in many cases (Scheme

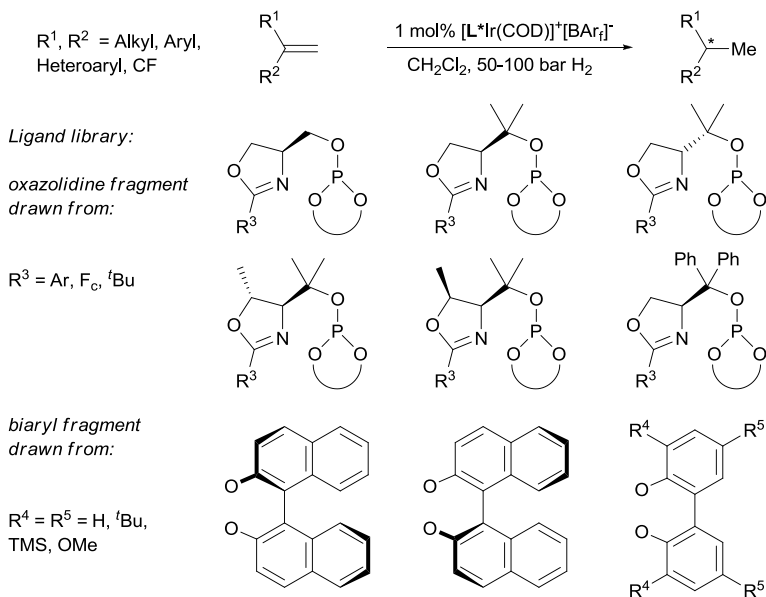
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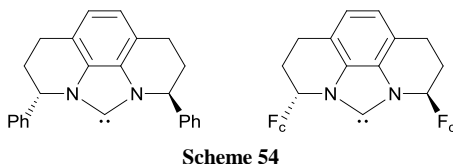
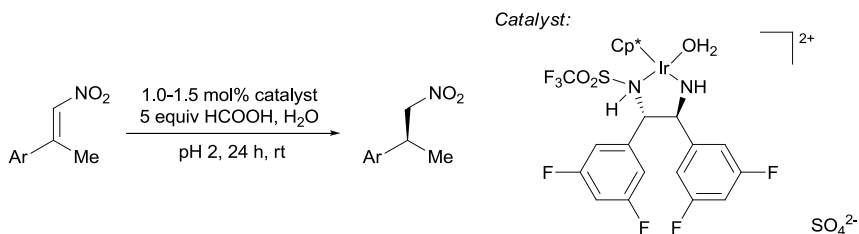
52). Indeed, several classes of alkene (1,1-heteroaryl-alkyl, 1,1-diaryl, etc.) are employed as substrates for asymmetric Ir-catalysed hydrogenation for the first time.  
 625 The paper also highlights the utility of propylene carbonate as a solvent which permits catalyst re-use.


**Scheme 50**

**Scheme 51**

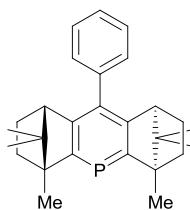
630


**Scheme 52**

Elsewhere, the Carreira group have described a transfer hydrogenation of  $\beta,\beta$ -disubstituted nitroalkenes in water.<sup>160</sup> The reaction employs formic acid as reductant and achieves up to 94% *e.e.* (Scheme 53). The Metallinos group report the use of phenanthroline-derived benzimidazolylidene ligands (Scheme 54) in Ir-catalysed reduction of MAA and MAC, observing *e.e.* values up to 81%.<sup>161</sup> Semeniuchenko and co-workers have described base-activated Ir-catalysed hydrogenation of electron-deficient alkenes.<sup>162</sup>



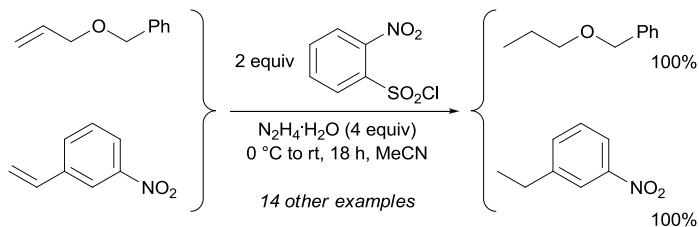
Pd catalysis of alkene hydrogenation also remains a fertile area. The idea of performing Pd-catalysed reduction in the presence of a homochiral modifier was applied by Sugimura and co-workers, who examined the reduction of various cinnamic acids in the presence of cinchona alkaloids, achieving up to 92% *e.e.*<sup>163</sup> The approach was then advanced by Rothenberg and co-workers, who demonstrated “chiral imprinting” of Pd by reducing a Pd salt in the presence of a cinchona dopant.<sup>164</sup> Crucially, they were able to demonstrate that the metal retained a degree of chiral character even after extraction of the dopant. Elsewhere, Cazin and co-workers report<sup>165</sup> mild alkene reduction with Pd(NHC)(PCy<sub>3</sub>) and the Zhang group report alkene reduction with encapsulated Pd catalysts under biphasic conditions.<sup>166</sup> Finally, the Garner group have reported the first homochiral C<sub>2</sub>-symmetric phosphinine ligand (Scheme 55).<sup>167</sup> In the single asymmetric transformation with this ligand examined so far (Pd-catalysed hydrosilylation of styrene), a modest 27% *e.e.* was obtained; rather, the report is highlighted due to the ligand’s structural novelty.



Reports have appeared on the use of other metals as catalysts for alkene hydrogenation. The Louis group have reported on the ability of supported Au catalysts to effect selective hydrogenation of 1,3-dienes in the presence of simple alkenes<sup>168</sup> and Ueno, Watanabe and co-workers describe the preparation and catalytic activity of Au/Pd bimetallic nanoparticles in Apo-ferritin.<sup>169</sup> De Vries and co-workers have communicated a facile preparation of soluble Fe nanoparticles (by reducing FeCl<sub>3</sub> with a Grignard reagent) and demonstrated their utility as catalysts for alkene/alkyne hydrogenation.<sup>170</sup> Elsewhere, Albrecht and co-workers have described robust Ru<sup>II</sup> *N*-heterocyclic carbene complexes that function as alkene

hydrogenation catalysts<sup>171</sup> and the Berke group have demonstrated the use of Re complexes as catalysts for alkene transfer hydrogenation with dimethylamine-borane complex as hydrogen donor.<sup>172</sup>

In the area of metal-free alkene reduction, the Carbery group has detailed a protocol for alkene reduction by means of one-pot *o*-nitrobenzenesulfonylhydrazide (NBSH) formation and diimide generation, for which no catalyst is necessary (Scheme 56).<sup>173</sup> The chemo- and regioselectivity of the reaction has been delineated and in addition to successfully reducing common substrates such as MAA, the reaction has been shown to be applicable in situations where the presence of hydrogenolytically-labile functionality precludes the use of direct hydrogenation methods (e.g. nitroarene or benzyloxy-containing substrates).



Scheme 56

## 2.2 Alkyne reduction

Publications on alkyne reduction in 2009 have been comparatively few. The partial reduction of alkynes to alkenes is the subject of a report from Ohkuma and co-workers who describe alkyne semihydrogenation with a Pd nanoparticle / tetrabutylammonium borohydride system.<sup>174</sup> In contrast, the Sajiki group report the use of a Pd<sup>0</sup>-polyethyleneimine complex as an alkyne semihydrogenation catalyst.<sup>175</sup> The Cho group have used a different metal, namely Ru, with which they are able to effect transfer semihydrogenations of alkynes with tributylamine.<sup>176</sup>

## 2.3 Arene reduction

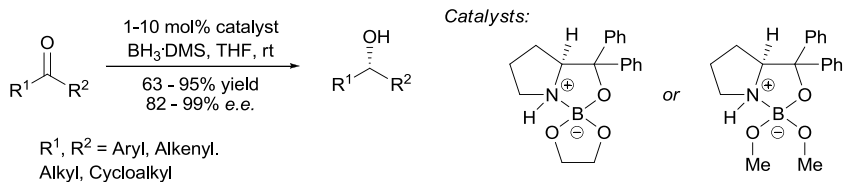
2009 has seen publications on several different approaches to achieving arene reduction. In the area of Birch reductions, near-simultaneous reports from the Jackson group<sup>177</sup> and from Costanzo, Vogt and co-workers<sup>178</sup> describe ammonia-free procedures at room temperature that utilise alkali metals stabilised in silica gel. Elsewhere, the Landais group has undertaken a comprehensive study of Birch reductive alkylations of biaryls.<sup>179</sup>

Rh remains the metal of choice for catalysing arene perhydrogenation and a noteworthy report from Motoyama describes the use of Rh nanoparticles supported on carbon nanofibres.<sup>180</sup> The point of note for this catalytic system is that it exhibits excellent tolerance of epoxide functionality elsewhere in the substrate. 2009 has also seen reports from the Zhou group<sup>181</sup> (Use of [Rh(cod)Cl]<sub>2</sub>, including for semihydrogenation of BINOLs), from Roucoux and co-workers<sup>182</sup> (imidazolium-stabilised Rh colloids), from Roucoux, Philippot and co-workers<sup>183</sup> (Rh nanoparticles supported on silica), and from the Savoia group<sup>184</sup> (Rh on graphite). In addition, the Sajiki group have contrasted Rh catalysts with other metal systems (Ru,

Pd, Pt, Ir)<sup>185</sup> and Monflier and co-workers have described a catalyst consisting of Ru nanoparticles stabilised by cyclodextrin inclusion complexes in water.<sup>186</sup>

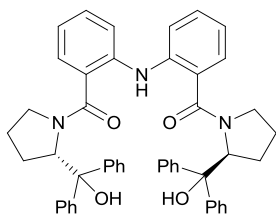
## 2.4 Ketone reduction

Cho published a tutorial review on 2009 on catalysed asymmetric ketone reductions with boron hydrides,<sup>187</sup> which includes extensive discussion of oxazaborolidine catalysts. Indeed, such oxazaborolidine systems remain a subject of much active research. The Corey–Bakshi–Shibata (CBS) oxazaborolidine catalytic system was the subject of a further disclosure from the Corey group,<sup>188</sup> who have elucidated the role of *N,N*-diethylaniline as an additive. This had previously been found to enhance enantioselectivities for the reduction of 2,2-disubstituted cycloalkan-1,3-diones or hindered 2,2-disubstituted cyclic ketones; it transpires that the role of the additive is to catalyse the conversion of a deleterious impurity in preparations of the catalyst to the active catalyst. The Meyer group has also published on the CBS system, disclosing detailed theoretical and experimental studies that employ kinetic isotope effects in an attempt to delineate the role of nonbonding interactions in determining stereoselectivity.<sup>189,190</sup> Other oxazaborolidine systems have also been described – the Kettouche group report an *in situ* oxazaborolidine preparation using amino alcohols diiodomethane and sodium borohydride,<sup>191</sup> although the highest *e.e.* value achieved (87%) was comparatively modest for such systems. Ortiz-Marciales and co-workers have described two oxazaborolidines: a dimethoxy(aminoalkoxy)borate<sup>192</sup> and a spiroaminoborate,<sup>193</sup> both derived from diphenylprolinol (Scheme 57). Both are able to catalyse the borane-mediated reduction of various prochiral ketones with good enantioselectivities; the latter has also been employed for the synthesis of  $\beta$ -hydroxy ethers and  $\beta$ -amino ethers.<sup>194</sup>

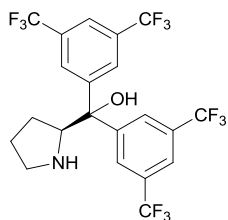


**Scheme 57**

Boron reducing agents are also employed in the work of the Soós group, who employ a “minimally fluorinated” diarylprolinol (Scheme 58) as an oxazaborolidine precatalyst.<sup>195</sup> The role of the trifluoromethyl groups is to impart hydrophobicity (as opposed to affinity for a fluorous phase) and the catalyst recovery is effected using extraction with a tuned aqueous-organic solvent system and a solid phase extraction approach. For the reduction of aryl alkyl ketones, *e.e.* values up to 98% were achieved. The Du group have reported the use of a bis(diarylprolinol) organocatalyst incorporating a diarylamine linker motif, achieving *e.e.* values up to 97% for the same substrate class (Scheme 58).<sup>196</sup> In contrast, sodium borohydride is employed as reductant in an enantio- and regioselective reduction of cyclic  $\alpha,\beta$ -unsaturated ketones reported by the Singaram group.<sup>197</sup> They use a tartrate-derived boronic ester (“TarB-NO<sub>2</sub>”) as catalyst, achieving *e.e.* values up to 99% (Scheme 59). One other non-metal methodology of note reported in 2009 is the Oestreich group’s use of *Si*-stereogenic silanes as stoichiometric reducing agents.<sup>198</sup>



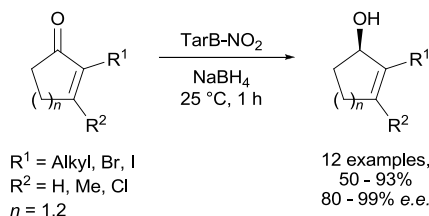
Du's Catalyst



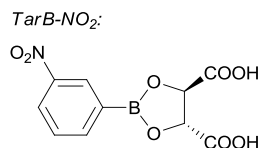
Soós' Catalyst

750

## Scheme 58



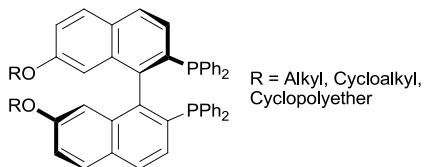
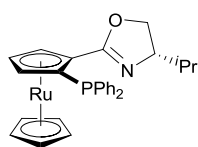
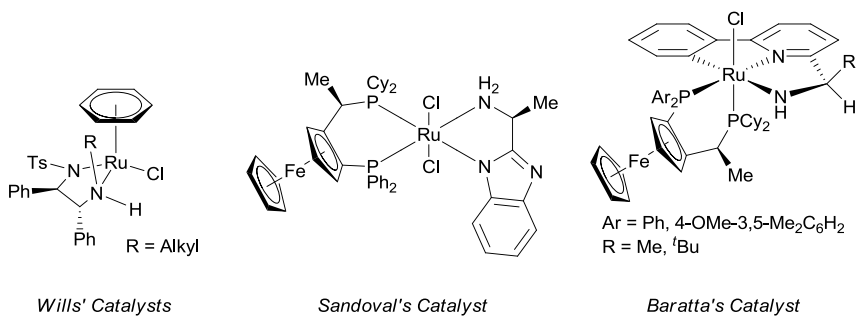
## Scheme 59



Amongst metal-catalysed ketone reduction methods, reports on Ru are prevalent. The Wills group have reported the use of *N*-alkylated TsDPEN Ru complexes as catalysts for ketone transfer hydrogenation (Scheme 60), achieving up to 98% *e.e.* and up to 94% *e.e.* for imine reduction.<sup>199</sup> (The Wills group have also reported Ir<sup>III</sup> complexes of DPEN<sup>200</sup> and TsDPEN<sup>201</sup> ligands, giving up to 85% *e.e.* for ketone reduction). Other reports of Ru-catalysed asymmetric ketone transfer hydrogenation include Adolfsson and co-workers' use of pseudodipeptide ligands<sup>202,203</sup> and the Ikariya group's use of various *N,S*-chelating ligands;<sup>204</sup> up to 99% *e.e.* was achieved with both ligand classes.

Ru-catalysed methods relying on H<sub>2</sub> gas as reductant include Sandoval's report of a catalyst complex comprising a JosiPhos ligand in combination with a benzimidazole ligand ("Me-bimAH").<sup>205</sup> This was able to effect the asymmetric reduction of aryl ketones with good *e.e.* values, in the range 92-99% (Scheme 60). In conjunction with Noyori and co-workers, Sandoval has also published a study on the role of NH/ $\pi$  attractive interactions in asymmetric ketone hydrogenation with Ru/BINAP/1,2-diamine catalysts.<sup>206</sup> Baratta and co-workers have disclosed catalysts that also employ JosiPhos, but in concert with *N,N,C* pincer ligands, whose coordination involves a CH activation step;<sup>207</sup> these were utilised in both transfer hydrogenation and with H<sub>2</sub> gas, with up to 99% *e.e.* being obtained in both cases. Elsewhere, Yuan, Gong and co-workers reported on the use of 7,7'-disubstituted BINAP ligands<sup>208</sup> and Zhang and co-workers describe ruthenocenyloxy phosphino-oxazoline ligands,<sup>209</sup> both of which can be used for Ru-catalysed ketone reduction, affording *e.e.* values of up to 99% and 98% respectively. (Scheme 61).

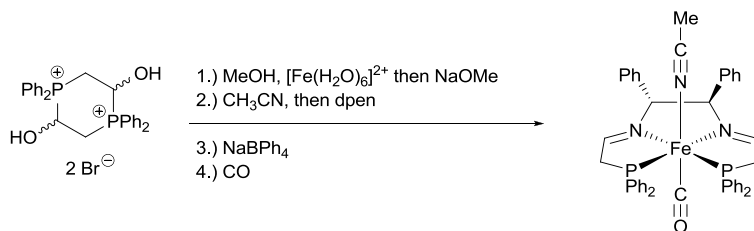
In the area of Rh-catalysed ketone reduction, the Adolfsson group have reported on the use of amino acid-derived thioamide ligands<sup>210</sup> (in up to 97% *e.e.*) and the Lee group describe using TsDPEN ligands for certain substrate classes:  $\alpha$ -functionalised aryl ketones<sup>211</sup> and, more specifically,  $\alpha$ -sulfonyloxy heteroaryl ketones.<sup>212</sup>



**Scheme 61**

785

Concerning Fe-catalysed ketone reduction, reports from the Morris group<sup>213,214</sup> merit attention. They describe the facile templated synthesis of a *P,N,N,P* tetradentate Fe chelate which is highly effective as a catalyst for ketone reduction (Scheme 62) – in transfer hydrogenation with isopropanol, up to 99% *e.e.* was achieved; the ability to employ an iron catalyst as opposed to platinum group metals is highly desirable from an economic standpoint. Elsewhere, the Campagne group have described Fe-catalysed “overreduction” of ketones and aldehydes to the corresponding alkanes with polymethylhydrosiloxane as reductant.<sup>215</sup>



795

A plethora of other metals have also been employed for ketone reduction. The Ley group have reported a continuous flow process using only catalytic amounts of lithium *tert*-butoxide in *isopropanol*.<sup>216</sup> The Shibata group have studied the generation and use of hafnium hydride as reductant,<sup>217</sup> observing that in the reduction of  $\alpha$ -alkoxyketones, the diastereoselectivity is highly dependent on solvent – the *erythro:threo* preference could be reversed upon going from THF to EtCN. The Hamada group have published a Ni-catalysed enantioselective hydrogenation of aromatic  $\alpha$ -aminoketone hydrochlorides by dynamic kinetic resolution<sup>218</sup> and Shimizu, Ohshima, Mashima and co-workers have described reduction of enones and heteroaromatic ketones with Cu<sup>I</sup> diphosphine complexes.<sup>219</sup> Finally, Collin and

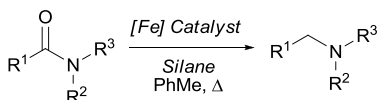
co-workers have disclosed Meerwein–Ponndorf–Verley reductions of ketones with chiral Sm complexes, albeit in modest *e.e.*<sup>220</sup>

## 810 2.5 Aldehyde reduction

The Breit group have described<sup>221</sup> a supramolecular catalyst for aldehyde hydrogenation, constructed from a Rh<sup>I</sup> salt and a bifunctional ligand incorporating both a triarylphosphine and an acylguanidinium motif. In contrast, it is Fe complexes (of cyclopentadienone) and their reduction of aldehydes which are the subjects of a full paper from the Casey group.<sup>222</sup> Naimi-Jamal, Kaupp and co-workers report on aldehyde (and ketone) reduction by ball-milling with sodium borohydride<sup>223</sup> (in the context of sustainable solvent-free chemistry) and Meyer has reported a theoretical study on alpine-borane reductions of benzaldehydes.<sup>224</sup> Plucinski and co-workers have reported nanoparticle-supported Pd catalysts for aldehyde hydrogenation which are easily recoverable and reusable.<sup>225</sup> Elsewhere, In a different mode of aldehyde reduction, Miyoshi, Shimizu and co-workers reported the reductive dimerisation of aldehydes to 1,2-diols (and imines to 1,2-diamines) mediated by Sr metal.<sup>226</sup>

## 825 2.6 Amide reduction

Two reports were published simultaneously in 2009 on the reduction of *N,N*-disubstituted amides to amines with silanes under conditions of Fe catalysis. The Beller group describe the reduction of a model substrate (*N,N*-dimethylbenzamide) with various silanes and various Fe catalysts, achieving the best yield (97%) with 2 mol% triiron dodecacarbonyl cluster and phenylsilane.<sup>227</sup> The Nagashima group employed 1,1,3,3-tetramethyldisiloxane (TMDS) as reductant and contrasted iron pentacarbonyl and triiron dodecacarbonyl as catalysts, finding the optimal catalyst choice was substrate dependent (Scheme 63).<sup>228</sup> Nagashima has further employed TMDS in Pt-catalysed amide reductions, giving a full account of the enhanced efficacy arising from the use of a *bifunctional* silane.<sup>229</sup> In addition, the group have described an Ir-catalysed reduction of amides, this time to enamines, with TMDS (Scheme 64).<sup>230</sup> Elsewhere, the An group have introduced lithium diisobutylisopropoxyaluminum hydride (LDBIPA) and demonstrated its efficacy in the semireduction of tertiary amides to aldehydes.<sup>231</sup>



Beller:

R<sup>1</sup> = Ph R<sup>2</sup>, R<sup>3</sup> = Me

[Fe] = Fe<sub>2</sub>(CO)<sub>9</sub>, Fe<sub>3</sub>(CO)<sub>12</sub>, Fe(OAc)<sub>2</sub>,

Fe(acac)<sub>2</sub>, Fe(stearate)<sub>2</sub>, FeF<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>

Silane = PhSiH<sub>3</sub>, Et<sub>3</sub>SiH, Me(EtO)<sub>2</sub>SiH, (EtO)<sub>3</sub>SiH,

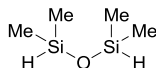
Et<sub>2</sub>MeSiH, TMSOSiMe<sub>2</sub>H, Ph<sub>2</sub>SiH<sub>2</sub>, PMHS

Nagashima:

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = Alkyl, Aryl, Cycloalkyl, Morpholino

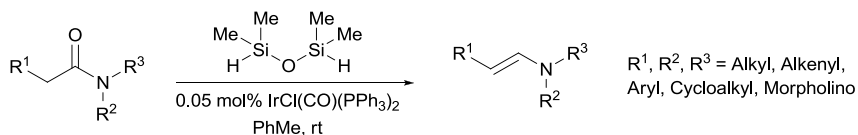
[Fe] = Fe(CO)<sub>5</sub>, Fe<sub>3</sub>(CO)<sub>12</sub>

Silane =



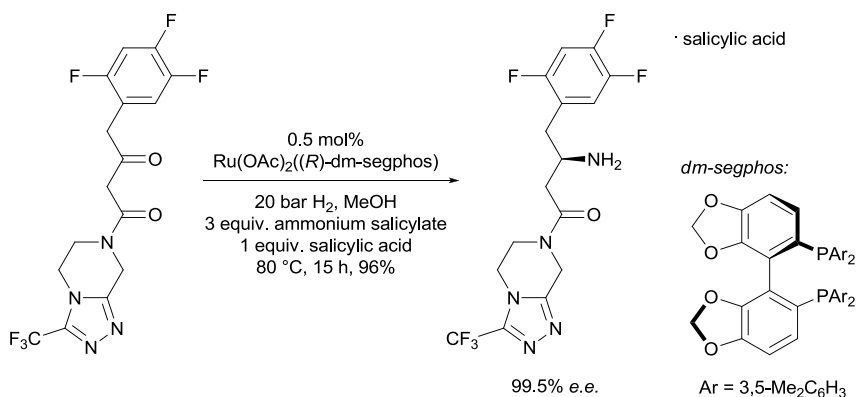
840

Scheme 63

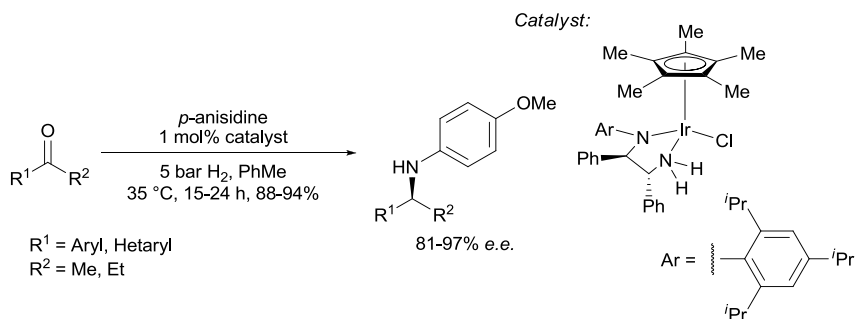

**Scheme 64**

## 845 2.7 Imine reduction and reductive alkylation

A significant disclosure from workers at Merck and Takasago is the direct asymmetric reductive amination of  $\beta$ -ketoamides to give *N*-unprotected  $\beta$ -aminoamides, using simple ammonium salts as nitrogen source.<sup>232</sup> The approach utilises a  $\text{Ru}^{\text{II}}$  dm-segphos catalyst and has been utilised to introduce the stereocentre in sitagliptin, a drug for treatment of type-II diabetes (Scheme 65).


**Scheme 65**

The Xiao group have also reported on direct asymmetric reductive amination,<sup>233</sup> employing an Ir complex with an *N*-tosyl dppe ligand and achieving up to 97% *e.e.* for the reductive amination of various aryl alkyl ketones with *p*-anisidine (Scheme 66). Mršić, Minnaard, Feringa and de Vries have employed Ir for *N*-aryl imine hydrogenation, achieving >99% *e.e.* with a monodentate phosphoramidite ligand<sup>234</sup> and Ikariya and co-workers have reported that the addition of silver salts to Ir-dppe catalysts effects an increase in *e.e.* for imine hydrogenation.<sup>235</sup>


**Scheme 66**

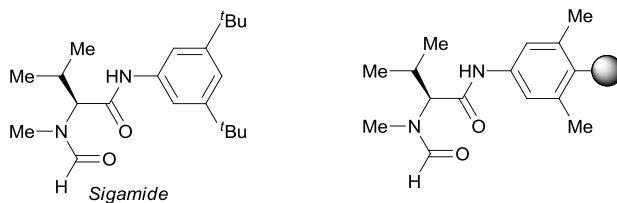
860



Complexes of several other metals were employed as catalysts for imine reduction in 2009. The Rubio-Pérez group have reported<sup>236</sup> Pd-BINAP complexes for direct asymmetric ketone reductive amination in up to 99% *e.e.* and the Santos group<sup>865</sup> describe a chiral auxiliary approach for Pd-catalysed asymmetric reduction of  $\beta$ -carboline imines in up to 13:1 *d.r.*<sup>237</sup> Silane-mediated imine reduction has been reported by the Yang group to be promoted by indium trichloride,<sup>238</sup> by Smith and co-workers to be catalysed by molybdenum dioxide dichloride,<sup>239</sup> and by the Legoupy group to be catalysed by an organotin chloride incorporated into an ionic<sup>870</sup> liquid (which aids purification).<sup>240</sup>

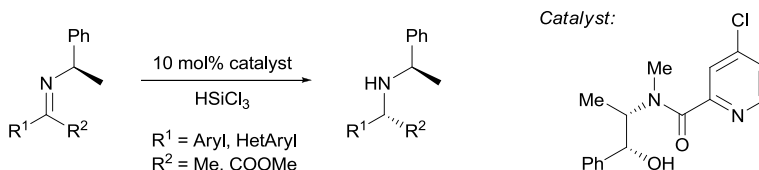
In the area of boron reductants, the Alinezhad group introduced *N*-methylpyrrolidine zinc borohydride (ZBHNMP) for reductive amination,<sup>241</sup> Shi and co-workers described stable 1,2,3-triazole-borane complexes for reductive amination in organic or aqueous solvent<sup>242</sup> and Priefer and co-workers have reported the<sup>875</sup> preparation and use of silica-supported cyanoborohydride for reductive amination.<sup>243</sup>

Several reports have appeared on the organocatalytic asymmetric reduction of imines with trichlorosilane. Malkov, Kočovský and co-workers have published on amino acid-derived formamide catalysts, both solution-phase (“sigamide”, giving up to 97% *e.e.*)<sup>244</sup> and, in collaboration with Cooke, in polymer-supported form,<sup>245</sup><sup>880</sup> giving up to 91% *e.e.* (Scheme 67). Elsewhere, Jones and co-workers have detailed an imidazole derived organocatalyst<sup>246</sup> (with which up to 87% *e.e.* was achieved for *N*-aryl imine reduction) and the Benaglia group have described *N*-acylated 1,2-aminoalcohol catalysts<sup>247</sup> (achieving up to 95% *e.e.*). In an extension of this latter methodology, Benaglia combined these catalysts with a (comparatively cheap)<sup>885</sup> stereochemically-matched chiral auxiliary ( $\alpha$ -methylbenzylamine) to achieve near-quantitative conversion and *d.r.* values >99:1 for a variety of aryl imines (Scheme 68).<sup>248</sup>



Malkov &amp; Kocovsky's Catalysts

Scheme 67



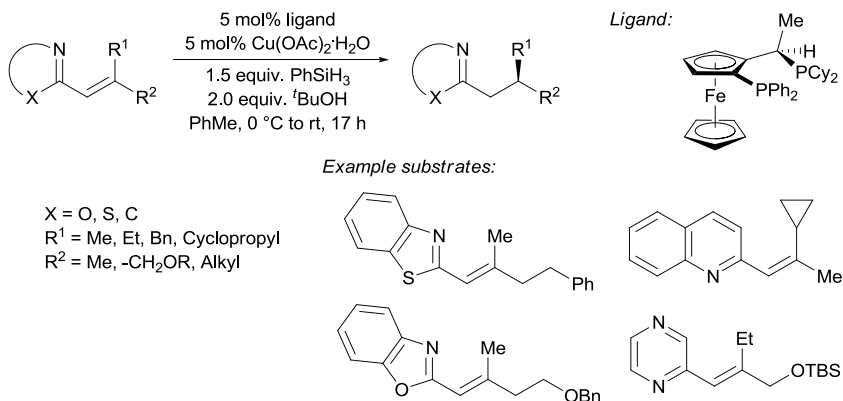
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Scheme 68

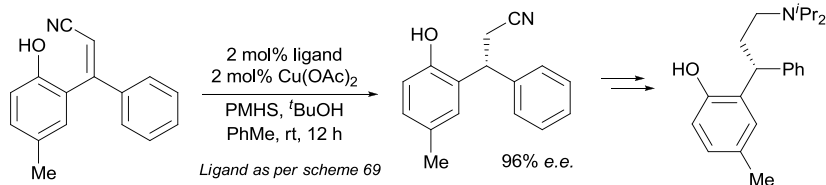
Other noteworthy reports on imine reduction include a theoretical study from the Himo group on organocatalytic reductive amination of  $\alpha$ -branched aldehydes,<sup>249</sup> a detailed mechanistic study from the Papái group on imine reduction with “frustrated<sup>895</sup> Lewis pairs”<sup>250</sup> and a disclosure from the Largeron group of a biomimetic electrocatalytic system for imine reduction catalysed by an *ortho*-iminoquinone.<sup>251</sup>

## 2.8 Conjugate reduction

Cu-catalysed methods dominated the area of conjugate reduction in 2009. The Lam group have reported the conceptually novel approach of considering aromatic heterocycles as activating groups for asymmetric conjugate addition.<sup>252</sup> They have been able to demonstrate enantioselective reduction of 2-vinylheteroarenes, achieving up to 99% *e.e.* (Scheme 69). Elsewhere the Yun group report the use of the same JosiPhos ligand (and analogues) to effect Cu-catalysed conjugate reduction of  $\beta,\beta$ -diaryl acrylonitriles<sup>253</sup> and applied this methodology to the asymmetric synthesis of tolterodine (Scheme 70).<sup>254</sup>



Scheme 69

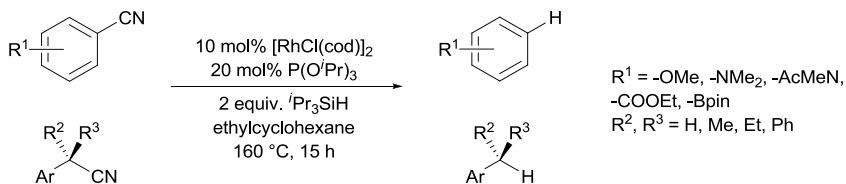


Scheme 70

Other reports of Cu-catalysed methods include the Koskinen group's report of conjugate reduction of stereochemically labile  $\alpha,\beta$ -unsaturated amino ketones<sup>255</sup> and Hu, Zheng and co-workers' report<sup>256</sup> of asymmetric conjugate reduction of  $\beta$ -substituted  $\alpha,\beta$ -unsaturated phosphonates (wherein the substrates are regioisomeric to the  $\beta,\gamma$ -unsaturated phosphonates they are able to reduce with a Rh-catalyst; see scheme 45). Non-copper methods of note include Arseniyadis, Cossy and co-workers' report of enantioselective conjugate reduction of  $\beta$ -azole-containing  $\alpha,\beta$ -unsaturated aldehydes<sup>257</sup> (catalysed by a homochiral imidazolidinone and proceeding in up to 94% *e.e.*), the Ashfeld group's titanocene-catalysed reduction of various  $\alpha,\beta$ -unsaturated carbonyls with Zn,<sup>258</sup> and Stephens, Scrutton and co-workers' enzymatic methodology employing pentaerythritol tetranitrate reductase, achieving >99% *e.e.* for many cyclic enone substrates.<sup>259</sup>

## 2.9 Nitrile reduction

925 A noteworthy disclosure in 2009 came from Tobisu, Chatani and co-workers, who described a Rh-catalysed reductive cleavage of C-CN bonds with triisopropylsilane (Scheme 71).<sup>260</sup> Both aryl and benzylic nitriles are viable substrates, with good yields (75-99%) achieved. Elsewhere, for the more well-precedented reduction of nitriles themselves to amines, the Beller group have described Ru *N*-heterocyclic carbene catalysts for nitrile hydrogenation,<sup>261</sup> Lemaire and co-workers describe the use of titanium isopropoxide and tetramethylidisiloxane<sup>262</sup> and the Singaram group detail the use of *diisopropylaminoborane*.<sup>263</sup>



Scheme 71

935

## 2.10 Nitroarene reduction

The selective reduction of nitroarenes appears to have been the subject of much research in 2009. A review has been published in the area by Blaser<sup>264</sup> (selective hydrogenation of functionalised nitroarenes).

940 Most abundant have been reports of reductions of nitroarenes to the corresponding amines. A highly significant disclosure from the Xu group described the use of fullerene as a catalyst for hydrogen activation; for the reduction of nitrobenzene they describe catalytic activity *comparable to noble metal catalysts*.<sup>265</sup>

Elsewhere, the Lu group have reported a selective monoreduction of dinitroarenes 945 to the corresponding nitroanilines with carbon monoxide, catalysed by Se.<sup>266</sup> Hydrogen gas as reductant was described by Liao, Shi and co-workers<sup>267</sup> (catalysed by tannin-stabilised Pd nanoparticles), by the Nagashima group<sup>268</sup> (catalysed by Pt in polysiloxane gels), by the Royo group<sup>269</sup> (catalysed by molybdenum dioxide dichloride) and by Tokunaga and co-workers<sup>270</sup> (catalysed by Au nanoparticles supported on Fe<sub>2</sub>O<sub>3</sub>). In this latter instance, *in situ* reductive aminations were also demonstrated. Other reductants have also been employed; Fernandes and co-workers disclose Re-catalysed reduction with silanes,<sup>271</sup> the Hamann group employed Zn in attempting one-pot reductive amidations of nitroarenes<sup>272</sup> and the Yutilov group describe the use of hydrazine for a specific substrate class (aminonitropyridines).<sup>273</sup>

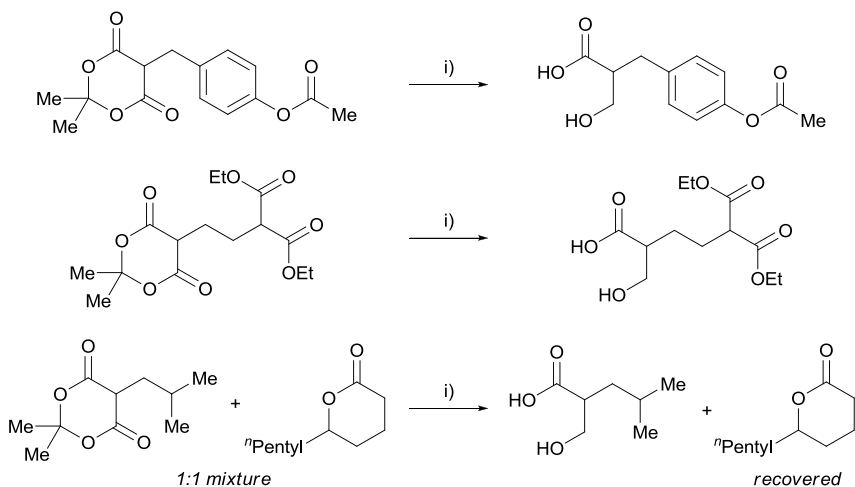
955 The reduction of nitroarenes to the corresponding *N*-arylhydroxylamines has been addressed by the Tomkinson group<sup>274</sup> (using Zn in water), by the Jiang group<sup>275</sup> (using Zn in a water/CO<sub>2</sub> system) and by Takenaka, Yasuda and co-workers<sup>276</sup> (using hydrogenation over supported Pt catalysts).

## 960 2.11 Other reductions

The Kuhn group disclose the first “absolute asymmetric reduction” (borohydride reduction of an alcohol).<sup>277</sup> Absolute asymmetric synthesis implies enantioselective synthesis from achiral starting materials without the use of chiral reagents or

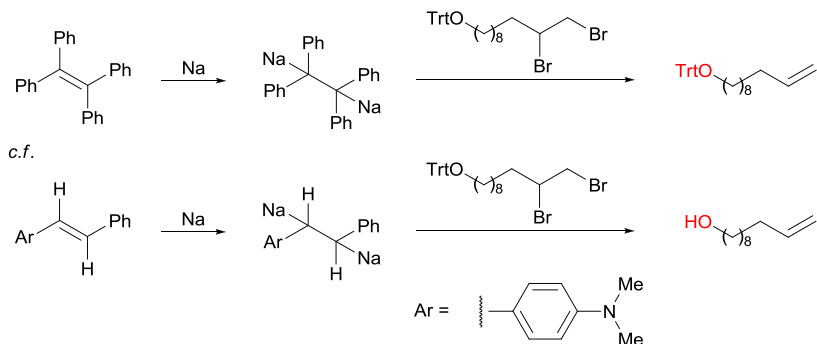
catalysts. In this example, the orientation and exposure of a selected face of an  
 965 achiral crystal to the achiral reagent imparts the chirality. Although *e.e.* values were low (9-26%), the authors contend this proof of concept is significant.

Procter and co-workers have reported the selective reduction of cyclic 1,3-diester  
 using samarium diiodide and water.<sup>278</sup> The reagent system is highly selective,  
 differentiating between the carbonyl groups of esters and lactones and also showing  
 970 ring size selectivity for  $\delta$ -lactones (Scheme 72).



**Scheme 72** Reagents and conditions: i) 7 equiv.  $\text{SmI}_2$ , THF,  $\text{H}_2\text{O}$ , rt, 67 – 87%

In other, miscellaneous disclosures, Kamal, Reddy and co-workers have reported  
 a highly chemoselective azide reduction, wherein aryl azides may be reduced  
 975 selectively in the presence of aliphatic azides.<sup>279</sup> Workers at Boehringer-Ingelheim  
 have studied the reduction of phosphinites, phosphinates, and other phosphorus  
 functionality with DIBAL.<sup>280</sup> The MacMillan group have reported the reductive  
 deamination of anilines by quaternisation and subsequent treatment with Na  
 metal.<sup>281</sup> Finally, Azzena, Antonello and co-workers have described their studies on  
 980 1,2-diaryl-1,2-disodiummethanes as reducing agents.<sup>282</sup> Variation of the substituents  
 on the aryl groups allows the electron donating ability of the alkylmetal to be  
 controlled, such that selective reductions may be effected (Scheme 73).



**Scheme 73**

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