

## V Summary

In this thesis the chemistry of iodine in its oxidation states +I to +V was studied. Special interest was laid on aryl-ligands and on the highly electronegative ligands fluorine and pentaorthotellurate group.

### *I(I) compounds and polyiodine cations*

Extensive research on the formation of IF and IOTeF<sub>5</sub> and also BrF has shown that their existence in substance is highly improbable. It is anticipated that they are formed as intermediates which disproportionate extremely fast. It is very interesting to note the unexpected formation of the polycations I<sub>5</sub><sup>+</sup> and I<sub>7</sub><sup>+</sup>. The X-ray investigations of these compounds have shown that I<sub>5</sub><sup>+</sup> is z-shaped while I<sub>7</sub><sup>+</sup> is w-shaped. The existence of I<sub>7</sub><sup>+</sup> was proven for the first time. Raman spectra of these compounds were measured and discussed.

### *I(III) compounds*

IF<sub>3</sub> was crystallized for the first time, its structure could be solved and a substantial gap in interhalogen chemistry could be filled. As expected, IF<sub>3</sub> showed the typical T-shape. However in contrast to other XF<sub>3</sub> compounds like ClF<sub>3</sub> and BrF<sub>3</sub> and to the dimeric ICl<sub>3</sub>, IF<sub>3</sub> builds polymeric layers. The iodine atom shows an expanded pentagonal-planar 3+2 coordination, reminiscent to the regular pentagonal structure of the IF<sub>5</sub><sup>2-</sup>.

Like ClF<sub>3</sub> and BrF<sub>3</sub>, IF<sub>3</sub> shows amphoteric behavior with respect to fluoride ions. For the first time the IF<sub>2</sub><sup>+</sup> cation was prepared and fully characterized. IF<sub>2</sub><sup>+</sup> has the highest Lewis-acidity and fluoride acceptor strength of all halF<sub>2</sub><sup>+</sup>-cations (hal = Cl, Br).

I(OTeF<sub>5</sub>)<sub>3</sub> and I(OTeF<sub>5</sub>)<sub>3</sub>·C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>F were crystallized for the first time and their structures have been determined. In the solid state they occur as dimeric units with unexpected I··F and I··O interactions. The fluoride atoms of the OTeF<sub>5</sub> group as well as the oxygen atoms of C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>F show basic properties in the presence of the I(III) center. The coordination number of iodine in solvate free I(OTeF<sub>5</sub>)<sub>3</sub> is 4, while in I(OTeF<sub>5</sub>)<sub>3</sub>·C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>F the CN is 5.

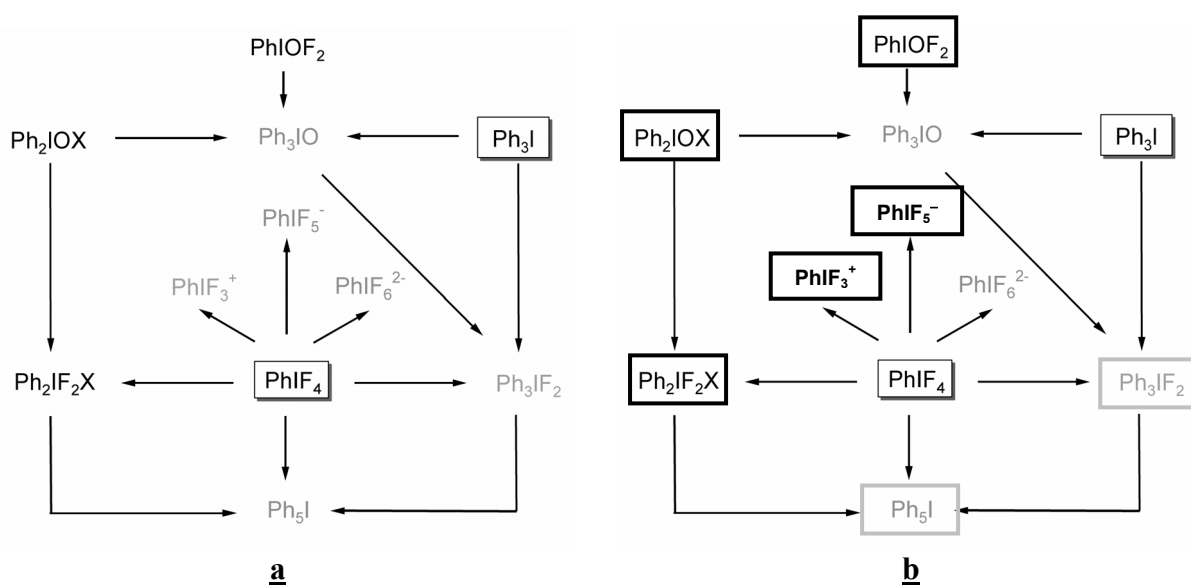
Ligand coupling reactions (LCR) are typical decomposition reactions for homoleptic aryl-main group compounds like SbPh<sub>5</sub> and BiPh<sub>5</sub>. This reaction proceeds with a radicalic or a

concerted mechanism. Through the specific choice of ligands it could be proven that LCR for non cyclic triaryliodanes proceeds via a concerted mechanism. Therefore extensive experiments on preparation of diverse mixed-type triaryliodanes were performed. For the investigation of LCR the knowledge of their structures was essential.  $\text{I}(\text{CF}_3\text{Ph})_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  is the first species of this class. It could be prepared and the crystal structure elucidated.

### *I(V) compounds*

For  $\text{F}(\text{IOTeF}_5)_4$  the crystal structure was determined and Raman spectra could be interpreted. The square-pyramidal molecules with the F atom in the apical position form a chain structure in the solid state. This is performed by  $\text{I} \cdots \text{F}$  interactions which is rarely observed for  $\text{OTeF}_5$  groups.

On the demanding field of organoperiodanes great progress was made. Prior to these investigations little was known about these compounds. The schematic figure 1 shows the situation before and after this work. Novel structures are marked by black frames while gray frames indicate compounds which exist almost certainly.



**Figure 1** Organic periodanes before (**a**) and after (**b**) this work.

With the preparation of the  $\text{PhIF}_3^+$  and  $\text{PhIF}_5^-$  cations the amphoteric property of  $\text{PhIF}_4$  regarding fluoride donating and accepting agents could be verified.  $\text{PhIF}_4$  was shown to have similar properties like  $\text{XeOF}_4$ .  $\text{PhIF}_3^+$  has the same pseudo-trigonal-bipyramidal structure as the oxide-fluorides  $\text{XeOF}_3^+$  and  $\text{IOF}_3$  and the halogen fluorides  $\text{XF}_4^+$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).

$\text{PhIF}_5^-$  has a pentagonal-pyramidal arrangement ( $C_{5v}$ ) and is the third known species of this kind besides  $\text{XeOF}_5^-$  and  $\text{IOF}_5^{2-}$ . In all three compounds,  $\text{PhIF}_3^+\text{SbF}_6^-$ ,  $\text{PhIF}_4$  and  $\text{pip}^+\text{PhIF}_5^-$ , the phenyl group occupy the same place as the oxygen atom in the xenon and iodine oxyfluorides. Phenyl group and oxygen atom seem to have similar features with regard to sterical requirements and probably to electronic qualities.

Because of the spectroscopic and crystal structure investigations on  $\text{PhIOF}_2$  and  $\text{Ph}_2\text{IOF}$ , data of mono- and di-phenyloxyfluorides are accessible for the first time. Both molecules have a pseudo-trigonal-bipyramidal structure and show relevant intermolecular contacts in their solid state. As a result, iodine is coordinated octahedrally with results of a chainlike arrangement.

Fluorination of  $\text{Ph}_2\text{IOTfa}$  and  $\text{Ph}_2\text{IOF}$  with  $\text{SF}_4$  resulted in the formation of the compounds  $\text{Ph}_2\text{IF}_2^+\text{CF}_3\text{CO}_2^-$  and  $\text{Ph}_2\text{IF}_2^+\text{F}^-$ . Both have ionic structures with a pseudo-trigonal-bipyramidal geometry for the  $\text{Ph}_2\text{IF}_2^+$  cations which can also be detected by Raman spectroscopy. The trifluoroacetate counter ion causes a dimeric arrangement while the fluoride ion leads to unusual hexameric units. In both compounds iodine prefers an octahedral environment formed by four covalent bonds and two  $\text{I}\cdots\text{F}$  or two  $\text{I}\cdots\text{O}$  contacts, respectively.

Two different methods were applied for the preparation of iodine(V) with three phenyl ligands. While the oxidation of triphenyliodine with ozone resulted only in a non identifiable, fastly decomposing substance, the fluorination with  $\text{XeF}_2$  led to  $\text{Ph}_3\text{IF}_2$  as a mixture of two isomers which could be proven by NMR-spectroscopy. Crystallization of  $\text{Ph}_3\text{IF}_2$  or 2,2'-biphenylphenyliodinedifluoride was not feasible. The latter can be prepared similarly and exists in three isomeric forms.

Despite the not very encouraging results of DFT calculations on pentaphenyliodine – decomposition of  $\text{Ph}_5\text{I}$  to  $\text{Ph}_3\text{I}$  and  $\text{Ph}_2$  releases 90 kcal/mol – extensive investigations for its preparation were made.

Phenylation of  $\text{PhIF}_4$  with  $\text{Ph}_2\text{Zn}$  or  $\text{PhLi}$  gave solids which exploded even at  $-80\text{ }^\circ\text{C}$ . Cautious decomposition of reacting solutions lead to  $\text{Ph}_3\text{I}$  and  $\text{Ph}_2$ . This results are taken as indication for the possible existence of  $\text{Ph}_5\text{I}$ .