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Organohypervalent heterocycles

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This review summarizes the structural and synthetic aspects of heterocyclic molecules incorporating an atom of a hypervalent main-group element. The term "hypervalent" has been suggested for derivatives of main-group elements with more than eight valence electrons, and the concept of hypervalency is commonly used despite some criticism from theoretical chemists. The significantly higher thermal stability of hypervalent heterocycles compared to their acyclic analogs adds special features to their chemistry, particularly for bromine and iodine. Heterocyclic compounds of elements with double bonds are not categorized as hypervalent molecules owing to the zwitterionic nature of these bonds, resulting in the conventional 8-electron species. This review is focused on hypervalent heterocyclic derivatives of nonmetal main-group elements, such as boron, silicon, nitrogen, carbon, phosphorus, sulfur, selenium, bromine, chlorine, iodine(III) and iodine(V).

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1. Introduction

A hypervalent molecule is generally defined as a main group element compound that contains a number of formally assignable electrons exceeding the octet in the valence shell around its central atom.[1–4] The expansion of the electronic valence shell beyond the classical Lewis–Langmuir octet, in particular

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the non-metallic elements, has opened an important era in the chemistry of these elements. Jeremy I. Musher,[3] in 1969, originally defined hypervalent molecules as those formed by the non-metals of groups 15–18 in any of their stable valence states higher than 3, 2, 1, and 0, respectively; however, recently this terminology has also been extended to the group 13 and 14 elements.[5] The special structural features and reactivity pattern of hypervalent compounds can be explained by hypervalent bonding, which involves a 3c-4e bond.[5–7] Sugden explained the subsistence of a two-centre one-electron (2c-1e) bond in hypervalent molecules, thus rationalized the bonding in these molecules without the need for expanded octets or ionic bond character, which was not widely accepted at that time.[8] In 1951, the molecular orbital description of a 3c-4e model was independently developed by G. C. Pimentel[9] and R. E. Rundle.[10] Recently, Parkin made a clear distinction between the main-group element compounds that attribute to 3c-4e interactions from those featuring the 3c-2e interactions.[11] The former are termed as 'electron-rich hypervalent molecules' while the latter ones are called as 'electron-deficient hypercoordinate molecules'.[12–20] Moreover, Braïda and Hiberty proposed the role of charge-shift bonding in hypervalent prototypes.[21] Further, Crabtree recently pointed out the similarity between hypervalency and other types of weak bonding.[22] The valence shell of the central atom is essentially an octet and the electrons beyond eight electrons (8e) are mainly located on the ligands, not on the central atom.

Hypervalent heterocycles are cyclic compounds containing a hypervalent main-group element in their ring. Typically, these heterocycles include polycoordinated heteroatoms bearing 10 electrons or 12 electrons and either a distorted trigonal-bipyramidal or pseudo-octahedral geometry. However, heterocycles with elements having double bonds are not categorized as hypervalent compounds due to their zwitterionic nature, resulting in 8-electron species.[23] Cyclic hypervalent molecules possess higher thermal stability compared to their acyclic analogues. The enhanced thermal stability of cyclic hypervalent molecules can be attributed to the fact that hypervalent molecules for carbon, boron and nitrogen are possible only in cyclic structures. Further, the enhanced thermal stability of cyclic versions may be attributed to the linking/bridging between equatorial and apical ligands,[24] which restricts the Berry pseudorotation and makes ligand coupling more difficult. Further, the overlap of the lone pair of pi-electrons on the hypervalent atom (such as iodine) with the aromatic ring (π-conjugation) may also enhance the stability.[25,26] Despite the fact that hypervalent heterocycles are associated with significantly higher thermal stability compared to their acyclic analogs, a systematic presentation on the chemistry of these compounds is still lacking.[27] This review is primarily focused on the chemistry of the hypervalent heterocycles of non-metal main group elements, such as, boron, carbon, silicon, nitrogen, phosphorous, sulfur, selenium, chlorine, bromine and iodine. Given that there are no significant reports on the synthetic applications of some of the cyclic hypervalent molecules, in some cases, only the synthesis and characterization of hypervalent heterocycles are discussed.

Viktor V. Zhdankin

Viktor V. Zhdankin was born in Ekaterinburg, Russian Federation. His MS (1978), PhD (1981), and Doctor of Chemical Sciences (1986) degrees were earned at Moscow State University in the laboratory of Nikolay S. Zefirov. He moved to the University of Utah in 1990, where he worked for three years as an Instructor of Organic Chemistry and Senior Research Associate with Peter J. Stang. In 1993, he joined the faculty of the University of Minnesota Duluth, where he is currently a Professor of Chemistry. His main research interests are in the areas of synthetic and mechanistic organic chemistry of hypervalent main-group elements and organofluorine chemistry.

2. General overview of hypervalent compounds

In 1980, the research groups of Martin, Arduengo and Kochi introduced the '*N*–X–*L*' nomenclature to classify the hypervalent compounds of main-group elements, where '*N*' represents the number of valence electrons present on the hypervalent atom 'X', and '*L*' denotes the number of ligands around the central atom 'X'.[28] Parkin proposed the $ML_lX_xZ_zH_h$ nomenclature, which gives a more comprehensive description of this '*N*–X–*L*' terminology.[11] However, compounds of elements containing double bonds are, in general, not included in the category of hypervalent species due to the zwitterionic nature of these bonds, leading to the classical 8e-species.[23] The hypervalent bonding and geometry have noteworthy implications in numerous existing growing areas of synthetic organic chemistry, such as hypervalent iodine(III) and iodine(V) reagents/catalysts, use of sterically constrained T-shaped phosphorus(III) compounds in small molecule activation and catalysis,[29–36] and utilization of novel heavier group Lewis acids in frustrated Lewis pair chemistry.[37–44] According to the IUPAC recommendations,[45] the position and valency of a 'hypervalent atom' in a molecule are indicated using the Greek letter 'λ'. Here, the symbol λ^n represents the heteroatom present in the non-standard valence state 'n' in a formally neutral molecule. Early considerations about the geometry of hypervalent molecules were described by the 'VSEPR model' for atomic bonding. Accordingly, AB_5- and AB_6-type molecules will acquire trigonal bipyramidal and octahedral geometry, respectively. However, the bond lengths, bond angles and violation of the octet rule were not fully justified, and hence alternative models were proposed. Further, the argument on the basic bonding descriptions of hypervalent

species to recognize why they do not fulfil to the conventional Lewis octet rule has almost come to end on the theoretical front.[4,13–16,46–57]

The widely used '3c-4e' bond explained the structural features and high reactivity of hypervalent compounds. The molecular description of the 3c-4e bond, developed by Rundel[10] and Pimentel[9] involved the formation of three molecular orbitals by the combination of a p-orbital on the central atom and one atomic orbital from each of the two ligands. The three molecular orbitals obtained by the combination of these atomic orbitals are bonding, non-bonding, and anti-bonding molecular orbitals. The bonding and non-bonding molecular orbitals each contain one pair of electrons. A representative example of type **1** of presentation from 10-I-3 is shown in Fig. 1. The interaction of the 5p orbital of the iodine atom and the half-filled orbitals of the two ligands forms three molecular orbitals. The node present in the non-bonding molecular orbitals results in the charge distribution of almost +1.0 on the iodine atom and −0.5 on each ligand. Further, a normal covalent bond exists between the carbon substituent and the iodine atom, and this carbon substituent occupies the equatorial position. Both the ligands are attached by the hypervalent bond and occupy the apical positions leading to a distorted trigonal bipyramidal geometry. Besides, the 12-I-5 species, RIL_4 has overall a square bipyramidal (or pseudooctahedral) geometry.

It is pertinent to mention here that hypervalent F, O, N, C and B compounds are rarely stable. In a recent report on computational studies pertaining to the hypervalent bonding in these elements, Machsdo and coworkers suggested that the synthesis of stable hypervalent second-period molecules may be achieved by destabilizing the competing non-covalent interations.[58] Further, computational studies suggest that the hypervalent bonding in these molecules is considerably weaker and has less covalency than the classical 2c-2e bonds.

Briefly, the structure and reactivity of hypervalent species can be best summarized as follows: (i) the pentacoordinated hypervalent compounds 10-X-5, 10-X-4, and 10-X-3 possess a trigonal pyramidal geometry with ligand at the apical positions; (ii) the hexacoordinated species 12-X-6 and 12-X-5 exist as square bipyramidal (or pseudooctahedral); (iii) the hypervalent bond, in general, is longer than the sum of the covalent radii of the bonded atoms, but shorter than ionic bonds; (iv) intramolecular positional isomerisation (known as 'Berry pseudorotation') significantly explains the reactivity of hypervalent species; and (v) ligand exchange and reductive elimination (ligand coupling) are typical for hypervalent compounds.

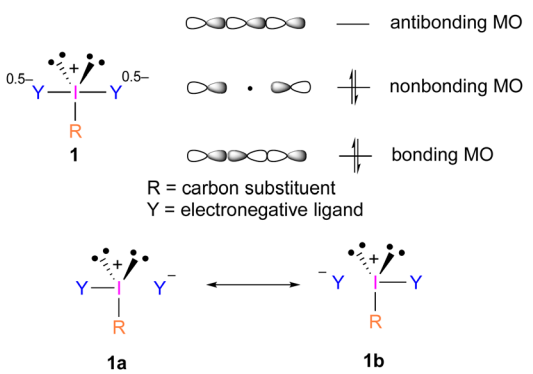


Fig. 1 Molecular orbital description of the 3c-4e bond in hypervalent 10-I-3 species **1**.

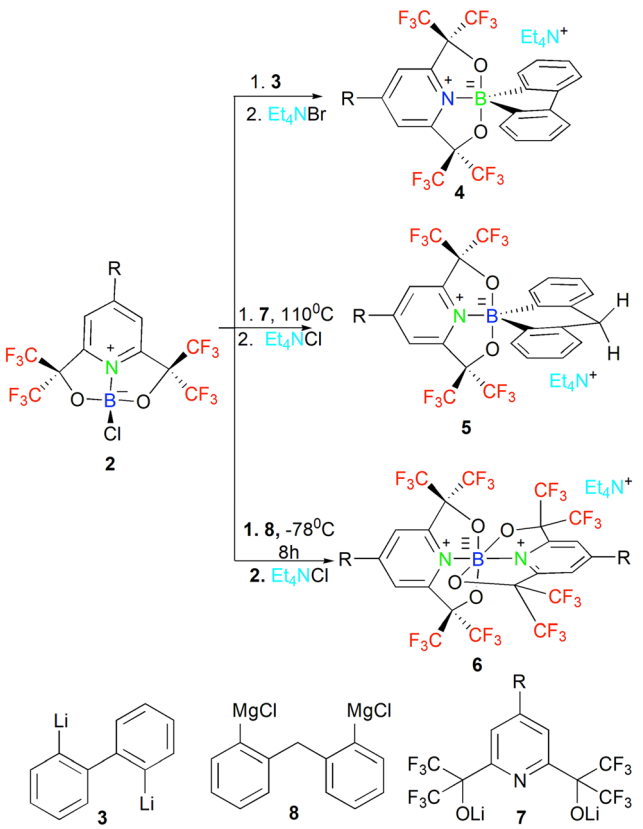
3. Hypervalent heterocyclic compounds of group 13 elements

Main group elements present in and below the third row of the periodic table are capable of expanding their valency to form hypervalent species, and numerous stable compounds with atoms formally containing 10 valence electrons have been reported in the literature.[5] In the case of the second row elements such as carbon and boron, their corresponding electron state lies in the transition state of the S_N2 reaction, which leads to the general conception that these elements are reluctant to form stable hypervalent compounds. The synthesis and isolation of these hypervalent compounds seem to be a challenging task.[1,59–62] Despite the challenges associated with their synthesis and isolation, numerous hypervalent heterocycles of 10-electron structures for group 13 elements have been reported in the literature.[63] This section elaborates the synthesis and structural aspects of hypervalent heterocycles of boron and aluminium, respectively.

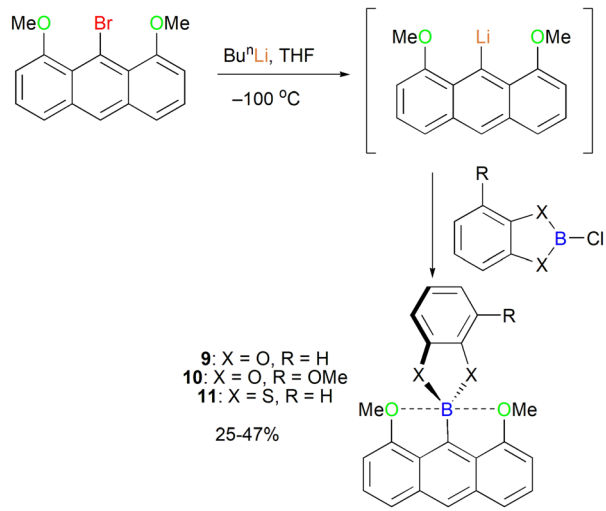
3.1. Hypervalent boron heterocycles

Lee and Martin first reported the anionic pentacoordinated and hexacoordinated boron species of the type 10-B-5 and 12-B-6 (Scheme 1), stabilized in a heterocyclic system by complexation.[61] Chloroborate **2** on reaction with dilithiobiphenyl-(**4**)[64] gives the yellow anion of **3**, which is stabilized as tetrabutylammonium salt, as shown in Scheme 1. The reaction of chloroborate **2** with Grignard reagent (**8**) in THF at −78 °C, followed by the addition of tetrabutylammonium chloride in dioxane gives another pentacoordinated boron species **5**. Further, hexacoordinated boron **6** was isolated as a white crystalline solid by the reaction of **7** with dilithio derivative at 110 °C followed by cation exchange.

The synthesis of pentacoordinated hypervalent boron species **9–11**, bearing a 1,8-disubstitued anthracene skeleton was reported by Akiba and coworkers in 2000, as outlined in Scheme 2.[65,66] The structures of these species and the intramolecular hypervalent interactions were elucidated base on X-ray diffraction and DFT calculations. The central boron atom is found to be planar in **9–11** with sp^2 hybridization given that the sum of the bond angles around the central boron atom is 360°. Thus, one of the lone pairs on the oxygen atoms present at the 1,8-positions in **9–11** interacts with the empty p-orbital of the central boron atom to form a 3c-4e bond, and the overall structure can be regarded as slightly distorted trigonal bipyramid. Further, the two hypervalent B–O bond lengths are 2.379 and 2.441 Å in **9**, 2.398 and 2.412 Å in **10**, and identical (2.436 Å) in **11**. The lengths are longer than covalent B–O bonds (1.39 to



Scheme 1 First report on anionic pentacoordinated and hexacoordinated hypervalent boron species of the type 10-B-5 and 12-B-6 by Lee and Martin, respectively.



Scheme 2 Synthesis of pentacoordinated hypervalent boron species **9–11** bearing a 1,8-disubstitued anthracene skeleton.

1.40 Å) but shorter than the sum of the van der Waals radii (3.48 Å).[65] The small difference in the B–O bond in **9** may be either due to the packing effect or linked to the electrophilicity of the boron atom, given that **9** bearing a more electron-donating methoxy (OMe) group exhibited a more symmetrical structure.

In another example, Yamamoto and coworkers reported similarly coordinated 10-methylacridinium-based hypervalent boron species **12** and confirmed its hypervalent nature by X-ray structural data (Fig. 2).[67] Further, hypervalent 10-B-5 species **13–15** (Fig. 2), bearing a flexible tridentate ligand based on 2,6-bis(*p*-tolyloxymethyl)benzene, was synthesized from the corresponding aryl bromides, and their structures were confirmed by single-crystal X-ray analysis.[68] As revealed from the X-ray analysis, the boron atoms of the diphenyl (**14**) and the catecholato derivative (**15**) were pentacoordinated; however, in the case of the pinacolato derivative (**13**), it was found to be tricoordinated. Moreover, the catecholato derivative (**15**) was found to have the strongest B–O interactions, indicating the close to the ideal trigonal bipyramidal structure typical of hypervalent 10-B-5 species.

In two representative examples, hypervalent boron–nitrogen heterocycles **16** and **17**, were reported.[69,70] The first hypervalent boron compound **16** (Fig. 3) with apical N coordination was synthesized by Yamamoto and coworkers using a tridentate ligand bearing two pyrimidine rings.[69] X-ray analysis and molecular orbital calculations indicated that compound **16** possesses a hypervalent pentacoordinate structure with a hypervalent N–B–N bond (Fig. 3). The crystal structure of **16** showed that the 1,3,2-dioxaborolane ring is planar, indicating that the boron atom is sp^2 hybridized and is perpendicular to the phenyl rings to which it is linked. The central boron atom and two nitrogen atoms of the pyrimidine rings were nearly colinear. The B–N distances (equal to 2.537 Å in both cases) are shorter compared to the sum of the van der Waals radii (3.62 Å). In another example, a terpyridine-based hypervalent boron–nitrogen compound, [(β-diketiminate)B(terpy)](OTf)$_2$ (**17**) (Fig. 3) was synthesized in 85% yield by Vidovic, Findlater and coworkers.[70] X-ray analysis of compound **17** suggested pentacoordination with four shorter B–N bonds (bond lengths

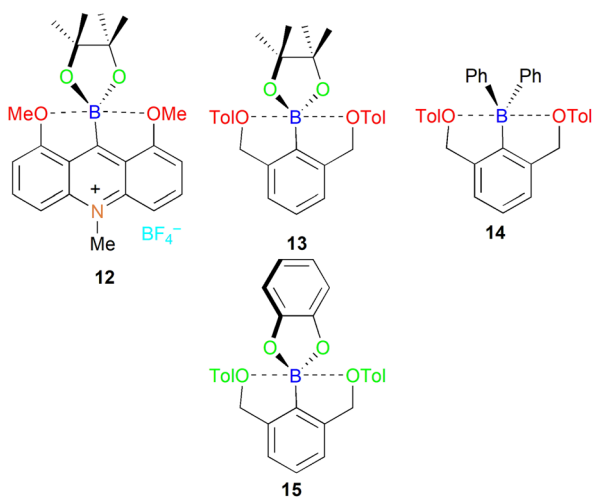


Fig. 2 Structures of 10-methylacridinium-based hypervalent boron species **12** and 2,6-bis(*p*-tolyloxymethyl)benzene-based hypervalent 10-B-5 species **13–15**.

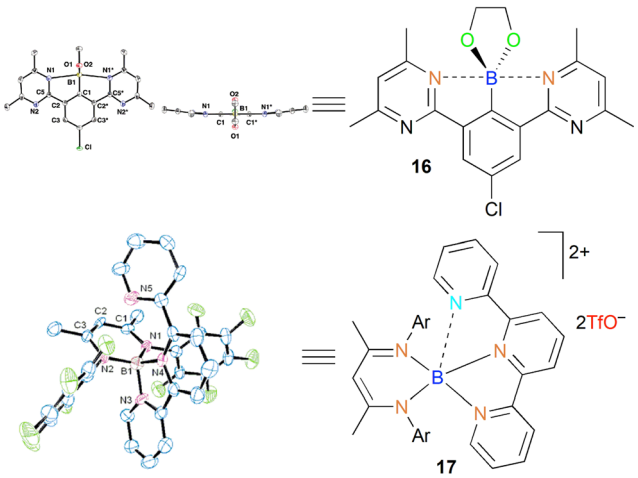
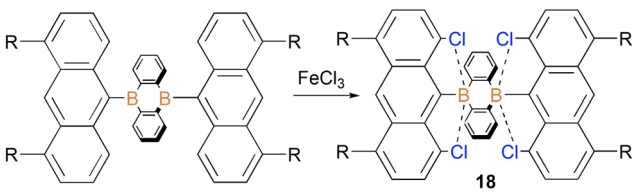


Fig. 3 X-ray structures of hypervalent boron–nitrogen heterocycles **16** and **17**.

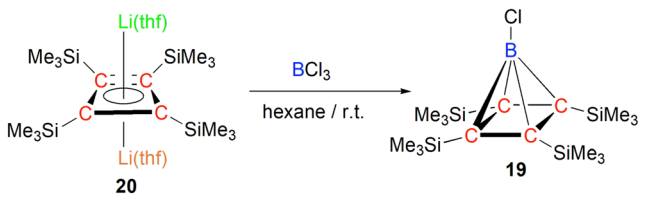
between 1.50 and 1.63 Å) and one B–N bond having a bond length of 2.94 Å. The authors described this molecule **17** as hypervalent; however, the geometry provided in the X-ray picture is not convincing. In particular, the boron atom is best described as tetrahedral and the N5 lone pair is not even directed toward boron. Boron is likely too small to sit in the terpy pocket and has a bonding interaction with all three nitrogen atoms.

A pentacoordinate organoboron compound, B,B-bis(1,8-dichloro-9-anthryl)-substituted 9,10-dydro-9,10-diboraanthracene (**18**), was developed by Yamaguchi and coworkers, as outlined in Scheme 3.[71] In these compounds, the orthogonal arrangement of the anthryl substituents may push the boron and chlorine atoms to form a 3c-4e bond.

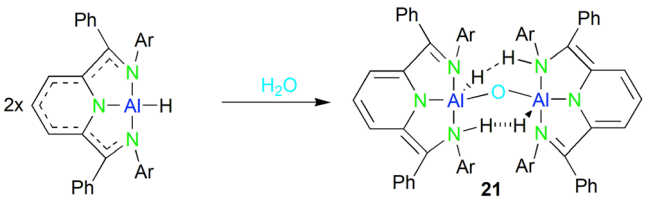
Lee, Sekiguchi and coworkers reported the first representative example of a pyramidal compound with the group 13 elements, chloroborapyramidane (**19**) (Scheme 4).[72] The reaction of $\mathbf{20}^{2-}[Li(thf)^{+}]_2$ with BCl_3 in hexane afforded compound **19** as pale-yellow crystals in 51% yield. The B–Cl bond length of 1.766 Å in **19** is shorter than the sum of the single bond covalent radii of the boron and chlorine atoms of 1.84 Å. The crystal structure of **19** suggested an unprecedented square pyramidal geometry with the central boron atom pulled above the centre of the carbon ring base.



Scheme 3 Synthesis of pentacoordinate organoboron compound, B,B-bis(1,8-dichloro-9-anthryl)-substituted 9,10-dydro-9,10-diboraanthracene (**18**).



Scheme 4 Synthesis of chloroborapyramidane **19**.



Scheme 5 Aluminium-amido-mediated heterolytic addition of water affording alumoxane **21**.

3.2. Hypervalent aluminium heterocycles

One of the representative examples of hypervalent aluminium heterocycles can be illustrated by alumoxane **21**, which is obtained by the aluminium-amido-mediated heterolytic addition of water, as shown in Scheme 5.[73]

In 2009, the Huang group demonstrated various deprotonation and reductive addition reactions of hypervalent aluminium dihydride compounds with primary and secondary amines, phenols, ketones, and phenyl isothiocyanate, leading to the synthesis of various hypervalent heterocycles **22–25** (Fig. 4).[74]

4. Hypervalent heterocyclic compounds of group 14 elements

In recent years, research interest in group 14 compounds with non-classical chemical bonds has increased extensively,[5,75] including derivatives of carbon, silicon, germanium, tin, and lead. The extension in the coordination sphere in these

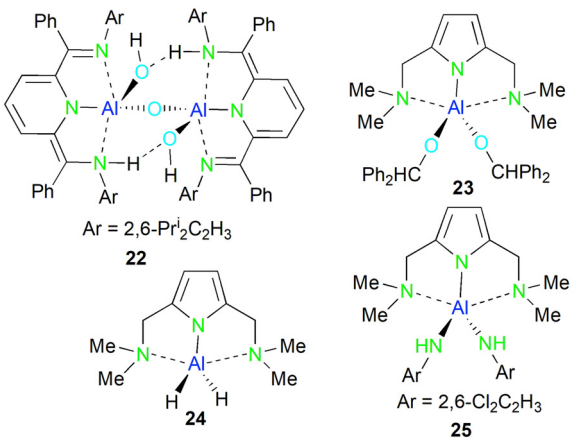


Fig. 4 Structures of hypervalent aluminium heterocycles **22–25**.

elements is generally due to the additional intra- or intermolecular coordination interactions. In the case of the hypervalent compounds of group 14 elements, the donor lone pair of electrons is usually provided by the ligand given that the central atom has no ns^2 lone pair. In the early 1960s, organotin compounds were shown to have the ability to expand their coordination spheres.[76,77] Hulme reported the first structurally characterized pentacoordinated organotin compound, $PyMe_3SnCl$, in 1963.[78] In the last three decades, five (TBP, SP)- and six (Oh)-coordinated Sn have been extensively studied. Interestingly, some studies on hypervalent carbon compounds were also reported mainly by the Martin group, as well by Akiba, Yamamoto and coworkers.

4.1. Hypervalent carbon heterocycles

Pentacoordinate carbon compounds, termed electron-deficient and electron-rich species depending on the number of formal valence electrons around the central carbon, have distinct structures and properties. Electron-rich species such as 10-C-5, generally found as the transition state of a fundamental bimolecular nucleophilic substitution, usually consist of an interaction of a vacant 2p orbital of the central carbon atom with two lone-pair electrons or an interaction between a vacant C–X σ* orbital and a lone pair of a nucleophile. These pentacoordinate carbon compounds bearing a 3c-4e bond are termed hypervalent carbon compounds. However, although hypervalent compounds of heavy main group elements are widespread, in the case of the light second row elements, their synthesis and isolation always present a significant challenge. The earlier synthesis of hypervalent carbon compounds includes the significant work done by Martin and coworkers;[1,59,61,79–81] however, due to the lack of solid-state X-ray crystallographic data, the existence of 3c-4e bonding in these compounds could not be confirmed. Martin and coworkers reported the synthesis of hypervalent carbon species **26** through the coordination of two sulfide moieties to a carbocation (Fig. 5).[60] This group presented evidence of the existence of hypervalent 10-C-5 using NMR study[4] and electrochemistry.[5]

Last two decades witnessed the substantial efforts by Akiba, Yamamoto and coworkers in this area, and a few examples of isolated and structurally confirmed penta-/hexa-coordinated carbon have been reported.[66,82–87] In this series, the first X-ray crystallographically characterized solid-state structure of a stable pentacoordinate carbon species, 1,8-dimethoxy-9-dimethoxymethyl anthracene monocation, was reported in 1999.[82] This group reported the synthesis and X-ray analysis of hypervalent carbon compound **27** bearing a tridentate anthracene ligand with two coordinating oxygen sites at the 1,8-positions (Scheme 6).[66,82] The distances between the apical 'C–O' bonds (2.44 Å) were found to be shorter than the distances between the *ipso* carbon atoms of the anthracene backbone linked to these three atoms (2.51 Å). The sum of the C–O covalent radii was found to be 1.39 Å. Further, the atoms in molecule (AIM) analysis indicated the presence of bond paths between the central carbon and the two oxygen atoms present at the 1,8-positions. However, the 'ρ' values indicate very weak interactions between the carbon and oxygen atoms.

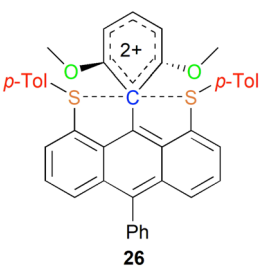


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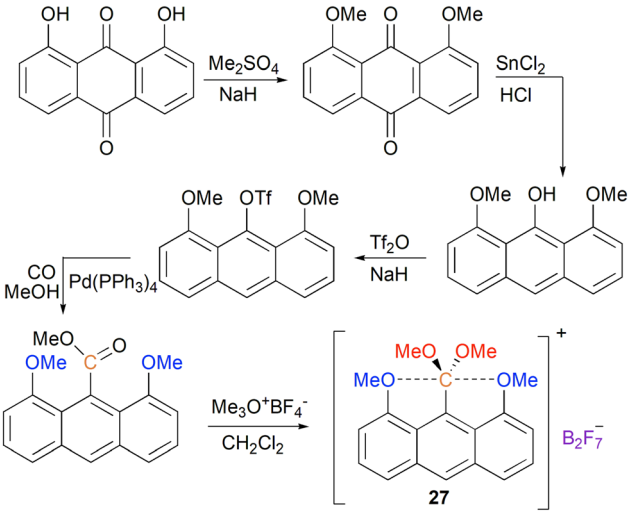
Fig. 5 Structure of hypervalent carbon species **26** bearing two sulfide linkages.

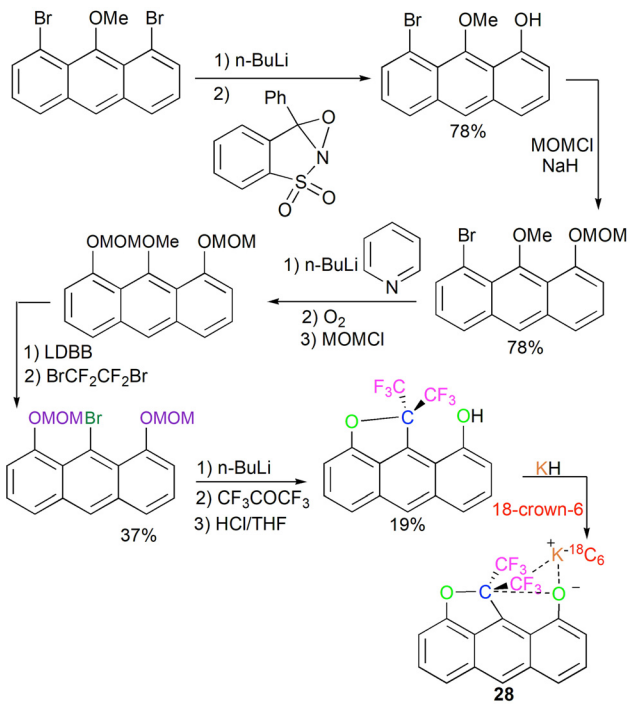


Scheme 6 Synthesis of hypervalent carbon compound **27** bearing a tridentate anthracene ligand with two coordinating oxygen sites at the 1,8-positions.

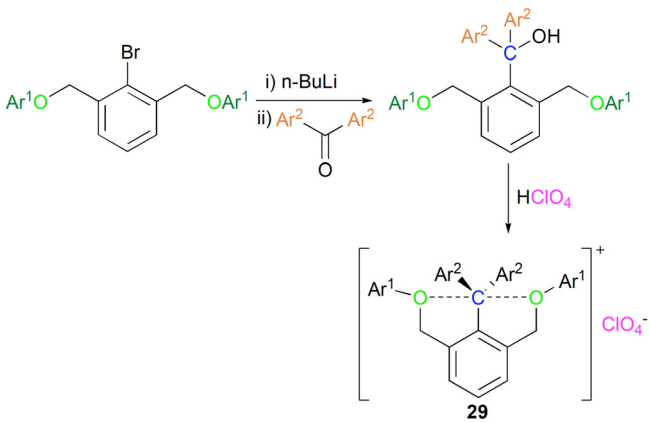
An anionic hypervalent pentacoordinate carbon compound **28** was synthesized by utilizing a ligand bearing two deprotectable methoxymethoxy groups, as depicted in Scheme 7.[83]

Yamamoto and Akiba group also developed certain other hypervalent carbon species **29**, bearing 2,6-bis(*p*-substituted phenyloxymethyl)benzene, utilizing a van Koten-type framework (Scheme 8).[84] These species bear flexible side arms supporting the apical donors, which result in significantly longer and weaker apical interactions. The X-ray analysis of the bis(*p*-fluorophenyl)methyl cation bearing a 2,6-bis(*p*-tolyloxymethyl)benzene ligand displayed a symmetrical structure, in which the two C-O distances are identical, although the distance (2.690 Å) is longer than that (2.43 and 2.45 Å) of the 1,8-dimethoxy-9-dimethoxymethylanthracene monocation. Further, the synthesis and experimental charge density analysis and DFT calculations of a hexacoordinate carbon species, 12-C-6, were also reported by the same group.[86,87]

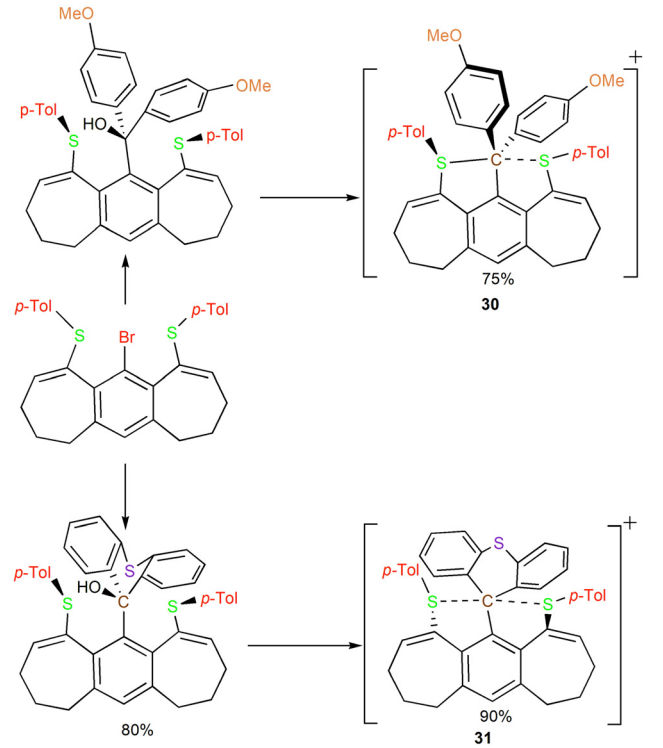
Recently, the synthesis and X-ray characterization of hypervalent pentacoordinate carbon compounds **30** and **31** bearing a 7-6-7 ring skeleton was reported by Yamamoto and coworkers. The synthesis of compounds **30** and **31** is outlined in Scheme 8.[88] In the case of compound **30**, bearing a *para*-OMe



Scheme 7 Synthesis of anionic hypervalent pentacoordinate carbon compound **28**.



Scheme 8 Synthesis of cation **29** bearing 2,6-bis(*p*-substituted phenyloxymethyl)benzene.



Scheme 9 Synthesis of hypervalent pentacoordinate carbon compounds **30** and **31** bearing a 7-6-7 ring skeleton.

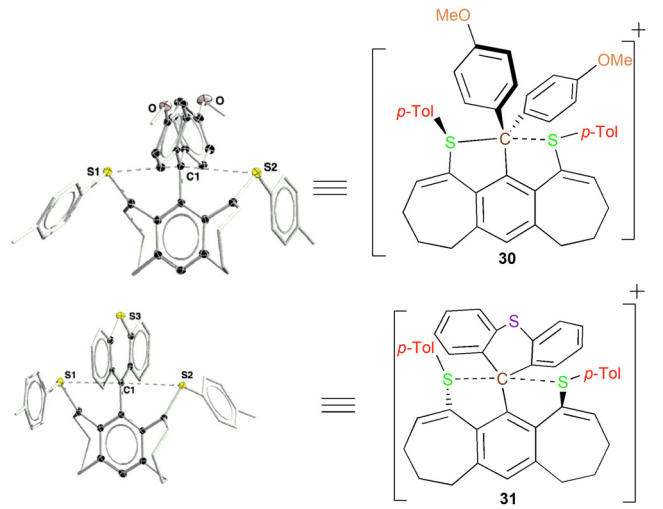


Fig. 6 X-ray structures of carbon heterocycles **30** and **31**.

substituent, and compound **31** with thioxanthylium moiety, hypervalent pentacoordinate structures were observed (Scheme 9).

Both structures featured an sp^2 hybridized central carbon atom with the sulfur atoms aligned at apical positions to form a trigonal bipyramidal geometry (Fig. 6). In both compounds **30** and **31**, a pair of nearly identical S/C distances (3.154/3.069 Å) and 3.020/3.041 Å) was observed, which is considerably shorter than the sum of the van der Waals radii of the two atoms (3.50 Å).

4.2. Hypervalent silicon heterocycles

Martin and coworkers reported the synthesis of stable, anionic hypervalent 10-Si-5 heterocycles **32** and **33** (Fig. 7).[89,90] The high electronegativity of the apical oxygen present in the fluoroalkoxy ligand and the electropositive carbon equatorial to the central atom increases the difference in electronegativity between the central atom and apical ligand, forming a stable hypervalent bond.[91,92] This ligand also provides stabilization through a 5-membered ring effect[93] and a *gem*-dialkyl (Thorpe-Ingold) effect,[94–96] which favors the ring-closed hypervalent species.

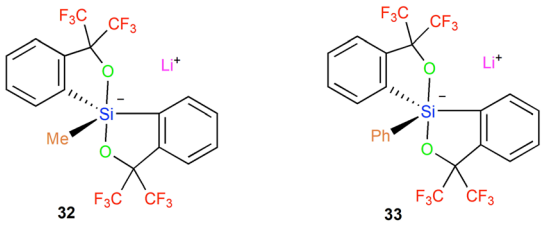


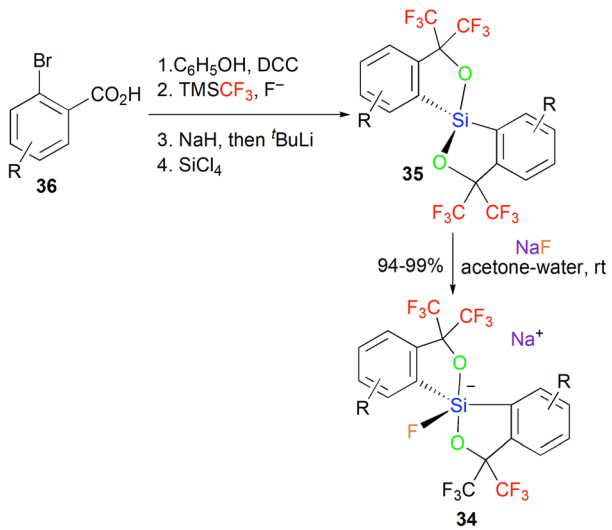
Fig. 7 Structures of anionic hypervalent 10-Si-5 heterocycles **32** and **33**.

A new synthetic route to access Martin's spirosilanes **34** was developed by Goddard, Fensterbank and coworkers (Scheme 10).[97] Hypervalent fluorosilicated **34** was prepared by the reaction of sodium fluoride with tetracoordinated silicate **35** in acetone–water at room temperature, while tetracoordinated silicate **35** could be easily obtained from the corresponding 2-bromobenzoic acids **36** by a simple synthetic sequence.

Further, X-ray analysis of spirosilane **34-OMe** bearing a methoxy substituent revealed the trigonal pyramidal structure of silicon with apical oxygen atoms and presence of an aromatic ring and fluorine atoms occupying the equatorial positions (Fig. 8).[97]

During the catalytic cross-Aldol reactions of aldehydes mediated by chlorosilanes, the intermediate formation of unstable 10-Si-5 silicon–oxygen heterocycles has been proposed.[98,99] Further, Ikeda and Inagaki theoretically investigated (electron-pair bond model) the structures and stabilities of three-membered rings containing hypervalent atoms X (X = Si, S or P).[100]

Another important class of cyclic hypervalent silicon compounds is triptych siloxazolidines (5-aza-2,8,9-trioxa-1-silabicyclo[3.3.3]undecane) (**37**), which was later termed silatranes (Fig. 9). Silatranes {X-Si(OCH$_2$CH$_3$)$_3$N} and their derivatives are a class of pentacoordinated silicon compounds with unique stereoelectronic and crystal structures. Several reviews



Scheme 10 Synthetic route to access Martin's spirosilanes **34**.

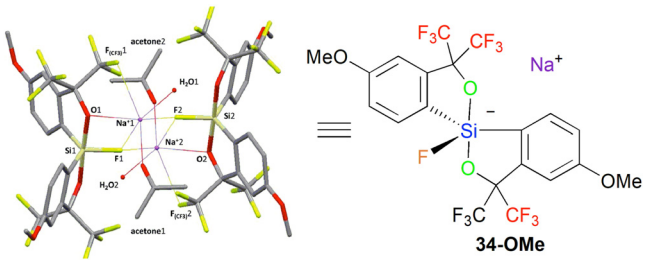


Fig. 8 X-ray structure of silicon hypervalent heterocycle **34-OMe**.

have appeared in the literature highlighting the synthesis, structure and reactivity of these compounds.[101–105] Besides, their unique chemical reactivity pattern, diverse biological activities, such as antiviral, anti-inflammatory, and anti-tumor as well as seed germination properties have been well investigated.[102]

X-ray diffraction suggests a tricyclic cage structure for silatranes that possess hypervalent silicon having a trigonal bipyramidal arrangement surrounded with three endocyclic oxygens placed at the equatorial position. Silatranes can exist in two conformations, *exo*- and *endo*-conformations (Fig. 9).[106,107] The concept of 3c-4e bonding in these compounds was established in 1977.[108] In the case of *exo*-conformation, the lone pair of electrons present on the nitrogen atom is directed out of the cage, while in the *endo*-form, the lone pair is directed towards the silicon atom, as depicted in Fig. 9. The transannular Si–N interactions may lead to the endo form, which results in the formation of a 3c-4e hypervalent bond.[108] A significant dipole moment (μ = 5.3–7.1 D) is present in these compounds due to the transfer of electron density from the N-atom to the Si–R bond. This dipole moment in conjunction with the strong electron-donating effect of the silatranyl group contributes to the high reactivity of these compounds.[109] The transannular Si–N dative bond distance is between the sum of their covalent and non-bonded radii (1.89 Å and 2.69 Å). This bond length indicates the weak interaction between silicon and nitrogen.[110]

4.3. Hypervalent germanium, tin, and lead heterocycles

The chemistry of the hypervalent germanium, tin, and lead compounds has been elaborated in several reviews and monographs. The inter- and intramolecular donor–acceptor bonds are usual characteristics of these compounds, in particular for tin(IV) compounds. In general, a trigonal bipyramid or more rarely a square pyramid as well as an octahedral arrangement of the metal atom, are distinct for germanium, tin, and lead in pentacoordinate '10-M-5' and hexacoordinate '12-M-6' compounds, respectively.

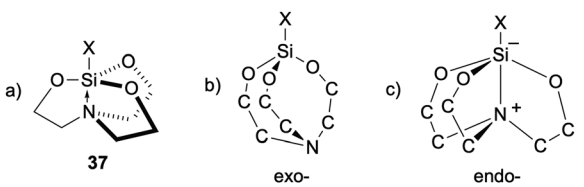


Fig. 9 (a) Structure of silatranes (**37**): exo- (b) and endo- (c) isomers.

According to Musher's classification, in view of 10-M-5 and 12-M-6, hypervalent compounds of germanium, tin and lead include hypervalent bonding of the second type, in which the central atom has no ns^2 lone pair electrons. This model implies that the trigonal bipyramidal metal atom can utilize its nsp^2 orbitals for bond formation with the equatorial ligands to form two-center bonds, while its np_z orbital can be involved in the interaction with an appropriate orbital of the axial substituent 'X' and a lone pair of electrons of the donor atom to form a hypervalent, 3c-4e bond in the axial moiety D → M–X. Baukov

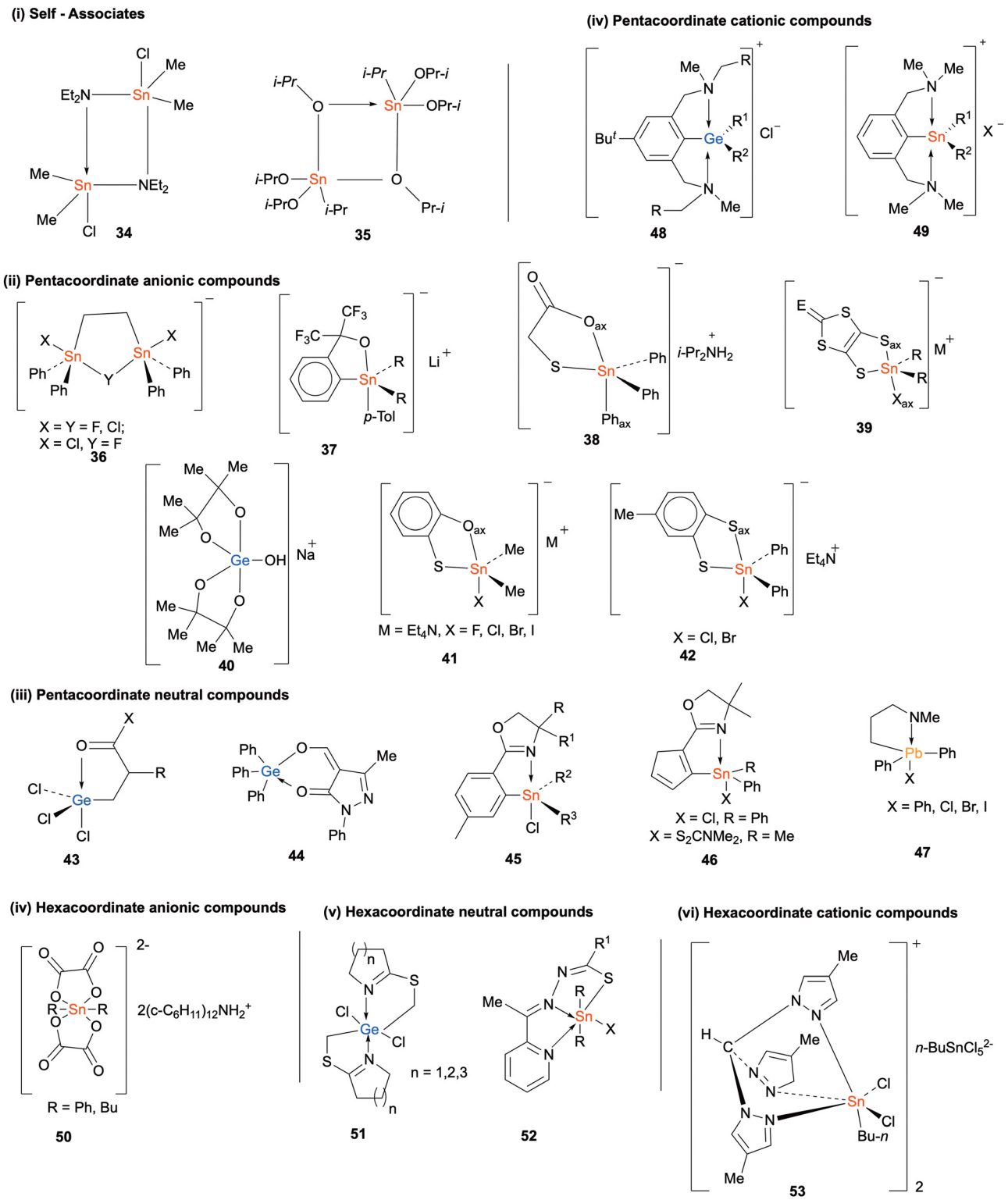
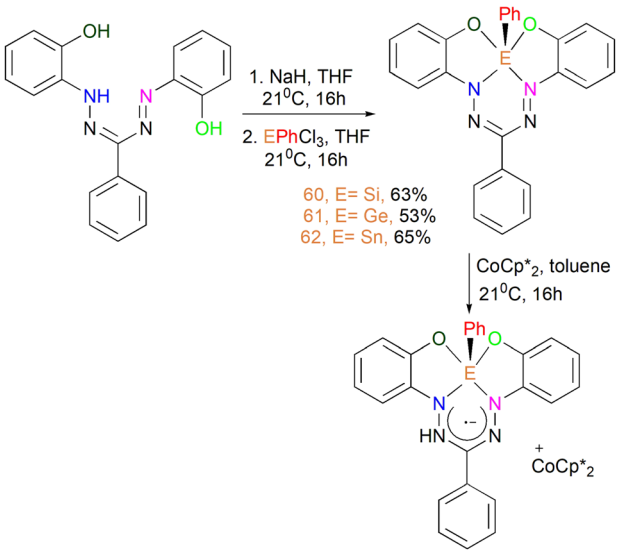


Fig. 10 Selected examples of hypervalent germanium, tin, and lead heterocycles **38–57 (types i–vi)**.

and Tandura[111] discussed the hypervalent compounds of germanium, tin and lead, classifying these compounds as self associates[112,113] of the type **38** and **39**, pentacoordinate anionic compounds **40–46**,[114–120] pentacoordinate neutral compounds **47–51**,[121–127] pentacoordinate cationic **52** and **53**,[128–130] and hexacoordinate anionic **54**,[131] neutral **55** and **56**[132–134] and cationic **57**[135] compounds (Fig. 10).

Other representative examples of these heterocyclic compounds are illustrated by germanium cyclic oxamide complexes **58**[136] and cyclic pentaorganostannate **59**,[137] as shown in Fig. 11.

In 2018, Gilroy and coworkers reported the preparation and characterization of a family of formazanate complexes **60–62** of hypervalent group 14 elements (Ge, Sn, Si) (Scheme 11).[138] The chemical reduction of these complexes using bis(pentamethylcyclopentadienyl)cobalt ($CoCp^*_2$) afforded radicals stabilized specifically by the square-pyramidal coordination geometry within the framework of the heteroatom-rich formazanate ligands.



Scheme 11 Preparation of formazanate complexes **60–62** of hypervalent group 14 elements (Ge, Sn, Si).

5. Hypervalent heterocyclic compounds of group 15 elements

Among the hypervalent heterocycles of group 15 elements, hypervalent nitrogen species have been recently characterized, while various types of hypervalent phosphorous compounds are described in the literature. Regarding other elements of this group, there are numerous reports on organobismuth and organotin compounds showing hypervalent coordination/hypercoordination.[139–141]

5.1. Hypervalent nitrogen heterocycles

Hypervalent pentacoordinated nitrogen species (10-N-5) have been some of the fundamental hypervalent compounds, with their synthetic attempts traced back to 1916.[142–150] Regardless of the theoretical calculations about the existence and stability,[151–156] the synthesis and isolation of thermally stable hypervalent nitrogen compounds of the type N–N–L (N > 10, L > 4) could not be achieved until 2020.[148,150,157,158] However, the detection,[159–163] isolation and structural characterization of transient, as well as stable[164–166] hypervalent tetracoordinate nitrogen radical species (9-N-4) have been reported. Recently, in 2020, Shang, Yamamoto and coworkers synthesized stable hypervalent pentacoordinate nitrogen cationic radical (11-N-5) species **63**, as depicted in Scheme 12.[167]

Furthermore, the N–O bond distance in cationic radical species **63a** is shorter than the sum of the N–O van der Waals radii, which indicates the attractive interactions between the N and O atoms. The single-crystal X-ray analysis and computational studies revealed that the nitrogen centre adopts a trigonal bipyramidal geometry, which features a 3c-5e hypervalent attractive interaction (Fig. 12).

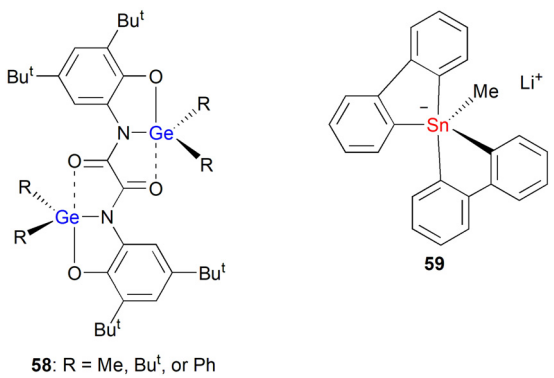
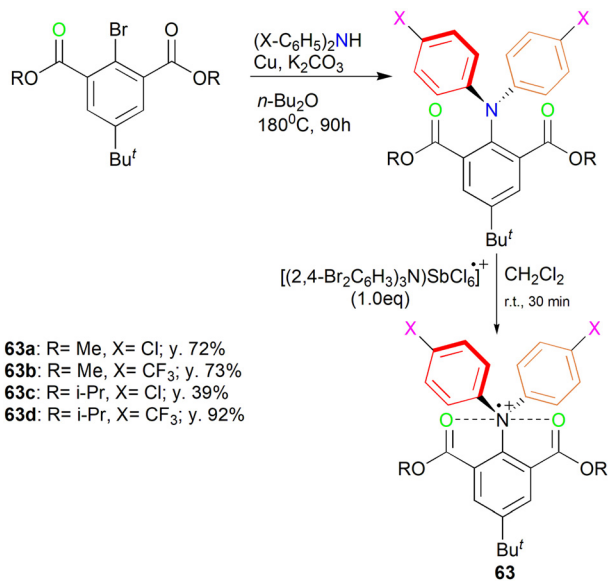


Fig. 11 Germanium cyclic oxamide complexes **54** and cyclic pentaorganostannate **55**.



Scheme 12 Synthesis of stable hypervalent pentacoordinate nitrogen cationic radical (11-N-5) species **63**.

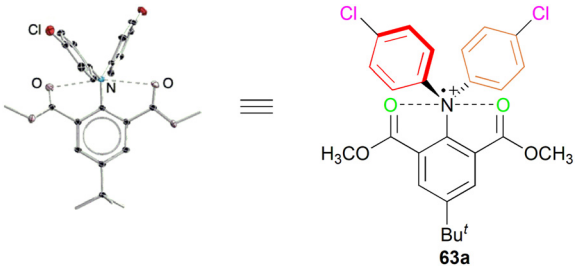
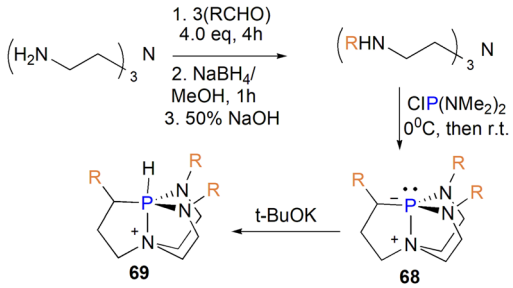


Fig. 12 X-ray structure of nitrogen hypervalent heterocycle **63a**.



Scheme 13 Preparation of pentacovalent 10-P-5 compound **69**.

5.2. Hypervalent phosphorous heterocycles

Various structural types of hypervalent phosphorus compounds have been reported in the literature.[5] Representative examples of stable hypervalent phosphorus heterocycles are 10-P-3 compounds **64**,[33] anionic 10-P-4 species **65**,[168] pentacovalent 10-P-5 compounds **66**,[169] and anionic hexacoordinated 12-P-6 species **67**[170] (Fig. 13). The first two structural types **64** and **65** are usually classified as low-coordinate hypervalent phosphorus compounds.[33]

The pentacovalent 10-P-5 compound, shown by the protonated form of proazaphosphatrane **69**, was reported by Kishanga and Verkade, as depicted in Scheme 13. Compounds **68**, a class of strong nonionic bases (Verkade bases, also known as superbases), serve as efficient catalysts and promoters of many chemical transformations.[171] The X-ray analysis showed that the P–Nax distance (2.047 Å) in cation **69** was within the experimental error (*i.e.* within 3× esds) Further, the NeqPNeq angles of 118–119° were also comparable to that in the aforementioned analogs reported previously. Another important class of hypervalent phosphorous heterocycles includes hypervalent 10-P-3 compounds. 3,7-Di-*tert*-butyl-5-aza-2,8-dioxa-1-phosphabicyclo[3.3.0]octa-2,4,6-triene (ADPO, **64**) is one of the important examples of this class, which possesses unique chemical properties.[33]

Kornev and coworkers reported the preparation and structural investigation of certain low-coordinate hypervalent phosphorus heterocycles, phenylpyrazole-based hypervalent phosphorus compounds **70** and **71** (Scheme 14).[172] The X-ray analysis revealed that the phosphorus atom in molecule **70** has an overall trigonal bipyramidal geometry with both chlorine atoms present at the apical position, and the N- and C-substituents as well as the lone pair of electrons occupy the equatorial positions. Further, the P–N and P–C bond distances are 1.771 Å and 1.831 Å, respectively.

Yamamoto and coworkers reported the first stereo-pure isolation of the pair of O-facial and O-meridional isomers of 12-P-6 oxaphosphates **72** and **73** using a modified Martin ligand[173–176] with two bulky C_2F_5 groups to slow down the Berry pseudorotation (BPR) of the precursors (Fig. 14).[177]

The single-crystal X-ray crystallographic structures of both oxaphosphates **72** and **73** are presented in Fig. 15 The X-ray crystallographic analysis of **72** revealed a hexacoordinate O-facial geometry, while its solid-state structure displayed facial coordination of the potassium to all the oxygen atoms.

5.3. Hypervalent arsenic, antimony, and bismuth heterocycles

Hypervalent structures are typical of arsenic, antimony, and bismuth heterocycles. The chemistry of these compounds was overviewed by K.-Y. Akiba[2] and Romanenko and Sotiropoulos.[178] Certain representative examples of these compounds are illustrated by structures **74** and **75** (Fig. 16).

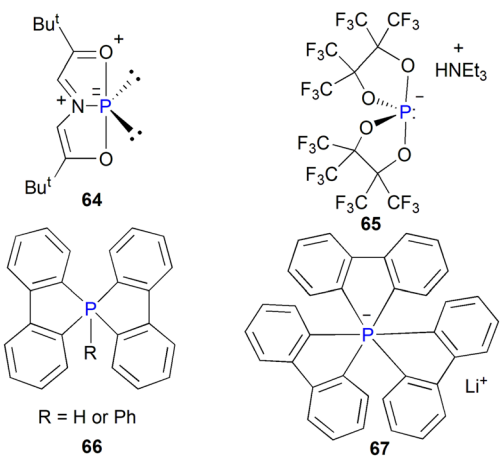
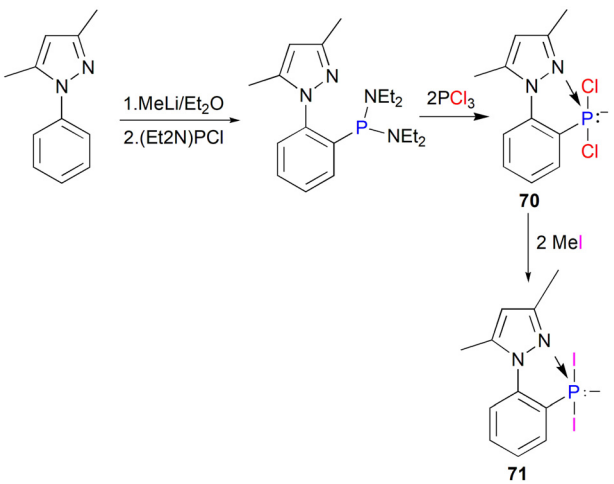


Fig. 13 Representative examples of stable hypervalent phosphorus heterocycles **64–67**.



Scheme 14 Synthesis of phenylpyrazole-based hypervalent phosphorus heterocycles **70** and **71**.

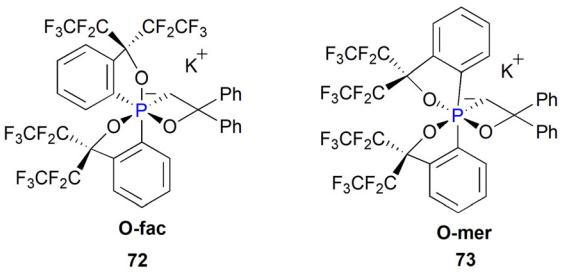


Fig. 14 Pair of O-facial and O-meridional isomers of 12-P-6 oxaphosphates **72** and **73**, respectively.

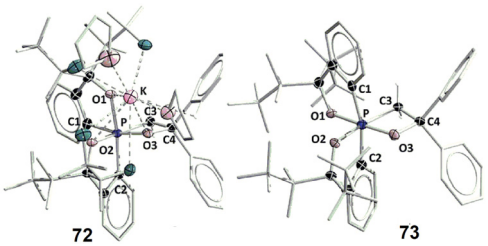


Fig. 15 X-ray crystallographic structures of oxaphosphates **72** and **73**.

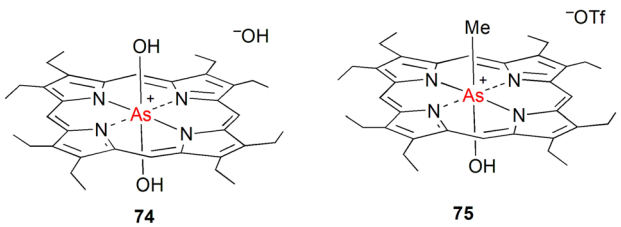


Fig. 16 Representative examples of hypervalent arsenic heterocycles **74** and **75**.

Further, selected examples of hypervalent heterocycles of antimony and bismuth elements **76–86** are presented in Fig. 17.

6. Hypervalent heterocyclic compounds of group 16 elements

The last few decades has witnessed tremendous growth in the interest in organochalcogen (S, Se, and Te) chemistry by chemists due to their immense utilization in the field of synthetic organic chemistry,[179–188] dyes,[189] and biological applications.[190–195] Certain hypervalent heterocycles of these elements have been synthesized and well-characterized. The hypervalent compounds of Se and Te have similar structures to that of sulfur.

6.1. Hypervalent sulfur heterocycles

Certain structural types of hypervalent compounds of sulfur(IV) and sulfur(VI) are known.[5] The representative examples of stable hypervalent sulfur heterocycles reported in the literature

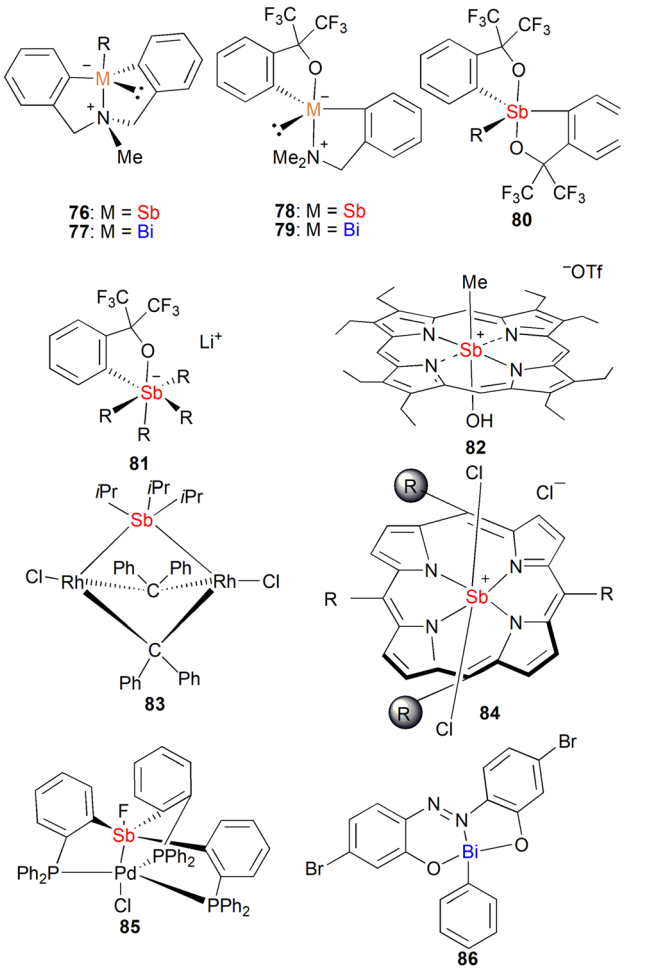


Fig. 17 Examples of hypervalent heterocycles of antimony and bismuth elements **76–86**.

include anionic 10-S-3 sulfuranes **87**,[196] 10-S-4 species **88**,[197] **89**,[198] pentacoordinated 10-S-5 sulfuranes **90**[199] and **91**[200] and hexacoordinated 12-S-6 species **92** (also known as persulfuranes)[201] (Fig. 18).

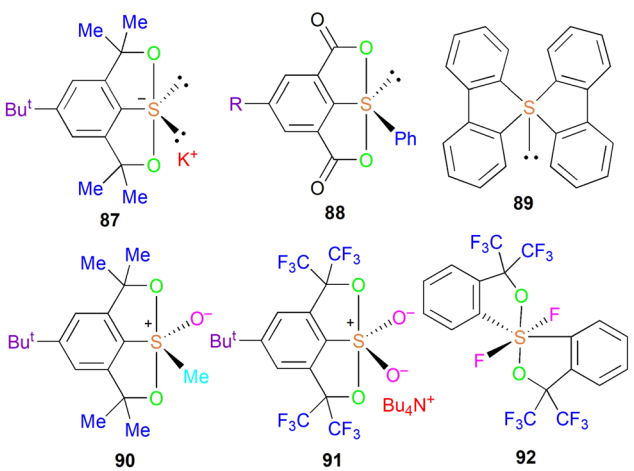


Fig. 18 Representative examples of stable hypervalent sulfur heterocycles **87–92**.

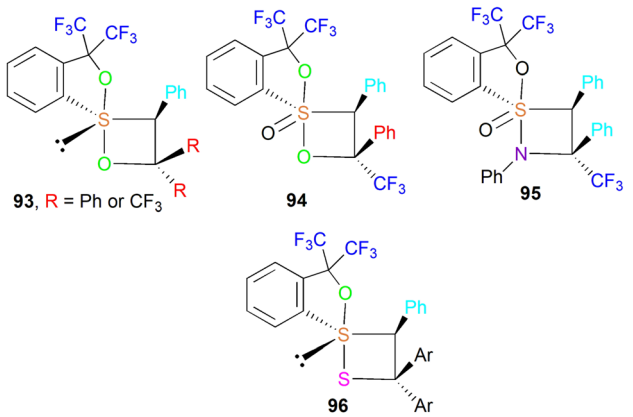
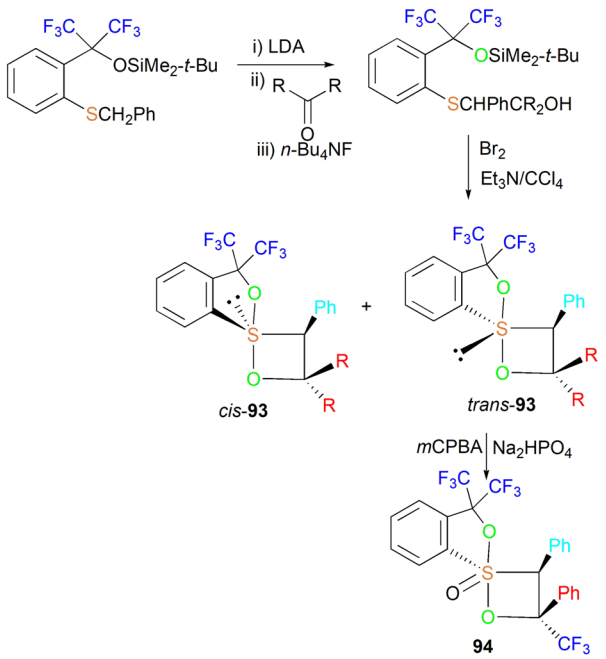


Fig. 19 Four-membered 10-S-4 and 10-S-5 heterocycles **93–96**.

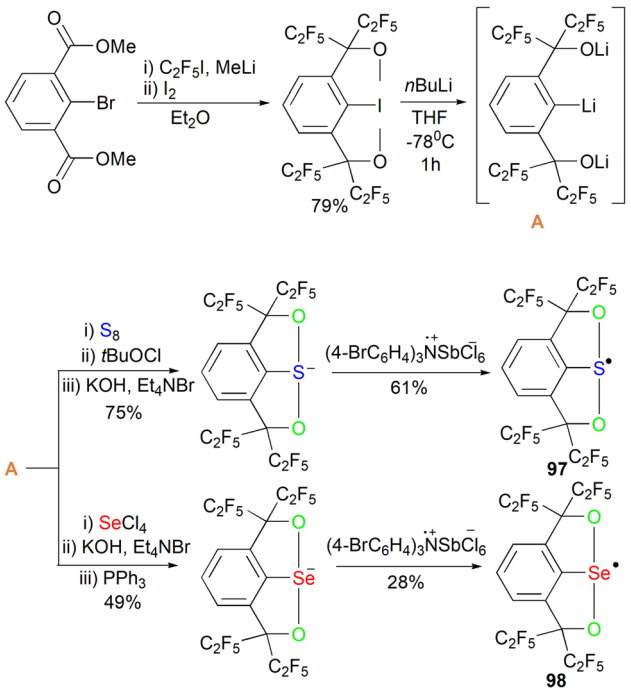
Kawashima reported the preparation and structural studies of various four-membered 10-S-4 and 10-S-5 heterocycles **93–96** (Fig. 19).[202]

In particular, this group synthesized tetracoordinated and pentacoordinated 1,2-oxathietanes **93** and **94**, as shown in Scheme 15, and reported their thermolysis. These compounds having a tetracoordinated or pentacoordinated hypervalent sulfur atom collectively with other heteroatoms were isolated as thermally stable products and structurally characterized through single-crystal XRD. The X-ray crystallographic analyses revealed that the hypervalent sulfur centers in these molecules possess a distorted trigonal bipyramidal geometry.

The isolation of hypervalent group 16 radicals and their applications in organic-radical batteries were reported by Yamamoto and coworkers.[203] Utilizing a tridentate ligand



Scheme 15 Synthesis of tetracoordinated and pentacoordinated 1,2-oxathietanes **93** and **94**, respectively.



Scheme 16 Hypervalent sulfur **97** and selenium radicals **98** utilizing tridentate ligand bearing C_2F_5 groups.

bearing C_2F_5 groups, hypervalent sulfur **97** and selenium radicals **98** were isolated for the first time (Scheme 16). This structures were characterized by X-ray crystallography, electron spin resonance spectroscopy, and density functional theory calculations, which revealed a three-coordinate hypervalent structure. Furthermore, by making use of the reversible redox reactions between the hypervalent radicals and corresponding anions, organic radical batteries as cathode-active materials were developed.

'π-Hypervalent' heterocyclic systems have attracted substantial attention because of their remarkable structure and reactivity.[204] A variety of sulfur heterocycles with endocyclic double bonds on sulfur is usually referred to as 10-S-3 ''π-hypervalent heterocyclic systems''. Compounds containing a 10-S-3 sulfurane species have extensively been studied. Further, these compounds can be represented as canonical structures with tetracovalent sulfur, for example, tetraazathiapentalenes **99** and trithiapentalenes **100** (Fig. 20).[205,206] However, a more

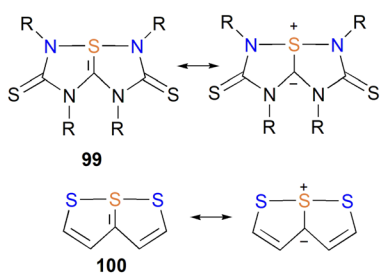
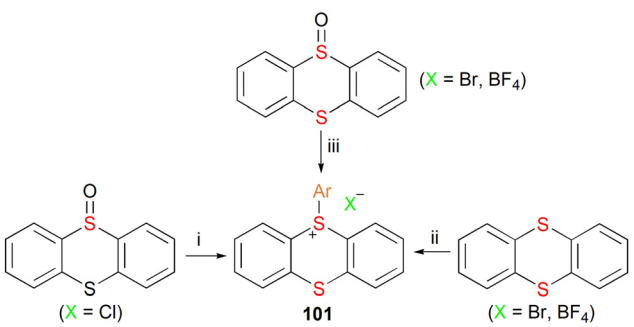


Fig. 20 Canonical structures of tetracovalent sulfur heterocycles tetraazathiapentalenes **99** and trithiapentalenes **100**.

precise illustration of these compounds involves 'non-hypervalent betaine structures' with eight electrons on the sulfur atom. These compounds are associated with extensive theoretical and synthetic interest[207–209] and a discussion on heterocyclic mesomeric betaines including sulfur or other elements has been well-reviewed.[210,211]

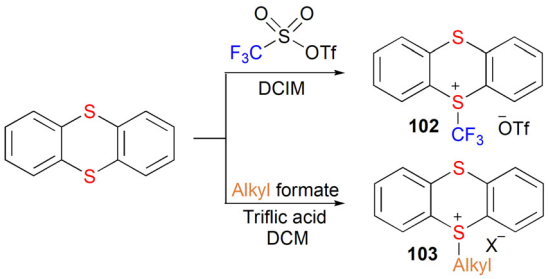
Thianthrenium salts represent a typical class of organosulfur compounds with exceptional potential applications in organic synthesis. These compounds have emerged as versatile precursors in a variety of chemical transformations.[211–227] Shu and co-workers recently summarized the synthesis and applications of aryl, alkyl, and alkenyl salts.[227] The seminal work reported by Calvin and coworkers,[228] Lucken[229] and Shine group[230] became the foundation for the development of different organothianthrenium salts. Shine developed the synthesis of aryl thianthrenium perchlorates by the treatment of thianthrenium perchlorates with e^--rich aromatics.[213–215] Other methods for the synthesis of aryl thianthrenium salts (**101**) include the reaction of thianthrene S-oxide with: (i) $AlCl_3$ followed by arenes[215,217] and (ii) aryl Grignard reagents or Ar_2Hg (Scheme 17). Recently, the Ritter[231] and Wang[232] research groups independently developed efficient protocols for the synthesis of aryl thianthrenium salts using thianthrene sulfoxides.

Besides, synthetic methods to access alkenyl thianthrenium salts have been developed through: (i) treatment of thianthrene with acetic anhydride followed by appropriate alkenes;[225] (ii) stereoselective C(sp^2-H) thianthrenation of aliphatic alkenes using trifluoroacetic anhydride (TFAA), followed by alkaline workup;[226] (iii) thianthrene sulfoxide reaction with alkenes using triflic anhydride and alkaline workup;[233] and (iv) electrochemical strategy developed by Wickens and coworkers.[234] The Ritter group reported an excellent example of the synthesis of trifluoromethyl thianthrenium salt (**102**) using trifluomethyl sulfonic anhydride (CF_3SO_3Tf),[235] while Shine and coworkers reported the excellent access to alkyl thianthrenium salts (**103**) utilizing alkyl formates and triflic anhydride[236] (Scheme 18). Recently, the Shi group achieved the synthesis of a diverse range of alkyl thianthrenium salts using triflic anhydride and aliphatic alcohols.[237]



i) 1. H_2SO_4, 2. $AlCl_3$, 3. ArH; ii) 1. $ON^+BF_4^-$, MeCN; 2. Ar_2Hg, MeCN; iii) ArMgX, Benzene

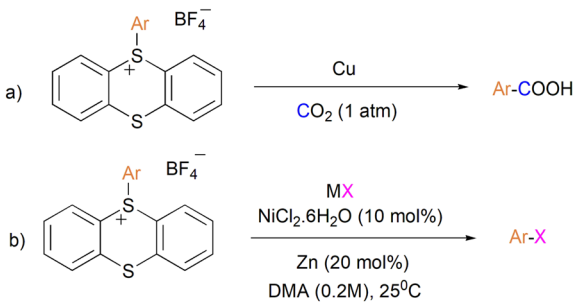
Scheme 17 Synthesis of aryl thianthrenium salts (**101**) including thianthrene S-oxide.



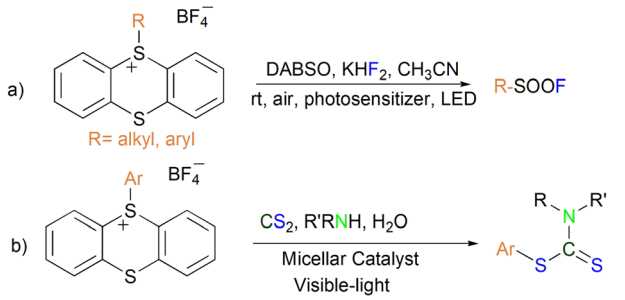
Scheme 18 Synthesis of trifluoromethyl thianthrenium salt (**102**) and alkyl thianthrenium salts (**103**).

Besides the significant achievements in the synthesis of thianthrenium salts, various reports pertaining to the versatile utilization of these salts have appeared in the literature.[222,227] An overview of their potential applications is presented here. A variety of aryl substituted compounds can be effectively accessed through transition metal-catalyzed cross-coupling reactions of aryl thianthrenium salts, where the majority of these are palladium-catalyzed reactions. Examples of these Pd-catalyzed coupling reactions are sulfination of arenes,[238] Suzuki–Miyaura coupling reaction,[239] one-pot conversion of C–H bond of arenes into C–Si bond bond,[240] α-arylation of carbonyl compounds,[241] reduction alkylation,[242] reductive deuteration/tritiation,[243] phosphination,[244] esterification,[245] and deuterated formylation.[246] Besides these applications, the copper-catalyzed carboxylation of aryl thianthrenium salts has been reported by Wang and coworkers recently[247] (Scheme 19(a)). This example provides an elegant illustration of site-selective C–H carboxylation, which may be utilized for late-stage carboxylation modification. Moreover, the Ritter group developed an unusual Ni(I)/Ni(III)-catalyzed regioselective late-stage arene halogenation method (Scheme 19(b)).[248]

Besides, several photoredox-catalyzed cross-coupling reactions of aryl thianthrenium salts have been explored, highlighting the versatility of these salts under free-radical pathways. The first report by Ritter, in 2019, gave a breakthrough in the development of numerous photoredox cross-coupling transformations of aryl thianthrenium salts.[249] Photoredox-catalysis involving aryl thianthrenium salts has been reported for the regioselective hydroxylation,[250] arene



Scheme 19 (a) Copper-catalyzed carboxylation of aryl thianthrenium salts. (b) Ni(I)/Ni(III)-catalyzed regioselective late-stage arene halogenation of aryl thianthrenium salts.



Scheme 20 (a) Visible-light-mediated fluorosulfonylation reaction of thianthrenium salts and (b) synthesis of *S*-aryl dithiocarbamates from thianthrenium salts.

fluorination,[251] para-selective arylation of monosubstituted arenes,[252] Sonogashira-type reaction,[253] late-stage heteroarylation,[254] (hetero)arylation,[255] radical hydroarylation of azine-substituted enamides,[256] thioetherification,[257] sulfonylation,[258] α-sulfonylation of carbonyl compounds,[259] C–H arylation of heterocycles,[260] and three-component synthesis of aryl sufonohydrazides.[261] Other recent examples in this area include visible-light-mediated fluorosulfonylation reaction for the synthesis of sulfonyl fluorides[262] (Scheme 20(a)) and synthesis of *S*-aryl dithiocarbamates *via* an electron donor–acceptor photoactivation strategy[263] (Scheme 20(b)). Besides, the Kong and Cao group developed a practical method for the fluorosulfonylation of thianthrenium salts (alkyl and aryl) without the use of any external redox reagent or metal catalyst.[264]

In addition to aryl thianthrenium salts, the application of alkyl and alkenyl thianthrenium salts has also been well explored towards various transformations. Alkenyl thianthrenium salts can be utilized for olefinic carbon–phosphorous cross-coupling,[265] Cu-catalyzed silylation and borylation,[233] vinylation reactions,[266] electrochemical synthesis of aziridines,[234] allylic C–H functionalization,[267] electrochemical synthesis of allyamines,[268] aziridination and cyclopropanation,[269] *etc.* The applications of alkyl thianthrenium salts include trifluoromethylations,[235,270] Cu-catalyzed Sonogashira coupling reactions,[237] thermal and photochemical borylation reactions,[271] and visible-light promoted hydroalkylation.[272]

6.2. Hypervalent selenium and tellurium heterocycles

The chemistry of hypervalent selenium (generally named selenuranes) and tellurium (known as telluranes) is similar to that of sulfur compounds.[5] Representative examples of stable hypervalent heterocyclic derivatives of selenium and tellurium include anionic 10-Se-3 **104** and 10-Te-3 species **105**,[273] 10-Se-4 selenuranes **106**[274] and 10-Te-4 telluranes **107**[275] and hexa-coordinated 12-Te-6 species **108** (pertellurane)[276] (Fig. 21). Mlochowski and coauthors presented a comprehensive review on the chemistry of selenaheterocycles.[277]

A one-pot Cu(I)-assisted synthetic approach was reported by Batabyal and coworkers for the preparation of biologically important benzoxytelluranes **109** from 2-bromo-*N*-aryl benzamides and the tellurium dianion (Te_2) under base-free conditions, as depicted in Scheme 21.[278]

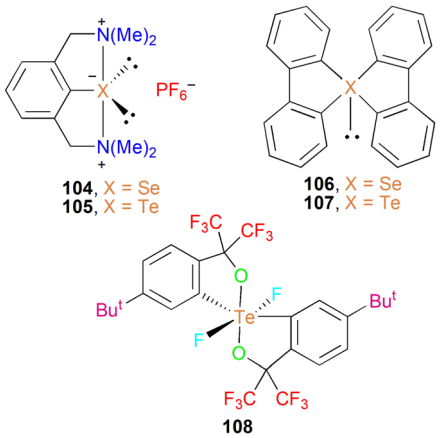
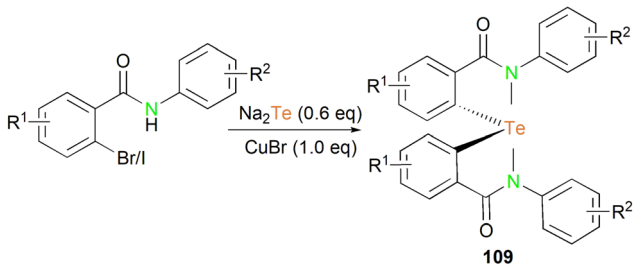


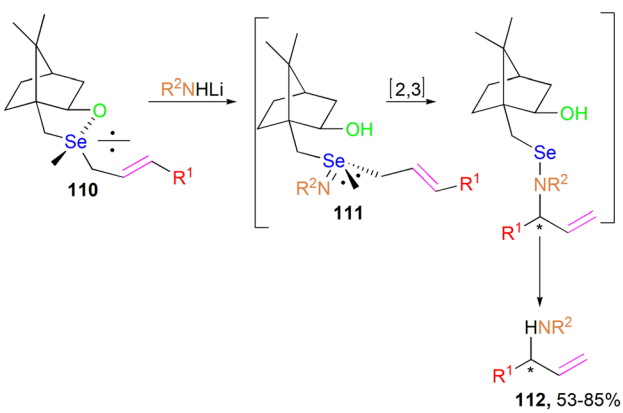
Fig. 21 Examples of hypervalent heterocycles selenium and tellurium **104–108**.



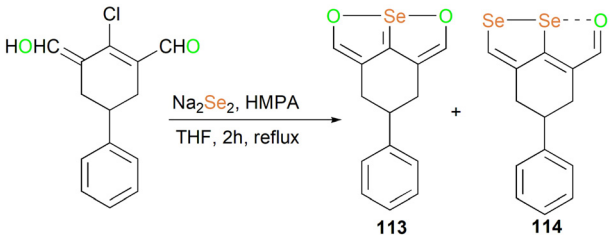
Scheme 21 One-pot Cu(I)-assisted synthesis of benzoxytelluranes **109**.

An interesting synthetic utilization of cyclic chloroselenurane **110** was reported to afford chiral allylic selenimides **111** on nucleophilic reaction with lithium N-protected amides as intermediates with the retention of its configuration. The sigmatropic [2,3]-rearrangement of **111** yielded chiral N-protected allylic amides **112** in up to 93% ee (Scheme 22).[279–281]

Similar to the 'π-hypervalent' heterocyclic systems in sulfur, the Butcher group synthesized organoselenium compounds



Scheme 22 Synthetic utilization of cyclic chloroselenurane **110** to afford chiral allylic selenimides **111** and further chiral N-protected allylic amides **112**.



Scheme 23 Synthesis of 'π-hypervalent' organoselenium compounds **113** and **114**.

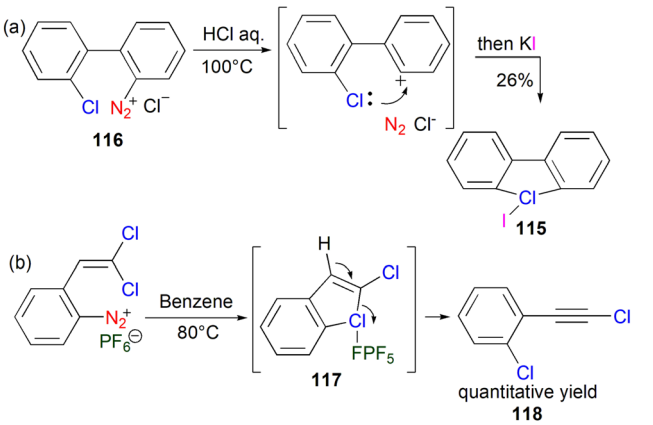
113 and **114** stabilized by intramolecular coordination, as shown in Scheme 23.[282]

7. Hypervalent heterocyclic compounds of group 17 elements

Hypervalent halogen compounds are generally classified into halogen(III), halogen(V), and halogen(VII) derivatives, and have been utilized as reagents for a variety of selective organic transformations. These compounds have always been the centre of attraction for researchers due to their exceptional chemical reactivity, in particular, electrophilic and oxidative reactions of organoiodine(III) and organoiodine(V) compounds have been extensively used in organic synthesis.[283] Compared to the enormous development in the area of hypervalent iodine chemistry, the chemistry of organobromanes and organochloranes has been relatively much less investigated. Only a few researchers has been actively involved in the development of these compounds and their synthetic utilization, which limits their priority in the literature. Even after the first report on the synthesis of a hypervalent iodine compound by Wilgerodt in 1886,[284] it took more than 60 years for the preparation of first hypervalent bromine and chlorine compounds. The first preparation of λ^3-chlorane and λ^3-bromane was reported in 1952 by Sandin and Hay;[285] however, the physicochemical properties of these compounds received little attention for many years, which may be broadly attributed to the lack of user-friendly preparation methods. In this section, an overview of the synthesis and synthetic applications of cyclic hypervalent halogens, highlighting some recent examples, is provided.

7.1. Hypervalent heterocyclic compounds of chlorine(III)

Despite the fact that inorganic λ^3-chloranes, such as sodium chlorite ($NaClO_2$) and chlorine trifluoride (ClF_3),[286] were discovered in 1922 and 1930, respectively, the organo λ^3-chloranes were not revealed until 1952. Even 70 years after the first synthesis of an organochlorine(III) compound, the development of the chemistry of organochloranes is still in its infancy.[287] In 1957, Nesemyanov predicted the utilization of diarylchloronium and diarylbromonium salts as excellent arylating agents, subject to the discovery of possible conditions for the production of these salts in higher yields.[288] The chemistry of organo λ^3-chloranes seems quite promising considering the higher ionization potential and electronegativity of the chlorine atom,



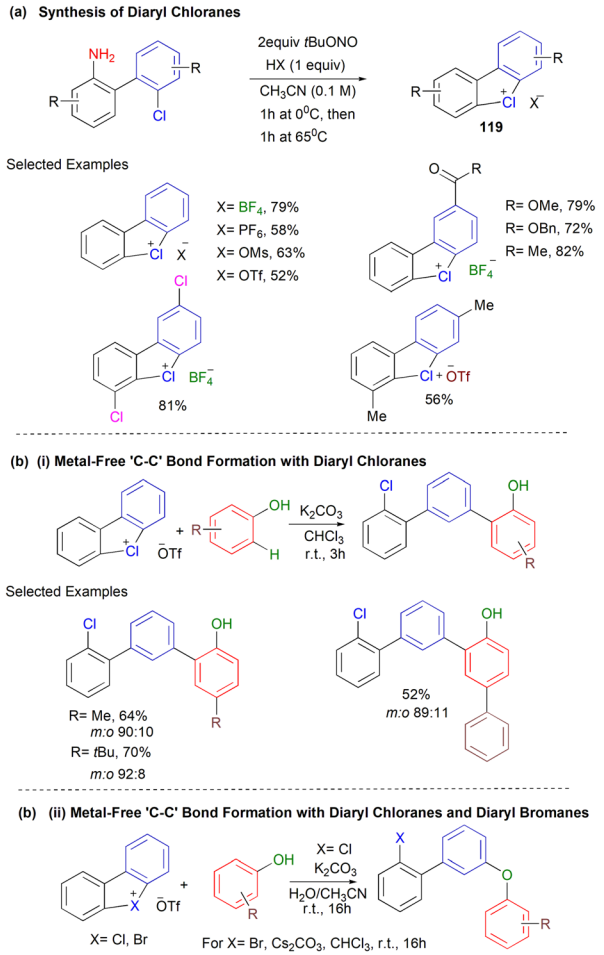
Scheme 24 (a) Synthesis of cyclic diaryl-λ^3-chlorane **115** and (b) attempted synthesis of benzochlorole **117**.

which tends to a decreased positive charge in the hypervalent chloranes, accounting for the enhanced reactivity of these compounds. Their distinctive electronic properties present reactivity that is complementary to that of iodanes and the promising bromanes.

Sandin and Hay prepared the first hypervalent chloronium compound, namely, *o*,*o*′-diphenylene(iodo)-λ^3-chlorane **115**, through intramolecular nucleophilic chlorine attack on aryldiazonium salt **116** (Scheme 24(a)).[285] The same synthetic strategy was applied for the synthesis of benzochlorole **117**; however, compound **117** underwent ring opening to give alkyne derivative **118** in quantitative yield (Scheme 24(b)).[289] It is pertinent to mention here that a similar strategy performed in intermolecular fashion to access acyclic diaryl-λ^3-chloranes gave relatively low yields of the desired products.[290–293] An improved synthetic strategy, in terms of yield, for acyclic diaryl-λ^3-chloranes has recently been reported using weakly coordinating anions.[294,295]

Recently, a simple and robust synthetic method for the preparation (Scheme 25(a)) of a series of cyclic diaryl-λ^3-chloranes **119** and their synthetic potential as versatile aryne precursors {Scheme 25(b)-(i)} were reported.[296] The enhanced reactivity of these λ^3-chloranes accounts for the unparalleled metal-free arylation reactions of phenols under base-mediated reaction conditions. Further, the chemo- and regio-selectivity observed in the reactions of these chloranes as well as the intermediacy of arynes were supported by DFT calculations and experimental mechanistic investigations. Cyclic diaryl-λ^3-bromanes were also utilized in a similar fashion for the metal-free 'C–O' coupling with phenols, as outlined in Scheme 25(b)-(ii).

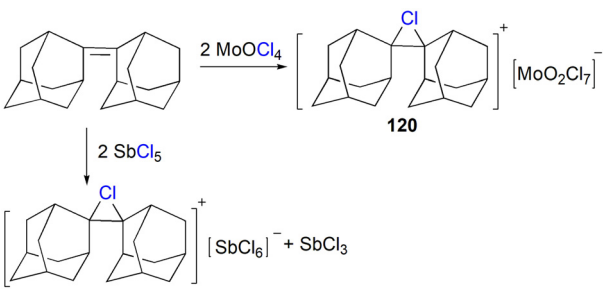
In addition to diaryl-λ^3-chloranes, many researchers have demonstrated the participation of diaryl-λ^3-chloranes as intermediates *via* kinetic studies, product identification, and/or by direct observation.[297,298] Olah and coworkers provided the first spectroscopic evidence of a bridged chloronium ion[299] and later synthesized the sterically crowded cyclic chloronium salt,[300] which was further isolated by Nugent[301] (Scheme 26). The solid-state structure of the salt was in contrast to that of



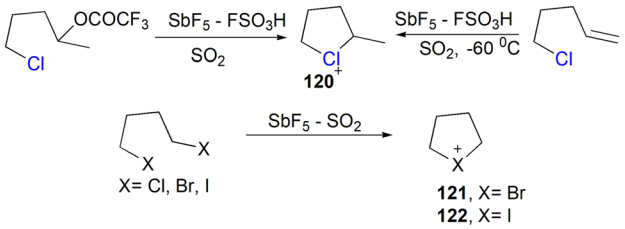
Scheme 25 (a) Synthesis of a series of cyclicdiaryl-λ^3-chloranes and (b) metal-free 'C–C' and 'C–O' coupling of cyclicdiaryl-λ^3-chloranes with phenols *via* aryne intermediates.

corresponding cyclic bromonium and iodonium salts and showed an unsymmetrical three-membered chloronium moiety.

Further, Olah and Peterson reported the formation of cyclic chloronium ion **120** *via* 1,4-halogen participation through ionization using an antimony pentafluoride (SbF_5)–sulfur dioxide (SO_2) solution, as outlined in Scheme 27.[302] Other cyclic halonium ions, bromonium **121** and iodonium **122** ions, were also formed using a similar synthetic strategy. Certain five-membered halonium ions were revealed to be stable by NMR investigation for short periods of time at temperatures in the range of −30 to 0 °C, depending on their structure.



Scheme 26 Synthesis of three-membered chloronium salts.



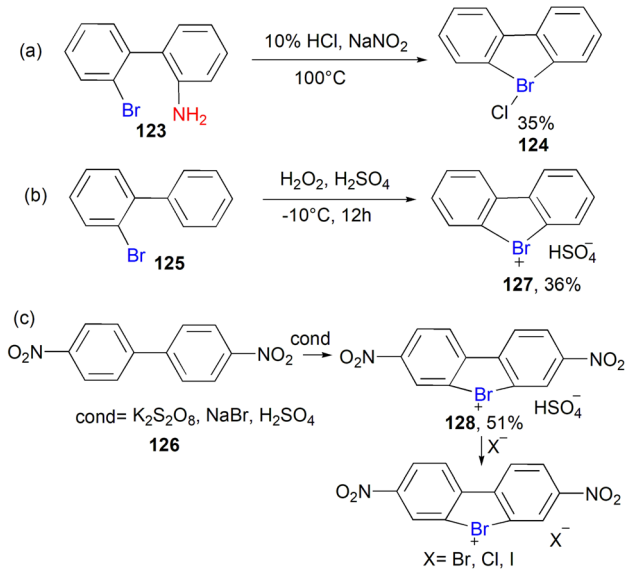
Scheme 27 Formation of five-membered cyclic halonium ions **120–122**.

7.2. Hypervalent heterocyclic compounds of bromine(III)

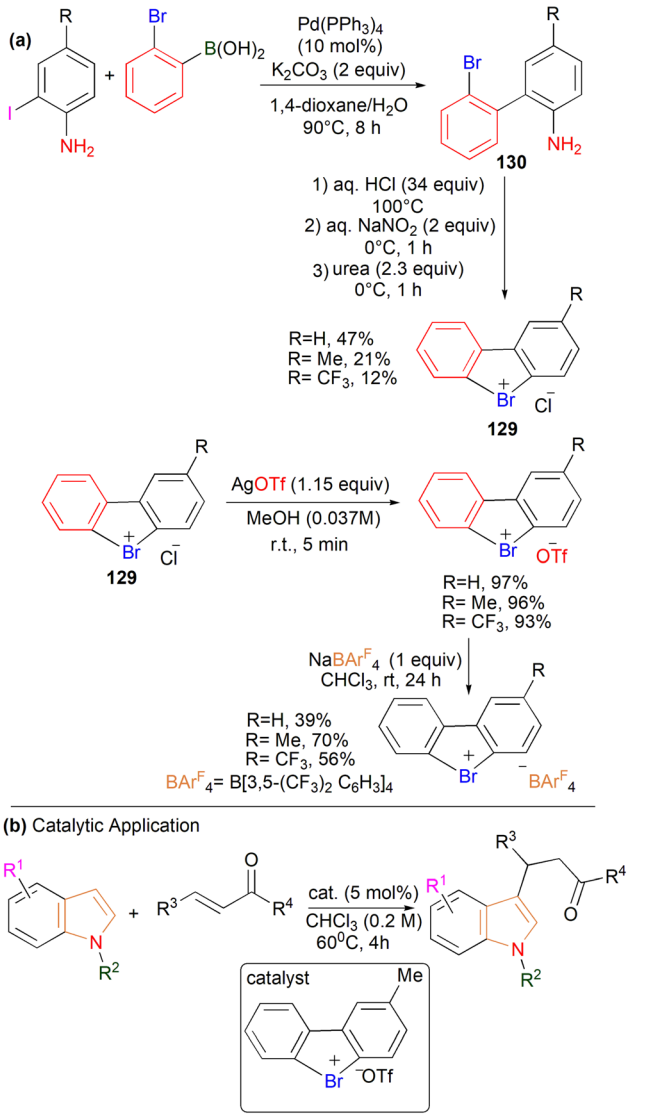
Among the hypervalent halogen compounds, the hypervalent iodine compounds have been the centre of attraction for researchers due to their unique characteristic properties, such as mild in reactivity, easy to handle, and environmentally benign class of compounds. Their hypervalent bromine analogues can be attributed to the higher reactivity pattern due to the higher nucleofugality, ionization potential and strong electrophilicity associated with them.[303–305] These properties of hypervalent bromine compounds have been the mainstay for the development of various synthetically useful transformations using bromanes, such as Bayer–Villiger-like oxidation,[303,304] oxidative coupling reactions of alkynes with primary alcohols,[306] metal-free C–O and C–N couplings,[307] and amination of unactivated alkanes.[308] Despite the fact that hypervalent bromine compounds offer a superior reactivity pattern, their synthesis remains a challenge owing to the inherent thermodynamic barrier for the oxidation of Br(I) to Br(III) in comparison to the conversion of I(I) to I(III). This disadvantage limits the synthetic utilization of these compounds. In this series, the synthesis of certain cyclic λ^3-bromanes (diaryl-/dialkyl-/Br–O) has been reported using various oxidizing agents. Recently, electrochemical oxidation was also developed by Francke, Suna and coworkers as an alternative approach for the preparation of these compounds.[309]

7.2.1. Cyclic diaryl-λ^3-bromanes. The first hypervalent bromonium compound **124** was prepared by Sandin and Hay through thermal decomposition similar to the preparation of cyclic diaryl-λ^3-chloranes *via* intramolecular nucleophilic bromine attack on an aryldiazonium salt, as outlined in Scheme 28(a).[285] 2-Amino-2′-bromobiphenyl (**123**) on diazotization using 10%HCl/$NaNO_2$ at 100 °C afforded the hypervalent bromonium compound **124** in 35% yield, as outlined in Scheme 28(a). Oxidative cyclization of 2-bromobiphenyl (**125**) using hydrogen peroxide[310] and that of 4,4′-dinitrobiphenyl (**126**) using $K_2S_2O_8$[311] in sulfuric acid afforded corresponding cyclic diaryl λ^3-bromanes **127** and **128**, as shown in Scheme 28(b) and (c), respectively.

Yoshida and coworkers synthesized cyclic bromonium salts **129** and evaluated their potential as excellent halogen-bonding organocatalysts.[312] Functionalized 2-amino-2′-bromobiphenyl



Scheme 28 Approaches (a)-(c) to the synthesis of cyclic bromonium compounds **124**, **127** and **128**.



Scheme 29 (a) Synthesis of cyclic diaryl λ^3-bromanes **129** and related λ^3-bromanes and (b) catalytic applications of cyclic diaryl λ^3-bromanes as halogen-bonding organocatalysts.

derivatives **130**, obtained through palladium-catalyzed Suzuki coupling reactions, were cyclized to produce the corresponding cyclic diaryl λ^3-bromanes **129** as chloride salts in 12–47% yield (Scheme 29). These salts were further converted to their triflates in up to 97% yield, which were then treated with $BAr^F{}_4$ anions. X-ray analysis of cyclic λ^3-bromanes **129** revealed an ion-pair structure rather than the covalently bonded form.[313] These cyclic bromonium salts were evaluated for their catalytic applications as halogen-bonding organocatalysts towards the Michael addition reaction of indoles with α,β-unsaturated ketones with the final product yield of up to 96%, as shown in Scheme 29(b).

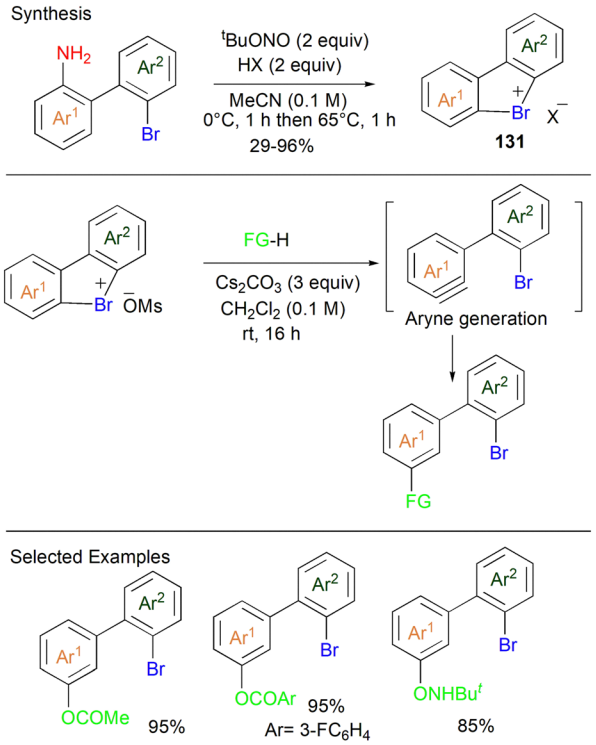
A series of cyclic diaryl λ^3-bromanes **131** was reported using *t*-butyl nitrite (^{t}BuONO) as a mild oxidant in the presence of Brønsted acid and utilized as aryne precursors (Scheme 30).[307]

Further, the X-ray analysis of **131-OMs** revealed a tricyclic planar structure with a dihedral angle of −1.04(4)° and carbon–bromine bonds slightly longer (1.928 Å and 1.932 Å, respectively) with respect to the bromobenzene (1.850 Å). Moreover, the angle between C–Br–C reflected a T-shape structure typical for 3c-4e bonding (Fig. 22).[283,314–319]

In addition to the achiral version, the synthesis and applications of chiral bromonium salts as asymmetric halogen-bonding donor catalysts have been recently reported in the literature. Yoshida and coworkers developed chiral binaphthyl-based cyclic bromonium salts **132** {Scheme 31(a)} with amide functionalities and utilized these salts for the vinylogous Mannich reaction of cyanomethyl coumarins with imines in up to 99% yield and 96% ee.[320] The corresponding iodonium salts were explored for the thiol addition reaction to isatin derived ketimines, which gave the products in up to 99% yield and 97% ee.[320] Further, chiral bromonium salts **133** bearing an *N*-nitroso group were prepared through a multi-step synthetic sequence, as shown in Scheme 31(b), and their reactivity was studied in the Mannich reaction of isatin-derived ketimines with malonic esters.[321]

7.2.2. Cyclic dialkyl-λ^3-bromanes. Olah and Bollinger reported that the ionization of 2-fluoro-3-bromo-2-methylbutane (**134**) in antimony pentafluoride (SbF_5)–sulfur dioxide solution at −78 °C gave a stable solution of cyclic dialkyl λ^3-bromane **135** {Scheme 32(a)}.[322] Later, in 1985, Brown and coworkers presented the synthesis and X-ray analysis of cyclic dialkylbromanes **136** {Scheme 32(b)}.[323] Compound **137** was obtained as a bright-yellow solid by the addition of bromine to adamantylideneadamantane (**136**) in dichloromethane.

7.2.3. Cyclic λ^3-bromanes containing Br–O bonds. In addition to the diaryl- and dialkyl-cyclic λ^3-bromanes, examples of cyclic bromanes containing Br–O bonds were also reported. In this series, as a representative example, cyclic bromine **139** was prepared in 99% yield for the first time by



Scheme 30 Synthesis of cyclic diaryl λ^3-bromanes **131** using *t*-butyl nitrite (^{t}BuONO) and their synthetic utilization as aryne precursors.

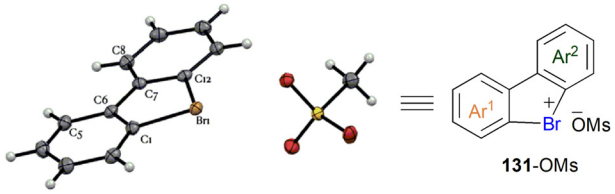
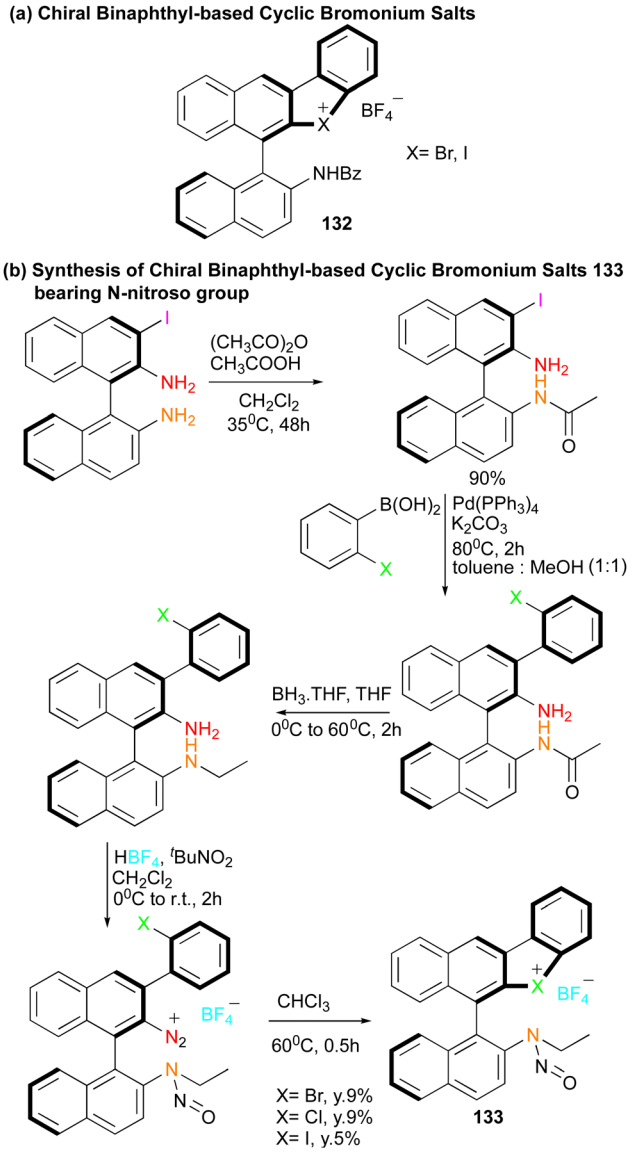


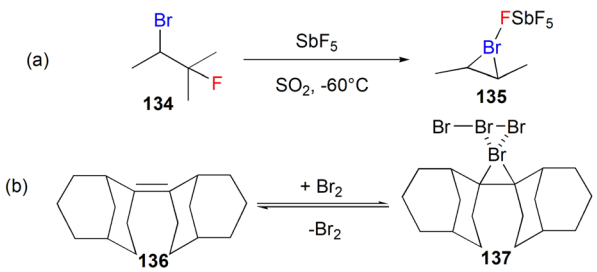
Fig. 22 X-ray structure of cyclic diaryl λ^3-bromane **131-OMs**.

the Martin group through the oxidative cyclization of compound **138** using BrF_3 (Scheme 33(a)).[324] The concern of using highly reactive BrF_3 in this synthetic methodology was recently resolved by utilizing electrochemical oxidation. Various cyclic bromanes **141** were synthesized by electrochemical oxidation of aryl bromides **140** in yields of up to 72% and utilized for the C–C coupling of arenes {Scheme 33(b)}.[309]

In another recent example, bench-stable cyclic λ^3-bromanes (**142**) were prepared using the cyclic 1,2-benzobromoxol-3-one (BBX) strategy.[325] The ligand exchange reaction of *N*-triflylimino-λ^3-bromane (**142**) with carbon nucleophiles and NaOH afforded diverse cyclic bromanes **143–145** in good yields, as depicted in Scheme 34. Two other cyclic bromanes, **146** and **147**, were also prepared from **145** in quantitative yield and 30% yield (2 steps), respectively. The synthetic utilization of these cyclic bromanes was investigated by reaction with various nucleophiles to realize the arylation of benzene and oxidation of alkanes, sulfides, enones and alcohols.

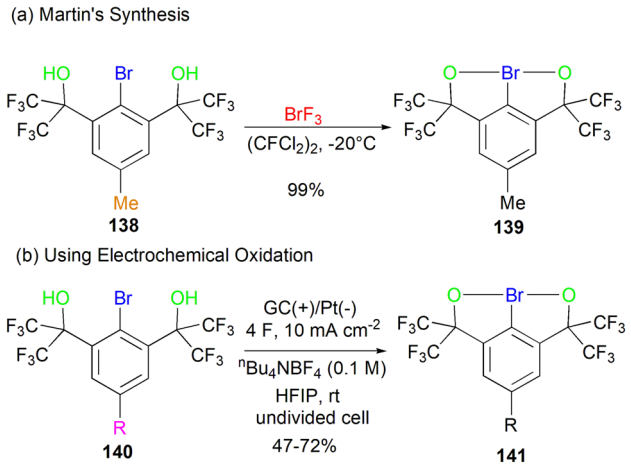


Scheme 31 (a) Structure of binaphthyl-based chiral bromonium salts **132** and (b) multi-sequence synthesis of **133**.

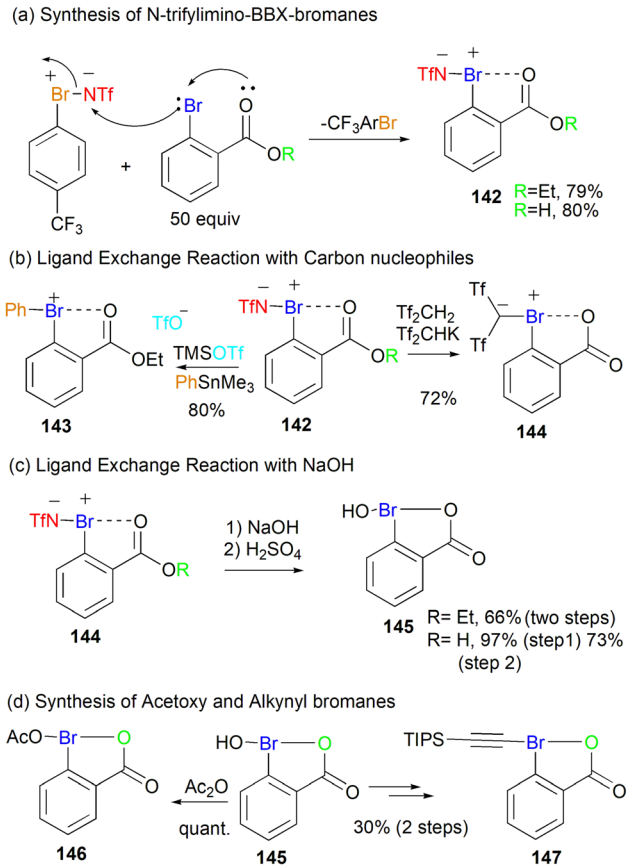


Scheme 32 Approaches (a) and (b) to the synthesis of cyclic dialkyl λ^3-bromanes **135** and **137**.

Recently, Sokolovs and Suna developed an excellent example of electrochemical synthesis of a range of diverse cyclic

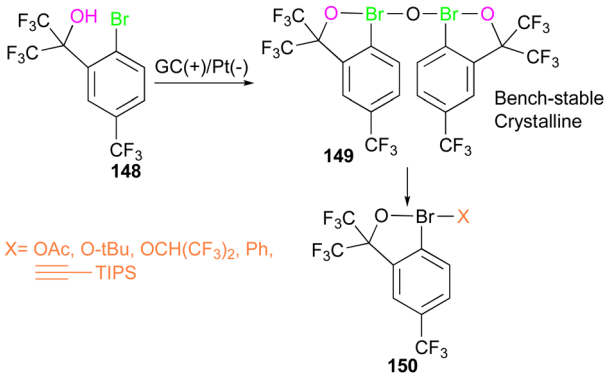


Scheme 33 Synthesis of cyclic bromanes **139** and **141** containing Br–O bonds through (a) Martin's synthesis using BrF_3 and (b) electrochemical oxidation, respectively.



Scheme 34 Approaches (a)–(d) to the synthesis of cyclic λ^3-bromanes **142–147**.

hypervalent bromine(III) compounds (**150**).[326] The dimeric benzobromoxole (**149**), obtained through anodic oxidation of aryl bromide (**148**), can be converted to numerous synthetically useful Br(III) compounds (**150**) (Scheme 35).



Scheme 35 Electrochemical synthesis of cyclic hypervalent bromanes **150**.

7.3. Hypervalent heterocyclic compounds of iodine(III)

Hypervalent iodine compounds have been widely utilized as reagents and catalysts in organic synthesis due to their environmentally benign and unique properties.[283,327–339] These compounds are associated with excellent oxidizing and electrophilic properties and reported to show similar structural properties and reactivity patterns as that of transition metals, such as Ag(I), Hg(II) and Tl(III). The low toxicity, high bench stability and easy handling of the hypervalent iodine compounds make them excellent alternatives to these heavy metals for diverse organic transformations. The hypervalent iodine compounds have emerged as reagents of choice for various selective oxidative transformations and shown paramount significance in organic synthesis for the development of organic transformations that are otherwise difficult to access. In particular, the diverse reactions of hypervalent iodine compounds include couplings,[340] oxidative rearrangements,[341] oxidations,[342] cyclizations,[343] atom-transfer reactions,[344] alkene functionalization,[345] C–H bond functionalization,[346] photochemical transformations,[347] α-functionalization of carbonyl compounds,[348] and organocatalysis.[349] A range of acyclic hypervalent iodine(III) (λ^3-iodanes) and hypervalent(V) (λ^5-iodanes) compounds was reported in the literature, and some representative examples are presented in Fig. 23.

Cyclic hypervalent iodine compounds are particularly vital reagents because of their higher thermal stability and modified reactivity compared to that of their acyclic analogues.[344,350–352] The higher thermal stability associated with cyclic iodanes can

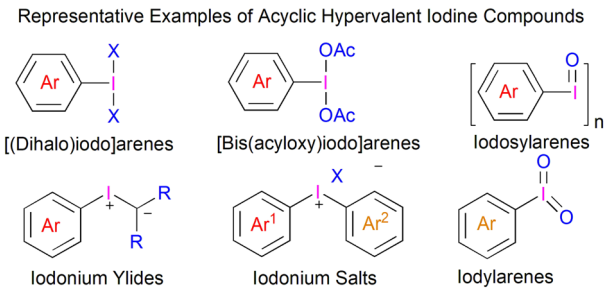


Fig. 23 Representative examples of acyclic hypervalent compounds.

be attributed to the link between apical and equatorial ligands present at the iodine centre, causing pseudorotation and reductive elimination, which makes thermal decomposition quite difficult.[24–27] The synthetically significant classes of cyclic iodanes are shown in Fig. 24. The cyclic hypervalent λ^3-iodanes can be generally classified as: (i) cyclic aryliodonium salts and (ii) benziodoxole derivatives.

Aryliodoniums have emerged as important synthons to access diverse structural motifs since the discovery of the iodonium salts in the 1890s.[353–360] Iodonium salts having two carbon atoms and a closely associated anionic part possess a pseudo-trigonal bipyramidal geometry with experimentally found 'C–I–C, bond angle close to 90°. These compounds are also referred to as 'λ^3-iodanes'. Usually, these salts have substantial bonding between the anion and central atom, rendering these salts as 'hypervalent'.[361] Despite the fact that acyclic aryliodoniums have made tremendous advancements, in particular as arylating agents, their cyclic counterparts have been reported to be more atom-economical due to the fact that the iodoarene, generated as byproduct/waste, remains part of the arylated products.[358,362,363] The reactivity patterns and thermal decomposition of cyclic iodonium salts, in concert with their reactions with diverse nucleophiles, was elaborated in the review articles by Grushin.[364,365] Recently, Wen, Gu and coworkers comprehensively reviewed the chemistry and synthetic applications of cyclic aryliodonium salts.[352] Prior to this, Han and coworkers[366] and the Fu group[367] provided brief illustration on these compounds. Goswami and coworkers[368] and Jiang *et al.*[369] presented the advancements of cyclic aryliodonium salts, focusing on their applications for the synthesis of polycyclic compounds and functionalized molecules. The preparation of cyclic diaryliodonium salts is well established. Mascarelli and Benati reported the first preparation of cyclic diaryliodonium salt **152** in 1909 *via* the diazotization of 2,2′-diaminobiphenyl (**151**) followed by addition of potassium iodide {(Scheme 36(a)}.[370] Similarly, diazotization of 2-amino-2′-iodobiphenyl (**153**) followed by the addition of NH_4PF_6 (or HBF_4) gave dibenziodonium compounds **154** {Scheme 36(b)}.[371]

The conventional synthetic strategies for the production of cyclic diaryliodoniums are, in general, associated with disadvantages, such as wastage of reagents, time consuming method, and requiring multiple synthetic sequences. Thus, several synthetic routes to address the above-mentioned disadvantages have been developed either using electrochemistry or one-pot sequences. Methods involving oxidation of the corresponding precursor by an appropriate oxidant, and then by ring closure using a suitable acid to afford cyclic aryliodoniums of the type **155** are well-documented (Scheme 37). The general methods include: (i) peracetic acid and sulfuric acid,[372–381] (ii) PhI(OH)OTs (Koser's reagent) as oxidant and *p*-toluenesulfonic acid (TsOH),[382] (iii) *m*-CPBA, and then TfOH,[353,358] (iv) oxone and sulfuric acid,[383] (v) He's method employing electrolysis in the presence of TfOH,[384] (vi) Moran's method involving oxidation *via* electrolysis and TfOH,[385] (vii) Oxone and TfOH,[386] (viii) Selectfluor and TfOH.[387]

The design and synthesis of several other types of cyclic diaryliodonium salts have also been well established.

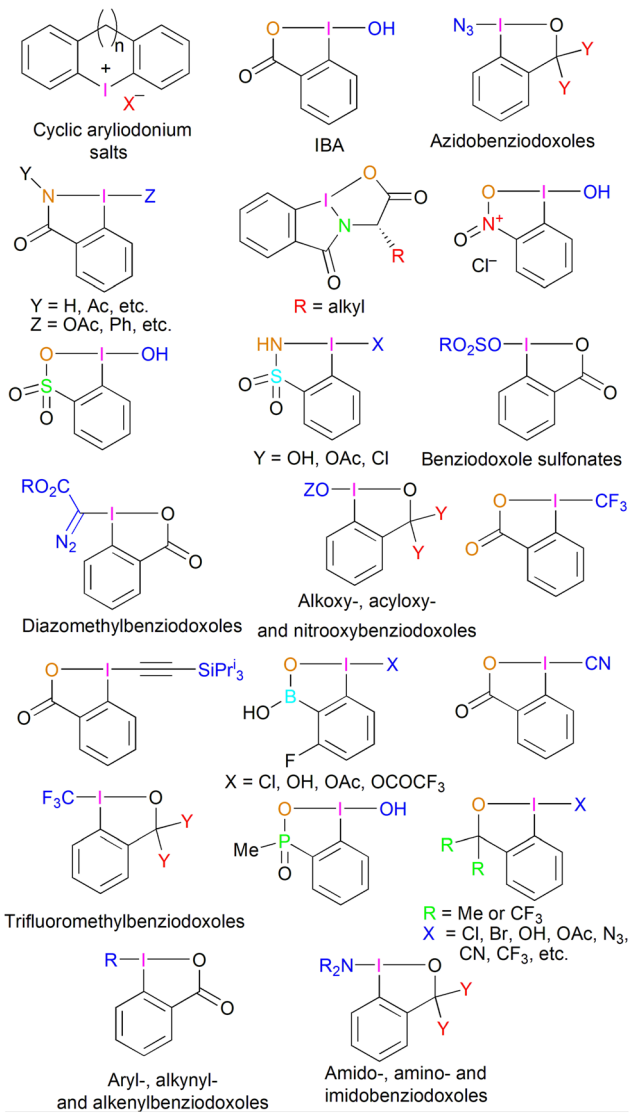
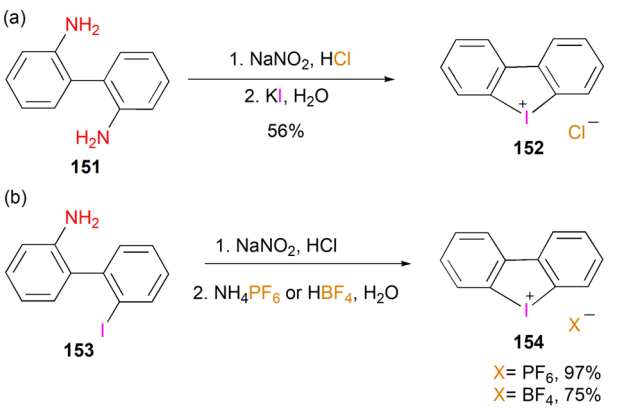
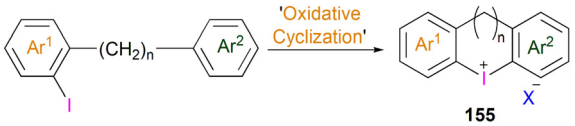


Fig. 24 Representative examples of cyclic hypervalent λ^3-iodanes.



Scheme 36 Approaches (a) and (b) to the synthesis of cyclic diaryliodonium salts **152** and **154**.



Scheme 37 General methods involving oxidative cyclization for the synthesis of cyclic diaryliodonium salts **155**.

Representative examples of heterocyclic iodoniums **156–161**,[388–392] vinyl(aryl)iodoniums **162–163**,[393,394] and polycyclic aryliodoniums **164–167**[395–398] are shown in Fig. 25.

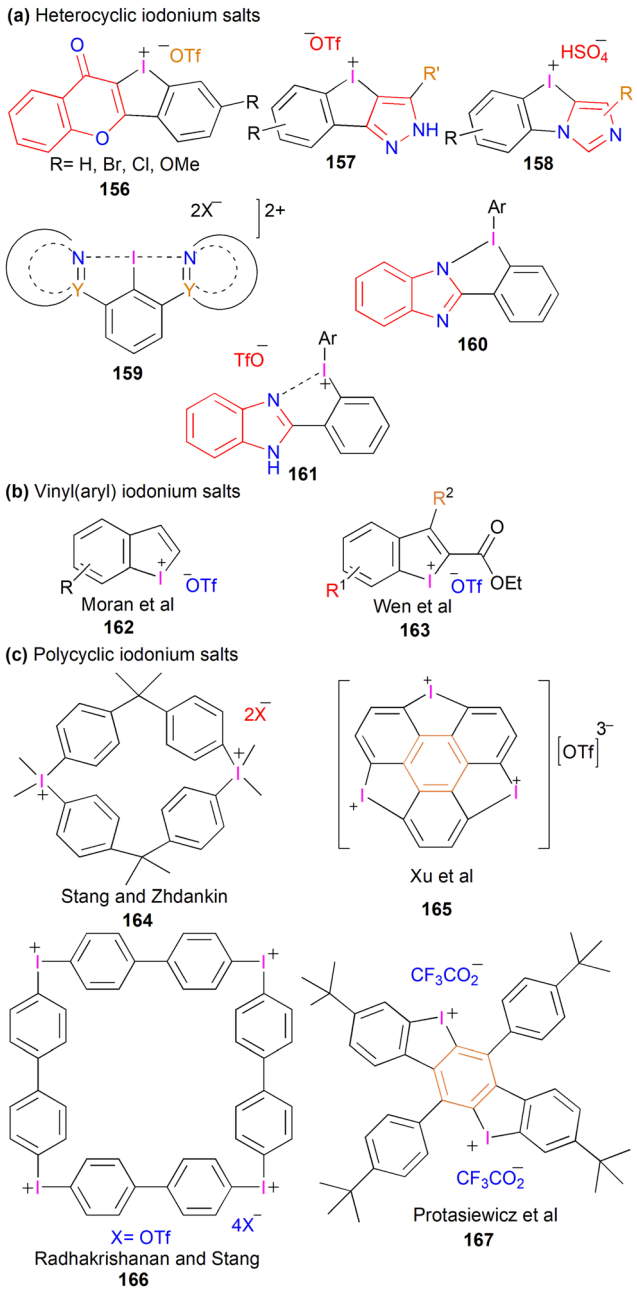


Fig. 25 Examples of (a) heterocyclic iodonium salts **156–161**; (b) vinyl(aryl)iodoniums **162–163**; and (c) polycyclic aryliodoniums **164–167**.

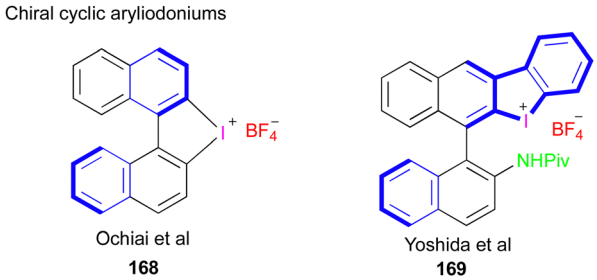
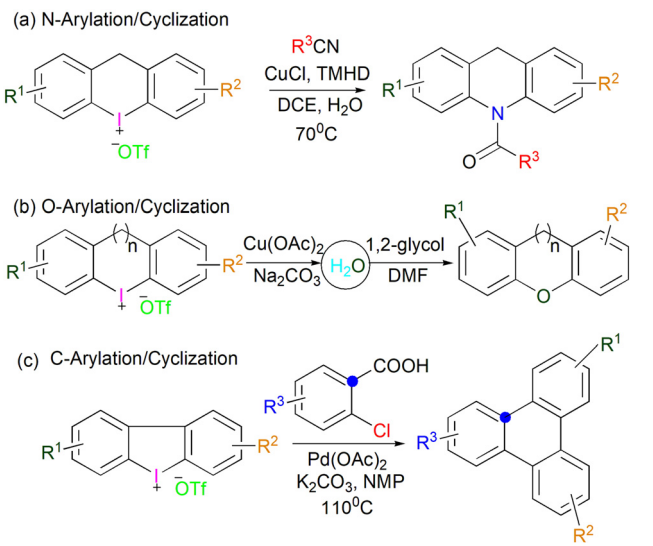


Fig. 26 Chiral cyclic aryliodoniums **168** and **169**.

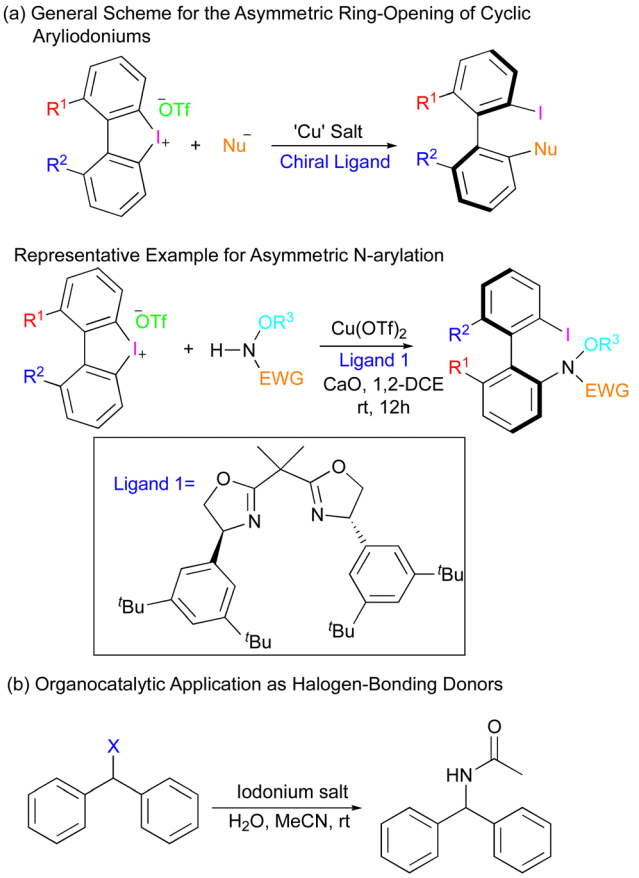
Chiral hypervalent iodine reagents have attracted significant attention in asymmetric synthesis.[399,400] The chiral hypervalent iodine-catalyzed reactions have been proven to be an excellent method to access enantioenriched molecules and intermediates that possess a broad array of applications in medicinal chemistry. In this series, the synthesis of binaphthyl-based chiral cyclic iodoniums **168** was reported by Ochiai and co-workers (Fig. 26),[302] while Yoshida *et al.* prepared new chiral iodoniums **169** *via* a three-step procedure.[401]

Cyclic aryliodoniums, due to their unique ring system and high electron-deficient properties, can be efficiently used for the construction of various polycyclic scaffolds.[402–407] Besides, cyclic aryliodoniums have been utilized in diverse transformations, and the past decade has witnessed a high demand for the design and synthesis of a broad range of cyclic aryliodoniums with varying substituents.[408–413] Certain recently selected arylation approaches for the construction of diverse compounds through C–N,[414] C–O,[415] and C–C[416] bond formation are highlighted in Scheme 38.

In recent years, much attention has also been directed toward the enantioselective ring-opening reactions of cyclic aryliodoniums with different nucleophiles to obtain axially chiral atropisomers.[417–421] Scheme 39(a) depicts some recently



Scheme 38 Arylation approaches (a)–(c) for the construction of diverse compounds using cyclic aryliodoniums.



Scheme 39 (a) General scheme for the asymmetric ring opening of cyclic aryliodoinum salts (asymmetric *N*-arylation). (b) Cyclic aryliodonium salts as halogen-bonding donors.

developed protocols for the synthesis of chiral biarylatropisomers. Besides, the efficient exploration of cyclic aryliodoniums as versatile halogen-bonding organocatalysts is shown in Scheme 39(b).[422,423]

Other cyclic hypervalent iodine reagents are represented by cyclic compounds, which incorporate iodine, oxygen, nitrogen, and some other elements in the ring (Fig. 24). In general, the name 'benziodoxoles' is used for cyclic iodanes that contain iodine and oxygen in the five-membered ring and different substituents are attached to the iodine. The most important compound of this class is 2-iodosobenzoic acid, abbreviated as 'IBA' (1-hydroxy-1,2-benziodoxol-3-(1*H*)-one), which was prepared for the first time over 100 years ago.[424] According to the X-ray analysis, the five-membered ring in benziodoxoles is quite distorted with the almost linear arrangement of two electronegative ligands. The endocyclic iodine–oxygen bond length in iodine-substituted benziodoxoles varies from 2.11 Å (in carboxylates) to 2.48 Å (in 1-phenyl benziodoxolone).

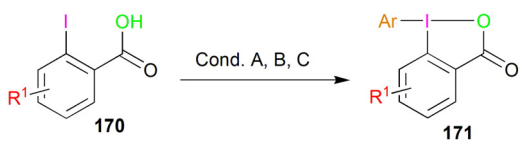
Benziodoxoles are extensively utilized in organic synthesis as umpolung iodine(III) reagents for the introduction of diverse functional groups, such as alkynyl, alkenyl, cyano, SCN, azido, CF_3, and Hal, and are generally termed 'atom-transfer reagents'.[344,425–428] Further, benziodoxole reagents that contain carbon-based functional groups at the iodine center (such as aryl-, alkynyl-, and alkenylbenziodoxoles) permit C–C and C–heteroatom bond-forming reactions under metal-free conditions or under mild and easy-to-handle catalytic conditions. The preparation, structural aspects, and recent synthetic applications of aryl-, alkynyl-, and alkenylbenziodoxoles for the direct arylation, alkynylation and alkenylation of various organic substrates have been comprehensively reviewed recently.[429,430] Herein, we present some of the representative examples to showcase their synthetic applications in organic synthesis.

Arylbenziodoxoles **170** can be easily prepared from the appropriate 2-iodobenzoic acids **171** and substituted benzenes[431–439] (Scheme 40). Moreover, these compounds can also be obtained from suitable hypervalent iodine reagents through ligand exchange reaction.[440–442] Single-crystal X-ray structures of several arylbenziodoxoles have been published.[436,443–445] Arylbenziodoxoles have been shown to possess a zwitterionic structure, as evidenced by the presence of a short internal interaction between iodine and oxygen atoms.[436–438,440–443] Further, the average distance of the intramolecular I···O bonds (2.5 Å) is longer compared to the average covalent I–O bond length (2.14 Å);[446,447] however, shorter than the sum of van der Waals radii for iodine atom and oxygen atoms (3.5 Å),[448] indicating a significant increase in the ionic nature of this bond.

Arylbenziodoxoles can be used as versatile aryne precursors,[449] as well as for the formation of benzoic acid derivatives.[450–454] A general schematic presentation for aryne generation and representative example for benzoic acid formation are outlined in Scheme 41(a) and (b), respectively.

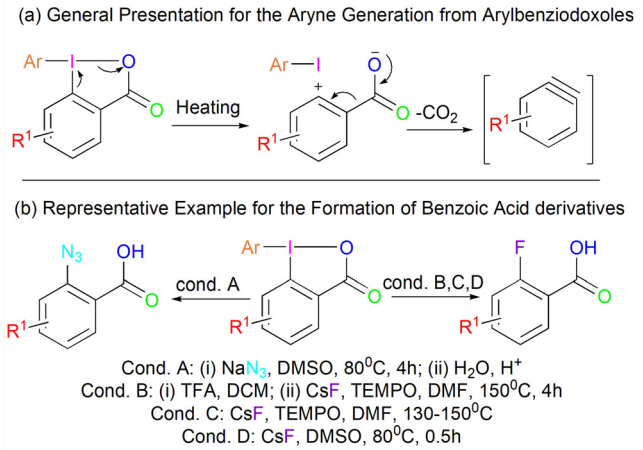
Besides, alkynylbenziodoxoles, also termed ethynylbenziodoxoles (EBXs), have evolved as excellent alkyne transfer reagents. These reagents can be successfully applied as electrophilic alkynylating reagents to wide range of organic substrates and their utilization is usually preferred over the classical methods.[344,426,427,455–460] The first example of EBX **172** was prepared by Ochiai and coworkers in 1991 (Scheme 42).[384]

The same group established the structure of cyclohexyl-EBX **172a** by X-ray diffraction analysis.[461] The X-ray structural data showed the presence of a distorted T-shaped geometry with an endocyclic C(sp^2)–I–O angle of 75.28° and a C(sp^2)–I–C(sp) angle of 90.9°. Later on, many X-ray structures of various aromatic and aliphatic alkynylbenziodoxoles and silyl alkynylbenziodoxoles were reported with almost the same bond



A: (i) $K_2S_2O_8$, H_2SO_4; (ii) ArH; (iii) aq. NH_3
B: (i) *m*CPBA, TfOH, ArH, DCM; (ii) 25% aq NH_3
C: (i) Oxone, H_2SO_4; (ii) ArH, DCM

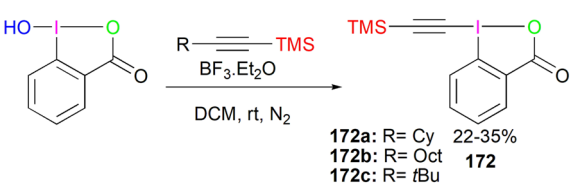
Scheme 40 Synthesis of arylbenziodoxoles **171** from 2-iodobenzoic acids **170** and substituted benzenes.



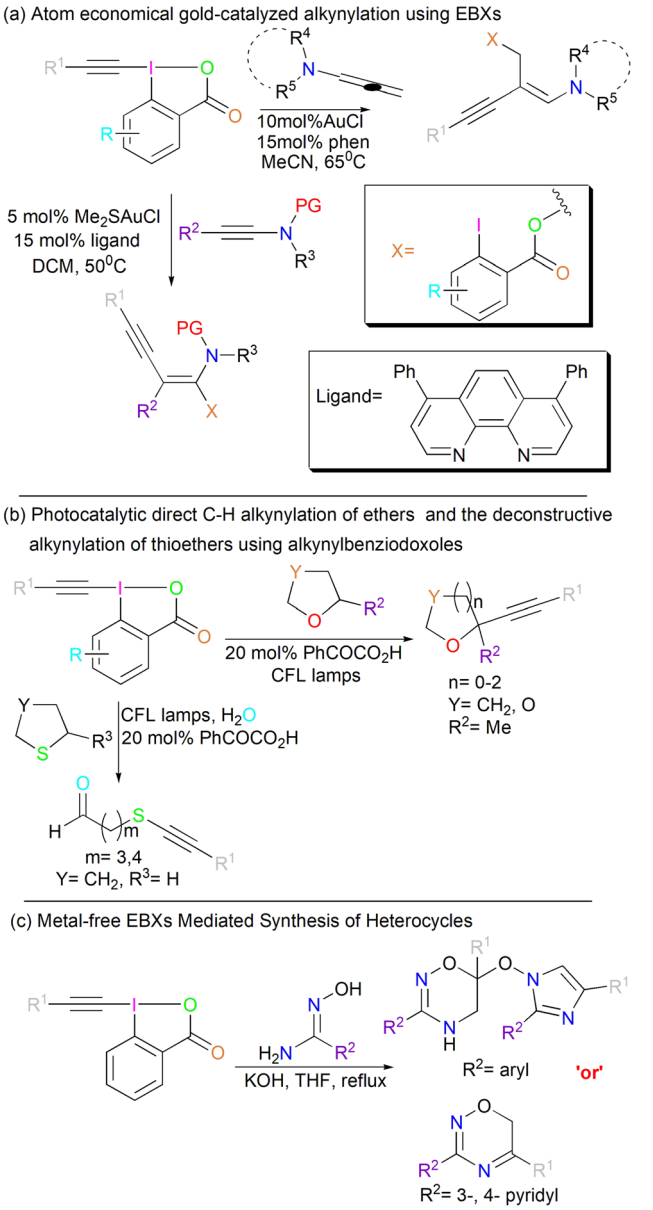
Scheme 41 (a) General presentation for aryne generation and (b) representative example for benzoic acid formation from arylbenziodoxoles.

lengths and angles at the iodine atom.[462] EBXs can be conveniently used in direct alkynylation or complex reactions involving the formation of several bonds in a single transformation.[344,426,427,455–460,463] The alkyne transfer reactions can be performed effectively under metal-catalyzed conditions using gold,[464–470] copper,[471–478] palladium,[479–483] *etc.* Ethynylbenziodoxoles have also been utilized for radical alkynylation reactions under photoredox conditions.[459,484–496] Besides, several metal-free alkynylation reactions have also been reported for the synthesis of numerous synthetically important targets, including heterocycles.[497–507] Representative examples for metal-catalyzed, photoredox and metal-free alkynylation reactions using EBXs are presented in Scheme 43.

Vinylbenziodoxoles (VBXs), also termed alkenylbenziodoxoles, have recently received significant attention. The formation of VBXs as products in various addition reactions of alkynylbenziodoxoles has been reported in earlier reports.[508–510] Waser and coworkers described synthetic approaches to access various VBX reagents and their reactivity in detail in 2020,[427] and recently elaborated by Zhdankin *et al.*[429] In general, VBXs are categorized as X-VBX and C-VBX, depending on the presence of heteroatom 'X' or carbon substituent at the β-carbon of the vinyl group, respectively. C-VBXs can be easily synthesized by coupling vinylboronic acids and suitable hypervalent iodine compounds,[511–514] whereas several synthetic methods have been reported recently for the synthesis of 'X-VBXs' through the addition reaction of S-, N-, O-, and X-nucleophiles to ethynylbenziodoxoles (EBXs).[515–524] A common



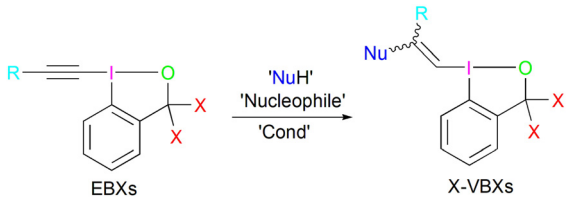
Scheme 42 First example of the preparation of ethynylbenziodoxoles (EBXs).



Scheme 43 (a) Atom-economical gold-catalyzed alkynylation using EBXs; (b) photocatalytic direct C–H alkynylation of ethers and the deconstructive alkynylation of thioethers using alkynylbenziodoxoles; and (c) metal-free EBX-mediated synthesis of heterocycles.

approach for the preparation of X-VBXs starting from EBXs is outlined in Scheme 44.

The cyclic structure of the styrylbenziodoxole (**173**) was confirmed by X-ray analysis (Fig. 27).[511] The molecular structure of VBXs showed a distorted T-shape with an O–IC(sp^2) angle of 165.88 Å, similar to that of reported arylbenziodoxoles[436,443–445] and alkynylbenziodoxolones.[461,462,525] The endocyclic I–O bond length of 2.51 Å was considerably longer than that in the case of alkynylbenziodoxoles, and in general close to the I–O bond in the structure of arylbenziodoxolones.[436,443–445] This bond length trend indicates the higher *trans* influence exerted by the vinyl and aryl groups in comparison to the alkynyl- and trifluoromethyl groups.



Scheme 44 Common approach for the preparation of X-VBXs starting from EBXs.

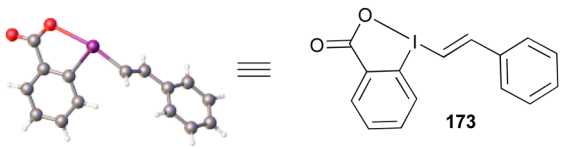
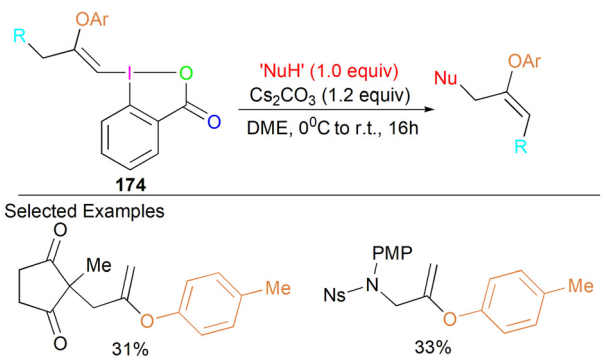


Fig. 27 X-ray structure of styrylbenziodoxole (**173**).

Further, VBXs are efficiently utilized as synthetic equivalents of the alkenyl group.[427,429] As one of the representative recent examples, an umpolung strategy of enol ethers to generate oxy-allyl cation equivalents from O-VBXs **174** is outlined in Scheme 45.[372]

The chemistry of benziodoxole sulfonates as oxidants and electrophiles was discussed in detail recently by Zhdankin and coworkers.[526] Iodine(III) benziodoxoles **175–178** and pseudo-benziodoxoles **179** and **180** are powerful electrophiles as well as mild oxidants towards a range of unsaturated compounds. Pseudocyclic benziodoxole-derived triflate (IBAOTf) **179**, in particular, has been shown to be an efficient reagent for oxidative heteroannulation reactions. Benziodoxole-derived organosulfonates **179** and **180** are shown in Fig. 28. Single-crystal X-ray diffraction of IBA-OTf (**179**) showed that the hydroxy(aryl)iodonium ion in **179** possesses a distorted T-shaped intramolecular geometry around the hypervalent iodine atom with an O–I–O angle of ~167°. Further, the I–OH bond of 1.92 Å is notably shorter than the dative secondary interaction between iodine and a carboxylate oxygen atom (2.34 Å), which is consistent with the proposed pseudocyclic structure of **179**.



Scheme 45 Generation of oxy-allyl cation equivalents from O-VBXs **174**.

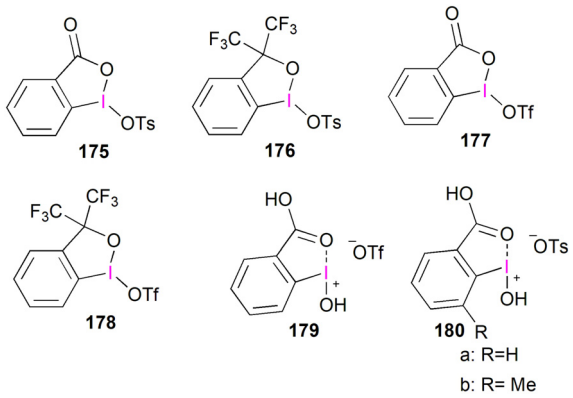
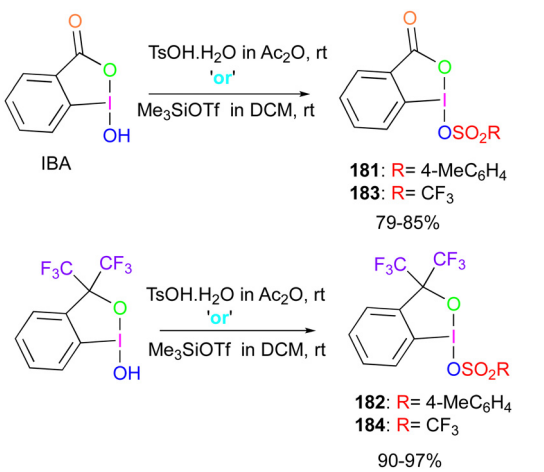


Fig. 28 Benziodoxole-derived organosulfonates **175–180**.

Benziodoxole-based tosylates **181–182** and triflates **183** and **184** were prepared by the reactions of 2-iodosylbenzoic acid (IBA) or 1-hydroxy-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (**185**) with *p*-toluenesulfonic acid or trimethylsilyl triflate, respectively (Scheme 46).[527,528] The cyclic structure of **175** and **177** was in agreement with the IR absorption at about 1615 cm^{-1}.[529] Further, the structures of the benziodoxole-based tosylates were independently confirmed by X-ray structural analysis by Stuart and coworkers.[530] Further, the preparation, structure, and reactions of 2-iodosylbenzoic acid triflate (IBA-OTf, **179**) were recently investigated by Zhdankin and coworkers.[531,532] The synthetic applications of IBA-OTf (**179**) as a catalyst in oxidative heteroannulations[533,534] and efficient precursor to novel sulfoximidoyl-substituted hypervalent iodine[535] have been recently investigated. Besides, the X-ray crystal structures and the reactions of certain other new pseudocyclic benziodoxole tosylates **180**, analogs of benziodoxole triflate, have also been invetsigated.[536]

Further, IBA-tosylate **180a**, was investigated for the synthesis of novel phenol-substituted benziodoxole, namely, 1-(4-hydroxyphenyl)benziodoxole.[444] The X-ray structure of tosylate **180b** is presented in Fig. 29. The X-ray data revealed a



Scheme 46 Preparation of benziodoxole-based tosylates **181** and **182** and triflates **183** and **184**.

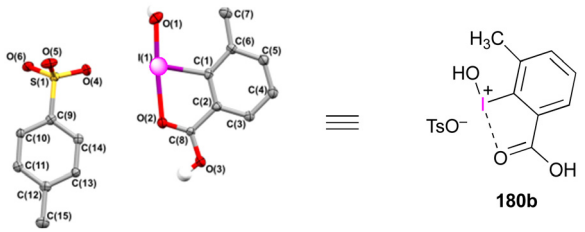


Fig. 29 X-ray structure of compound **180b**.

pseudocyclic structure for the compound with a secondary bond of 2.362(3) Å between the iodine and carboxylate oxygen. Compound **180b** possesses a tetracoordinated iodine center with a I–C covalent bond (1.926 Å), one I–O covalent bond (1.926 Å), and two iodine–oxygen secondary bonds to the carboxylate and tosylate oxygen atoms. This geometry is similar to that of benziodoxole triflate **179**. The iodine center in the cationic fragment of **180b** has a distorted T-shaped geometry typical of hypervalent iodine compounds with as intermolecular distance between iodine and the tosylate oxygen (2.947 Å). Considering the primary and secondary bonding, the iodine(III) center in **180b** has a pseudo square-planar coordination.

Recent progress in the synthetic applications of other classes of benziodoxole reagents, including azido-, amido-, amino-, imino-, cyano-, trifluoromethyl-, trifluoromethylthio-, alkoxy, nitrooxy-, acyloxy- and diazomethyl- has been comprehensively discussed in a 2023 review.[351] Azidobenziodoxoles (Fig. 24) have been effectively utilized as electrophiles or radical azidation reagents for transferring the azido group to a diverse range of substrates.[425,426,444,537–539] These reagents can be prepared by the addition of $TMSN_3$ to the corresponding acetoxybenziodoxoles or the benziodazoles.[540–543] The X-ray analysis of these compounds was reported by Zhdankin and coworkers in 1996 (Fig. 30).[540] The I–N bond in azidobenziodoxoles has a lower bond dissociation energy (BDE) compared to cyclic hypervalent iodine compounds with any other ligands.[537,544–546] Differential scanning calorimetry results suggested that the azidobenziodoxoles derived from *tert*-butyl-substituted benziodoxoles are expected to be safer than the unsubstituted benziodoxles.[547,548] Organic azides can be transformed to the corresponding amines or amides by suitable synthetic methods. Alternatively, amino groups can be directly converted to other organic substrates by utilizing the corresponding benziodoxole derivatives as group transfer reagents, which can be efficiently prepared by ligand exchange reactions of substituted benziodoxoles with the corresponding nitrogen compounds.[535,549–558] Most of these reagents are stable and are easy to handle. The structures of these compounds have been established by X-ray structural analysis.[549,550,552–554,556–558] Certain recently developed synthetic protocols utilizing azidobenziodoxoles such as azido sulfonylation of terminal alkynes,[559] C(sp^3)–H bond functionalization,[560] bromoazidation of olefins[561] and photocatalytic ring opening of 1,4-dioxane, affording the corresponding iodobenzoyloxy derivative,[562] are summarized in Scheme 47.

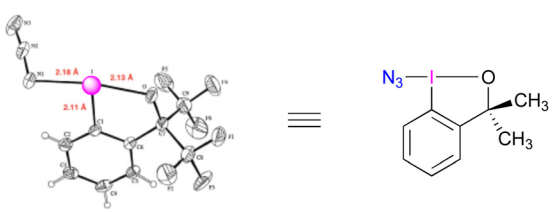
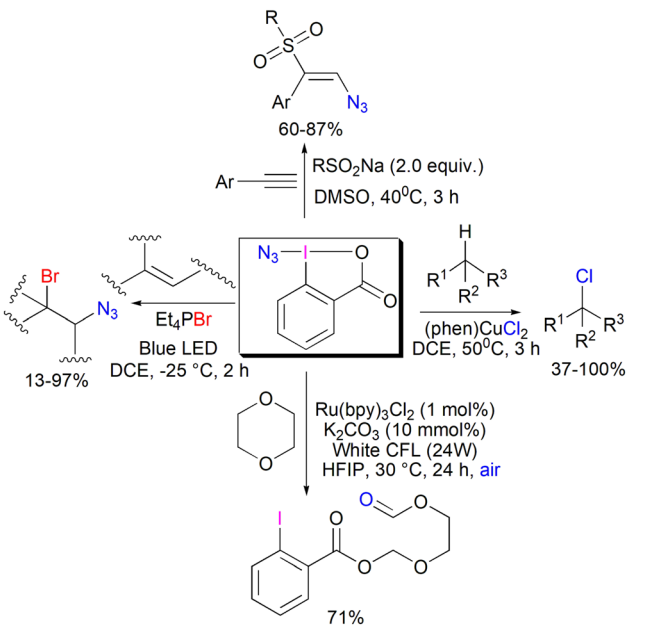


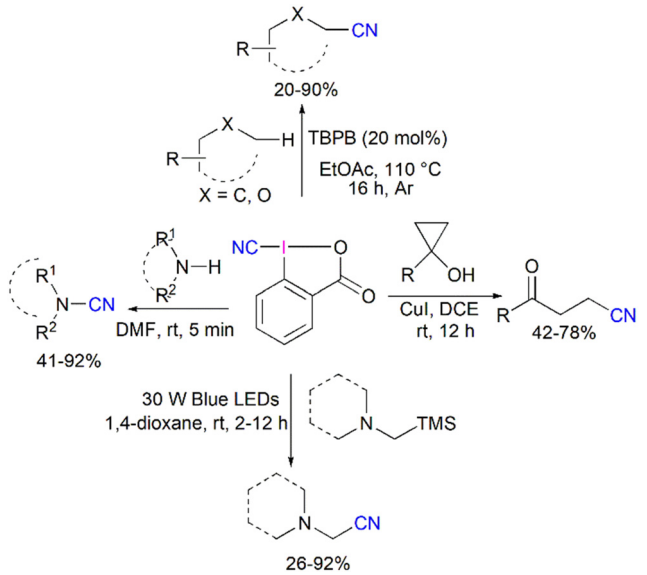
Fig. 30 X-ray structure of a stable azidobenziodoxole.

In addition to azidobenziodoxoles, various cyclic cyano-substituted iodanes are known in the literature and have been efficiently used for the transfer of the cyano group to organic substrates.[563,564] Cyclic cyano iodanes were first prepared and investigated more than 25 years ago.[541] Several cyclic cyano iodanes have been synthesized *via* ligand exchange reaction using TMSCN and their structures have been confirmed by X-ray analysis.[542,565,566] Representative recent examples highlighting the use of cyanobenziodoxoles include the cyanation of C(sp^3)–H bonds,[567] photo cyanation of tertiary amines,[568] α-cyanation of cyclopropanol,[569] and cyanation of primary and secondary amines[570] (Scheme 48).

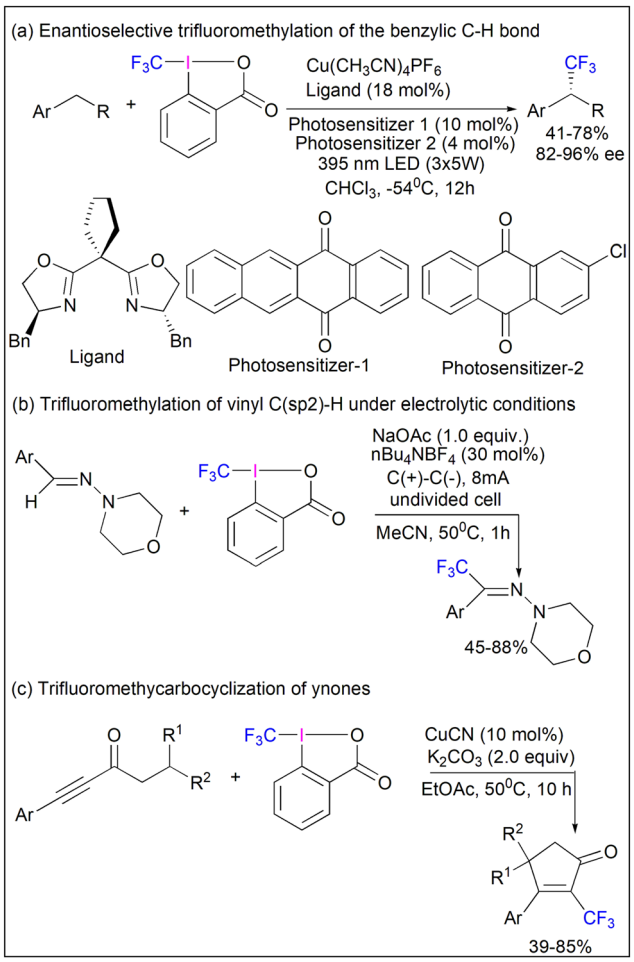
Benziodoxoles containing a trifluoromethyl group (–CF_3 group) as a ligand are known as Togni's reagents.[571–574] Trifluoromethylbenziodoxoles can be conveniently prepared from the corresponding acetoxy- or methoxybenziodoxoles by the addition of $TMSCF_3$. These compounds are excellent reagents for the selective transfer of the –CF_3 group to various substrates under metal-free, transition metal-catalyzed, or photocatalyzed conditions. A wide range of cyclic trifluoromethyl-substituted iodanes has been prepared and their structures and reactivity in trifluoromethylation reactions reported.[575–581] Cyclic trifluoromethyliodane reagents are comparatively stable and safe to handle compared to their corresponding acyclic compounds,



Scheme 47 Examples for the synthetic utilization of azidobenziodoxoles.



Scheme 48 Examples highlighting the synthetic applications of cyanobenziodoxoles.



Scheme 49 Synthetic utilization of trifluoromethylbenziodoxoles (Togni's reagents) for diverse trifluoromethylation reactions (a)–(c).

which are, in general, unstable due to the weak C–I bond between the carbon atom of the CF_3 group and the hypervalent iodine center. The reactions of these reagents with alkene or alkyne substrates can give the addition of trifluoromethyl groups, as well as trifluoromethylation followed by cyclization.[571–573,582] Other reactions are the insertion of the CF_3 group into C(sp^3)–H and C(sp^2)–H bonds and trifluoromethylation at heteroatoms.[583–585] Recently reported representative examples include: (i) enantioselective trifluoromethylation of the benzylic C–H bond;[586] (ii) trifluoromethylation of vinyl C(sp^2)–H under electrolytic conditions;[587] and (iii) trifluoromethycarbocyclization of ynones,[588] as depicted in Scheme 49.

Cyclic iodanes bearing alkoxy groups are known for transferring alkoxy groups to appropriate substrates,[589–597] as well as one-electron oxidizing reagents.[589–591] Alkoxybenziodoxoles can be easily accessed by reacting substituted benziodoxoles with alcohols[592,594,595,598] and utilized as starting materials for the synthesis of various cyclic hypervalent iodine compounds.[596,599–604] Besides alkoxybenziodoxoles, acyloxybenziodoxoles and nitrooxybenziodoxoles[605] were also reported in the literature. It is worthwhile to mention here that nitrooxybenziodoxole is shock-insensitive and does not undergo decomposition even when stored at room temperature for more than one year.[606] Certain examples of recently reported transformations using these reagents are presented in Scheme 50.

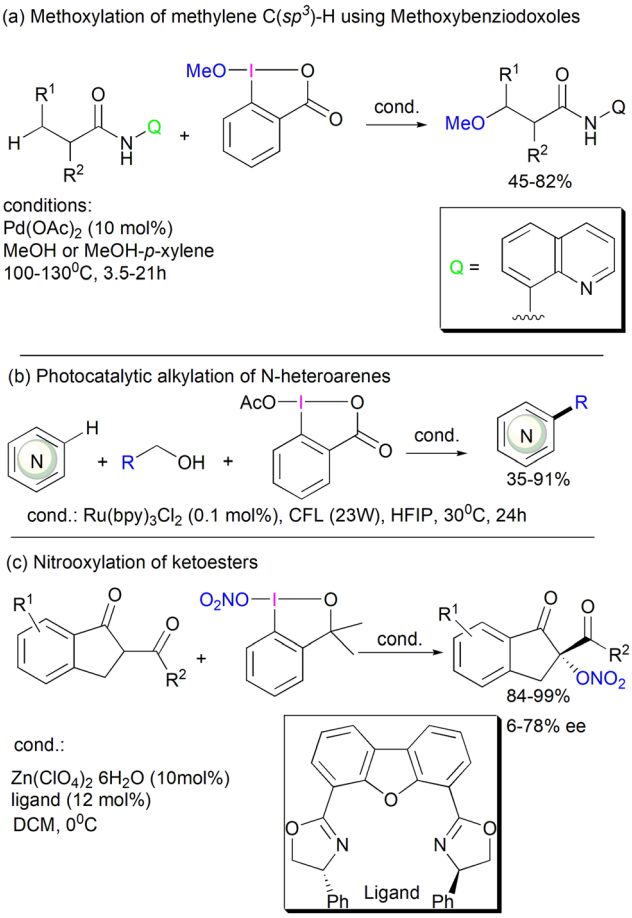
Further, in the area of cyclic hypervalent iodine compounds, Suero and coworkers developed cyclic or pseudocyclic hypervalent iodine reagents with diazomethyl groups and reported their structures and reactivity pattern.[607] These compounds are bench stable and substituted diazomethyl radicals can be generated from these compounds under photocatalytic conditions.[334,607] An interesting example of C–H diazomethylation of arenes using pseudocyclic diazomethylbenziodoxole is outlined in Scheme 51. In addition to this, significant transformations utilizing Rh-carbenoid species generated from pseudocyclic diazomethylbenziodoxoles and dinuclear rhodium complexes were reported in the literature.[608–610]

In recent years, numerous cyclic and pseudocyclic heterocycle-substituted iodanes have been developed and selected examples of λ^3-iodanes **185–191** are presented here (Fig. 31) and the related λ^5-iodanes are discussed in the next section. Recently, Nachtsheim, Postnikov and coworkers presented a systematic investigation on the thermal stability of these iodanes.[611]

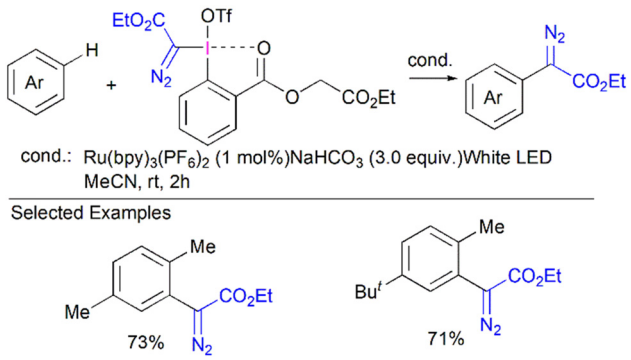
In addition, various chiral cyclic and pseudocyclic hypervalent iodine(III) derivatives were described in the literature.[349,399,400] These compounds have been reported to play an important role in asymmetric synthesis, and various oxidative transformations have been achieved in excellent yield and enantioselectivity using these reagents. Examples of cyclic and pseudocyclic hypervalent λ^3-iodanes **192–205** are presented in Fig. 32.

7.4. Hypervalent heterocyclic compounds of iodine(V)

The chemistry of hypervalent iodine(V) compounds has witnessed remarkable expansion in recent years.[333,612–614]



Scheme 50 (a) Methoxylation of methylene C (sp^3)–H using methoxybenziodoxoles; (b) photocatalytic alkylation of N-heteroarenes; and (c) nitroxylation of ketoesters.



Scheme 51 C–H diazomethylation of arenes using pseudocyclic diazomethylbenziodoxole.

Organoiodine(v) heterocycles are represented by several typical classes **206–222**, as shown in Fig. 33. One of the main representatives of these compounds, 2-iodoxybenzoic acid (IBX, **206**), was first synthesized in 1893 by Hartman and Meyer.[615] Later, Mullin and coworkers reported the synthesis of IBX through the oxidation of 2-iodobenzoic acid using potassium bromate

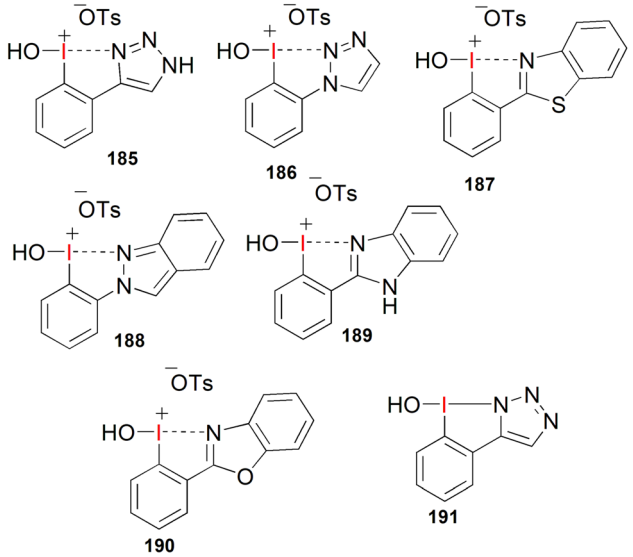


Fig. 31 Examples of cyclic and pseudocyclic heterocycle-substituted λ^3-iodanes **185–191**.

under acidic conditions.[616] However, the existence of bromate impurities imparted explosive nature to IBX at elevated temperature; thus, IBX could not be developed as a potential oxidant, especially for many years until the synthetic method reported by Frigerio *et al.*[617] Since then, IBX has been utilized in a plethora of oxidative transformations, involving the oxidation of alcohols, amines, benzylic carbon and phenols[333,612–614] and oxidative cyclization to diverse heterocyclic rings has been well-documented.[618] A. R. Katritzky and coworkers confirmed the cyclic structure of IBX derivatives by X-ray crystallographic study.[619] Martin and coworkers reported the synthesis, structure, and properties of several cyclic λ^5-iodanes in the 1980s–1990s.[620–623]

Iodine(v) heterocycles have found broad practical application as mild and selective reagents for the oxidation of alcohols and some other useful oxidative transformations. Numerous reviews on the chemistry and synthetic applications of IBX (**206**) and related iodine(v) heterocycles were published previously.[624–626] Recently, the synthetic applications of iodine(v)-based oxidants in numerous oxidation reactions were systematically reviewed.[613,614] Further developments in this area include the preparation of safer hypervalent iodine(v) variants with enhanced solubility in common solvents and greater thermal stability. Certain structural analogs of IBX were synthesized to solve the solubility challenges of IBX.[623,627–633] Besides, pseudocyclic iodine(v) compounds, 2-iodoxybenzoate esters (**219**) (Fig. 33), are also important oxidants possessing intramolecular secondary I···O interactions between the iodine and oxygen atom present in the *ortho*-substituent.[634,635]

Another important λ^5-iodane is triacetoxybenziodoxolone, known as Dess–Martin periodinane (DMP) (**210**).[620] DMP was prepared by heating IBX with acetic anhydride and has emerged as the one of the preferred reagents for the oxidation of alcohols to the respective carbonyl compounds. The synthetic applications of DMP as an oxidation reagent were

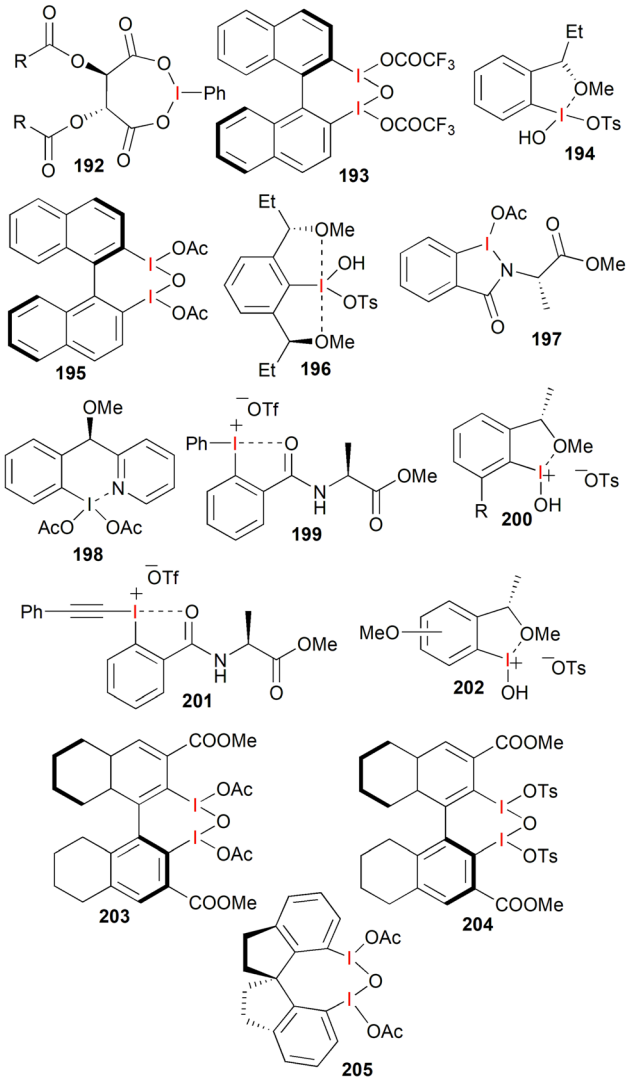


Fig. 32 Examples of chiral λ^3-iodanes **192–205**.

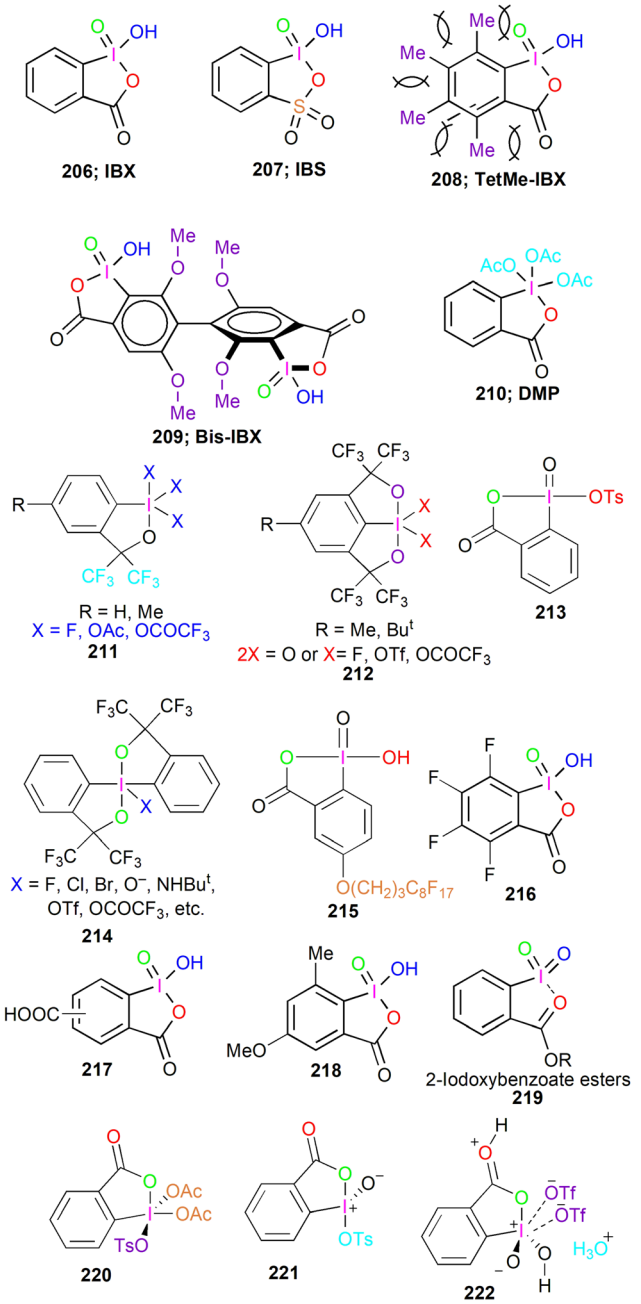


Fig. 33 Examples of cyclic hypervalent iodine(v) compounds **206–222**.

recently reviewed by Kupwade[636] and in the total synthesis by Heravi and coworkers.[637] Moorthy and coworkers reported the synthesis of a highly reactive iodine(v) oxidant, tetramethyl-IBX (TetMe-IBX, **208**).[638,639] TetMe-IBX is capable of oxidizing alcohols in common organic solvents even at room temperature due to its hypervalent 'twisting-promoted' rate enhancement.[640] In another report, Moorthy and coworkers designed and synthesized the twisted 3,3′-diiodo-2,2′,6,6′-tetramethoxybiphenyl-4,4′-dicarboxylic acid (**DIDA**), another modified IBX-precatalyst for the *in situ* generation of Bis-IBX.[641] Bis-IBX, containing perpendicular aromatic planes, presumably undergoes insufficient aggregation, which results in good solubility and enhanced reactivity. Bis-IBX oxidizes the primary alcohols to either the corresponding carboxylic acid or aldehydes depending on the solvent system used.

The tosylate derivative of 2-iodoxybenzoic acid (IBX-tosylate, **213**) can be prepared by the reaction of IBX with *p*-toluenesulfonic acid in acetic anhydride.[642] 2-Iodoxybenzenesulfonic acid (IBS, **175**), a thia-analog of IBX and a powerful oxidizing reagent, exists in the cyclic tautomeric form of 1-hydroxy-1*H*-1,2,3-benziodoxothiole 1,3,3-trioxide.[630] Ishihara and coworkers established that the thia analog is the most powerful catalyst in the iodine(v)-catalyzed oxidation of alcohols using oxone as a terminal oxidant. Recently, Zhdankin and coworkers reported the preparation and reactivity of the strongest iodine(v) oxidant, 2-iodoxybenzoic acid ditriflate (**222**, Fig. 33).[643] Performing X-ray structural studies of compound **222** has been reported to be an extremely challenging task due to its exceptional oxidizing properties. The X-ray analysis demonstrated a very complex solid-state assembly formed by primary bonds and various intermolecular secondary interactions.[643] The hypervalent iodine atom in molecule **222**

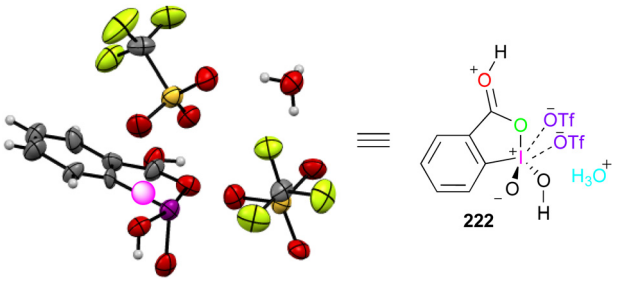


Fig. 34 X-ray structure of compound **222**.

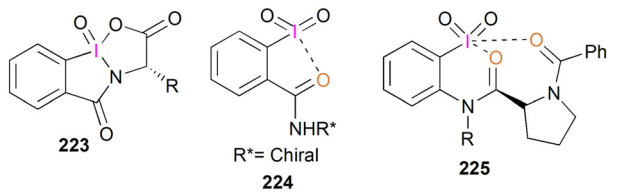


Fig. 35 Examples of chiral λ^5-iodanes **223–225**.

has short primary bonds to carbon and three oxygen atoms and secondary contacts to the oxygen atoms (2.985 Å and 2.820 Å), having significant ionic character (Fig. 34). The set of four primary and three secondary contacts indicate the pseudopentagonal bipyramidal geometry at the hypervalent iodine center. The considerable ionic character of compound **222** can be a probable reason for its exceptionally high electrophilicity and oxidizing reactivity.

2-Iodoxybenzoic acid (IBX) and Dess–Martin periodinane (DMP) are examples of frequently used stoichiometric hypervalent iodine(v) reagents, although the recovery of these reagents from the reaction mixture is low yielding. Thus, to overcome this, numerous recyclable (polymeric as well as non-polymeric) cyclic hypervalent iodine(v) compounds have also been developed and utilized in diverse organic transformations.[644]

Moreover, Zhdankin and coworkers reported the first chiral cyclic hypervalent λ^5-iodanes (**223**)[645] (Fig. 35). These amino-acid-derived benzioazole oxides (**223**) were prepared by the oxidation of 2-iodobenzamides, which were obtained from 2-iodobenzoyl chloride with amino acids or their methyl esters, with potassium bromate. Later, this group reported the synthesis of chiral IBX amides (**224**) by the dioxirane oxidation of 2-iodobenzamides[646] and pseudo-benziodoxazines (**225**)[647] (Fig. 35).

8. Conclusions

In conclusion, this review demonstrated the significant current interest in the chemistry of heterocyclic compounds incorporating an atom of a hypervalent main-group element. Hypervalent heterocycles possess significantly higher thermal stability compared to their acyclic analogs, which adds special features to their chemistry. The increased stability of the cyclic derivatives is especially important for hypervalent bromine and iodine, allowing the preparation and broad synthetic application of numerous valuable reagents. In particular, benziodoxole-based hypervalent iodine heterocycles are used as reagents for transferring the substituent on iodine to the organic substrate or as versatile oxidants. We expect that the interest in synthetic applications of hypervalent heterocyclic compounds as versatile reagents for organic synthesis will continue to grow in the future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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