Organic & Biomolecular Chemistry

REVIEW

View Article Online
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Cite this: *Org. Biomol. Chem.*, 2021, **19**, 4852

Reactions promoted by hypervalent iodine reagents and boron Lewis acids

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Received 16th April 2021,
Accepted 13th May 2021

DOI: 10.1039/d1ob00740h

rsc.li/obc

Understanding the role of boranes in hypervalent iodine chemistry will open up new reactivities which can be utilised in organic synthesis. Due to similar reactivities, λ^3-iodanes have presented themselves as viable alternatives for many transformations dominated by transition metals whilst mitigating some of the associated drawbacks of metal systems. As showcased by recent reports, boranes can adopt a dual role in hypervalent iodine chemistry that surpasses mere activation of the hypervalent iodine reagent. Increased efforts to harness this potential with diverse boranes will uncover exciting reactivity with high applicability across various disciplines including adoption in the pharmaceutical sciences. This review will be relevant to the wider synthetic community including organic, inorganic, materials, and medicinal chemists due to the versatility of hypervalent iodine chemistry especially in combination with borane activation or participation. We aim to highlight the development of hypervalent iodine compounds including their structure, bonding, synthesis and utility in metal-free organic synthesis in combination with Lewis acidic boranes.

Introduction

Since the discovery of dichloro(phenyl)-λ^3-iodane (**1**) by Willgerodt,[1] chemical curiosity regarding hypervalent iodine compounds has resulted in numerous publications concerning their preparation, structure and application. Aside from Willgerodt's reagent, the initial spark that fuelled interest was the discovery of reagents **2** and **6**, known as Koser's reagent[2] and Dess–Martin periodinane (DMP)[3] respectively, that are useful in various oxidative processes of organic molecules.[4–6] Further prominent representatives include (diacetoxyiodo)benzene (PIDA, **3**), [bis(trifluoroacetoxy)iodo]benzene (PIFA, **4**),

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Dr Christian Thiehoff studied chemistry at the Westfälische Wilhelms–Universität Münster (Germany) and received his M.Sc. in 2014. During this time, he spent several months in the group of Prof. R. A. Batey at the University of Toronto (Canada) in 2013. He completed his doctoral studies under the supervision of Prof. R. Gilmour at the Westfälische Wilhelms–Universität Münster (Germany) where his research focused on the use of stereoelectronic effects in the design of functional small molecules. After a postdoctoral stay in the research group of Dr R. L. Melen at Cardiff University, he is currently working at Evotec (UK) Ltd.

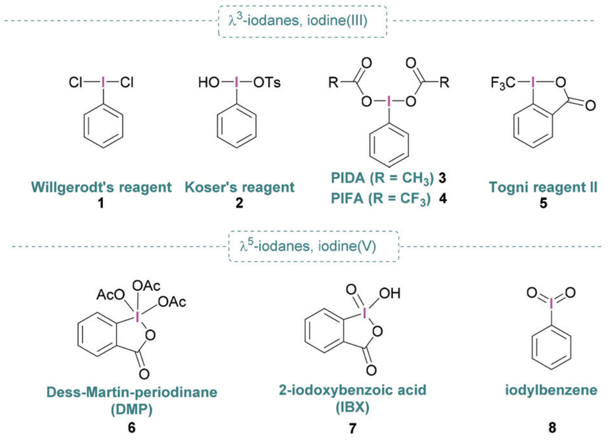
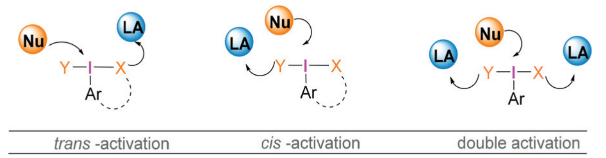


Fig. 1 Representative examples of common λ^3 and λ^5-iodanes.

Togni reagent II (**5**), and 2-iodoxybenzoic acid (IBX, **7**) (Fig. 1) are also commercially available and remarkably useful for metal-free synthesis due to their high nucleofugality, controllable reactivity, high stability and easy handling. Hypervalent iodine compounds are valuable reagents, having broad applicability in organic synthesis,[6] and present themselves as non-toxic and environmentally benign alternatives to heavy metals.[7] Moreover, hypervalent iodine compounds are commonly used in oxidation reactions,[8–10] they have also found widespread utilisation in functionalisations, and are ideally suited for applications in total synthesis as well as the pharmaceutical industry.[11,12] When combined with boranes, typically Lewis acid, activation of the hypervalent iodine compound occurs as shown in Scheme 1.



Scheme 1 Different mode of acid activation of λ^3-iodane.

However, in some cases, the borane can also play a dual role that goes beyond mere activation, for example by transferring one of its substituents to the hypervalent iodine compound.

Reactivities of hypervalent iodine compounds

The different types of hypervalent iodine compounds reported to date can be classified according to the oxidation state of the iodine atom.[13] Two oxidation states, +3 and +5, are commonly found in these compounds which are generally represented as λ^3- and λ^5-iodanes.

Here the superscript states the number of bonds to an atom in comparison with its real or hypothetical parent hydride. λ^7-Iodanes are also known in which the iodine atom has a +7 oxidation state. The unique structural features of hypervalent

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Dr Paul D. Newman obtained his PhD in 1991 under the guidance of Prof. P. Williams at Cardiff University (UK). He then worked as a PDRA with Dr R. Cross and Dr R. Peacock at the University of Glasgow (UK) followed by a return to Cardiff to work with Prof. P. G. Edwards. From 2003–2009 he was a research fellow in the Cardiff Catalysis Institute to which he remains affiliated in his current senior Lecturer role. He has a long-standing interest in asymmetric coordination compounds and their application notably with phosphine and/or NHC-based ligands and has authored or co-authored 66 publications in the field.

Thomas Wirth

Dr Thomas Wirth is professor of organic chemistry at Cardiff University (UK). He received his PhD after studying chemistry at Bonn (Germany) and the Technical University of Berlin (Germany). After a postdoctoral stay at Kyoto University (Japan) as a JSPS fellow, he worked independently at the University of Basel (Switzerland) before taking up his current position at Cardiff University in 2000. He was invited as a visiting professor to a number of places: Toronto (1999), Tokyo (2000), Osaka (2004, 2008), Kyoto (2012). He was awarded the Werner-Prize from the New Swiss Chemical Society (2000), the Furusato Award from JSPS London (2013), the Wolfson Research Merit Award from the Royal Society (2016) and the Bader-Award from the Royal Society of Chemistry (2016). In 2016, he was elected as a fellow of The Learned Society of Wales. His main interests of research concern stereoselective electrophilic reactions, oxidative transformations with hypervalent iodine reagents and flow chemistry performed in microreactors.

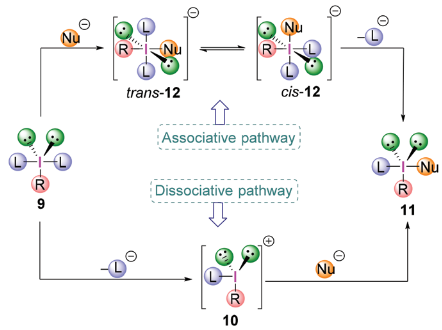
iodine compounds is the formation of linear, polarisable, formal 3-centre 4-electron bonds (3c–4e$^-$ bonds)[14] between the iodine atom and its two *trans* ligands. These bonds are composed of two electrons in the unhybridised 5p-orbital of the iodine atom and an electron of each ligand. This bonding type renders the iodine atom partially positively charged (polarised hypervalent bond) and highly electrophilic making it susceptible towards nucleophilic attack.

The typical reactivity of λ^5- and λ^7-iodanes involves oxidative processes, whereas λ^3-iodanes display two types of reactivity which are determined by the number of heteroatom and carbon-ligands.[15] The first group of compounds within λ^3-iodanes are of the type RIL_2 and can act as potent oxidising agents. The presence of two heteroatom ligands is an essential requirement for this reactivity. The oxidation reaction consists of a two step process of initial ligand exchange followed by reductive elimination. These two processes constitute the fundamental reactivity behaviour of hypervalent iodine compounds. The second group, of the type R_2IL, comprises two carbon-based ligands and one heteroatom ligand on the iodine atom. These compounds act as group transfer reagents of one carbon ligand (R) to a range of nucleophiles *via* reductive elimination of RI and are poor oxidising reagents.[15]

The exact mechanism of the ligand exchange reaction of λ^3-iodanes is still unclear however, a dissociative or an associative pathway (Scheme 2) can be operative, depending on the nature of the λ^3-iodanes.[15,16] The former would proceed *via* the dissociation of a ligand L from λ^3-iodane **9** generating iodonium ion **10** as an intermediate followed by nucleophilic attack to give compound **11**. For the latter, the order of events would be reversed. The coordination of a nucleophile (Nu^-) to the electrophilic iodine centre in **9** gives the square planar [12-I-4] species *trans*-**12** with a *trans*-arrangement of the ligands (L) which is in equilibrium with its *cis*-form (*cis*-**12**). Subsequent loss of a ligand L yields the iodine(III) compound **11**.

Rebecca Melen

Dr Rebecca Melen studied for her PhD degree at the University of Cambridge (UK). Following Postdoctoral studies in Toronto (Canada) with Prof. D. W. Stephan and Heidelberg (Germany) with Prof. L. H. Gade, she took up a position at Cardiff University (UK) in 2014 where she is now a Reader in Inorganic Chemistry. In 2018, she was awarded an EPSRC early career fellowship and she was the 2019 recipient of the RSC Harrison Meldola Memorial Prize. Her research interests include diverse aspects of main group reactivity and catalysis, including the applications of main group chemistry in organic synthesis.



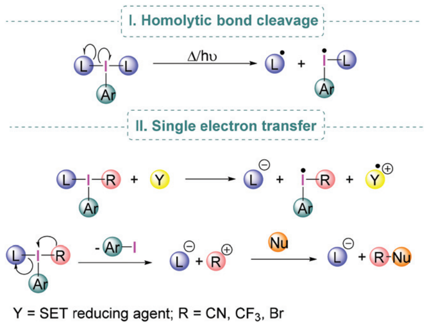
Scheme 2 Ligand exchange reaction of λ^3-iodanes *via* the associative or dissociative pathway.

Although the dicoordinated intermediate **10** has been observed in gas phase experiments,[17] solution phase based experimental data indicate the presence of trivalent species due to coordination by anions or solvent molecules. On the other hand, isolation and X-ray crystallographic analysis of stable tetracoordinated hypervalent iodine species with a square planar geometry such as the tetrachloroiodate anion strongly corroborates the associative pathway to be most likely.[18]

Hypervalent iodine compounds commonly undergo reductive elimination to liberate an iodine(I) species. The exceptionally good leaving group aptitude of a λ^3-iodane arises from the facile and energetically favourable generation of the monovalent iodine compound in a reductive process.[19] By studying the solvolysis rates of cyclohexenyl derivatives, Ochiai and co-workers[20] identified the phenyliodo group as having a remarkably good leaving group capability. It is referred to as a hypernucleofuge (super leaving group) because it was determined to be about 10^6 times better as a leaving group than the corresponding triflate. Despite the homonymy, reductive elimination in transition metal catalysis differs from that of hypervalent iodine and the same reactivity in the context of hypervalent iodine chemistry should be referred to as ligand coupling, the concerted process retains the stereochemical configuration of the ligands. The actual pathway of the reductive elimination reaction in λ^3-iodanes depends strongly on the nature of the ligands on the iodine(III) species, the reaction partner, and the reaction conditions.

Other distinct reaction pathways exhibited by λ^3-iodanes are nucleophilic substitution, elimination, or fragmentation. The nucleophilic substitutions are most common and can proceed through either S_N2 or S_N1-type processes depending on the capability of the ligand to stabilise the positively charged intermediate. In either case, the same product(s) are formed. Base-mediated elimination reactions occur in systems where an acidic proton is present in the α- or β-position of one of the ligands. While β-elimination generates double bonds,[21] α-elimination results in the generation of carbenes.[22] Less common are processes where the reductive elimination includes a fragmentation.[23]

Under suitable reaction conditions, iodine(III) compounds may also facilitate transformations which involve the gene-



Scheme 3 Radical pathways in λ^3-iodane chemistry.

ration of radical species either by homolytic cleavage of the I–L bond (Scheme 3, I) or by Single Electron Transfer (SET) to the λ^3-iodane (Scheme 3, II).[24]

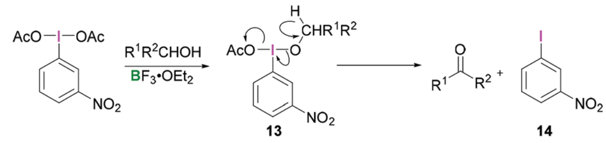
Activation of hypervalent iodine compounds

Most reactions employing λ^3-iodanes require activation of the hypervalent iodine compound[25] which is often achieved by addition of a Lewis or Brønsted acid or base. Lewis bases can be additives, the solvent or a substrate. Acid activation is arguably the most frequently employed method among the above mentioned activation modes. A range of Lewis (*e.g.* TMSOTf, $BF_3 \cdot OEt_2$, or metal cations such as Zn, Al, or Mg) or Brønsted (*e.g.* TfOH, TsOH, AcOH, TFA, or HF) acids that are competent in activating the λ^3-iodane have been investigated.[26] Although Lewis/Brønsted acid mediated *cis*-activation or *trans*-activation of λ^3-iodane are common, recently a double-activation mode for hypervalent iodine reagents has also been reported by Liu (Scheme 1).[27]

Tricoordinated boron Lewis acids are a popular choice for the activation of hypervalent iodine compounds, such as BF_3, BAr_3 and borosilicates. Pervasive use of trivalent boron compounds (typically BF_3) to activate hypervalent iodine compounds can be explained due to their high Lewis acidity. The empty p-orbital of the central boron atom can easily be accesed by a lone pair of electrons from a Lewis site in the hypervalent iodine compound enabling activation through increased electrophilicity. This is especially true for iodosylbenzene (**15**) which is an amorphous, pale yellow solid.[28] Its polymeric zigzag structure with O–I···O linkages renders it insoluble in most organic solvents.[27] In 1982, Ochiai and coworkers[29] suggested that $BF_3 \cdot OEt_2$ activates iodosylbenzene (**15**) *via* coordination of the boron Lewis acid to the oxygen atom breaking up the polymeric structure. Analogously, $BF_3 \cdot OEt_2$ coordination to the acetate oxygen of diacetoxy(*m*-nitrophenyl)iodane was assumed to activate the λ^3-iodane at room temperature to effectively oxidise alcohols to carbonyl compounds (Scheme 4).[30]

Presumably, the transformation consists of two steps, both of which are catalysed by BF_3. The initial ligand exchange reaction on λ^3-iodanes with the alcohol afforded **13** with subsequent β-elimination generating aryliodide **14** along with the respective carbonyl compound. A detailed study of the commercially available PIDA (**3**)/$BF_3 \cdot OEt_2$ combination utilised a combined experimental and computational approach for the full investigation of the activation phenomenon.[31] Comparison of the ^{1}H NMR spectra of PIDA (**3**) and a mixture of PIDA/$BF_3 \cdot OEt_2$ (1 : 1) in $CDCl_3$ indicated a downfield shift of the aromatic signals in the latter (*ca.* 0.1 ppm) which implies the formation of an electron-deficient species. ^{1}H NMR analysis of the titration of PIDA/$BF_3 \cdot OEt_2$ mixture resulted in the gradual downfield shift of the aromatic and acetyl resonances, confirming the initial finding (Scheme 5). Upon cooling a solution of PIDA/$BF_3 \cdot OEt_2$ in $CDCl_3$, the single resonance for the acetate ligands splits into two separate signals. This suggests the change of either a fast equilibrium between the BF_3 coordinated and the non-coordinated acetate ligand, or an unsymmetrical species with two distinct acetates. X-ray crystallographic analysis[31] of the PIDA-BF_3 adduct further corroborates the solution phase NMR analysis as the BF_3 unit is coordinated to the carbonyl oxygen of one acetate group. Structural comparison of the adduct and PIDA shows a lengthening of d = 0.13 Å for the I–O bond of the $BF_3 \cdot OAc$ ligand (d_{I-O} = 2.15 Å in PIDA, d_{I-O} = 2.28 Å in the adduct) associated with a contraction of the other I–O bond of $d \approx$ 0.07 Å (d_{I-O} = 2.076 Å in the adduct) indicative of the existence of the cationic acetoxy(phenyl)iodonium. However, no interaction was observed when PIDA (**3**) was replaced by PIFA (**4**) which was attributed to the lower basicity of the latter.

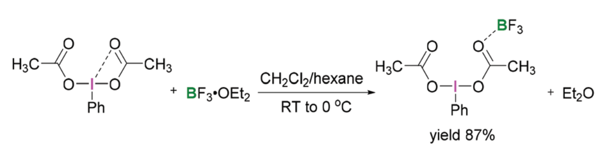
A recent study by Hopkins and Murphy revealed that borosilicates can also be used to activate λ^3-iodanes and successfully employed for the *gem*-difluorination reaction. For these reactions, borosilicate was found to be a better activator compared with $BF_3 \cdot OEt_2$ (Scheme 6).[32]



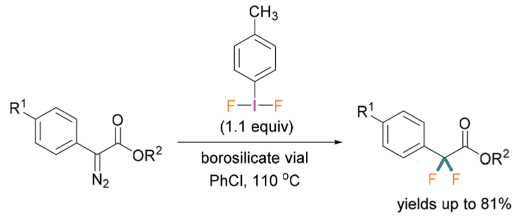
Scheme 4 Lewis acid mediated activation of the λ^3-iodane.

BF_3-mediated synthesis of iodonium salts

Structurally simple iodine(III) compounds are readily obtained by direct oxidation of the corresponding aryliodide precursor



Scheme 5 Synthesis and structure of $PhI(OAc)_2 \cdot BF_3$.

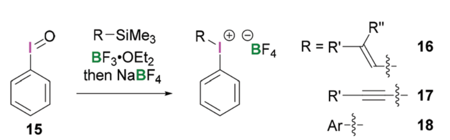


Scheme 6 Borosilicate activation of (difluoroiodo)toluene.

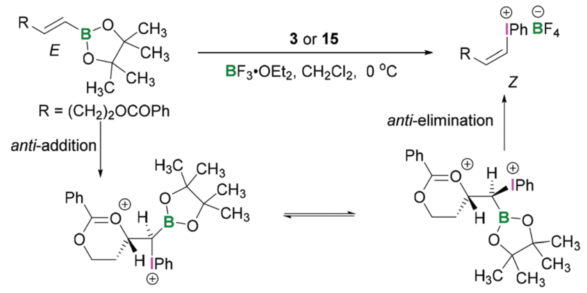
under suitable conditions.[33] For example, PIDA (**3**) can be synthesised by treating iodobenzene with peracetic acid in the presence of acetic acid.[34]

Some λ^3-iodanes, most often iodosylbenzene (**15**) and PIDA (**3**), can themselves serve as precursors for the synthesis of more complex alkenyl(aryl)iodonium (**16**),[35] alkynyl(aryl)iodonium (**17**)[36] or diaryliodonium salts (**18**) (Scheme 7).[35] Alkenyl (aryl)iodonium compounds represent versatile intermediates providing access to functionalised alkenes upon reaction with a variety of nucleophiles *via* an addition–elimination process (a formal S_N2-type reaction). Additionally, they can undergo α or β-elimination reactions to yield alkylidene carbenes or alkynes, respectively. Reaction of a nucleophilic alkene with **15** or **3** in the presence of $BF_3{\cdot}OEt_2$ followed by anion exchange with $NaBF_4$ yields the corresponding alkenyl(aryl)iodonium tetrafluoroborates **16** in a stereospecific fashion. Synthesis of vinyliodonium salts can be obtained from the reaction between the corresponding β,β-disubstituted vinylsilanes, vinylboronic acid esters and iodine(III) species. It's noteworthy that this electrophilic substitution reaction leads to retention of configuration of the olefin. Using this reaction condition, (*E*)-alk-1-enylboronates stereoselectively afforded (*E*)-alk-1-enyliodonium salts.

Okuyama reported that alkenylboronic esters bearing an acyloxy, alkoxy, or methoxycarbonyl group reacted with PIDA (**3**) in the presence of $BF_3{\cdot}OEt_2$ to give the alkenyliodonium tetrafluoroborates with complete inversion of configuration.[37] Thus (*E*)- and (*Z*)-boronates gave (*Z*)- and (*E*)-iodonium salts, respectively (Scheme 8).[37] A strong solvent effect was evident as selectivity was reversed upon addition of ether to the dichloromethane solution. Neighbouring oxy group participation in the reaction was found to be responsible for the stereoselectivity of these reactions. The *anti*-addition of an internal oxy group to the electrophilic carbon centre (β-position of the boronic ester) and iodine(III) compound led to the formation of a six membered cyclic intermediate. Concerted *anti*-elimination of the oxy group and boronic ester afforded the iodonium salts with inversion of configuration of the olefin.



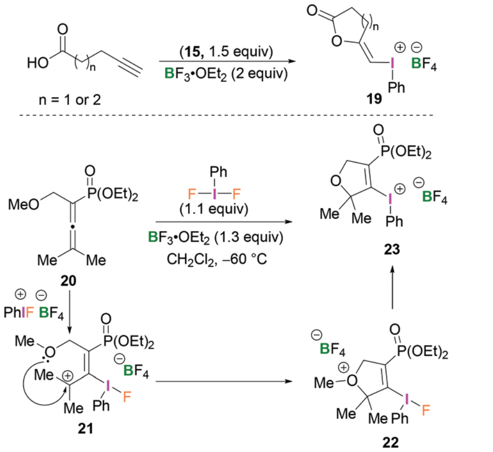
Scheme 7 Common strategy for the synthesis of alkenyl-(**16**) and alkynylaryl iodonium (**17**) as well as diaryliodonium tetrafluoroborates (**18**).



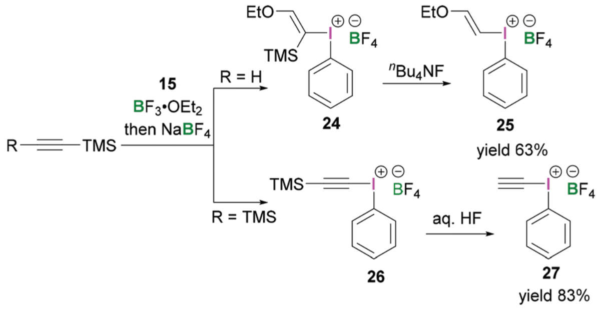
Scheme 8 Lewis acid mediated activation of the λ^3-iodane.

Compounds **19** and **23** constitute rather unusual examples of vinyl(phenyl)iodonium species. Ochiai and coworkers described the cyclisation of alkynoic acids to iodine(III)-enol species **19** mediated by BF_3-activated **15** (Scheme 9, top).[38] Stang reported the synthesis of dihydrofuranyl (phenyl)iodonium salt **23** which was obtained from the reaction of allenylphosphonate **20** and $PhIF_2$ in the presence of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at −60 °C (Scheme 9, bottom).[39] Presumably, the initially formed allyl cation **21**, obtained from the regioselective addition of the BF_3-activated λ^3-iodane to **20**, undergoes intramolecular cyclisation (**22**) followed by loss of the methyl group to afford **23**.

Furthermore, Ochiai demonstrated a mild reaction protocol for the synthesis of alkynyl(phenyl)iodonium salts.[40] Reaction between alkynyltrimethylsilanes and iodosylbenzene (**15**) in the presence of a Lewis acid led to the formation of iodonium salts **25** and **26** with the trimethylsilyl group replaced by a phenyliodonium group in the product. Initially ethynyltrimethylsilane reacted with **15** and $BF_3{\cdot}OEt_2$ in CH_2Cl_2 to afford (*E*)-ethoxy(vinyl)iodonium tetrafluoroborate (**24**). Protodesilylation of **24** using stoichiometric tetrabutylammonium fluoride in THF at −78 °C produced **25** in 63% yield (Scheme 10, top). The reaction was found to be highly



Scheme 9 Accessing alkenyliodonium compounds *via* cyclisation of alkynoic acids (top) or allenylphosponate (bottom).

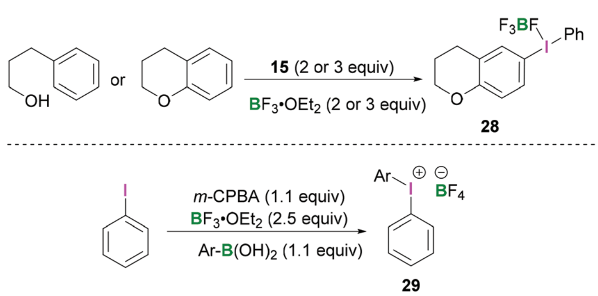


Scheme 10 Access to α-silyl substituted (*E*)-configured vinyliodonium salt **24** and subsequent stereoretentive protodesilylation to give **25** and synthesis of ethynyl(phenyl)iodonium tetrafluoroborate (**27**).

stereoselective and retention of configuration was observed. However, when commercially available bis(trimethylsilyl) ethyne was employed for the reaction with **15** in the presence of $BF_3{\cdot}OEt_2$, phenyl(trimethylsilylethynyl)iodonium tetrafluoroborate (**26**) was obtained (Scheme 10, bottom).[41] Treatment of **26** with hydrogen fluoride afforded the ethynyl(phenyl)iodonium tetrafluoroborate **27** in 83% yield.

Employing similar reaction conditions, Ochiai demonstrated the tandem oxidative intramolecular cyclisation of 3-phenylpropanol.[42] Formation of 6-chromanyl(phenyl)-λ^3-iodanes **28** (Scheme 11, top) originates from the reaction of **15** with either chromane or 3-phenylpropan-1-ol in the presence of $BF_3{\cdot}OEt_2$. The reported work described the tandem oxidative cyclisation and λ^3-iodanation of phenylpropanol in which a hypervalent phenyl-λ^3-iodanyl group was regioselectively introduced at the C6-position of chromane. A more general approach to access these structures was reported by Olofsson *et al.* (Scheme 11, bottom).[43] After *in situ* oxidation of an aryl iodide using *meta*-chloroperoxybenzoic acid (*m*-CPBA) in the presence of $BF_3{\cdot}OEt_2$, an arylboronic acid was added to the reaction mixture, resulting in the formation of the iodonium borate salt **29**.

This protocol enables the rapid synthesis of a variety of symmetrical and unsymmetrical diaryliodonium compounds with electron-withdrawing or donating substituents in moderate to good yields.



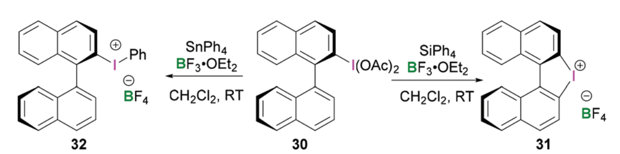
Scheme 11 Regioselective synthesis of chromanyl(phenyl)-λ^3-iodanes **28** (top) and one-pot synthesis of diaryliodonium tetrafluoroborate **29** (bottom).

Other noteworthy examples include chiral binaphthyliodonium tetrafluoroborates **31** and **32**, both of which can be synthesised from (*S*)-[1,1′-binaphthalen]-2-yl-λ^3-iodanediyl diacetate **30** (Scheme 12).[44] Interestingly, the reaction of tetraphenylsilane with 2-(diacetoxyiodo)-1,1′-binaphthyl in the presence of $BF_3{\cdot}OEt_2$ resulted in an intramolecular arylation yielding chiral diaryliodonium salt **31** (intramolecular cyclisation at the C2′ position). However, use of reactive organostannane (tetraphenylstannane), on the other hand, enables Sn–I(III) exchange resulting in binaphthaleneyl(phenyl) iodonium **32** in 76% yield.

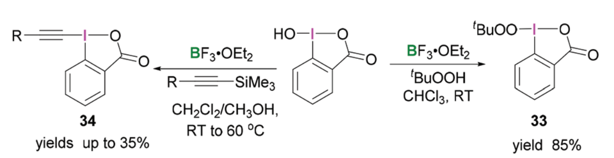
An extensive study by Ochiai demonstrated the synthesis of different iodinane derivatives. Using 1-hydroxy-1,2-benziodoxol-3(1*H*)-one as progenitor, *tert*-butylperoxy iodinane **33**[45] and alkynyliodinane **34**[46] were prepared from *tert*-butylperoxide or alkynylsilane, respectively, upon activation with $BF_3{\cdot}OEt_2$ (Scheme 13).

Whilst $BF_3{\cdot}OEt_2$ is the most widely used Lewis acidic borane for the activation of hypervalent iodine compounds, we have demonstrated their activation with the highly Lewis acidic tris(pentafluorophenyl)borane [$B(C_6F_5)_3$].[47] The reaction between triacetoxyiodane, $B(C_6F_5)_3$ and 2,6-lutidine in CH_2Cl_2 at −40 °C afforded the ion pair **35**. X-Ray crystallographic analysis revealed the formation of a lutidine-stabilised diacetoxyiodonium cation, originating from the abstraction of one acetate unit by $B(C_6F_5)_3$ generating acetoxytriarylborate as the counterion. The reported structure of **35** showed a bidentate binding mode of one acetate with the second acetate being covalently bound *via* one oxygen atom (Scheme 14). Reaction of $B(C_6F_5)_3$ and 2,6-lutidine with the related tris(trifluoroacetoxy)iodane yielded diaryliodonium **36** and perfluorophenyliodane **37** (Fig. 2) by double and single ligand exchange, respectively.

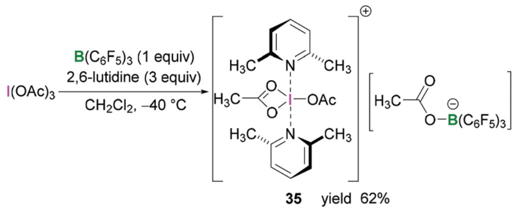
Functionalisation of aryl boronates using trivalent iodine were demonstrated by Kita.[48] Lewis acidic boron-substituted aromatic compounds were reacted with PIFA (**4**) in the presence of acetic acid using hexafluoro-2-propanol (HFIP) and CH_2Cl_2 (5 : 1) to afford boron-substituted diaryliodonium salts (Scheme 15). In these reactions the less bulky neopentylglycol



Scheme 12 Synthesis of binaphthyl-based iodonium salts **31** and **32**.



Scheme 13 Transformation of benzoiodaoxolone into the corresponding alkylperoxyiodinane **33** and alkynyl derivative **34**.



Scheme 14 Synthesis of diacetoxy iodonium **35** from I(OAc)$_3$ and B(C$_6$F$_5$).

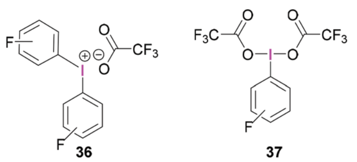
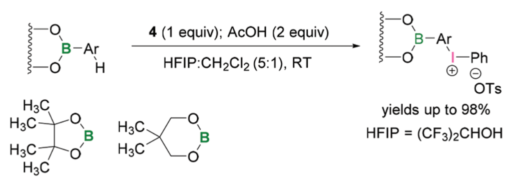


Fig. 2 Structure of diaryliodonium **36** and bis(trifluoroacetoxy)iodo pentafluorobenzene (**37**).



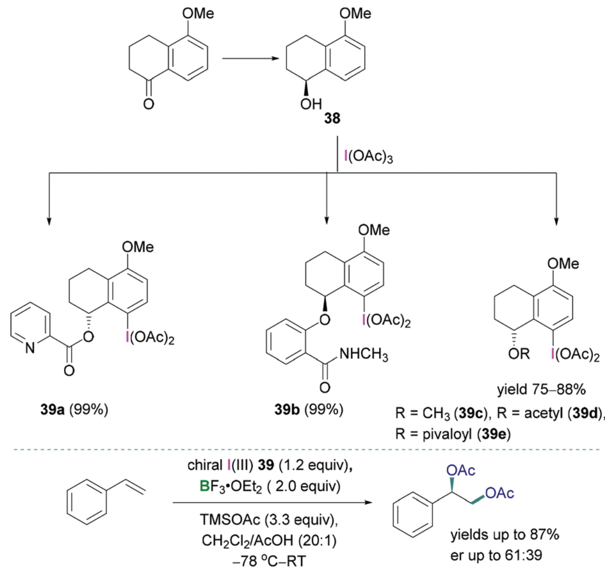
Scheme 15 Synthesis of boron-substituted iodonium salts.

boronate ester afforded better yields than BPin. Due to the lower Lewis-acidity of the boronates, it is unlikely that a direct activation of the iodine(III) reagent occurs.

Synthetic applications of the BF$_3$·OEt$_2$/iodane system

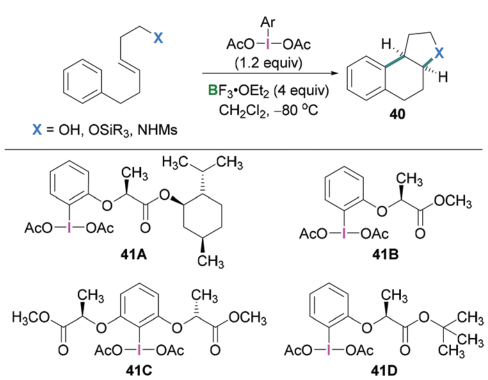
Stereoselective 1,2-difunctionalisation of alkenes provides the simplest way to introduce useful vicinal bifunctional groups onto a hydrocarbon chain.[49] Hypervalent iodine reagents can replace the ubiquitous use of transition metals, commonly utilised as catalysts for such transformations. Lewis acidic boranes, mostly BF$_3$·OEt$_2$, in combination with chiral trivalent iodine compounds have been employed successfully as powerful facilitating tools for enantioselective 1,2-difunctionalisation of alkenes.[50]

The synthesis of a variety of chiral trivalent iodine compounds bearing an α-tetralol was reported recently by Wirth.[51] The alcohol was subsequently employed for the synthesis of iodine(III) species **39a–e** (Scheme 16, top) in excellent yields (up to 88%). Pyridine containing substituents **39a** (*N*-methyl salicylamide), amide containing substituents **39b**, and 5-methoxy-1-tetralone-based substrates **39c–e** were introduced at the oxygen centre of α-tetralol to generate the corresponding iodine(III) species. A mild, efficient, and practical reaction protocol has been demonstrated to prepare such chiral trivalent iodine compounds which can be employed as catalysts in combination with boranes for the stereoselective diacetoxylation of styrene (Scheme 16, bottom). Although good to excellent yields of the diacetoxylated compounds were obtained (yields up to 87%), the enantioselectivities (enantiomeric ratio: up to 61 : 39) were modest. The enantioselective oxyarylation of internal alkenes has also been studied using BF$_3$·OEt$_2$ in combination with a lactate-based chiral iodine(III).



Scheme 16 Synthesis of the tetralol-based chiral trivalent iodine compounds (top); stereoselective diacetoxylation using trivalent iodine compounds (bottom).

In 2010, Fujita described the enantioselective oxyarylation of (*E*)-6-aryl-1-silyloxylhex-3-ene to afford **40** (Scheme 17, top).[52] Different Lewis and Brønsted acids were screened for the cyclisation reaction and BF$_3$·OEt$_2$ was found to be the most efficient. To test the effect of the steric bulk, different silyl groups were employed for the cyclisation reaction with slightly better enantioselectivity being observed with the bulky *tert*-butyldiphenyl silane (TBDPS) compared to the *tert*-butyldi-



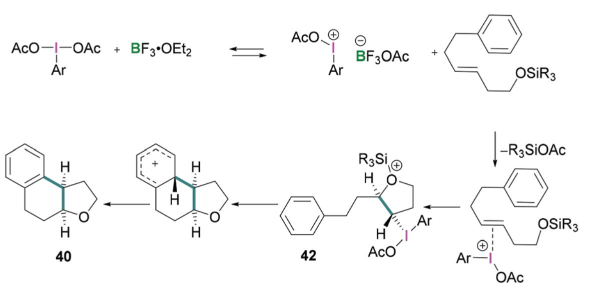
Scheme 17 Enantioselective oxyarylation reaction using λ^3-iodanes.

methylsilyl ether (TBS) group. Several substrates were examined and good yields (up to 88%) of the desired products with high enantioselectivities (up to 93%) were observed. Mechanistic studies (Scheme 18) revealed that the Lewis acidic boranes are required to activate the hypervalent iodine compound which facilitates the electrophilic addition to the olefins. The nucleophilic addition of the internal oxy group afforded **42**, and product **40** formed after further nucleophilic addition of the aryl group. The authors determined that the lactate-based hypervalent iodine reagent **41** reacts particularly well with one of the enantiotopic faces of the olefin (which is the rate-determining step) and induces the formation of the cyclised product.

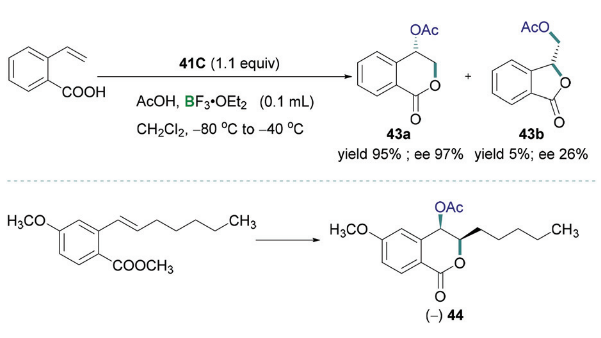
Preparation of biologically useful isochromanone scaffolds have been carried out using λ^3-iodane. In 2010, Fujita demonstrated the regio- and diastereo-selective oxidative lactonisation of 2-vinylbenzoic acid to 4-oxyisochroman-1-one **43a** using λ^3-iodane as a catalyst (Scheme 19, top).[53] $BF_3{\cdot}OEt_2$ was used as the Lewis acidic component to activate the iodine reagent. Vast studies revealed that different oxy groups such as methoxymethyl and hydroxymethyl in the alkenyl moiety does not affect the formation of δ lactone. The reported methodology can be utilised to prepare synthetically useful biologically active compounds **44** (Scheme 19, bottom).

Prévost and Woodward reactions for dioxyacetylation of alkenes using chiral hypervalent iodine compounds have also been carried out by Fujita (Scheme 20). An optically active hypervalent iodine reagent (**45**) in combination with a Lewis acidic boron $BF_3{\cdot}OEt_2$ and acetic acid were employed for the reaction with different cinnamyl derivative (**46**) at −80 °C to afford enantioselective dioxyacetylated products (**47**).[54] Diastereoselectivities (*syn*/*anti* selectivity) in the dioxyacetylated products showed a dependence on the reaction temperature. When the reaction was carried out at −80 °C to −40 °C, a regioisomeric mixture of monoacetoxy and diacetoxy compounds were obtained. Further treatment with pyridine enabled full conversion to the diacetoxy compounds **47a** (Scheme 20, top). High enantioselectivity (up to 96%) of the *syn* product (1*S*,2*S*) and excellent diastereoselectivity between the *syn* and *anti*-conformer (98 : 2) was observed. Intriguingly, the reaction at −80 °C to room temperature afforded the *anti*-configured diacetoxy compound **47b** (1*R*,2*S*) as the major product with excellent enantioselectivity (up to 96%) and diastereoselectivity (*syn* : *anti* 2 : 98) (Scheme 20, bottom).

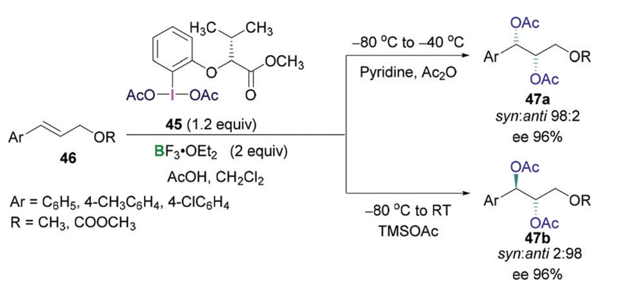
Wirth and coworkers investigated the enantioselective synthesis of α-acetoxylated ketones using catalytic amounts of chiral λ^3-iodanes.[55] The λ^3-iodanes were generated *in situ* from the reaction of chiral λ^3-iodanes **48** and an oxidising agent in the presence of acetic acid. Lewis acidic $BF_3{\cdot}OEt_2$ was employed to activate the hypervalent λ^3-iodanes and then subsequent reaction with the enol ether **49** afforded an intermediate in which the activated λ^3-iodane was attached to the α-carbon of the carbonyl functional group. Nucleophilic attack by an acetate anion (S_N2 reaction) led to the formation of the desired product **50** (Scheme 21). Excellent yields (up to 97%) of the α-acetoxylated ketones and good enantioselectivities (up to 88%) were obtained. However, cyclic substrates (for



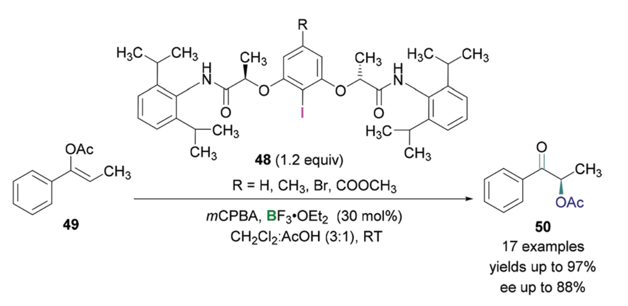
Scheme 18 Proposed reaction mechanism for enantioselective oxy arylation reaction.



Scheme 19 Tosyloxylactonization of 2-ethenylbenzoic acid (top) and synthesis of useful biologically active compound **44** (bottom).



Scheme 20 Enantioselective diacetoxylation of olefins using λ^3-iodanes.

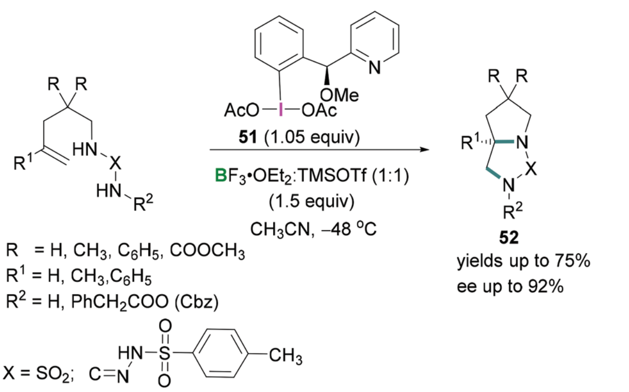


Scheme 21 Enantioselective acetoxylation reaction using chiral λ^3-iodanes.

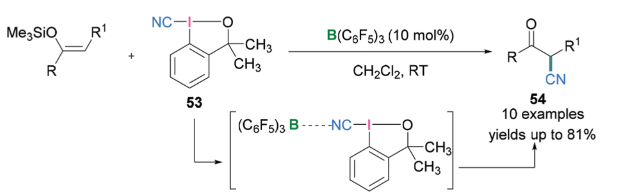
example, 3,4-dihydronaphthalen-1-yl acetate) showed poor enantioselectivities.

Further investigations by Wirth[56] on the stereoselective intramolecular diamination reaction of alkenes using a chiral hypervalent iodine reagent **51** revealed that equimolar mixtures of trimethylsilyl triflate (TMSOTf) and $BF_3{\cdot}OEt_2$ afforded $BF_2OTf{\cdot}OEt_2$ which acted as a Lewis acid to activate the λ^3-iodanes **51** (Scheme 22). Excellent enantioselectivities (up to 92%) were observed in the products **52**.

Hypervalent iodine compounds in combination with Lewis acidic boranes have also been used to introduce the nitrile functionality into an organic molecule. Electrophilic cyanation using iodanes provides an alternate to metal catalysed reactions which are useful for the generation of several biologically active compounds.[57] Further investigations revealed that the cyano group can also be introduced enantioselectively into an organic molecule utilising chiral hypervalent iodanes. In 2017, Minakata described the use of 1-cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (CDBX) **53** as the source of a CN group which can be activated by the strongly Lewis acidic borane $B(C_6F_5)_3$ and successively employed for catalytic electrophilic cyanation of silyl enol ethers to afford β-ketonitriles **54** (Scheme 23).[58] Commonly used Lewis acidic boranes such as $BF_3{\cdot}OEt_2$ and BEt_3 both failed to activate **53** and no product formation was observed, but the more Lewis acidic $B(C_6F_5)_3$ would activate the CDBX reagent. Mechanistic studies revealed that coordination between the cyano functionality of **53** and $B(C_6F_5)_3$ (which was confirmed from *in situ* IR and ^{13}C NMR spectroscopy, see later) resulted in the generation of a highly electrophilic species which facilitates the cyanation reaction. The interaction between the cyano functionality of **53** and $B(C_6F_5)_3$ was examined spectroscopically. The C≡N stretch in the IR spectrum was shifted from 2137 cm^{-1} (starting material-**53**) to 2216 cm^{-1} (**53** + $B(C_6F_5)_3$). Moreover, when an equimolar mixture of $B(C_6F_5)_3$ and **53** in CD_2Cl_2 was monitored using ^{13}C NMR, a significant downfield shift of the carbon atom of the C≡N group was seen. Moreover, the tertiary carbon adjacent to the oxygen also exhibits a downfield shift. Based on these observations, it was concluded that the cyano group was coordinated to the Lewis acidic boranes to assist cyano group transfer to silyl enol ethers to generate β-ketonitriles.



Scheme 22 Enantioselective cyclisation reaction using chiral λ^3-iodanes.



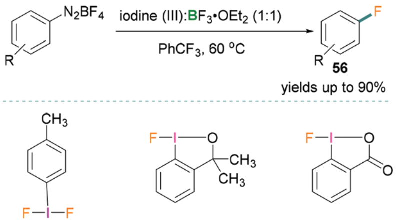
Scheme 23 Electrophilic cyanation reaction using Lewis acidic boranes and hypervalent λ^3-iodanes.

Kita demonstrated the oxidative cyanation[59,60] of electron-rich heterocycles including pyrroles, thiophenes, and indoles. Initial investigations showed that direct oxidative cyanations of electron-rich heterocyclic compounds were possible using a hypervalent iodine(III) reagent (PIFA, **4**) and $BF_3{\cdot}OEt_2$. TMSCN was used as the source of the CN group. Premixing of PIFA (**4**) and TMSCN *in situ* generated the hypervalent iodine(III)–CN species which was further activated by $BF_3{\cdot}OEt_2$. Cyanation of 1*H*-pyrrole was investigated but only poor yields of the desired products were obtained. The authors observed that the presence of a strong electron withdrawing group at the nitrogen-position significantly improved the yields of the desired product. Therefore, a tosyl group was introduced and employed for the cyanation reaction. Using the optimised reaction conditions, *N*-tosylpyrrole was selectively converted to 2-cyano-*N*-tosylpyrrole in 83% yield but 2 equivalents of PIFA (**4**) were required. To demonstrate a broad substrate scope, *N*-tosylpyrroles, substituted thiophenes, and *N*-tosylindole were tested with satisfactory yields of the products **55** being obtained (Scheme 24).

The reactivity of λ^3-iodanes was further investigated and successfully employed for the halogenation reaction.[61] Metal-free facile synthesis of organofluorine compounds are desirable as they are ubiquitous structural motifs in pharmaceutical compounds and agrochemicals.[62]

In 2018, Hu reported the fluorination of aromatic diazonium salts (Scheme 25).[63] Catalytic Balz–Schiemann fluorination reactions were investigated using different trivalent iodine compounds and $BF_3{\cdot}OEt_2$. All reactions were carried out in trifluorotoluene and many examples with yields of the products **56** up to 90% were reported using this methodology. Reactive functional groups (iodo, ketone, ester, carboxylic acid, nitrile, and sulfamide) remained intact and formation of undesirable products was not observed. To highlight the mechanistic

Scheme 24 PIFA-mediated oxidative cyanation of heteroarenes.



Scheme 25 Catalytic Balz–Schiemann fluorination reaction using Lewis acidic boranes and hypervalent λ^3-iodanes.

details, the authors suggested that the Lewis acidic component BF_3·OEt_2 activated the aryliodonium(III) and generated the aryl cation intermediates.[63] Addition of the borane increased the leaving group aptitude of dinitrogen which resulted in the formation of an $Ar^+BF_4^-$ salt and successive nucleophilic attack by a fluoride anion afforded the fluorinated product.

In 2017, Murphy used phenylallene derivatives **57** for the synthesis of α-difluoromethyl styrene compounds **58** which can be employed as fluorinated building blocks.[64] Stoichiometric amounts of difluoro(*p*-tolyl)-λ^3-iodane and BF_3·OEt_2 were reacted with phenylallenes to afford the α-difluoromethyl styrenes **58**. The reaction was found to be highly chemoselective with high functional group tolerance and proceeded *via* a fluorinative rearrangement mechanism. Several substrates such as substituted phenylallenes (phenylallenes bearing phenyl and α-allenyl substituents) and diphenylallenes were investigated.

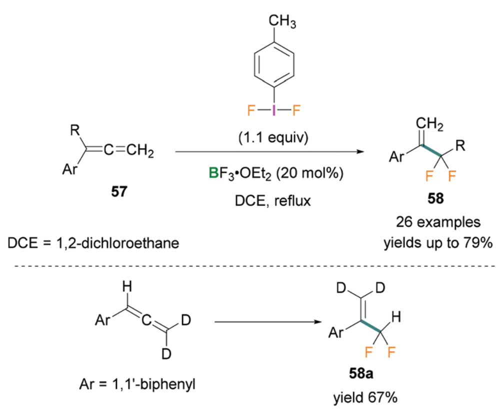
Moderate to good yields of the desired products (many examples, yields up to 79%) were obtained (Scheme 26, top). To investigate the reaction mechanism, deuterated phenylallene [D2] was used (Scheme 26, bottom) and the crude reaction mixture analysed by multinuclear NMR spectroscopy (^{1}H, ^{2}H, or ^{19}F NMR). As no deuterium scrambling was observed in the product (**58a**) it was concluded that the terminal double bond of the allene was not reacting (Scheme 26, bottom).

Combinations of hypervalent iodine reagents and Lewis acidic boranes are also capable of promoting C–C cross coupling reactions.[65] Following Kita's cyanation reaction conditions, Ramírez de Arellano demonstrated the four-component coupling reaction between naphthalene and substituted benzenes using stoichiometric amounts of PIFA (**4**) along with an excess of BF_3·OEt_2.[66] Here the functionalisation of C–H bonds using regioselective intermolecular four-component coupling reactions afforded novel C–C cross coupled products (Scheme 27). Direct oxidative coupling between naphthalene and different arenes such as tetramethylbenzene afforded linear tetraarenes with a binaphthalene core. Using this methodology, 1,1′-binaphthalene afforded linear hexaarene (**59**) chemo-selectively in excellent yields (up to 90%) and formation of tetraarene (**60**) as a by-product (yields up to 11%). However, when pentamethylbenzene reacted with 1,1′-binaphthalene, the tetraarene **60** was the major (93%) component compared to hexaarene **59** (3%) (Scheme 27).

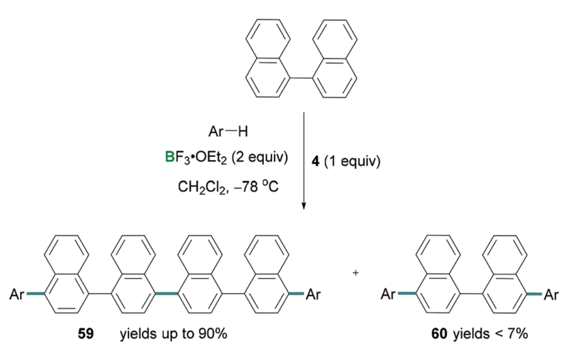
Recently, Shafir investigated the iodine directed *ortho* and *para* C–H alkylation of (diacetoxyiodo)benzene (**3**) to afford poly-substituted arenes.[67] A new synthetic strategy for *para*-selective C–H benzylation, and *ortho*-selective sulfonylation have been reported (Scheme 28). The reaction between $PhI(OAc)_2$ (**3**) and $ArCH_2SiMe_3$ in the presence of BF_3·OEt_2 afforded C–C cross-coupled products **61** selectively at the *para* position to the iodine in good to excellent yields (Scheme 28, top). When *para* substituted (4-benzylphenyl)-λ^3-iodanediyl diacetate (**62**) was employed for the oxidation reaction with different silane compounds **63** and **64**, using the optimised reaction conditions, *ortho* alkylation (*ortho* to iodine) compounds **65** and **66** were formed in 63% and 53% yields respectively (Scheme 28, bottom). Further treatment of **66** with cyclic allylsilane **63** led to the formation of **69** (76%), and reaction of **65** with trimethyl(prop-2-yn-1-yl)silane **67** afforded compound **68** in 42% yield. A [3,3] sigmatropic rearrangement mechanism was proposed to account for the formation of these products.

Additionally, hypervalent iodine compounds were tested for multicomponent coupling reactions. A mild reaction protocol was developed by Hu for the synthesis of *N*-substituted benzimidazolones **70** (Scheme 29).[68]

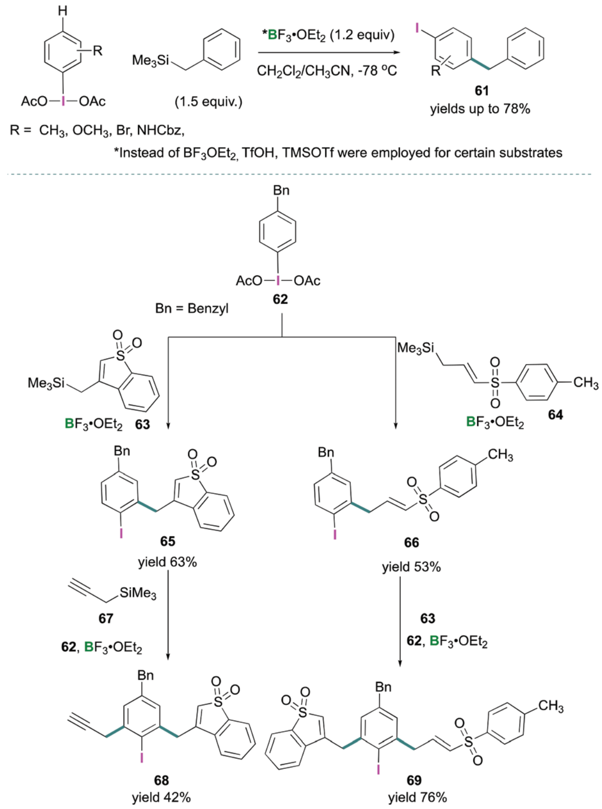
Aromatic hydroxylamines, aldehydes, and TMSCN were reacted together in the presence of stoichiometric amounts of $PhI(OAc)_2$ (**3**) and excess BF_3·OEt_2 to afford benzimidazolone derivatives in good yields (Scheme 29). Mechanistic details revealed that the aromatic hydroxylamines and aldehydes



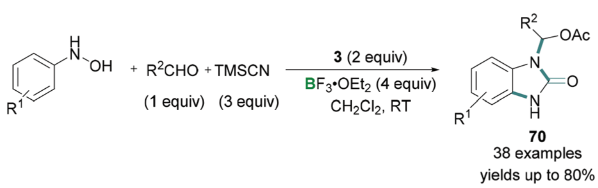
Scheme 26 Fluorinative rearrangement of phenylallene using Lewis acidic boranes and λ^3-iodanes.



Scheme 27 Oxidative four-component Kita coupling reaction.



Scheme 28 Iodine directed *ortho* and *para* C–H alkylation of PhI$(OAc)_2$.



Scheme 29 Synthesis of benzimidazolones **70**.

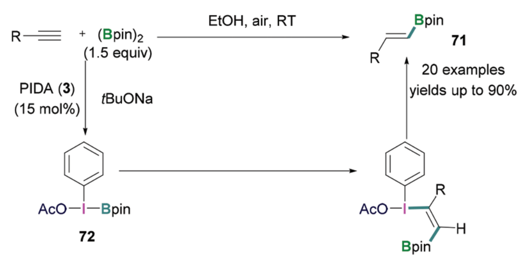
reacted together to afford a nitrone. Initial activation of the PhI$(OAc)_2$ (**3**) by $BF_3{\cdot}OEt_2$ and subsequent ligand exchange with TMSCN produced intermediate PhI(OAc)(CN). PhI(OAc)(CN) then underwent a ligand exchange reaction with the nitrone to give a reactive intermediate which undergoes [3,3] rearrangement to afford the final benzimidazolone product. Although high functional group tolerance for these reactions was observed, heterocyclic aldehydes, aliphatic aldehydes, and ketones failed to produce the desired product.

Beyond mere activation: dual role of the borane

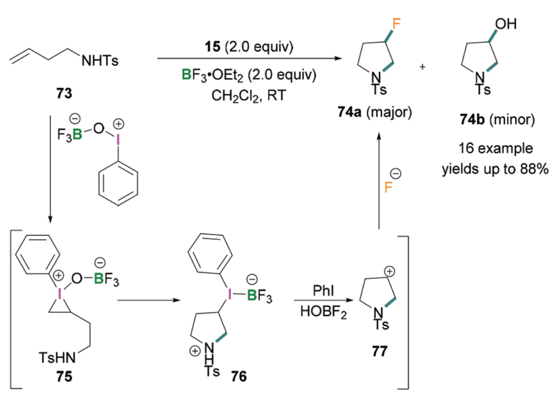
In certain cases, the Lewis acidic boranes do not only activate the hypervalent iodine compounds, but also actively participate in the reaction. Hypervalent iodine compounds in combination with Lewis acidic boranes have successfully been employed for hydroboration and fluorination reactions.

In 2017, Wei demonstrated the PhI$(OAc)_2$ (**3**) mediated hydroboration reaction of terminal alkynes with bis (pinacolato)diboron (B_2pin_2) using *t*BuONa (Scheme 30).[69] A simple reaction protocol has been discussed for the synthesis of various vinyl boronates **71**. It was suggested that PhI$(OAc)_2$ initially reacted with *t*BuONa to generate PhI(OAc)(O*t*Bu). Likewise, pinacol diborane also reacted with *t*BuONa to afford *t*BuOBpin. Subsequent reaction between PhI(OAc)(O*t*Bu) and *t*BuOBpin afforded PhI(OAc)(Bpin) **72**. In the next step, **72** reacted with the terminal alkyne stereoselectively to afford the desired vinyl boronates (**71**) in good to excellent yields (up to 90%).

Zhang demonstrated the use of $BF_3{\cdot}OEt_2$ as a fluorinating agent with iodosylbenzene for the fluorination of homoallylic amines.[70] *N*-(But-3-en-1-yl)-4-methylbenzene sulfonamide **73** exemplifies the intramolecular aminofluorination of homoallylic amines to prepare 3-fluoropyrrolidines **74** (Scheme 31). The reaction proceeds *via* the activation of PhIO by $BF_3{\cdot}OEt_2$ to afford a λ^3-iodane intermediate which reacts further with homoallylic amines to produce an iodonium intermediate **75**. This reactive intermediate readily undergoes intramolecular nucleophilic attack by the amino functional group to afford an intermediate iodonium borane pyrrolidine derivative **76** which, upon reductive elimination, formed the cyclic carbo-



Scheme 30 Hydroboration of various terminal alkynes.

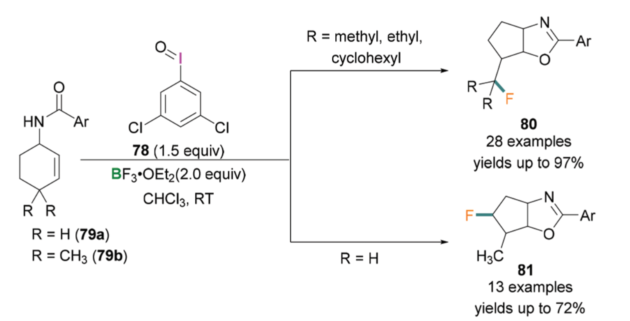


Scheme 31 Intramolecular aminofluorination of homoallylic amines.

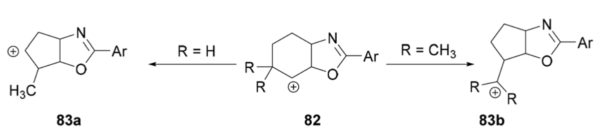
cation intermediate **77**. This cationic intermediate was readily trapped by the fluoride anion to produce the desired fluoropyrrolidines **74**.

In 2017, Zhang demonstrated the use of hypervalent iodine compounds towards the ring-contraction monofluorination reaction using BF_3 etherate as the fluorine source.[71] In the reported work, *N*-(cyclohex-2-en-1-yl)benzamide **79** was reacted together with iodosobenzene and $BF_3{\cdot}OEt_2$ in CH_2Cl_2 to afford monofluorinated fused five-membered oxazoline ring products (yields up to 35%). A dramatic change in the yield of the product was observed when 3,5-dichloroiodosobenzene **78** was employed as the oxidant instead of iodosobenzene. Different *N*-cyclohexenyl amides **79** were tested and good to excellent yields of the desired products were obtained. In contrast with **79a** (no substitution at C4 of the cyclohexenyl ring) which afforded **81** in satisfactory yield (up to 72%) (Scheme 32, bottom), when **79b** (two methyl groups at C4 of the cyclohexenyl ring) was employed for the fluorination reaction, a very different product (**80**) with yields up to 97% were obtained (Scheme 32, top). The formation of the different products can be explained based on the stability of the carbocation intermediate. In the reaction, λ^3-Iodanes **78** and $BF_3{\cdot}OEt_2$ react together to form an iodine(III) intermediate which activates the double bond of **79** and form the iodonium intermediate.

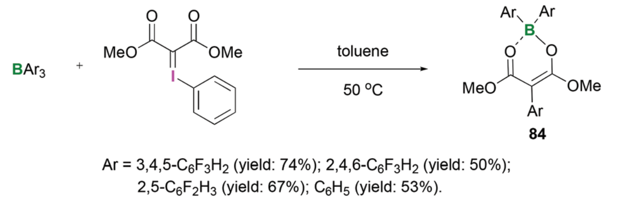
Intramolecular nucleophilic attack by the oxygen atom of the amide followed by reductive elimination formed the intermediate **82** (Scheme 33). Depending on the nature of the R group, different products were formed. When R = H, alkyl and double hydride shifts generated the carbocation intermediated **83a** and successive fluoride attack afforded the product **81**. However, when R = CH_3, **82** undergoes an alkyl migration to form a more stable tertiary carbocation **83b** which reacts with the fluoride ion to afford **80**.



Scheme 32 Ring-contraction monofluorination reactions using λ^3-iodanes (**78**) and Lewis acidic boranes.



Scheme 33 Formation of intermediate **83a** and **83b**.



Scheme 34 Reaction between iodonium and triarylfluoroboranes to afford the 1,3-carboboration compounds **84**.

The reactions between hydrazones and hydrazides with Lewis acidic triarylfluoroboranes have also been investigated. Recently, we demonstrated the synthesis of different boron dienolates **84** from the iodonium ylides in moderate to good yields (up to 74%).[72] Acyclic iodonium ylides reacted with several triarylfluoroboranes to afford the 1,3-carboboration compounds in which aryl group transfer from boron to the iodonium ylide had occurred (Scheme 34). In these reactions, the mechanism of activation was found to be the initial coordination of a boron Lewis acid to the carbonyl group. Cyclic iodonium ylides failed to afford the 1,3-carboboration products.

Conclusions

Expanding the toolbox of the synthetic chemist is crucial for the development of enabling strategies for metal-free synthesis while simultaneously simplifying the formation of ever more complex structures. Hypervalent iodine chemistry is presented as a reliable source to achieve these goals and inspires further development. However, the prerequisite activation of λ^3-iodanes by boranes has been limited almost exclusively to $BF_3{\cdot}OEt_2$ with just a few examples with triarylboranes and borosilicate. The few reported examples of other borane-based Lewis acidic activators indicate sufficiently exciting reactivity to promise a great future potential for the further advancement of synthetic protocols. The increased availability of boron reagents and understanding of their Lewis acidities and reactivities will allow the field of hypervalent iodine to expand into novel areas of synthetic applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

A. D. and R. L. M. are grateful to the EPSRC for funding and the awarding of an EPSRC Early Career Fellowship (R026912/1). We are grateful to the Leverhulme Trust for a research project grant (C. T., P. D. N. and R. L. M. RPG-2016-020).

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