Tri- and pentavalent iodine compounds are called $\lambda^3$- and $\lambda^5$-iodanes. Ligand exchange, i.e. displacement of heteroatom ligands of $\lambda^3$- and $\lambda^5$-iodanes with external nucleophiles, is a facile low energy process. A very high leaving group ability of $\lambda^3$-iodanyl groups is among the most important features of $\lambda^3$-iodanes, which makes it possible to generate highly reactive species such as carbenes, nitrenes, cations, and arynes under mild conditions and to oxidize a wide range of functionalities such as alcohols, amines, sulfides, alkenes, alkynes, and carbonyl compounds. The leaving process is termed reductive elimination, in which the $\lambda^3$-iodanyl group eliminates with energetically preferable reduction to univalent iodides. The process is also associated with an increase in entropy. Pseudorotation and ligand coupling on iodine(III), and homolytic cleavage of hypervalent iodanes are also discussed. Finally, recent progress in the structural elucidations of $\lambda^3$-iodanes is shown here.

**Keywords.** Iodane, Hypervalent, Reductive elimination, Ligand coupling, Ligand exchange
Introduction

The term iodane refers to hydrogen iodide (HI), a colorless non-flammable gas. According to IUPAC rules, compounds with nonstandard bonding number are shown by the lambda notation; thus, H₃I is called \( \lambda^3 \)-iodane and H₅I \( \lambda^5 \)-iodane. The most common ArIL₂ (L: heteroatom ligands) with decet structure is named aryl-\( \lambda^3 \)-iodane and ArIL₄ with dodecet structure aryl-\( \lambda^5 \)-iodane.

Aryl-\( \lambda^3 \)-iodanes (ArIL₂) have a geometry of a pseudotrigonal bipyramid with an aryl group and lone pairs of electrons in equatorial positions and two heteroatom ligands (L) in apical positions. Bonding in ArIL₂ uses an essentially pure 5p orbital in the linear L-I-L bond. This is a hypervalent three-center four-electron bond (3c–4e bond) with two electrons from the doubly occupied 5p orbital on iodine and one electron from each of the ligands L. The aryl group is bound by a normal two-electron covalent bond with 5sp² hybridization to form CAr-I \( \sigma \)-bond [1, 2].

The two lower energy molecular orbitals, bonding and nonbonding orbitals, of the three produced for hypervalent 3c–4e bond are filled (Fig. 1). Partial positive charge develops on the central iodine atom, while partial negative charge on the apical heteroatom ligands, because the filled nonbonding molecular orbital has a node at the central iodine. The partial positive charge on the iodine of the highly polarized 3c–4e bond makes the aryl-\( \lambda^3 \)-iodane an electrophilic agent. The inherent nature of 3c–4e bond explains the preferred orientation of more electronegative ligands in the apical positions. The presence of more electropositive central atoms is energetically favorable for hypervalent species: thus in general, \( \lambda^3 \)-iodanes are more stable than analogous \( \lambda^3 \)-bromanes and \( \lambda^3 \)-chloranes [1, 2].