ChemPubSoc Europe

DOI: 10.1002/ejoc.201600018

EurJOC European Journal of Organic Chemistry

Microreview

Manganese Catalysis

Recent Advances of Manganese Catalysis for Organic Synthesis

Jonathan R. Carney,[a] Barry. R. Dillon,[b] and Stephen P. Thomas*[a]

Abstract: Manganese is a non-toxic, inexpensive and earth abundant metal, so is a perfect candidate for catalysis whether as a replacement for precious metals or in the search for novel reactivity. Despite this, manganese catalysis has not undergone the same development of other earth-abundant metals (particularly iron and cobalt). This review details recent synthetic methodologies using manganese catalysts, including C–H activation, late stage fluorination, hydrosilylation and cross-coupling.

1.1 Introduction

Earth abundant metals offer a sustainable alternative to precious metals for the synthesis of bulk and fine chemicals and the advancement of sustainable chemical manufacturing. Cobalt- and nickel-catalysed reactions have seen great advances, but suffer from the inherent toxicity of these metals. Of the first-row transition metals, iron and manganese have the unique features of being non-toxic and environmentally benign. Iron catalysis is now well established for cross-coupling,[1,2] oxidation[3] and reduction reactions.[4] However, manganese has remained relatively unexploited with research only accelerating in the last 3–5 years.

Manganese has great potential redox activity due to the number of available oxidation states (–3 to +7) and the ability to form compounds with a coordination number of up to 7.[5] This allows a range of reactivity to be explored, with high oxidation-state manganese species being used as strong oxidising agents e.g. MnO_2 and $KMnO_4$ and with low oxidation-state manganese compounds displaying chemistry akin to main group compounds (for instance, $RMn^{II}X$ reagents have similar reactivity to Grignard reagents).[6] Manganese(II) is the most sta-

[a] *EaStCHEM School of Chemistry, University of Edinburgh*
Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, UK
E-mail: stephen.thomas@ed.ac.uk
http://www.chem.ed.ac.uk/staff/academic-staff/dr-stephen-p-thomas
[b] *AstraZeneca,*
Alderley Park, Macclesfield, Cheshire, SK10 4TG, United Kingdom

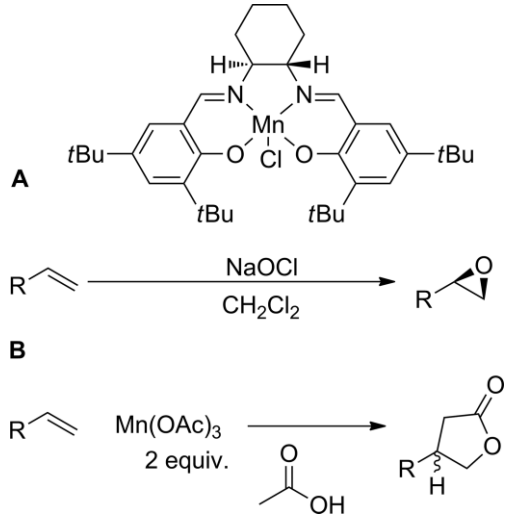
Raised in the Staffordshire Moorlands, Jon undertook his MChem. at the University of York, graduating in 2014. His final year project was completed under the supervision of Prof. Ian Fairlamb, investigating the catalytic potential of novel succinimide containing palladium(II) complexes. Jon moved to Edinburgh in September 2014 to start his PhD exploring earth-abundant metal catalysis.

Barry Dillon started his career in 1996 at GlaxoWellcome as a process R&D chemist. In 2001 he moved to undertake a PhD in natural product synthesis at Imperial College London under the supervision of Prof. Donald Craig, completing in 2004. In the same year he joined the Chemical Research and Development laboratories at Pfizer, Sandwich leading synthesis teams on a number of projects across the allergy & respiratory, pain and oncology portfolios. In 2011 he Joined AstraZeneca as a senior environmental adviser aligned to green chemistry, lifecycle analysis and other sustainability aspects.

Stephen Thomas was born in Toronto, Canada, and moved to the South West of the UK at a young age. After completing his MChem. at Cardiff University working with Prof. Nick Tomkinson, he moved to Churchill College, Cambridge University in 2007 for a PhD working with Dr Stuart Warren. Postdoctoral work with Prof. Dr Andreas Pfaltz at the University of Basel, Switzerland, was shortly followed by an appointment as a Lecturer at the University of Bristol. In 2012 Stephen was awarded a Chancellor's Research Fellowship at The University of Edinburgh, and moved with his research group to take up this position. His research interests are based on organometallic catalysis, synthetic methodology and mechanism, with a focus on the use on non-precious metals to replace and expand upon the reactivity of traditionally used 2nd and 3rd row transition-metals.

ble oxidation state, although manganese(III) can be stable but tends to disproportionate to manganese(II) and manganese(IV). Due to the half-shell effect, manganese(II) breaks the trend for electronegativity and is more electropositive than chromium and vanadium.[7]

The use of manganese for the epoxidation of alkenes[8] and radical-mediated oxidative cyclisations[9–11] has been extensively reviewed. This review will focus on alternative transformations,[12,13] particularly those reported in the last 5–10 years (Scheme 1). These include catalysts acting as replacements for platinum group metals, such as hydrosilylation and cross-coupling reactions, as well as reactions exhibiting more novel reactivity such as C–H activation to form alcohol, azide and halogenated products.



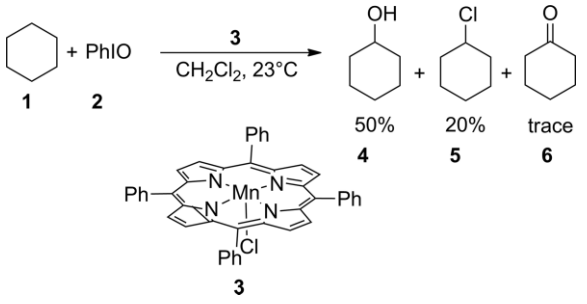
Scheme 1. A) Formation of enantioenriched epoxides catalysed by a manganese(III) salen compound B) radical cyclisation of an alkene and acetic acid mediated by $Mn^{III}(OAc)_3$.

2. Manganese Catalysis

2.1. Carbon–Oxygen Bond Formation by C–H Activation

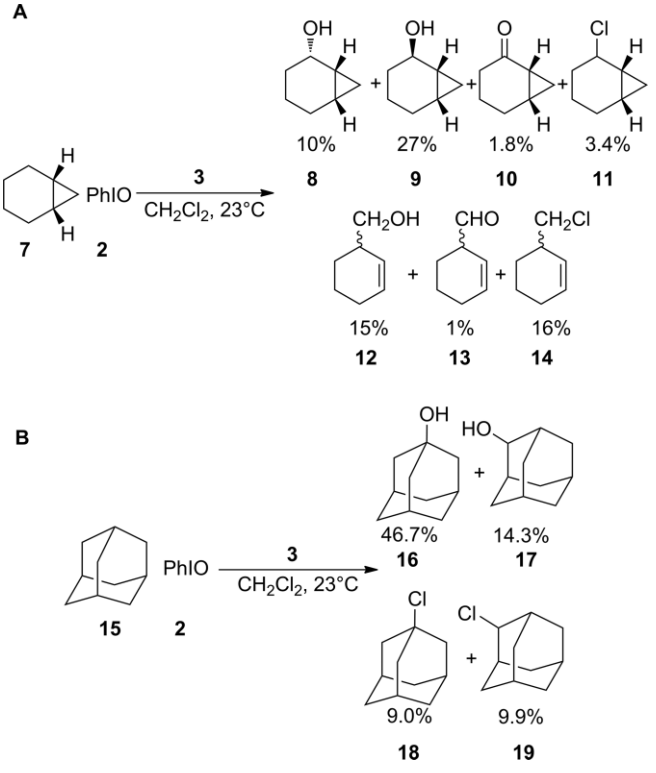
The activation of C–H bonds is an important area of research as this negates the requirement for pre-functionalisation of a substrate and can therefore lead to a decrease in waste products. Challenges lie in the need for selectivity between different C–H bonds in a substrate, over-oxidation, and chemoselectivity when substrates contain other functionalities susceptible to oxidation. The hydroxylation of unactivated C–H bonds by metalloporphyrin compounds is a biomimetic approach to this challenge. Groves and co-workers reported the oxidation of hydrocarbons using this strategy with a manganese porphyrin catalyst **3** (Scheme 2).[14]

Norcarane gives different products when subjected to oxidative conditions based on the mechanism of the oxidation reaction. Radical-mediated reactions give cyclohexene products whilst ionic reactions produce cycloheptene products. When norcarane was subjected to the manganese-porphyrin C–H hydroxylation conditions, it gave a range of oxygenated or



Scheme 2. Manganese-porphyrin-mediated oxidation or chlorination of cyclohexane, yields are based on the oxidant.

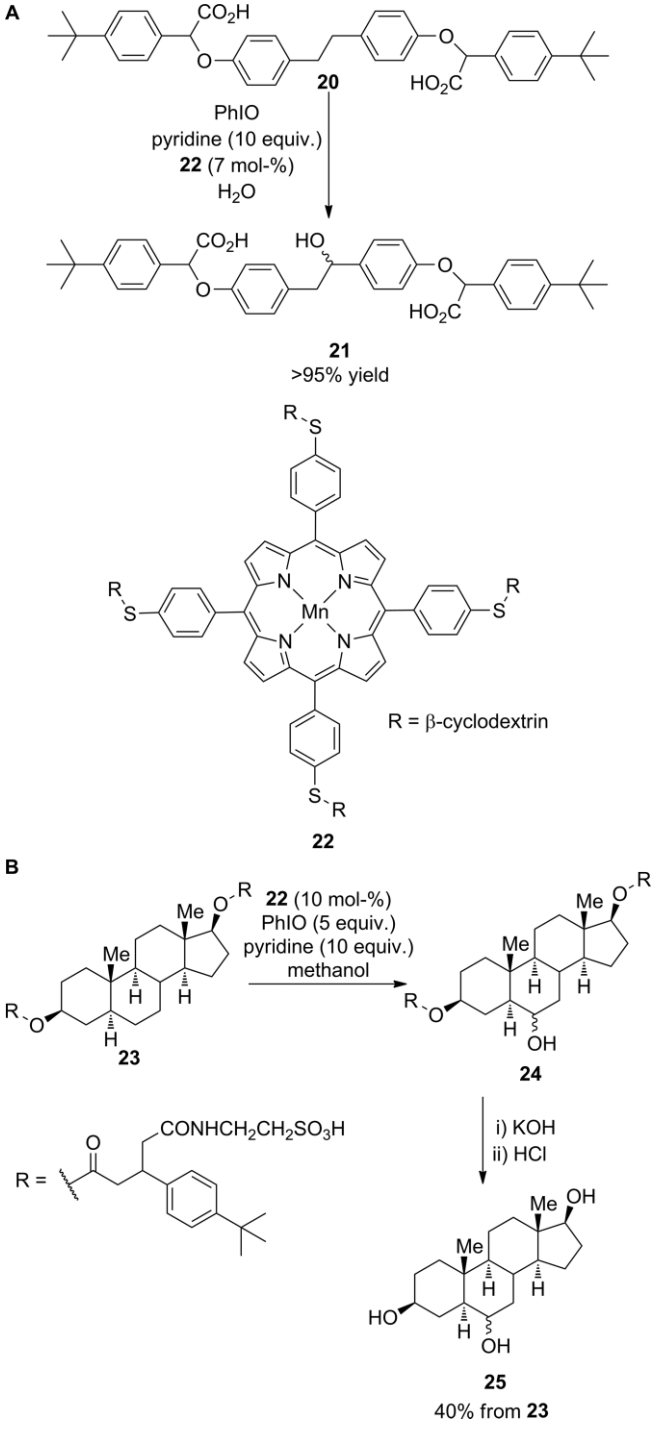
chlorinated cyclohexene products **12**–**14** suggesting the reaction proceeded by a radical pathway.[14] Manganese porphyrin catalysts show good chemoselectivity for the oxidation of tertiary C–H bonds over secondary and primary C–H bonds, as expected for a reaction involving a radical intermediate (Scheme 3, B).



Scheme 3. A) Product distribution of norcarane oxidation by manganese-porphyrin-catalyst, B) Manganese-porphyrin-mediated oxidation or chlorination of adamantane, yields are based on the oxidant.

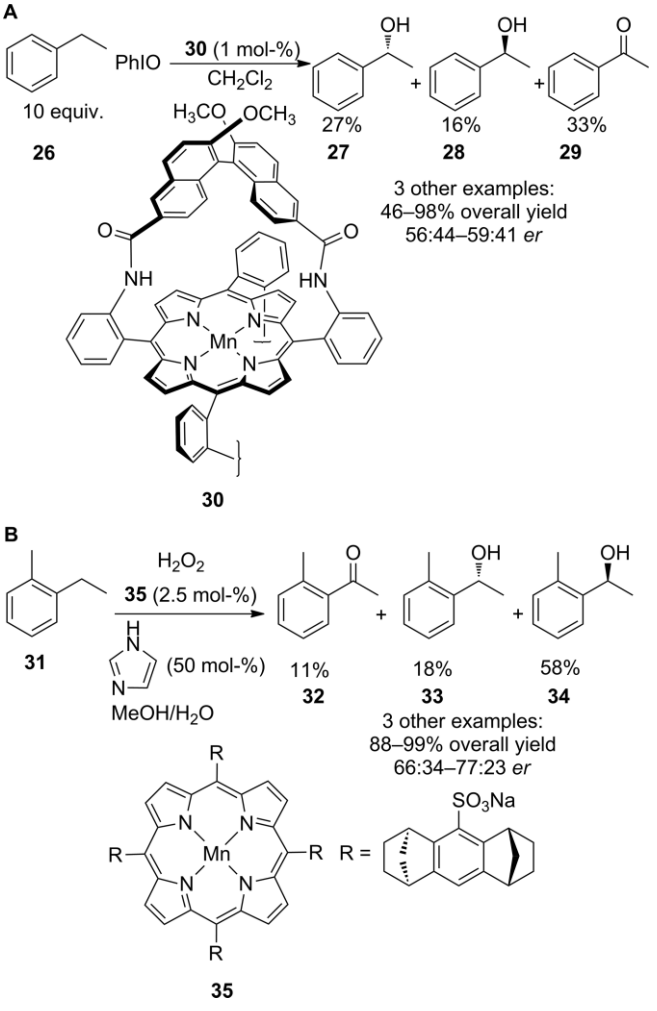
It was possible to increase selectivity for primary C–H bonds by increasing the steric bulk at the substituents at the *meso*-position of the porphyrin ligand. This increased selectivity was amplified if the substrate used was also sterically demanding.[15] Breslow et al. achieved selectivity by using a porphyrin bearing cyclodextrin groups, **22**, which allowed non-covalent binding at multiple points to steroid analogues through the hydrophobic effect.[16–18] This new catalyst displayed an increased turn-over number (TON) compared to previous catalysts for some substrates. It also gave novel chemoselectivity, albeit with low con-

version (2–3 catalyst turnovers), for steroids with hydrophobic arms (Scheme 4).



Scheme 4. Manganese-porphyrin-catalysed selective hydroxylation in the presence of **22**: A) hydroxylation of benzylic C–H bonds and B) selective hydroxylation in a steroid.

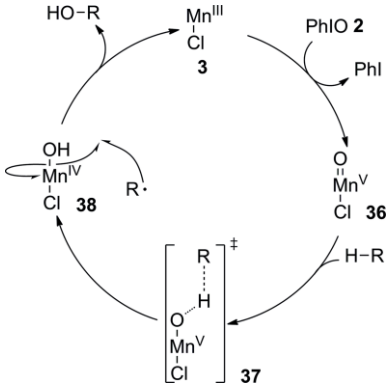
Initial stereoselective oxidations, using a manganese porphyrin with a bridging binaphthyl group **30**, revealed an enantiomeric ratio (*er*) of 56:44 to 63:37 favouring the (*R*)-enantiomer of the benzylic alcohol **27** (Scheme 5A).[19] A porphyrin ligand with a *meso*-substituent consisting of two norborane units fused to a central arene[20] was found to give improved enantioselectivity reaching 76:24 *er* for the hydroxylation of ethyltoluene (Scheme 5).[21] This reaction used H_2O_2 as an oxidant and water/methanol as the solvent system.



Scheme 5. Enantioselective manganese catalysis: A) using a porphyrin ligand containing a bridging binaphthyl group and B) using a porphyrin ligand bearing arene-fused norbornane substituents.

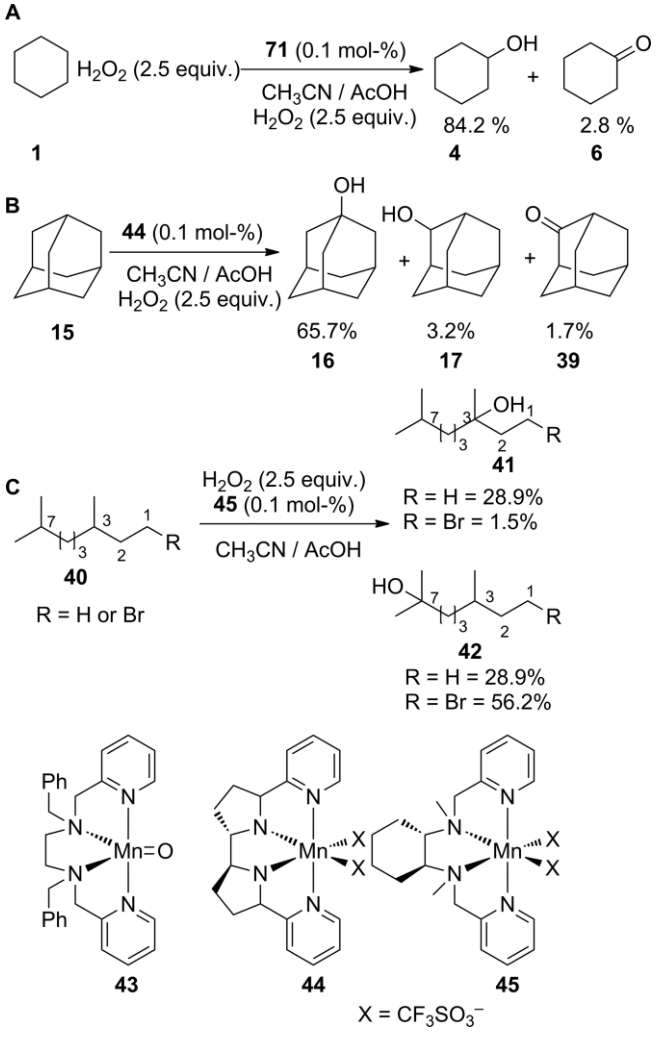
The mechanism of C–H oxidation by metalloporphyrins remains under investigation, although a general catalytic cycle is now well established (Scheme 6). The active catalyst for hydrogen abstraction is proposed to be a Mn^{V} oxo intermediate **36**, which is generated by oxidation of the Mn^{III} precatalyst **3** by iodosylbenzene **2**. This generates an alkyl radical and a Mn^{IV} complex with the hydroxo- and chloro-ligands in a *trans*-orientation. The alkyl radical then recombines with the hydroxide ligand in the oxygen rebound step.[14,22,23] This mechanism is commonly referred to as the heteroatom-rebound mechanism or Heteroatom-Rebound-Catalysis (HRC).

The oxidation of C–H bonds has also been achieved with a range of related tetradentate amine ligands on Mn^{II} centres. Nam et al. reported the oxidation of alkanes using a manganese oxo complex **43**[24] and this was expanded upon by Bryliakov and co-workers who showed that similar complexes, **44** and **45**, were capable of the chemoselective oxidation of C–H bonds, with hydrogen peroxide, in high yield (Scheme 7, A).[25] The



Scheme 6. Heteroatom rebound mechanism for manganese porphyrin catalysis.

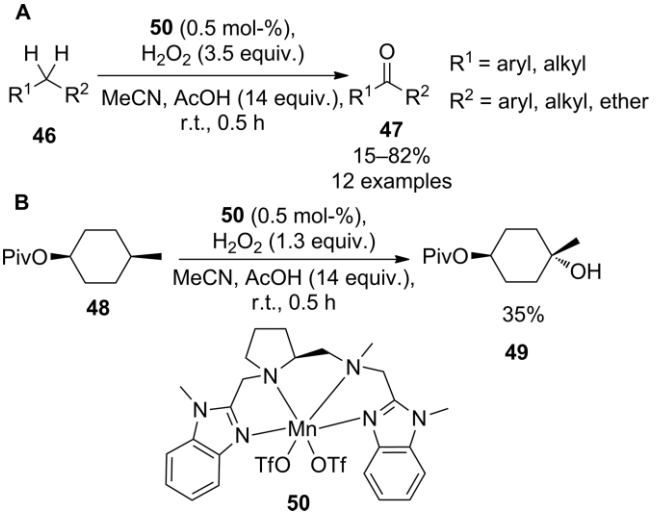
manganese complexes **44** and **45** were chemoselective for the oxidation of tertiary over secondary centres and for positions more remote from electronegative substituents. For instance, 1-bromo-3,7-dimethyloctane **40** was chemoselectively oxidised at



Scheme 7. Use of an amidopyridine manganese complex to catalyse: A) the hydroxylation of simple cyclic alkanes, B) the chemoselective hydroxylation of a tertiary carbon over a secondary carbon and C) the selective hydroxylation of a more remote (from bromine) tertiary centre.

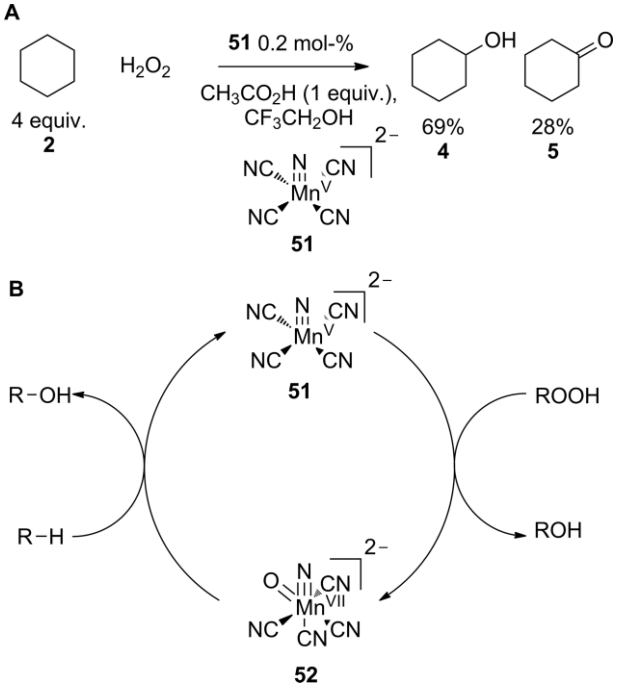
the distant C^7 tertiary centre, over the C^3 tertiary centre, **42** (Scheme 7, C).

A benzimidazole ligated manganese complex **50** has also been used in C–H oxidation (Scheme 8).[26] Unlike the previous catalysts, preferential oxidation to the ketone was observed where only secondary sites were available. However, chemoselective oxidation of tertiary sites over secondary sites to give tertiary alcohols **76** was still observed.



Scheme 8. Manganese-catalysed oxidation to: A) ketones, from a secondary carbon centre and B) alcohols from a tertiary carbon centre.

A square pyramidal tetracyano Mn^V **51** was used to oxidise C–H bonds with a variety of oxidants (Scheme 9).[27] Notably the system achieved better yields (>95 %) for C–H oxidation than had previously been reported. A different mechanism was



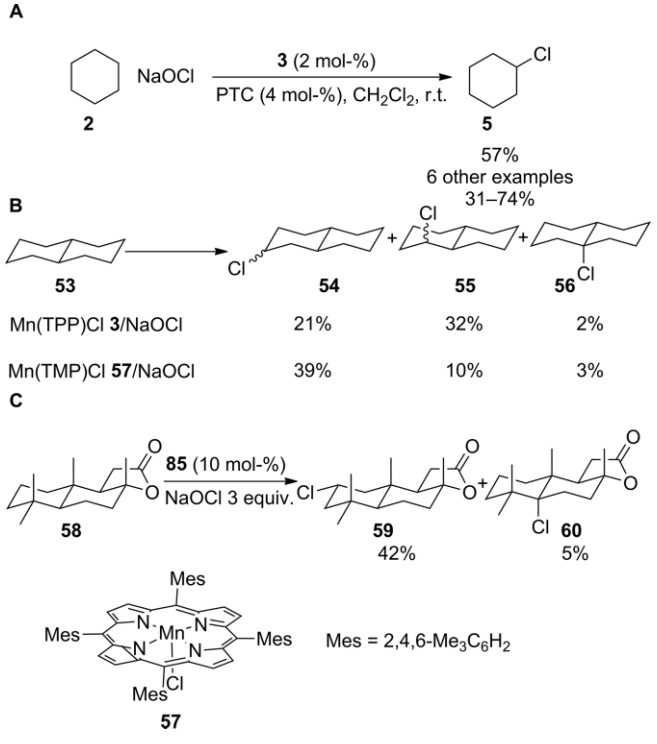
Scheme 9. Manganese(V) complex catalysed oxidation A) of cyclohexane and B) proposed mechanism of oxidation.

proposed for this catalyst: a Mn^{VII} nitride oxo intermediate was suggested to mediate hydrogen abstraction as opposed to a more conventional Mn^{V} intermediate.

2.2. Carbon–Halogen Bond Formation

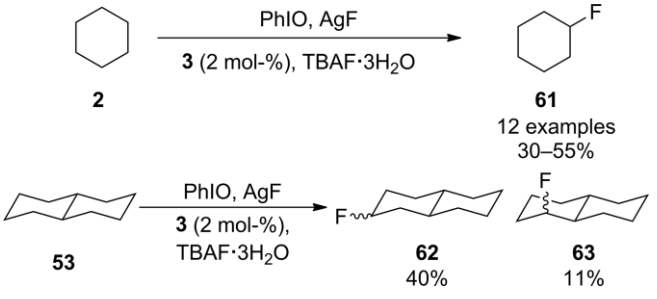
2.2.1 Carbon–Halogen Bond Formation by C–H Activation

The chlorination and bromination of C–H bonds has been reported as a side product in C–H oxidation reactions using manganese porphyrin catalysts.[28,29] However, these reports remained unexploited for almost thirty years as establishing control for halogenation over oxygenation was not possible. The understanding of the heteroatom-rebound mechanism (see Section 2.1) meant the crucial influences on selectivity could be more easily identified and therefore used to increase the yield of the halogenated product.[30] This was achieved by changing the axial ligand to a stronger donor ligand (F^- or Cl^- compared to imidazole, pyridine, acetonitrile). This was proposed to slow the rate of hydroxyl transfer and thus allow halogenation to dominate. This was first applied to C–H chlorination by Groves and co-workers, where the reaction was chemoselective for the activation of secondary C–H bonds as opposed to tertiary C–H bonds.[31] The chlorination of decalin was selective for the CH_2 groups and as was the chlorination of biologically relevant molecules such as sclareolide **58** (Scheme 10).

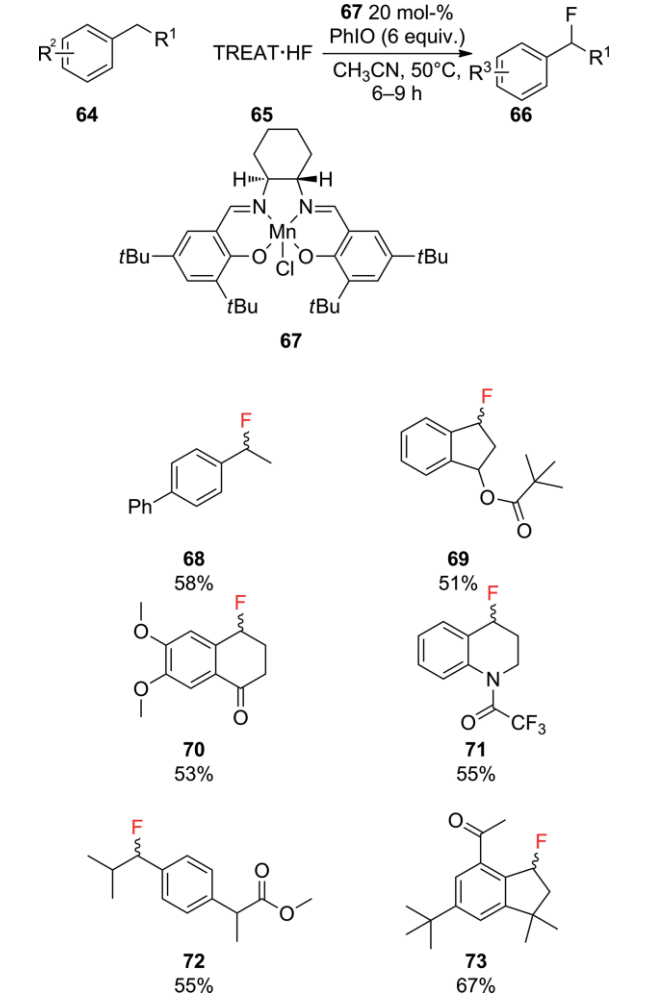


Scheme 10. The chlorination of C–H bonds A) simple cyclic hydrocarbons, B) selectivity of reaction and C) the application to biologically relevant molecules.

This methodology was expanded to include the fluorination of C–H bonds. Fluorinated molecules exhibit high biological activity and the incorporation of ^{18}F atoms allows these compounds to be used as tracers for medical imaging.[32] Fluorination was achieved using silver(I) fluoride as a halide source in place of NaOCl, and with the addition of sub-stoichiometric amounts of tetrabutyl ammonium fluoride (TBAF). A possible limitation of this methodology was the lower yields observed for the fluorination of benzylic positions due to the production of large amounts of oxygenated product. The use of a Mn(salen) complex with triethylamine trihydrofluoride (TREAT·HF) and AgF suppressed the oxygenation reaction and increased the yield of fluorination (Scheme 11). Minor modification of this method allowed for the functionalisation of benzyl C–H bonds with ^{18}F atoms which could then be used in Positron Emission Tomography (PET) imaging (Scheme 12). This method removes

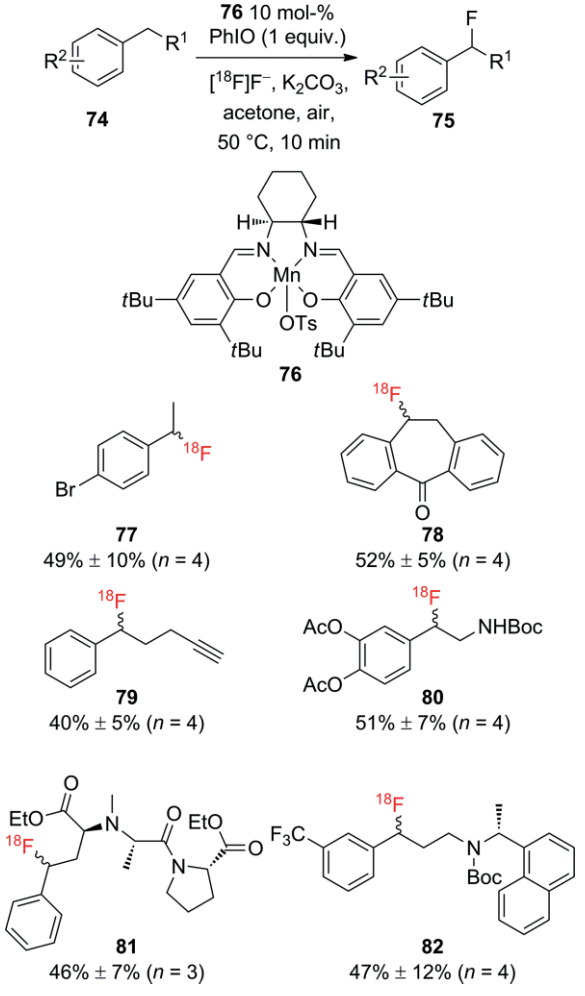


Scheme 11. Fluorination of C–H bonds.



Scheme 12. Fluorination of benzylic C–H bonds.

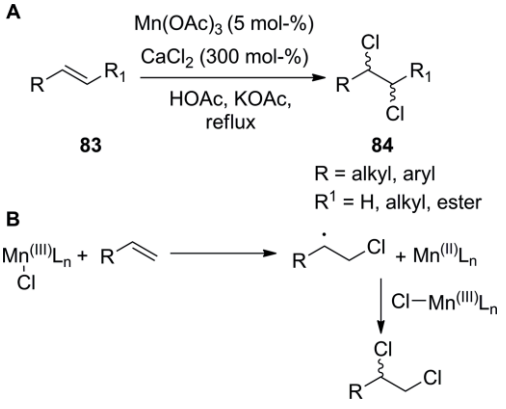
the need for prefunctionalisation of the substrate and allows for more rapid screening of target substrates. Given ^{18}F has a half-life of 110 min, it was important that the reaction was completed in 10 min allowing the methodology to become a viable imaging strategy (Scheme 13). This area of hugely influential research has been thoroughly reviewed by Groves.[30]



Scheme 13. Fluorination of benzylic C–H bonds using ^{18}F, yields reported are radiochemical conversions (RCC), are decay corrected, and averaged over (*n*) experiments.

2.2.2. Carbon–Halogen Bond Formation by Reduction of an Alkene

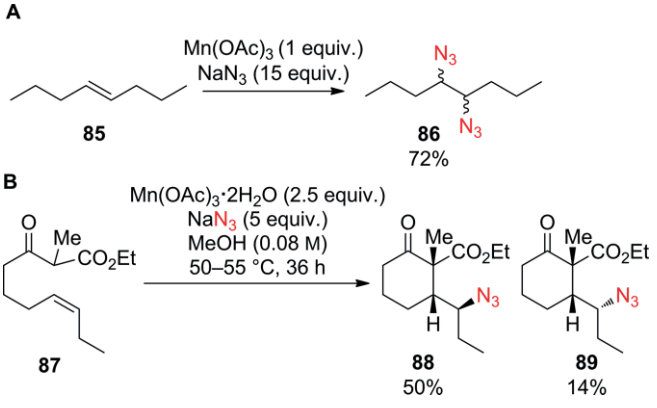
The dichlorination of alkenes has been reported using a manganese acetate catalyst and calcium chloride.[33] The reaction proceeds with good yields for a range of unsaturated hydrocarbons and a moderate yield with methyl cinnamate. Preliminary mechanistic investigations indicated a radical mechanism whereby the alkene is functionalised in two steps through an alkyl radical to give the dichloro-product (Scheme 14).



Scheme 14. A) Dichlorination of alkenes and B) the proposed mechanism.

2.3. Azide Formation

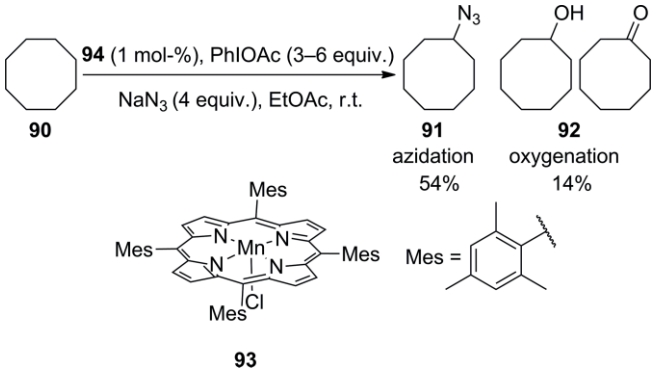
Fristad et al. reported the conversion of alkenes to diazides using a stoichiometric Mn^{III} acetate as a radical initiator and NaN_3 as the source of azide (Scheme 15).[34] Although the original report required high reaction temperatures and a large excess of NaN_3, Snider and co-workers optimised the system and applied it to the oxidative cyclisation of malonates bearing pendant alkenes and with termination by the radical trapping of azide.[35]



Scheme 15. A) The diazidation of alkenes and B) oxidative cyclisation terminated by azide trapping.

The activation of secondary, tertiary or benzylic C–H bonds to incorporate azides in a range of molecules (including bioactive molecules and pharmaceuticals) has been performed in moderate to good yields.[36] Building upon previous work using Heteroatom Rebound Catalysis (HRC), manganese porphyrin **93** or a salen complex gave good azidation yields for linear and cyclic alkanes as well as benzylic C–H bonds and followed the expected selectivity for HRC (Scheme 16).

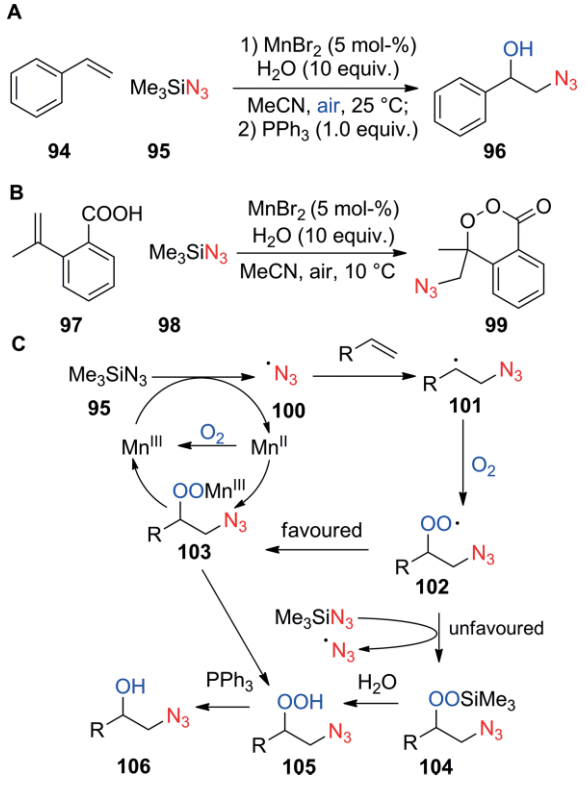
The hydroxyazidation of alkenes was reported by Jiao et al. using Me_3SiN_3 as an azide source, $MnBr_2$ as catalyst and air as the stoichiometric oxidant.[37] Internal and terminal styrene derivatives and aliphatic alkenes all successfully underwent hydroxyazidation. The reaction was found to tolerate nitro and ester functionalities on the arene. The method was used to incorporate azides in bioactive molecules including a steroid bearing a pendant alkene. An unexpected side product of the



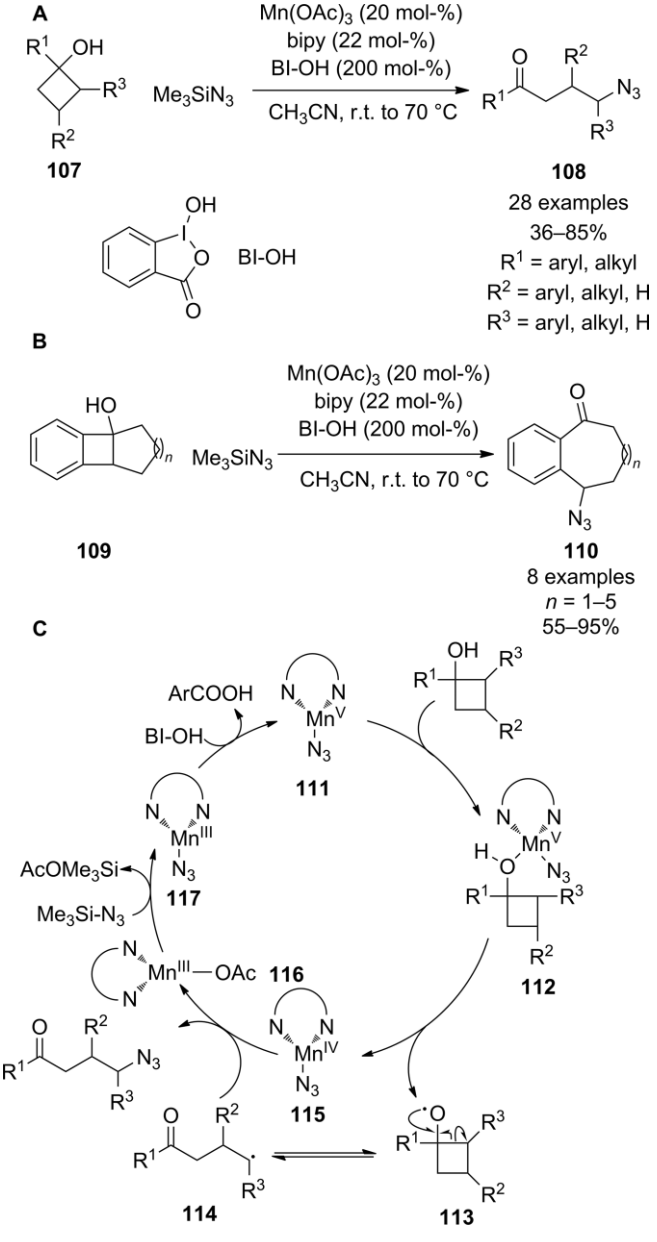
Scheme 16. Mn porphyrin used to catalyse the azidation of C–H bonds.

attempted hydroxyazidation of benzoic acids derivatives was the formation of a cyclic peroxyester product **99** (Scheme 17, B). Using detailed mechanistic studies and DFT calculations a radical mechanism was proposed (Scheme 17, C). Initially, O_2 oxidises trimethylsilylazide to the N_3 radical **100** which reacts with the alkene to give a secondary carbon radical **101**. A second reaction with O_2 forms a peroxo-radical **102**. At this point, the mechanism can proceed in two ways. The favoured route is proposed to involve single-electron transfer (SET) from Mn^{II} to give a peroxide **105** and the Mn^{III} compound used in the first step. The disfavoured route consists of peroxo radical attack on another equivalent of Me_3SiN_3 which leads to the silyl protected peroxide **104**. This then reacts with H_2O to give the same peroxide product **105** as that from the favoured route. Finally, PPh_3 reduces the peroxide to an alcohol to give the hydroxyazide **106**.

$Mn(OAc)_3$ combined with bipyridine (bipy) ligand can catalyse the azidation of cyclobutanols by C–C bond cleavage (Scheme 18).[38] This work requires a hypervalent iodine oxidant (BI–OH) to facilitate catalyst turnover. A range of cyclobutanol starting materials were transformed by this methodology to form primary, secondary and tertiary azides. Mechanistic studies showed that the reaction proceeded by a radical mechanism. The active catalyst was proposed to be a manganese(V) azide **111** which radically abstracted a proton from the alcohol



Scheme 17. A) The hydroxyazidation of alkenes, B) formation of cyclic peroxyester products from benzoic acid derivatives and C) the proposed mechanism.

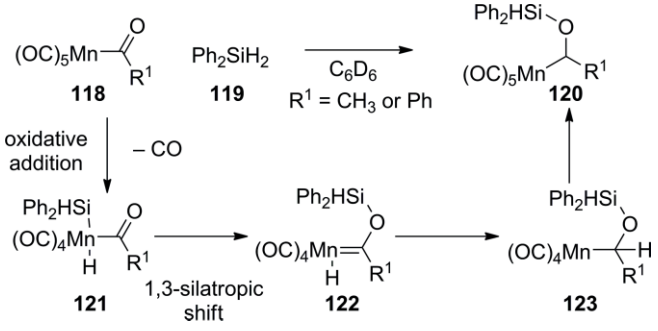


Scheme 18. The manganese-catalysed cleavage of cyclobutanes: A) to give alkyl azides, B) to give ring-expanded benzylic azides and C) the proposed mechanism.

before the alkyl radical **114** was terminated by trapping of the azide. Manganese(III) acetate **116** would then react with Me_3SiN_3 to give manganese(III) azide **117** which would be oxidised to the active manganese(V) catalyst.

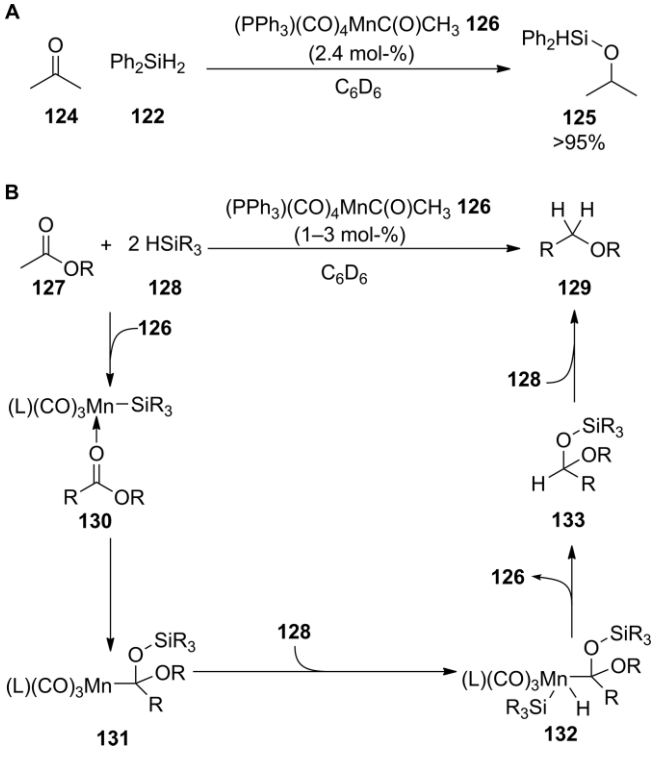
2.4. Hydrosilylation

Hydrosilylation of an acyl manganese species **118** was achieved using Ph_2SiH_2 (Scheme 19). The manganese centre is thought to undergo oxidative addition to the silane and 1,3-silatropic shift from manganese to oxygen is followed by a hydride migration to give silyl ether **120**.[39]



Scheme 19. Hydrosilylation of manganese acyl compounds.

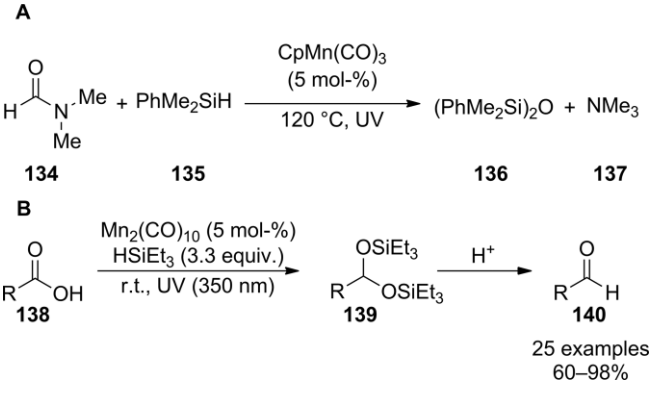
The addition of a ketone showed that these acyl manganese compounds were competent catalysts for the reduction of ketones with primary, secondary or tertiary silanes (Scheme 20, A).[40] The most active catalyst was $(PPh_3)(CO)_5MnC(O)CH_3$ with



Scheme 20. Reduction of carbonyl functionalities by sub-stoichiometric manganese compounds A) Reduction of ketones and B) reduction of esters to ethers.

increased activity noted with pre-stirring in silane for 20 min. This system has also been used to reduce esters to ethers (Scheme 20, B).[41] The proposed mechanism for ester hydrosilylation was more complex than that for the hydrosilylation of ketones. Initially, the pre-catalyst is transformed to the active manganese(I) silyl species **130**. Coordination of the carbonyl to the manganese(I) centre preceeds insertion of the ester into the Mn–Si bond. Oxidative addition into the silane gives an 18-electron manganese(III) complex **132** which undergoes reductive elimination of the silyl acetal to form a C–H bond and give silyl hemi-acetal **133**. Finally hydride transfer from a disilyl manganese compound gives the ether product **129**.

Manganese carbonyl compounds under photoirradiation have been shown to be active catalysts for the reduction of dimethylformamide (DMF) and diethylformamide (DEF) (Scheme 21A).[42] The reduction of carboxylic acids to aldehydes by hydrosilylation was reported under similar conditions (Scheme 21, B).[43] A range of phenyl acetic acids, alkenyl and alkyl carboxylic acids were successfully reduced. Benzoic acid derivatives were also reduced but with low conversions (ca. 30 %). The reduction of α,β-unsaturated carbonyl groups proceeded with concurrent reduction of the alkene. Carboxylic acids bearing pendant terminal alkenes saw both functionalities undergo hydrosilylation but internal, isolated, alkenes were unreactive.

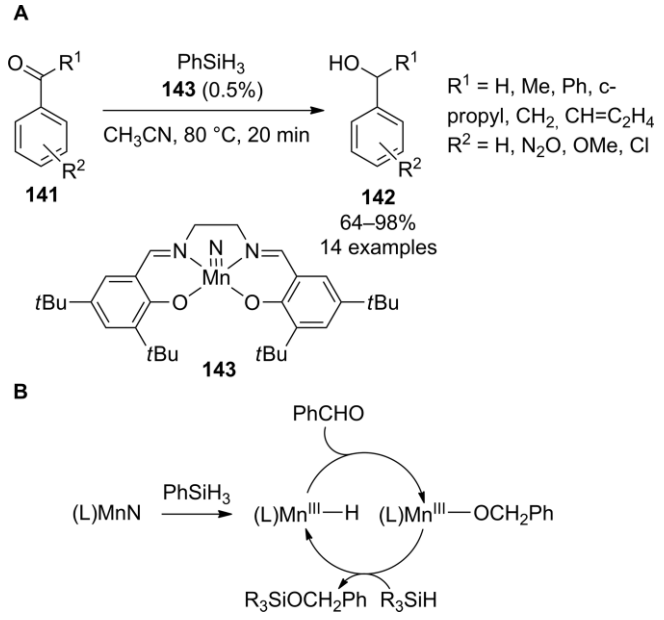


Scheme 21. A) Reduction of DMF to trimethylamine and a disilyl ether, B) hydrosilylation of a carboxylic acid to give an aldehyde.

A Mn^V nitride salen complex **143** was used for the hydrosilylation of aldehydes and ketones with primary, secondary and tertiary silanes in good yields at low catalyst loadings (Scheme 22, A).[44] It was suggested that the active catalyst was a manganese(III) hydride species. Carbonyl insertion to the Mn–H bond, before the silane was proposed to drive catalyst turnover and lead to silyl ether formation.

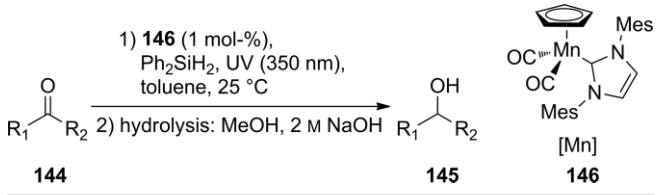
Lavigne et al. reported that the manganese *N*-heterocyclic carbene (NHC) complex **146** would catalyse the reduction of a variety of aryl and aliphatic aldehydes and ketones under UV irradiation (Table 1).[45] The electronics and sterics of the substituents on the carbene ligand were altered with mesityl substituents giving the best yields.

The use of a redox non-innocent bis(imino)pyridine (BIP) ligand was reported by Trovitch (Scheme 23).[46] This highly ac-



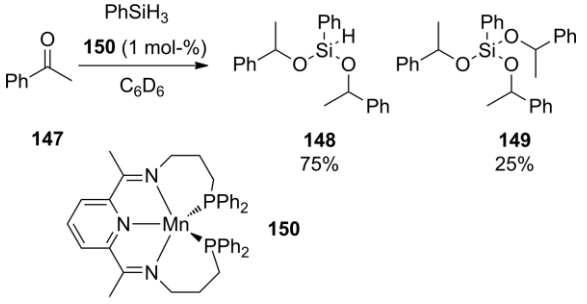
Scheme 22. Hydrosilylation of carbonyls with a manganese(salan) nitride complex: A) reaction scope and B) proposed mechanism.

Table 1. Hydrosilylation of carbonyls with a manganese carbene complex.



R^1	R^2	Conversion [%]	Yield [%]
Ph	H	> 97	90
4-$CH_3(O)CPh$	H	> 97	55
Pyridine	H	> 97	97
$CH_2=CH-(CH_2)_{10}$	H	> 97	71
Ph	Me	> 97	65
$CH_3(CH_2)_8$	Me	59	–

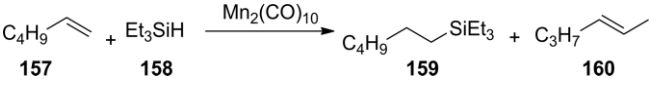
tive complex **150** exhibited a TOF of 76,800 h^{-1}, far exceeding that of other first-row transition metals (Fe, Co, etc).[47] Although highly active, a mixture of both tertiary **148** and quaternary silanes **149** were formed. Notably, the reaction was suggested to proceed by a radical mechanism.



Scheme 23. Hydrosilylation of carbonyls with a manganese bisiminopyridine complex.

Although a number of manganese systems have been used to catalyse the hydrosilylation of carbonyls, very few systems have been published for the hydrosilylation of alkenes. The first reported alkene hydrosilylation used a silylmanganese(I) catalyst which could be activated either thermally or photochemically (Scheme 24).[48] Thermal activation gave a range of products, including dehydrosilylation and alkene isomerisation, and was proposed to proceed by a radical mechanism. In contrast, the photochemical activation gave the hydrosilylation product and was proposed to proceed by a coordination mechanism akin to the Chalk–Harrod mechanism.

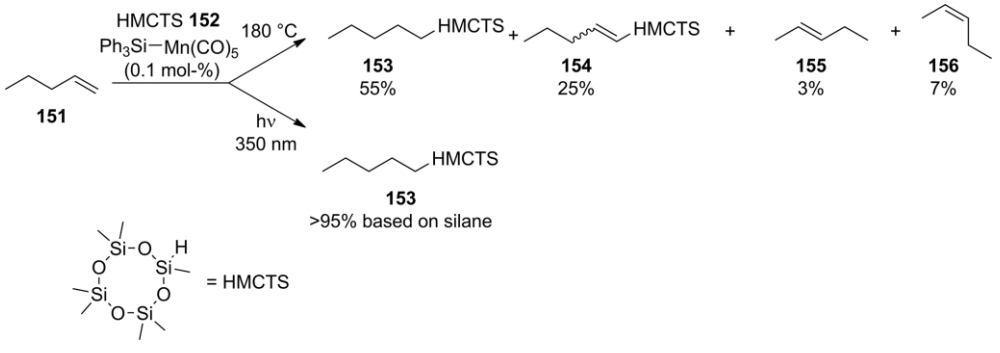
$Mn_2(CO)_{10}$ was used as a hydrosilylation catalyst to give the linear silane regioselectively without alkene isomerisation **160** (Scheme 25).[49] However the $Mn_2(CO)_{10}$ catalyst showed low activity and the use of a manganese carbonyl compound negates the inherent non-toxicity of manganese.



Scheme 25. Hydrosilylation of alkenes using a manganese carbonyl compound.

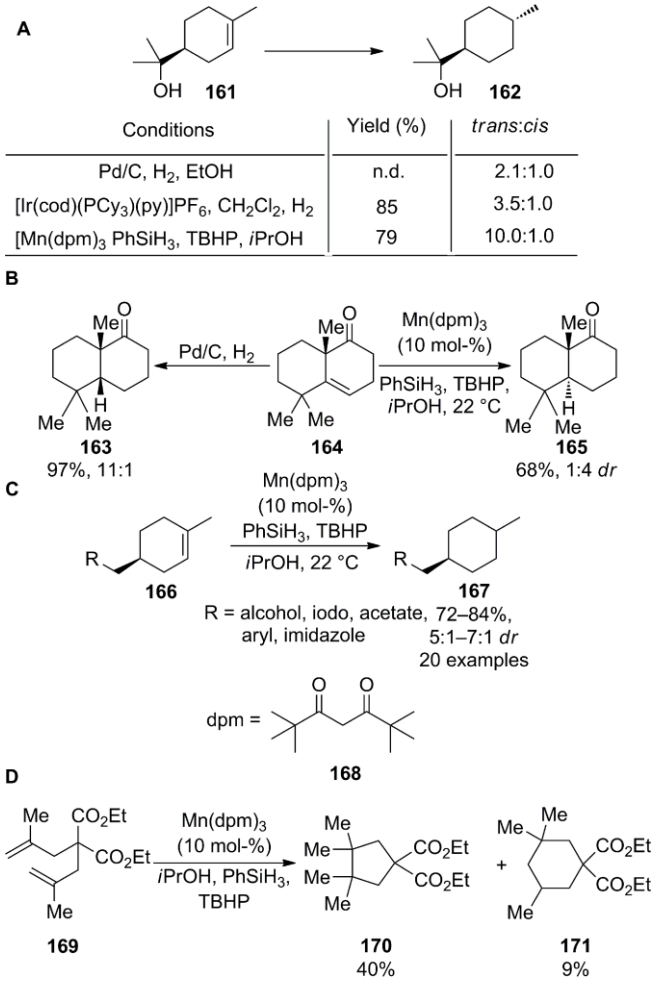
2.5. Formal Hydrogenation and Other Hydrofunctionalisations

$Mn(dpm)_3$ has been used in the formal hydrogenation of cyclic alkenes to give the thermodynamically favoured *trans*-dia-



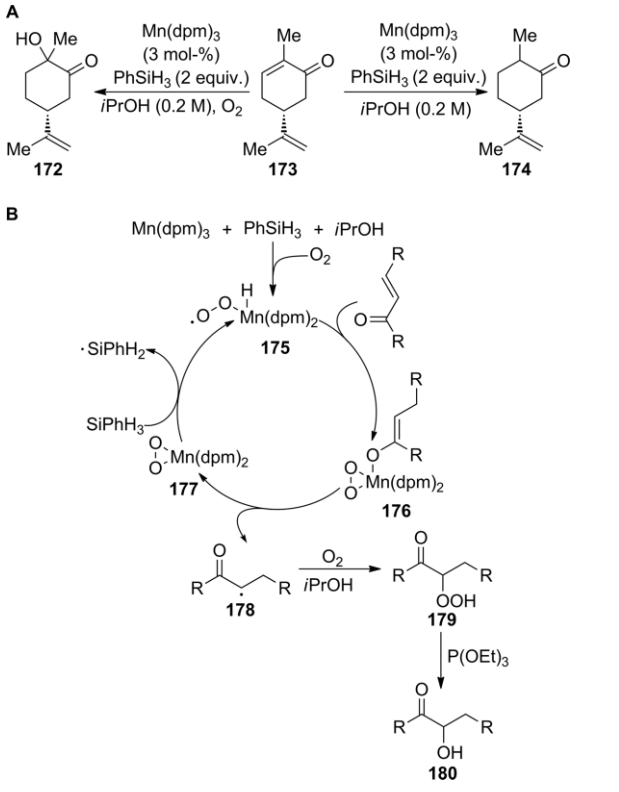
Scheme 24. Hydrosilylation of carbonyls with a manganese bisiminopyridine complex.

stereomer (Scheme 26, B).[50] This was observed to be more diastereoselective than common hydrogenation catalysts (such as Pd/C) (Scheme 26, A) and offers a complementary methodology. The system tolerated alcohol, iodide, acetate, ester, ketone and imidazole functionalities and also reduced primary, secondary and tertiary alkenes (Scheme 26, C). The application of the reaction conditions to diethyl dimethallylmalonate gave the cyclopentane derivative suggesting that the reaction proceeds by a radical mechanism (Scheme 26, D).

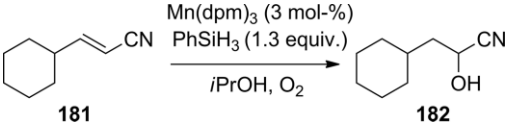


Scheme 26. The hydrogenation of alkenes by a manganese salt A) comparison to precious metal systems, B) stereoselectivity of the transformation compared to Pd/C, C) reaction scope and D) cyclisation of 1,6-dienes.

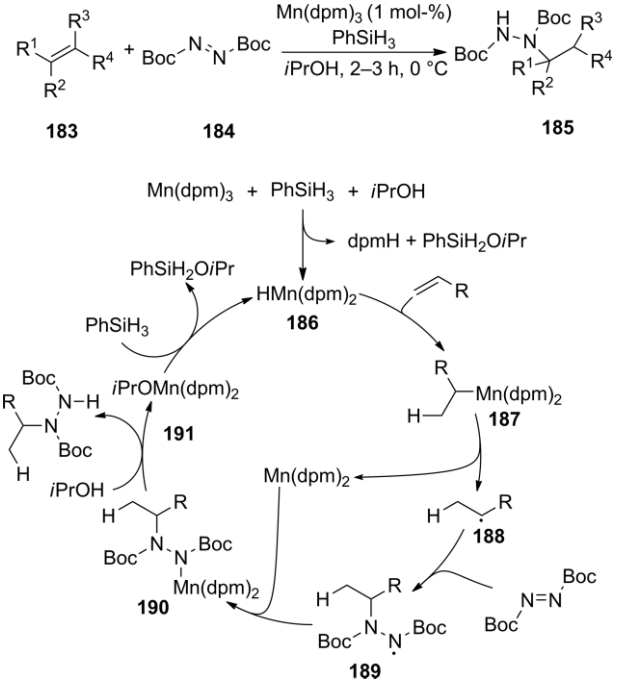
$Mn(dpm)_3$ has also been reported to catalyse the chemoselective alkene reduction of α,β-unsaturated ketones.[51] When the reaction was carried out under an atmosphere of air formal hydration of the alkene was observed as opposed to hydrogenation to give a mixture of α-hydroperoxy ketone **179** or α-hydroxy ketone **180** (Scheme 27).[52] The addition of $P(OEt)_3$ was used to reduce the peroxide to the α-hydroxy ketone. The active catalyst was proposed to be a manganese(V)peroxo intermediate **176** which mediates hydrogen atom transfer to the alkene to give the alkylradical **178** which can then react with O_2. When α,β-unsaturated nitriles were used, a majority of α-hydroxylation of the double bond was observed (Scheme 28).[53]



Scheme 27. A) The hydroxylation of alkenes and B) the proposed mechanism and C) the hydrohydroxylation of α,β-unsaturated alkenes.



Scheme 28. The hydroxylation of alkenes bearing nitrile substituents.

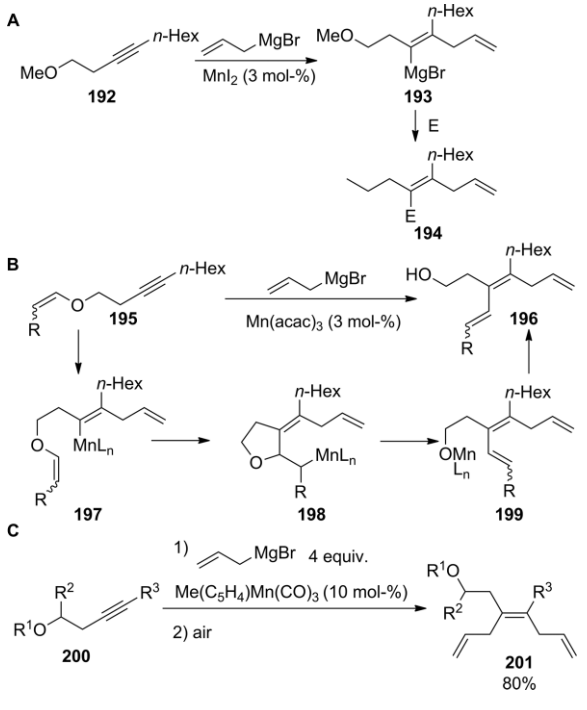


Scheme 29. The hydrohydrazination of alkenes.

Carreira et al. used the same conditions to catalyse the hydrohydrazination of alkenes (Scheme 29).[54] The manganese system proved to be more active (if less selective) than an analogous copper-catalysed reaction.[55] A variety of primary, secondary and tertiary alkenes underwent hydrohydrazination to give the amine product **185** using di-*tert*-butyl azodicarboxylate as the amine source. A variety of silanes could be used as the stoichiometric reductant due to the increased reactivity of the manganese system.

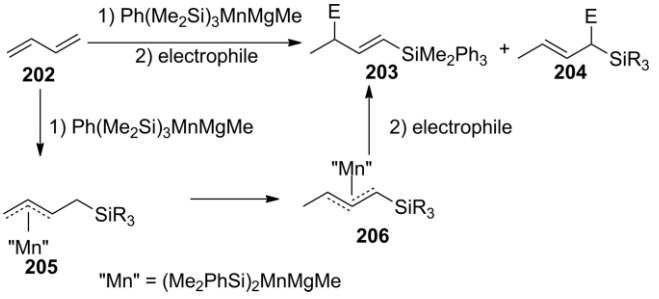
2.6. Carbometallation

The carbometallation of olefins gives access to a range of diversely functionalised products by formation of carbon–carbon or carbon–heteroatom bonds. Oshima and co-workers used allylmagnesium bromide and simple manganese salts to perform a range of transformations from alkyne starting materials **192** (Scheme 30).[56] The manganese-catalyst created an alkenyl Grignard reagent which could then react further with a range of electrophiles. For alkynes with a vinyl ether substituent **195**, rearrangement to a diene product **196** was observed and proposed to proceed through a cyclic intermediate **198**. Additionally, if after two hours, the reaction was exposed to air, diallylation of the alkyne was observed.

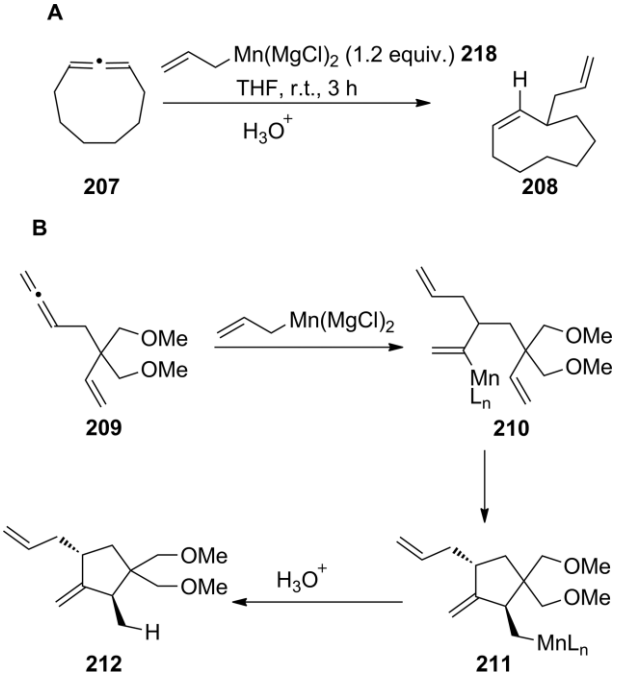


Scheme 30. The carbometallation of alkynes A) further reaction with electrophile, B) rearrangement reaction and C) diallylation of an alkyne.

Oshima and co-workers reported the carbometallation of isoprene and derivatives to give either a vinylsilane **203** or 1,4-hydrosilylation product **204** (Scheme 31).[57] Allenes were reduced to alkenes and then further functionalised by the addition of an electrophile (Scheme 32, A).[58] If a pendant alkene was present, the substrate would undergo cyclisation to a five-membered ring (Scheme 32, B). Again, exposure of the reaction to air after 9 hours allowed for the diallylated product to be formed.



Scheme 31. Carbometallation of butadiene.



Scheme 32. Carbometallation of allenes to give A) functionalised cyclic alkene and B) a five-membered ring.

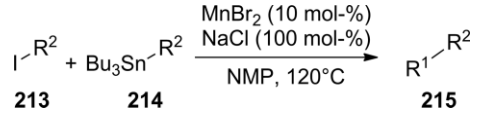
2.7. Cross-Coupling

Transition-metal-catalysed C–C, C–N and C–O bond forming reactions are powerful synthetic tools. Many modern methodologies rely on the use of precious metals, typically palladium. The high catalytic activity, wide substrate scope and operational simplicity has drawn palladium-catalysed protocols to the forefront of modern synthesis. Powerful methods using earth-abundant alternatives are now emerging, and within these manganese catalysts have shown tremendous promise. One significant challenge in cross-coupling using metals such as cobalt, iron or manganese lies in aryl(Csp^2)–aryl(Csp^2) bond forming reactions. Although limited examples exist using iron,[59,60] these rely on challenging synthetic methods.

Manganese has been used to catalyse Stille-type cross-coupling reactions to give aryl-aryl bonds in high yields (Table 2).[61] However, more forcing reaction conditions were

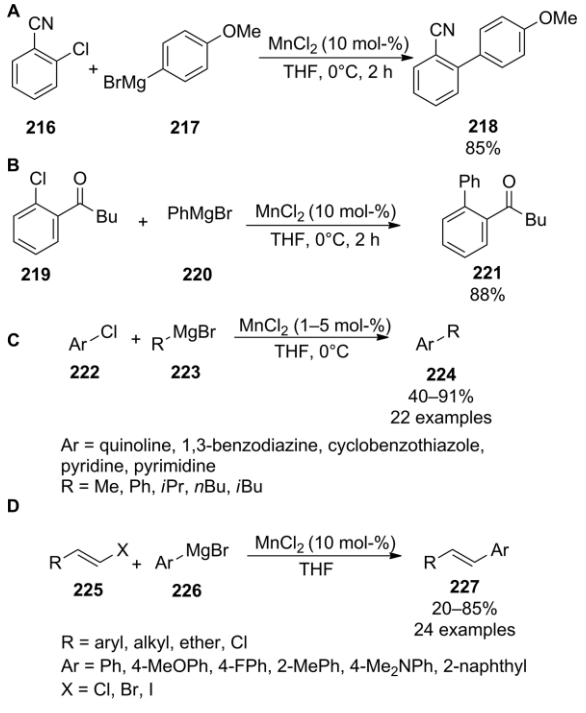
needed then those using the analogous palladium-catalysed reactions. NaCl was required as an additive and only aryl- and alkynyl-iodine reagents were suitable electrophiles. Both aryl and alkenyl stannanes underwent successful cross-coupling reactions and the use of 1,4-diiodoaryl electrophiles allowed for a double cross-coupling reaction in high yields.

Table 2. Manganese-catalysed Stille cross-coupling.



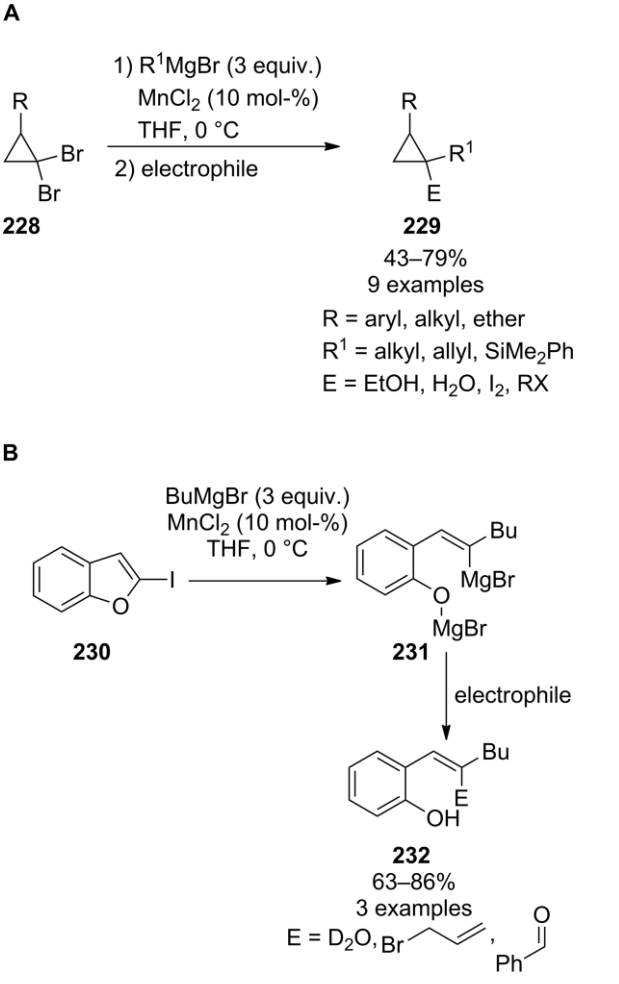
R^1	R^2	Time [h]	Yield [%]
Ph	4-CH_3Ph	10	81
PhCH=CH	PhCH=CH	15	81
Ph	2-thiophene	13	75
4-MeOPh	2-furan	8	90
Ph	PhC≡C	9	88

Cahiez and co-workers reported the formation of aryl-aryl bonds catalysed by a simple manganese salt, using Grignard reagents and aryl chlorides as the coupling partners (Scheme 33, A).[6] The method was found to tolerate some ketone functionalities when PhMgBr was used (Scheme 33, B).[62] More reactive Grignard reagents (i.e. BuMgBr) led to nucleophilic addition at the ketone. The substrate scope of the aryl halide was limited to arenes bearing electron-withdrawing substituents. This was expanded by Rueping and leawsuwan to incorporate a range of nitrogen containing heterocycles which underwent successful cross-coupling reactions with aryl- and alkyl Grignard reagents (Scheme 33, C).[63] This was developed further by Cahiez to include unactivated alkenyl halides (Scheme 33, D).[64] The stereochemistry of the vinyl halide was, in most cases, retained.



Scheme 33. Cross-coupling reactions of Grignard reagents with aryl and alkenyl halides A) coupling of aryl Grignard reagents with aryl chlorides bearing electron-withdrawing groups, B) in the presence of a ketone, C) with nitrogen containing heterocycles as electrophiles and D) with alkynyl halides acting as electrophiles.

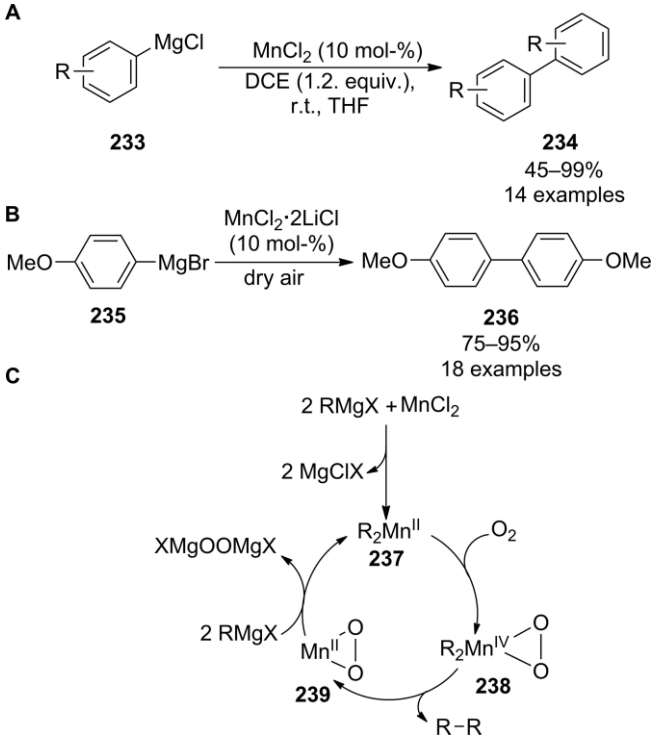
The coupling of Grignard reagents to *gem*-dibromocyclopropanes followed by further functionalisation with an electrophile was achieved using a $MnCl_2$ pre-catalyst (Scheme 34).[65] It was proposed that [$R_3MnMgBr$] was the active species and that the cross-coupling reaction preceeded manganese–halide exchange and was terminated by electrophilic trapping. This method could be applied to iodobenzofuran but with concurrent cleavage of the C–O bond. Again the organomanganese intermediate could be quenched by an electrophile allowing easy access to a diverse range of functionalities.



Scheme 34. Cross-coupling of A) *gem*-dibromo cyclopropanes and B) iodobenzofuran to give a ring-opened product.

In addition to cross-coupling reactions, the oxidative homocoupling of Grignard reagents has also been developed using $MnCl_2$ as the pre-catalyst (Scheme 35), with either atmospheric oxygen[66] or dichloroethane (DCE)[67] as the stoichiometric oxidant. Using DCE, arenes bearing electron-withdrawing groups and electron-donating groups gave good yields, but aryl groups with multiple substituents required longer reaction times. Heteroaromatic substrates were unreactive in this methodol-

ogy. Ethynylmagnesium chloride was successfully homocoupled in a 68 % yield. The high reactivity of aryl rings bearing electron-withdrawing substituents suggested that transmetallation was not the rate-limiting step – as is the case with palladium catalysis.

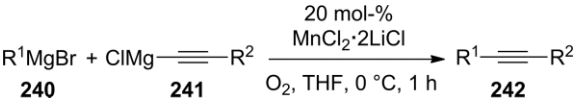


Scheme 35. The manganese-catalysed homocoupling: A) with DCE as an oxidant, B) with air as an oxidant and C) proposed mechanism when using air as an oxidant.

Using oxygen as the oxidant, the reaction was proposed to proceed by a Mn^{II}/Mn^{IV} cycle with a Mn^{IV} peroxo intermediate **263** (Scheme 35, C). Key to this mechanism was the need for rapid reductive elimination to avoid direct oxidation of the Grignard reagent to the corresponding phenol. Diaryl manganese(II) compounds were too stable for reductive elimination to occur at a sufficient rate, therefore it was necessary for the catalyst to be oxidised to Mn^{IV} and thus substantially increasing the rate of aryl-aryl reductive elimination. A range of arenes bearing both electron-donating and electron-withdrawing groups were tolerated although those with electron-donating substituents gave higher yields. Heteroaromatic compounds could also be homocoupled along with alkenes and alkynes. The coupling of alkenes to produce dienes proceeded with high stereoselectivity.

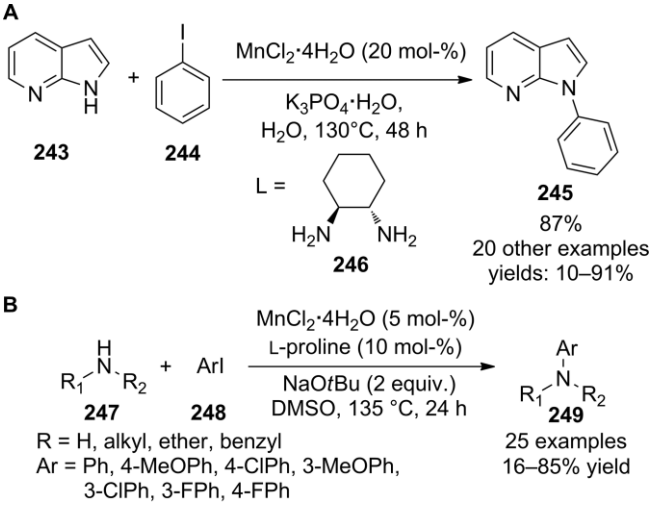
The oxidative coupling of Grignard reagents to prepare a range of unsymmetrical products was also reported (Table 3).[68] It was noted that homocoupling was highly dependent on the electronic and steric properties of the Grignard reagents used. Sterically encumbered Grignard reagents and those with arenes bearing electron-withdrawing groups heavily disfavoured homocoupling. Alkynylmagnesium halides were observed to undergo homo-coupling at a significantly slower rate than that of phenylmagnesium bromide. Therefore, the combination of aryl Grignard reagent with electron-donating substituents and a non-bulky alkynyl Grignard reagent proved to favour oxidative coupling over the homo-coupling of either reagent.

Table 3. Manganese-catalysed oxidative coupling of Grignard reagents.



R^1	R^2	Yield [%]	Yield R^1–R^1 [%]
4-MeOPh	pentyl	72	17
Naphthyl	$SiMe_3$	89	5
4-ClPh	pentyl	81	12
4-MeOPh	Ph	80	12
Naphthyl	4-Me_2NPh	68	6
5-EtO_2C-furyl	thiophene	69	7

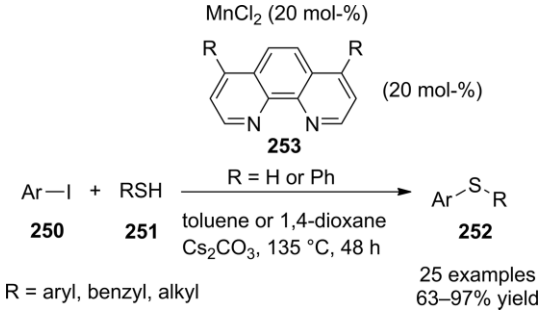
Teo and co-workers reported the cross-coupling reaction of pyrazoles, 7-azaindoles, indazoles and indoles with aryl iodides (Scheme 36) using $MnCl_2{\cdot}4H_2O$, *trans*-1,2-diaminocyclohexane and $K_3PO_4{\cdot}H_2O$.[69] A range of aryl iodides were successfully coupled and variation of the electronic character of the aryl iodide did not appear to affect reactivity, however *ortho*-substituents gave poor yields. This was later expanded to a range of aliphatic amines by using L-proline as the ligand and NaO*t*-Bu as the base.[70]



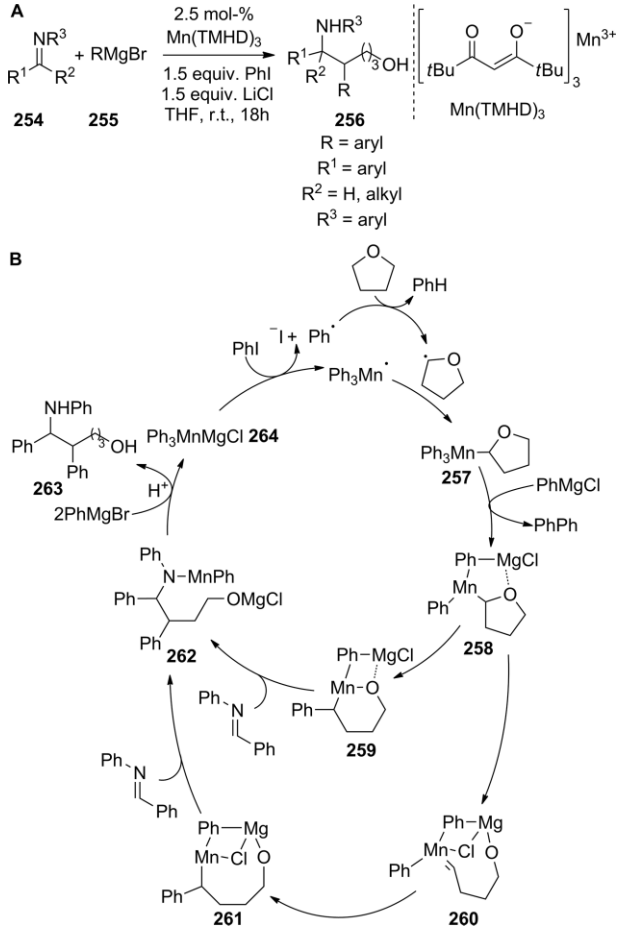
Scheme 36. Cross-coupling of aryl iodides with nitrogen nucleophiles: A) with heteroaromatic nitrogen nucleophiles and B) with alkyl nitrogen nucleophiles.

Liu et al. used $MnCl_2$ and a phenanthroline ligand to couple thiols and aryl iodides to form a variety of thioethers in moderate to good yields (Scheme 37).[71]

Wang reported the alkylation and radical cleavage of tetrahydrofuran, with trapping of the intermediate organomanganese species by imines or nitriles (Scheme 38). Primary and secondary imines were tolerated, although aromatic substituents were needed on both components of the imine. Other cyclic ethers, such as 2-methyl tetrahydrofuran and 1,4-dioxane, were unreactive.



Scheme 37. Cross-coupling of aryl iodides with sulfur nucleophiles.

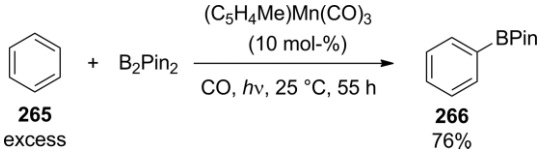


Scheme 38. The cleavage of THF and incorporation of nucleophile and electrophile: A) substrate scope and B) mechanism.

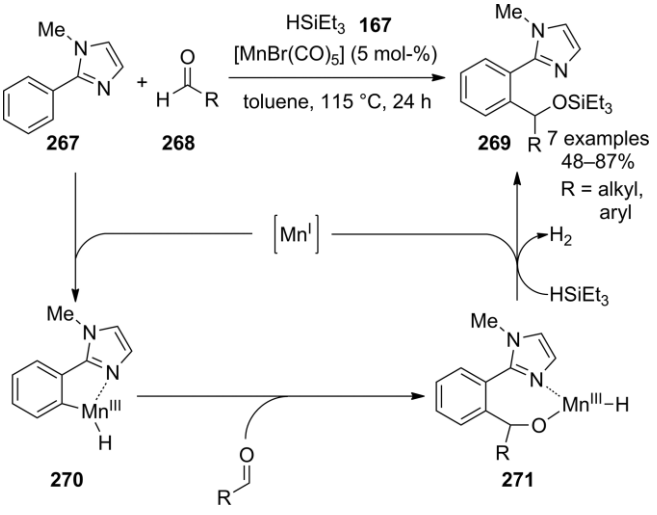
2.8. C–H Borylation and C–C Bond Formation by C–H Activation

Chen and Hartwig reported the borylation of C–H bonds using a manganese(I) carbonyl compound (Scheme 39). Under photoirradiation, this catalyst was shown to borylate benzene and pentane in good and moderate yields (with respect to B_2Pin_2), respectively.[72]

The insertion of aldehydes into unactivated aryl C–H bonds was reported by Takai and co-workers, initially using stoichiometric $[MnBr(CO)_5]$ to give benzyl alcohols (Scheme 40).[73] The addition of $HSiEt_3$ allowed the regeneration of the active catalyst **270** and the production of benzylic silyl ethers. The use of an imidazole directing group gave *ortho*-selectivity for the C–H activation and using an enantiopure imidazole gave up to 97:2 *dr*.

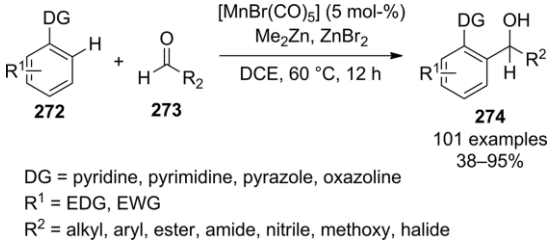


Scheme 39. The borylation of C–H bonds by a manganese carbonyl compound.



Scheme 40. Formation of benzyl silyl ether through insertion of an aldehyde to a C–H bond.

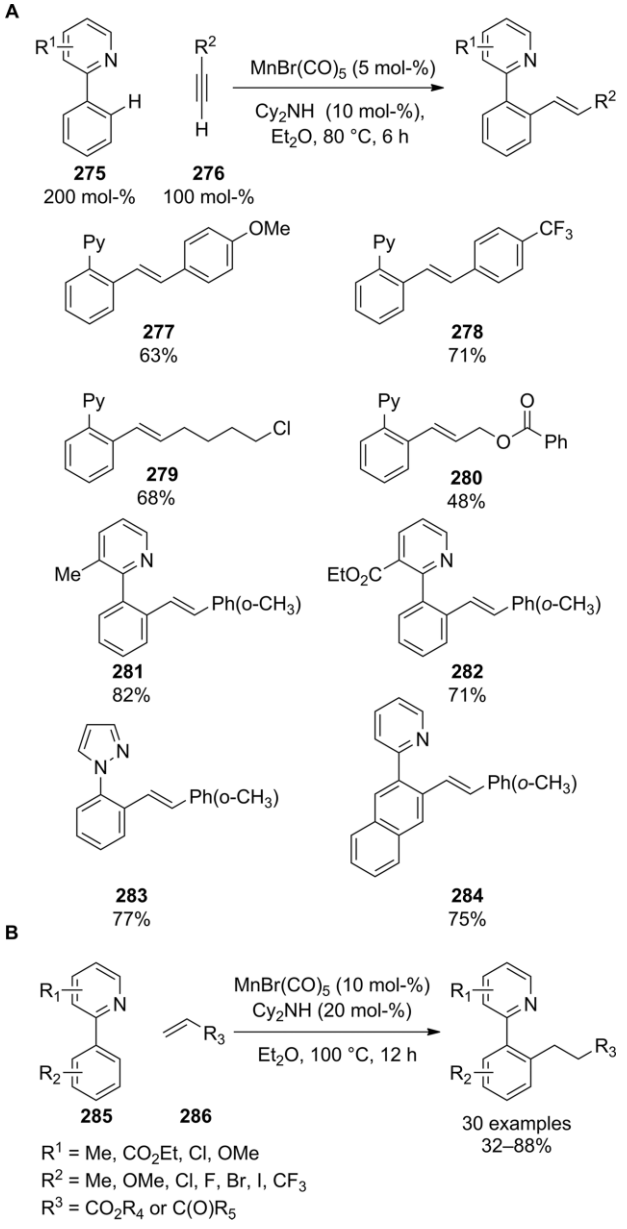
This methodology was expanded by Wang, by enabling the reaction to proceed without the need for silane by instead using a Lewis acid (Scheme 41).[74] The substrate scope of the reaction was also improved with a range of aldehydes, arenes and directing groups tolerated. The reaction occurred if the arene was replaced with an olefin where the vinylic Csp^2 C–H bond was used to nucleophilically add into the aldehyde. Additionally a nitrile could be used in place of the aldehyde, giving a ketone.



Scheme 41. Formation of alcohols by insertion of an aldehyde into an aryl C–H bond.

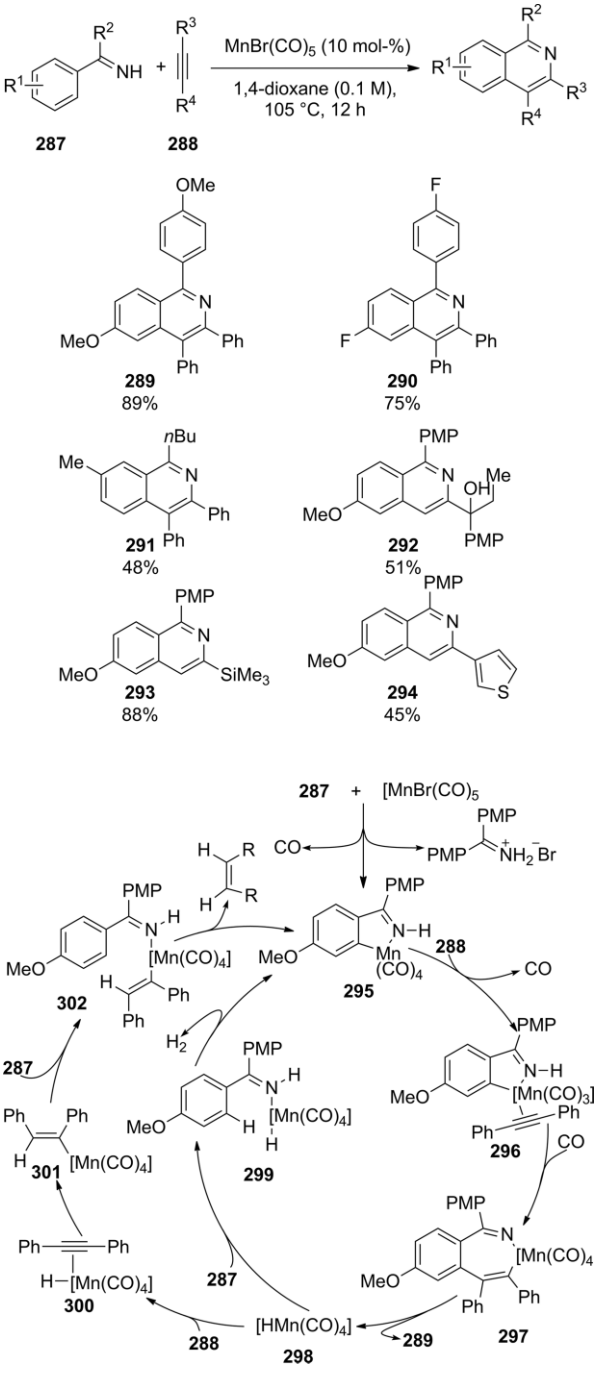
Wang reported a similar activation of an aryl C–H bond, with a pyridine directing group, and subsequent insertion of an alkyne into the intermediate five-membered manganacycle to give styrene derivatives (Scheme 42). Crucial to the C–H activation step is the presence of substoichiometric amounts of dicyclo-

hexylamine, which was suggested to deprotonate the arene and thus facilitate manganacycle formation. Aryl, alkyl, chloro and ester substituted alkynes were tolerated along with a wide variety of substituents on the aryl pyridine. This methodology was expanded by the replacement of alkynes with terminal alkenes bearing electron-withdrawing substituents to give *ortho* substituted biaryls.[75]



Scheme 42. Manganese catalysed C–H activation: A) With alkyne partners to form styrene derivatives and B) the insertion of alkenes into a C–H bond.

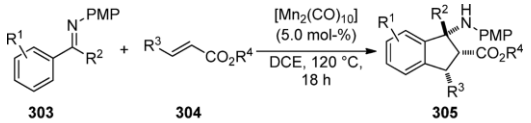
Wang also developed a [4+2] annulation system also using [MnBr(CO)$_5$] (Scheme 43).[76] Instead of a pyridine directing group, a benzylic imine was used. The H_2 generated in the reaction was proposed to mediate the catalyst turnover, unlike other C–H activation reactions where an oxidant is used for catalyst turnover. A range of electron-withdrawing and electron-donating substituents were tolerated on the arene. Both internal and terminal alkynes were used and a range of alkyl and aryl substituents were tested.



Scheme 43. Manganese-catalysed annulation to form isoquinolines.

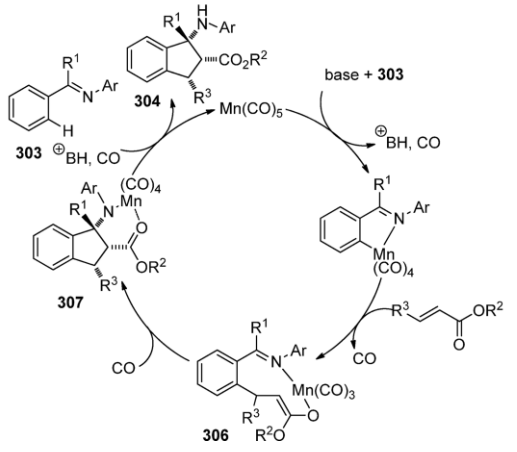
The benzyl imine system was also used to develop a C–H activation methodology for the synthesis of cyclic *cis*-β-amino acids, using alkenes with ester substituents as the coupling partner (Scheme 44).[77] Internal and terminal alkenes could be incorporated with good yields. The electronic properties of the imine substituent had a relatively minor effect on reactivity with chloro, fluoro, ester, ether and cyclopropanol functionalities were all tolerated.

A range of indoles and pyrroles were directly functionalised at the 2-position by the addition of an isocyanate to give the amide products (Scheme 45).[78] The proposed mechanism in-

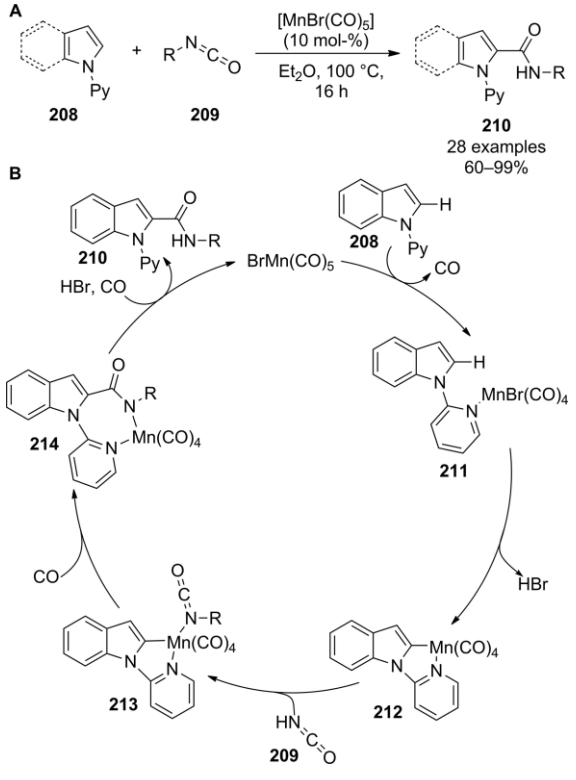


303 304 305

R^1	R^2	R^3	R^4	Yield
4-Me	Me	H	Et	94%
4-F	Me	H	Et	75%
4-Me	Me	Me	Me	64%
4-Me	4-MePh	H	Et	72%



Scheme 44. Manganese-catalysed annulation reaction (PMP = *p*-methoxyphenyl).

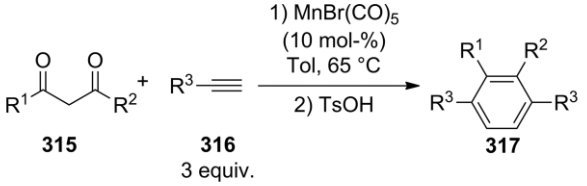


Scheme 45. Formation of amide substituted heterocycles by C–H activation catalysed by a manganese carbonyl species.

volves a C–H manganisation followed by a nucleophilic-type attack on the coordinated isocyanate.

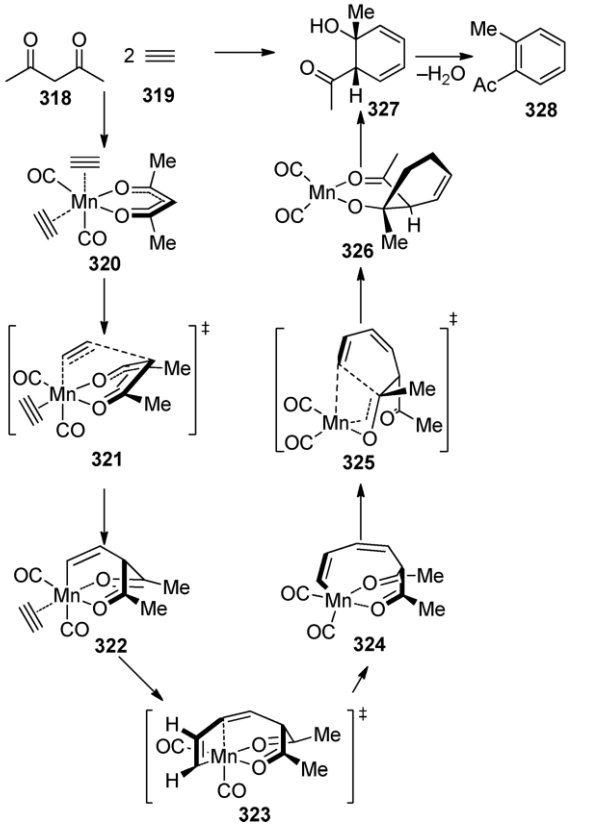
2.9. Cyclisation Reactions

The first example of a cyclisation reaction catalysed by a manganese species was a formal [2+2+2] cyclisation of a ketone and two equivalents of an alkyne to give benzene derivatives (Scheme 46).[79,80] The reaction is proposed to proceed by keto–enol tautomerism of the 1,3-dicarbonyl followed by coor-



315 316 317
3 equiv.

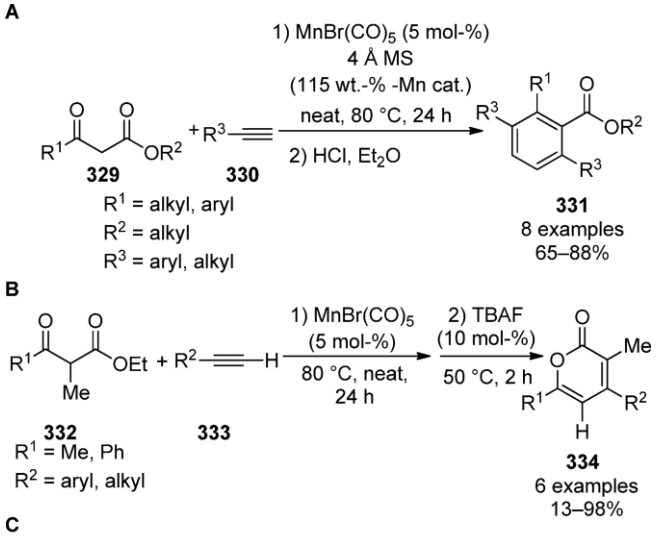
R^1	R^2	R^3	Time	Yield
Me	OEt	Ph	48 h	87%
*t*Bu	OEt	Ph	72 h	0%
Ph	Me	Ph	3 h	33%
Ph	OEt	4-OMePh	3 h	77%
Ph	OEt	4-B(Pin)Ph	12 h	65%



Scheme 46. Manganese-catalysed [2+2+2] cyclisation to form an aryl ring.

dination of manganese to give a manganese enolate **320**. This is followed by C–C bond formation at the α-carbon of the dicarbonyl and the *cis*-coordinated alkyne, to give a vinyl manganese species **322**. Alkyne insertion into the vinylic-manganese bond gave an eight-membered manganacycle **324**. At this point the manganesediene undergoes nucleophilic addition to the carbonyl. Finally, water is eliminated to gain aromaticity, assisted by sub-stoichiometric amounts of tosic acid. Only 1,3-dicarbonyl species were successful partners for the cyclisation and dicarbonyls bearing sterically demanding substituent groups showed no reactivity.

The reaction was also reported using neat conditions, with molecular sieves, and subsequent treatment with HCl instead of tosic acid (Scheme 47).[81,82] This was expanded to the synthesis of pyrones by changing the acid used to encourage the elimination of water. In these reactions TBAF was used and was proposed to initiate a base-catalysed intramolecular cyclisation.[83] Cyclooctanones could be prepared by inserting an alkyne into the carbon–carbon bond of a 1,3-dicarbonyl compound.[84]



R^1	R^2	Yield
OEt	C_6H_5	84%
OEt	4-$CF_3C_6H_5$	18%
OEt	2-Furyl	23%
Me	C_6H_5	23%

Scheme 47. Manganese-catalysed [2+2+2] cyclisation A) to form an aryl ester, B) to form pyrone derivatives and C) in the expansion of cyclic alkanes.

3. Conclusion

A range of transformations involving manganese catalyst have been reported and shown to have great promise in synthetic chemistry. Importantly manganese has provided solutions to difficult transformations, including the chemoselective oxidation of C–H bonds to alcohols, halides and azides. Research into C–H activation by insertion into an aryl C–H bond has been used to drive arene activation and further investigation of the mechanism and scope for this reaction is greatly important, and will only lead to further reactivity and utility.

Manganese has also been used as an alternative to precious metals in hydrosilylation and cross-coupling reactions. In both of these instances manganese has been reported as having increased TOF's in comparison to other earth abundant metals, although this increased activity has yet to be fully explored. Neither the hydrosilylation of alkenes or aryl-aryl cross-coupling has received the attention that it has garnered with other non-precious metals despite promising results.

The physical properties of manganese, its availability, low cost and low toxicity, make it is an obvious choice for sustainable catalysis and synthetic chemistry. For manganese catalysis to become routine a deeper understanding of mechanism and fundamental catalyst behaviour must be developed. The understanding of the HRC mechanism has allowed for the development of a range of different transformations, even though for 20 years only C–O bonds could be formed. Novel and interesting reactivity, such as Shenvi's hydrogenation and Nakamura's cyclisation reactions will only heighten the awareness of manganese catalysis and increase use.

Acknowledgments

J. R. C. thanks AstraZeneca, U.K. and the School of Chemistry, University of Edinburgh for the provision of a PhD studentship. S. P. T. thanks the University of Edinburgh for Chancellor's Fellowships, the School of Chemistry for continued support and the Royal Society for a University Research Fellowship.

Keywords: Homogeneous catalysis · Manganese · C–H activation · Fluorination

[1] W. M. Czaplik, M. Mayer, J. Cvengroš, A. J. von Wangelin, *ChemSusChem* **2009**, *2*, 396.
[2] B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500.
[3] A. Correa, O. Garcia Mancheno, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108.
[4] B. A. F. Le Bailly, S. P. Thomas, *RSC Adv.* **2011**, *1*, 1435.
[5] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*; 6th ed., Wiley Interscience, **1999**.
[6] G. Cahiez, C. Duplais, J. Buendia, *Chem. Rev.* **2009**, *109*, 1434.
[7] N. N. Greenwood, A. Earnshaw, *Chemistry Of The Elements*, Pergamon, Oxford, UK, **1989**.
[8] T. Katsuki, *Synlett* **2003**, 281.
[9] B. B. Snider, *Chem. Rev.* **1996**, *96*, 339.
[10] M. Mondal, *Synlett* **2012**, *24*, 137.
[11] M. Mondal, U. Bora, *RSC Adv.* **2013**, *3*, 18716.
[12] D. A. Valyaev, G. Lavigne, N. Lugan, *Coord. Chem. Rev.* **2016**, *308, Part 2*, 191.
[13] R. I. Khusnutdinov, A. R. Bayguzina, U. M. Dzhemilev, *Russ. J. Org. Chem.* **2012**, *48*, 309.

[14] J. T. Groves, W. J. Kruper, R. C. Haushalter, *J. Am. Chem. Soc.* **1980**, *102*, 6375.
[15] K. Suslick, B. Cook, M. Fox, *J. Chem. Soc., Chem. Commun.* **1985**, 580.
[16] R. Breslow, Y. Huang, X. Zhang, J. Yang, *Proc. Natl. Acad. Sci. USA* **1997**, *94*, 11156.
[17] J. Yang, B. Gabriele, S. Belvedere, Y. Huang, R. Breslow, *J. Org. Chem.* **2002**, *67*, 5057.
[18] R. Breslow, X. Zhang, Y. Huang, *J. Am. Chem. Soc.* **1997**, *119*, 4535.
[19] J. T. Groves, P. Viski, *J. Org. Chem.* **1990**, *55*, 3628.
[20] R. L. Halterman, S. T. Jan, *J. Org. Chem.* **1991**, *56*, 5253.
[21] H. Srour, P. L. Maux, G. Simonneaux, *Inorg. Chem.* **2012**, *51*, 5850.
[22] R. V. Ottenbacher, E. P. Talsi, K. P. Bryliakov, *ACS Catal.* **2015**, *5*, 39.
[23] P. Battioni, J. P. Renaud, J. F. Bartoli, M. Reina-Artiles, M. Fort, D. Mansuy, *J. Am. Chem. Soc.* **1988**, *110*, 8462.
[24] X. Wu, M. S. Seo, K. M. Davis, Y.-M. Lee, J. Chen, K.-B. Cho, Y. N. Pushkar, W. Nam, *J. Am. Chem. Soc.* **2011**, *133*, 20088.
[25] R. V. Ottenbacher, D. G. Samsonenko, E. P. Talsi, K. P. Bryliakov, *Org. Lett.* **2012**, *14*, 4310.
[26] D. Shen, C. Miao, S. Wang, C. Xia, W. Sun, *Org. Lett.* **2014**, *16*, 1108.
[27] L. Ma, Y. Pan, W.-L. Man, H.-K. Kwong, W. W. Y. Lam, G. Chen, K.-C. Lau, T.-C. Lau, *J. Am. Chem. Soc.* **2014**, *136*, 7680.
[28] C. L. Hill, J. A. Smegal, T. J. Henly, *J. Org. Chem.* **1983**, *48*, 3277.
[29] I. Tabushi, N. Koga, *Tetrahedron Lett.* **1979**, *20*, 3681.
[30] W. Liu, J. T. Groves, *Acc. Chem. Res.* **2015**, *48*, 1727.
[31] W. Liu, J. T. Groves, *J. Am. Chem. Soc.* **2010**, *132*, 12847.
[32] W. Liu, X. Huang, M.-J. Cheng, R. J. Nielsen, W. A. Goddard, J. T. Groves, *Science* **2012**, *337*, 1322.
[33] K. D. Donnelly, W. E. Fristad, B. J. Gellerman, J. R. Peterson, B. J. Selle, *Tetrahedron Lett.* **1984**, *25*, 607.
[34] W. E. Fristad, T. A. Brandvold, J. R. Peterson, S. R. Thompson, *J. Org. Chem.* **1985**, *50*, 3647.
[35] B. B. Snider, J. R. Duvall, *Org. Lett.* **2004**, *6*, 1265.
[36] X. Huang, T. M. Bergsten, J. T. Groves, *J. Am. Chem. Soc.* **2015**, *137*, 5300.
[37] X. Sun, X. Li, S. Song, Y. Zhu, Y.-F. Liang, N. Jiao, *J. Am. Chem. Soc.* **2015**, *137*, 6059.
[38] R. Ren, H. Zhao, L. Huan, C. Zhu, *Angew. Chem. Int. Ed.* **2015**, *54*, 12692; *Angew. Chem.* **2015**, *127*, 12883.
[39] B. T. Gregg, P. K. Hanna, E. J. Crawford, A. R. Cutler, *J. Am. Chem. Soc.* **1991**, *113*, 384.
[40] M. D. Cavanaugh, B. T. Gregg, A. R. Cutler, *Organometallics* **1996**, *15*, 2764.
[41] Z. Mao, B. T. Gregg, A. R. Cutler, *J. Am. Chem. Soc.* **1995**, *117*, 10139.
[42] R. Arias-Ugarte, H. K. Sharma, A. L. C. Morris, K. H. Pannell, *J. Am. Chem. Soc.* **2012**, *134*, 848.
[43] J. Zheng, S. Chevance, C. Darcel, J.-B. Sortais, *Chem. Commun.* **2013**, *49*, 10010.
[44] V. K. Chidara, G. Du, *Organometallics* **2013**, *32*, 5034.
[45] J. Zheng, S. Elangovan, D. A. Valyaev, R. Brousses, V. César, J.-B. Sortais, C. Darcel, N. Lugan, G. Lavigne, *Adv. Synth. Catal.* **2014**, *356*, 1093.
[46] T. K. Mukhopadhyay, M. Flores, T. L. Groy, R. J. Trovitch, *J. Am. Chem. Soc.* **2014**, *136*, 882.
[47] R. J. Trovitch, *Synlett* **2014**, *25*, 1638.
[48] S. L. Pratt, R. A. Faltynek, *J. Organomet. Chem.* **1983**, *258*, C5.
[49] H. S. Hilal, M. Abu-Eid, M. Al-Subu, S. Khalaf, *J. Mol. Catal.* **1987**, *39*, 1.
[50] K. Iwasaki, K. K. Wan, A. Oppedisano, S. W. M. Crossley, R. A. Shenvi, *J. Am. Chem. Soc.* **2014**, *136*, 1300.
[51] P. Magnus, M. J. Waring, D. A. Scott, *Tetrahedron Lett.* **2000**, *41*, 9731.
[52] P. Magnus, A. H. Payne, M. J. Waring, D. A. Scott, V. Lynch, *Tetrahedron Lett.* **2000**, *41*, 9725.
[53] P. Magnus, D. A. Scott, M. R. Fielding, *Tetrahedron Lett.* **2001**, *42*, 4127.
[54] J. Waser, E. M. Carreira, *Angew. Chem. Int. Ed.* **2004**, *43*, 4099; *Angew. Chem.* **2004**, *116*, 4191.
[55] J. Waser, B. Gaspar, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* **2006**, *128*, 11693.
[56] K. Okada, K. Oshima, K. Utimoto, *J. Am. Chem. Soc.* **1996**, *118*, 6076.
[57] K. Fugami, S. Nakatsukasa, K. Oshima, K. Utimoto, H. Nozaki, *Chem. Lett.* **1986**, *15*, 869.
[58] T. Nishikawa, H. Shinokubo, K. Oshima, *Org. Lett.* **2003**, *5*, 4623.
[59] A. K. Steib, O. M. Kuzmina, S. Fernandez, D. Flubacher, P. Knochel, *J. Am. Chem. Soc.* **2013**, *135*, 15346.
[60] I. Bauer, H.-J. Knölker, *Chem. Rev.* **2015**, *115*, 3170.
[61] S.-K. Kang, J.-S. Kim, S.-C. Choi, *J. Org. Chem.* **1997**, *62*, 4208.
[62] G. Cahiez, D. Luart, F. Lecomte, *Org. Lett.* **2004**, *6*, 4395.
[63] M. Rueping, W. Ieawsuwan, *Synlett* **2007**, 247.
[64] G. Cahiez, O. Gager, F. Lecomte, *Org. Lett.* **2008**, *10*, 5255.
[65] H. Kakiya, R. Inoue, H. Shinokubo, K. Oshima, *Tetrahedron* **2000**, *56*, 2131.
[66] G. Cahiez, A. Moyeux, J. Buendia, C. Duplais, *J. Am. Chem. Soc.* **2007**, *129*, 13788.
[67] Z. Zhou, W. Xue, *J. Organomet. Chem.* **2009**, *694*, 599.
[68] G. Cahiez, C. Duplais, J. Buendia, *Angew. Chem. Int. Ed.* **2009**, *48*, 6731; *Angew. Chem.* **2009**, *121*, 6859.
[69] Y.-C. Teo, F.-F. Yong, C.-Y. Poh, Y.-K. Yan, G.-L. Chua, *Chem. Commun.* **2009**, 6258.
[70] F.-F. Yong, Y.-C. Teo, *Tetrahedron Lett.* **2010**, *51*, 3910.
[71] T.-J. Liu, C.-L. Yi, C.-C. Chan, C.-F. Lee, *Chem. Asian J.* **2013**, *8*, 1029.
[72] H. Chen, J. F. Hartwig, *Angew. Chem. Int. Ed.* **1999**, *38*, 3391; *Angew. Chem.* **1999**, *111*, 3597.
[73] Y. Kuninobu, Y. Nishina, T. Takeuchi, K. Takai, *Angew. Chem. Int. Ed.* **2007**, *46*, 6518; *Angew. Chem.* **2007**, *119*, 6638.
[74] B. Zhou, Y. Hu, C. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 13659; *Angew. Chem.* **2015**, *127*, 13863.
[75] B. Zhou, P. Ma, H. Chen, C. Wang, *Chem. Commun.* **2014**, *50*, 14558.
[76] R. He, Z.-T. Huang, Q.-Y. Zheng, C. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4950; *Angew. Chem.* **2014**, *126*, 5050.
[77] W. Liu, D. Zell, M. John, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 4092; *Angew. Chem.* **2015**, *127*, 4165.
[78] W. Liu, J. Bang, Y. Zhang, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 14137; *Angew. Chem.* **2015**, *127*, 14343.
[79] H. Tsuji, K.-i. Yamagata, T. Fujimoto, E. Nakamura, *J. Am. Chem. Soc.* **2008**, *130*, 7792.
[80] N. Yoshikai, S.-L. Zhang, K.-i. Yamagata, H. Tsuji, E. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 4099.
[81] Y. Kuninobu, M. Nishi, S. Yudha, S. K. Takai, *Org. Lett.* **2008**, *10*, 3009.
[82] Y. Kuninobu, M. Nishi, A. Kawata, H. Takata, Y. Hanatani, Y. S. Salprima, A. Iwai, K. Takai, *J. Org. Chem.* **2010**, *75*, 334.
[83] Y. Kuninobu, A. Kawata, M. Nishi, H. Takata, K. Takai, *Chem. Commun.* **2008**, 6360.
[84] Y. Kuninobu, A. Kawata, M. Nishi, S. Yudha, S. J. Chen, K. Takai, *Chem. Asian J.* **2009**, *4*, 1424.

Received: January 7, 2016
Published Online: July 4, 2016