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Review

Intermolecular hypervalent I(III)· · ·O interactions: A new driving force for complexation of crown ethers

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Contents

Abstract

In this account, we show that intermolecular hypervalent I(III)· · ·O interactions play an essential role in the complexation of organo-λ^3-iodanes with crown ethers. In addition to the well-known driving force for the complexation of crown ethers, ion–dipole interaction, and hydrogen bonding interaction, our result provides a new class of interaction in supramolecular chemistry of crown ethers. Both solid state structure analysis and solution chemistry indicate that diaryl-, 1-alkynyl(phenyl)-, and 1-alkenyl(phenyl)-λ^3-iodanes as well as 1-alkynyl(aryl)-λ^3-bromanes form stable complexes with 18-crown-6 through hypervalent I(III)· · ·O or Br(III)· · ·O interactions. In these complexes, hypervalent iodine(III) or bromine(III) atom contacts with the three adjacent oxygen atoms of 18-crown-6. The complexation not only increases the stability of these hypervalent compounds but also increases the solubility toward polar solvents. The highly labile, activated iodosylbenzene monomers were isolated as stable crystalline complexes by the coordination of 18-crown-6. These iodosylbenzene monomer complexes serve as versatile oxidizing agents, especially in water as a solvent.

Keywords: I(III)· · ·O; Complexation; Crown ethers; Hypervalent interactions; Iodine; Bromine; Iodosylbenzene; Oxidations

1. Introduction

Cyclic polyethers are very unique in their ability to bind metal cations and small neutral or ionic molecules selectively. For complexation of cyclic polyethers, two kinds of binding forces are well recognized: ion–dipole interaction and hydrogen bonding. Metal ions form complexes with crown ethers through ion–dipole electrostatic interactions, the oxygen lone pairs being attracted to the cation positive charge (Fig. 1(a)) [1]. By complexing the cations in the cavity, crown ethers solubilize many salts in nonpolar organic solvents.

A variety of organic molecules with acidic hydrogens bind to crown ethers via hydrogen bonding [2]. For instance, alkylonium ions such as alkylammonium [3a], alkylsulfonium [3b], and alkylphosphonium ions [3c] as well as hydronium ion with acidic hydrogens bind crown ether hosts via X–H· · ·O (X = C, N, and O) hydrogen bonding in a perching arrangement. Fig. 1(b) shows a structure of hydronium ion complex with 18-crown-6 (18C6), in which three acidic hydrogens of the ion are hydrogen bonded to three alternate oxygens of 18C6 in a tripod arrangement with 180° O–H· · ·O bond angles [2a,4]. Solid complexes of certain neutral molecules such as MeCN, $MeNO_2$, Me_2SO_2, DMSO, MeOTs, and $CHCl_3$ having polar C–H bonds with 18C6 show

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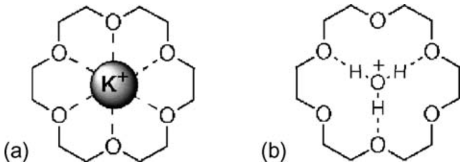


Fig. 1. Ion–dipole interaction ($K^+ \cdot 18C6$ complex) (a) and hydrogen bonding ($H_3O^+ \cdot 18C6$) (b).

C–H· · ·O interactions [2b]. Because of its relatively strong and highly directional nature, hydrogen bonding has been described as the masterkey interaction in supramolecular chemistry [1b].

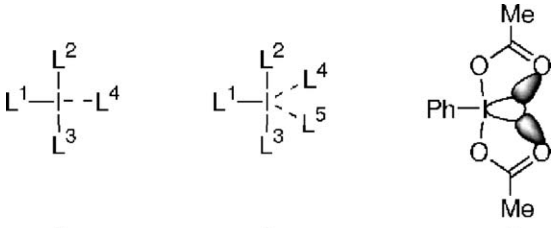
In this account, we show that, in addition to these binding forces (ion–dipole electrostatic interaction and hydrogen bonding), the third interaction, that is, hypervalent interaction [5] plays an essential role in the complexation of crown ethers with hypervalent organohalogen(III) compounds. Some highly labile organo-λ^3-iodanes are stabilized by the complexation with crown ethers through hypervalent interactions. Solubility of organo-λ^3-iodanes toward polar solvents, especially water, was much improved by the complexation with crown ethers.

2. Complexation of diaryl-λ^3-iodanes with crown ethers

Iodobenzene shows no evidences for formation of a complex with 18C6 in chloroform solution (by ^{1}H NMR and UV absorption spectra). Molecular iodine, however, forms 1:1 complexes with crown ethers, but the interaction is moderate: binding constants of molecular iodine in cyclohexane at 25 °C are 4.93 M^{-1} for 18C6, 4.78 for 15-crown-5 (15C5), 5.36 for 12-crown-4 (12C4), 2.54 for THF, and 0.94 for diethyl ether [6,7]. Hence, the binding of iodine to these crown ethers does not involve the cavity of the macrocyclic polyethers but rather involves a single oxygen–iodine interaction with a linear orientation of the halogen molecule with the donor oxygen atom [6]. A similar single oxygen–bromine interaction was observed in a molecular bromine·18C6 complex [8].

Hypervalent λ^3-iodanes (IL_3) exhibit a T-shaped geometry and are regarded as pseudotrigonal bipyramidal structures including two lone pairs at the iodine(III) [9]. In the solid states, most of the λ^3-iodanes exist as tetra- or penta-coordinated species through intramolecular and/or intermolecular secondary contacts. Tetracoordinated λ^3-iodanes **1** virtually adopt a square planar arrangement as a result of hypervalent secondary interactions [10]: the fourth ligand L^4 irrespective of neutral or anionic species interacts with I–L^1 antibonding orbital of the λ^3-iodanes and donates an electron pair into the σ* orbital forming a nearly linear L^1–I· · ·L^4 triad (Fig. 2) [11].

Penta-coordinated λ^3-iodanes generally exist in a pentagonal planar geometry **2** in the solid states [12]: for instance, the crystal structure of (diacetoxyiodo)benzene (**3**) exhibits two intramolecular secondary contacts between the iodine atom and the carbonyl oxygen atoms resulting in a pentagonal planar arrangement. To interpret the pentagonal planar geometry, Alcock et al. proposed the three-center secondary bonding model **3**, i.e., the overlap of the I–C σ* orbital with two lone pair orbitals of the carbonyl oxygen atoms, in which the two intramolecular secondary contacts are forced into the same plane as the primary bonds by repulsion from the lone pairs on iodine(III) [12a].



1 **2** **3**

Fig. 2. Tetra- and penta-coordination of λ^3-iodanes.

In conjunction with the facts that the hypervalent bonding of L^2–I–L^3 in **1** is highly polarized and the central iodine atom is positively charged, these solid state structure analyses suggested to us that the λ^3-iodanes might form discrete complexes with crown ethers through cooperative interactions between iodine(III) and oxygen atoms of crown ethers, in marked contrast to a simple interaction in molecular iodine–crown ether complexes [13].

We found that evaporation of a dichloromethane–diethyl ether solution of a 1:2 mixture of diphenyl-λ^3-iodane Ph_2IBF_4 (**4a**) and 18C6 in a refrigerator afforded a 1:1 $Ph_2IBF_4 \cdot 18C6$ complex **5a** [14]. On the other hand, when the solvent was changed to dichloromethane–hexane and twice amounts of **4a** relative to 18C6 were used, a 2:1 $Ph_2IBF_4 \cdot 18C6$ complex **5b** was obtained. These complexes are highly stable and no decomposition was observed on standing at room temperature for over 2 months. This is the first example of complexation between λ^3-iodanes and crown ethers.

For both the complexes **5**, the diphenyl-λ^3-iodanyl groups protrude above one face (for **5a**) and both faces (for **5b**) of the host to provide a perching type of host–guest relationship (Fig. 3). Both complexes **5** adopt a distorted pentagonal planar coordination about the iodines, in which each iodine atom contacts with the three adjacent oxygen atoms of 18C6: O1–O3 for I1 of **5a**; O1, O2*, and O3* for I1 of **5b**. The I1· · ·O1 and I1· · ·O3 distances (2.949(2) and 3.143(2) Å) in **5a** are longer than the average covalent bond (2.14 Å) [15] but definitively shorter than the sum (3.5 Å) of the van der Waal's radii [16]. Because both the C19–I1· · ·O1 and C13–I1· · ·O3 triads are near-linear (163.7(1)° and 167.6(1)°), these close contacts are indicative of hypervalent interactions, in which the oxygen donates an electron pair into an I–C σ* orbital [11]. The other I1· · ·O2 contact (3.201(2) Å) is weak and considerably deviates from the linearity of **3c–4e** σ bonding. In the complex **5a**, a water molecule appears to be hydrogen bonded to the 18C6 from the side opposite the λ^3-iodane. Thus, we can imagine a free and easy scene that a butterfly is resting on a leaf with spreading the wings and with drinking water. The 2:1 complex **5b** is centrosymmetric and coordination at the I1 similarly includes two hypervalent secondary bonding (I1–O2* and I1–O1) with a near-linear C–I· · ·O triad, and a weak contact (I1–O3*).

^{1}H and ^{13}C NMR experiments showed the complex formation in solution (CD_2Cl_2). Observation of an upfield shift of a methylene singlet of 18C6 by the addition of Ph_2IBF_4 (**4a**) and

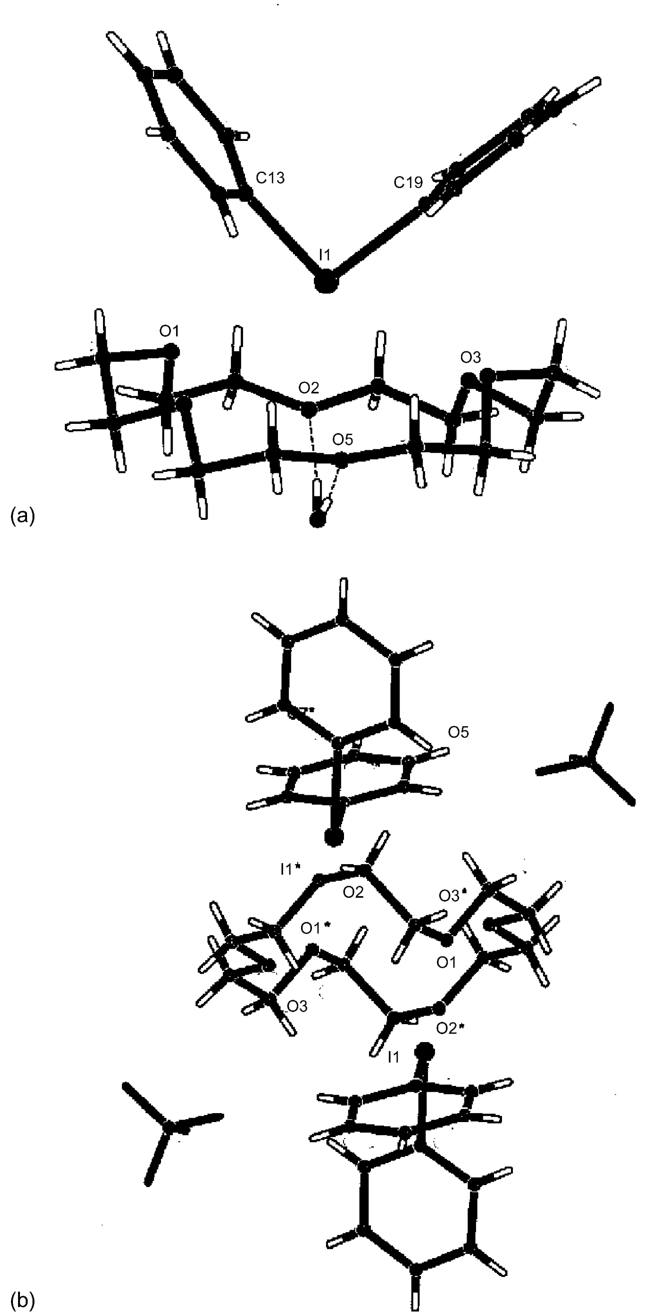


Fig. 3. X-ray crystal structures: (a) $Ph_2IBF_4 \cdot 18C6 \cdot 1.5\ H_2O$ complex **5a** (BF_4 was omitted for clarity) and (b) $(Ph_2IBF_4)_2 \cdot 18C6$ complex **5b**.

of the nuclear Overhauser effects (NOEs) for the *ortho* protons of **4a** by the irradiation of the 18C6 methylene protons suggests the formation of a stable complex in solution, which is similar to the solid state structure. The coldspray ionization (CSI) MS spectrum [17] for 2:1 complex **5b** in dichloromethane showed the most prominent ion peak of the 1:1 complex but a peak corresponding to the 2:1 complex was not detected, which suggests that in dichloromethane solution **4a** exclusively forms the 1:1 complex **5a**. The 1:1 stoichiometry between **4a** and 18C6 in CD_2Cl_2 solution was further confirmed from the Job plots by the ^1H NMR experiments [18]: a plot of complex concentration versus [**4a**]/([**4a**] + [18C6]) showed a maximum at near 0.5.

Table 1
Solvent effects: binding constants (K_a) between Ph_2IBF_4 (**4a**) and 18C6 at 24 °C

Entry	Solvent	DN[a]	K_a (M^{-1})
1	CD_2Cl_2	0	1.02×10^3
2	$CDCl_3$	0	5.45×10^2
3	CD_3COCD_3	17.0	6.33×10
4	THF-d_8	20.0	3.30×10
5	CD_3CN	14.1	1.92×10
6	CD_3OD	25.7[b]	5.55
7	D_2O	33.0[b]	2.30

[a] Donor numbers of Gutmann.

[b] Bulk donor numbers.

Table 2
Ligand effects: binding constants (K_a) of Ph_2IX with 18C6 at 24 °C[a]

X	K_a (M^{-1})	X	K_a (M^{-1})
PF_6	6.65×10^3	ClO_4	8.13×10^2
AsF_6	5.45×10^3	OTf	2.83×10^2
BF_4 **4a**	1.02×10^3	BPh_4	1.47×10^2

[a] In CD_2Cl_2.

Solvent effects on the complexation are shown in Table 1. The solvent donor ability presumably affects the binding constants, which decrease with the increased donor ability [19]: the logarithm of the binding constants correlates well with Gutmann's donor number (DN) of solvents (correlation coefficient $r = 0.96$). A competing hydrogen bonding between $CDCl_3$ and 18C6 decreases the binding constant in the solvent to one-half of the value in CD_2Cl_2 [2b].

The magnitude of the interactions with 18C6 seems to depend on the nature of heteroatom ligands X in Ph_2IX (Table 2). Changing the ligand from BF_4 to the less nucleophilic PF_6 and AsF_6 increased the binding constant about six times greater, while diphenyl-λ^3-iodanes with a highly nucleophilic ligand (X = Br or I) did not show any evidences for the complexation with 18C6.

Table 3 shows the substituent effects on the complexation. Introduction of an electron-donating methyl group onto the *ortho* and *para* position(s) of diphenyl-λ^3-iodane **4a** tends to decrease the complex stability to one-half. In the case of arenediazonium salts, the presence of sterically demanding *ortho* methyl group inhibits the complexation with 18C6, because the diazonium group must deeply penetrate the hole to complex well [3a]. Thus, the small *ortho* methyl effect in **4b** reflects a perching type of host–guest relationship in solution. Electron-withdrawing *p*-chloro and *p*-trifluoromethyl groups increase the binding con-

Table 3
Substituent effects: binding constants (K_a) between **4** and 18C6 at 24 °C[a]

Entry	ArAr′IBF$_4$ **4**		K_a (M^{-1})
	Ar	Ar′	
1	Ph	*o*-MeC_6H_4 **4b**	4.79×10^2
2	Ph	*p*-MeC_6H_4 **4c**	6.70×10^2
3	Ph	*p*-ClC_6H_4 **4d**	1.30×10^3
4	Ph	*p*-$CF_3C_6H_4$ **4e**	2.58×10^3
5	*p*-MeC_6H_4	*p*-MeC_6H_4 **4f**	5.07×10^2

[a] In CD_2Cl_2.

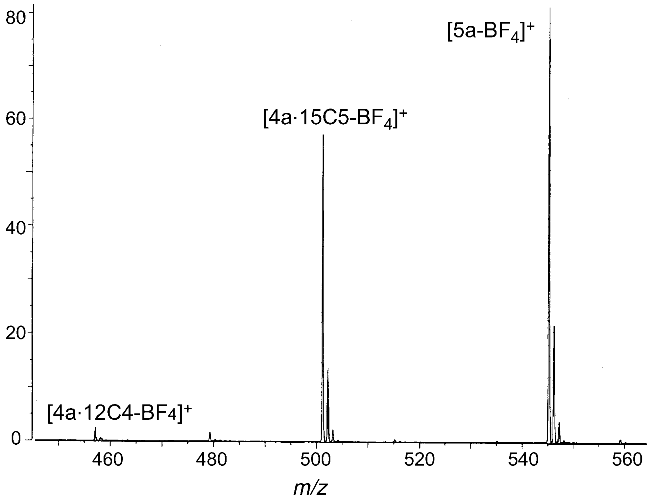


Fig. 4. CSI mass spectrum of a 1:1:1:1 mixture of 18C6, 15C5, 12C4, and **4a** in CH_2Cl_2.

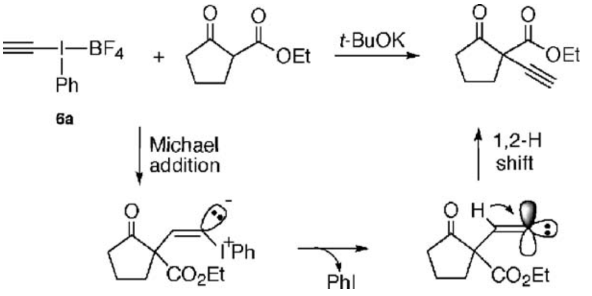
stants. A linear Hammett relationship ($\rho = 0.59$) between $\log K_a$ and σ_p^+ values for the substituent effects indicates that the λ^3-iodanes **4** with electropositive iodine(III) interact more efficiently with 18C6.

The binding magnitude of **4a** also depends on the ring size of crown ethers: the binding constant with 15C5 decreased to $1.58 \times 10^2\ M^{-1}$, and that with 12C4 was negligibly small. Very interestingly, the measurements of the CSI-MS spectrum for a mixture of an equal amount of 18C6, 15C5, and 12C4 in the presence of **4a** exhibit a similar difference in the binding efficacy (Fig. 4). Dibenzo-18C6 showed a slightly decreased interaction ($K_a = 7.48 \times 10^2\ M^{-1}$) compared to 18C6, owing to the decreased basicity of the oxygen atoms. Because of the macrocyclic effect, acyclic pentaglyme exhibited a significantly lower affinity than that of 18C6 [1b]. Use of [18]aneS_6 gave no evidences for interaction with **4a**: this is probably due to the decreased apicophilicity of sulfur ligands relative to oxygen ligands and of the conformational restriction [20].

X-ray crystal structure analysis of diphenyl-λ^3-iodane–crown ether complexes indicated that the cooperative hypervalent interactions between iodine(III) and oxygen atoms of crown ethers are critical to the complex formation. The occurrence of these hypervalent bonding involving crown ether oxygens will provide a new tool of forming supramolecular synthons in the field of crystal engineering.

3. Complexation of alkynyl- and alkenyl-λ^3-iodanes with crown ethers

Because of the powerful electron-withdrawing nature of phenyl-λ^3-iodanyl groups with large Hammett substituent constants (for instance, $\sigma_p = 1.37$ for $PhIBF_4$) [21], ethynyl(phenyl)-λ^3-iodane [HCCI(Ph)X] **6** is a highly electron deficient species and hence acts as a good Michael acceptor toward a variety of soft nucleophiles. Commercially available ethynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**6a**: $X = BF_4$) undergoes direct ethynylation of alkali metal enolates derived from 1,3-dicarbonyl compounds and nitroalkanes under mild conditions (Scheme 1) [22]. This direct ethynylation of nucleophiles with λ^3-iodane **6a** probably involves tandem Michael addition–reductive elimination-alkylidene carbene rearrangement pathway [23]. High migratory aptitude of α-hydrogens in alkylidene carbenes is responsible for this facile ethynylation.



Scheme 1. Tandem Michael addition-alkylidene carbene rearrangement.

Synthetic use of ethynyl-λ^3-iodane **6a**, however, is limited due to the relatively low thermal stability: in fact, the iodane **6a** gradually decomposes even on standing at room temperature. The heteroatom ligand BF_4 is a weak nucleophile and, therefore, its coordination (by a fluorine atom) to the iodine(III) through hypervalent bonding is relatively loose [24], which in turn increases the positive charge on the iodine of **6a**. These features tend to enhance the reactivity of **6a** toward nucleophiles as well as to decrease the stability. Introduction of more nucleophilic ligands such as halogens instead of BF_4 is expected to decrease the susceptibility of **6a** toward decomposition, because of the decreased positive charge on the iodine(III); however, the attempted ligand exchange of ethynyl-λ^3-iodane **6a** with halide ions results in the Michael addition to the β-carbon atom, instead of the formation of ethynyl(phenyl)(halo)-λ^3-iodanes [25]. 18C6 serves as a new type of heteroatom ligand that efficiently coordinates to the iodine(III) but not undergoes Michael additions, and the coordination of 18C6 increases the stability of **6a** [26].

Treatment of ethynyl-λ^3-iodane **6a** with 18C6 in dichloromethane–diethyl ether solution at −20 °C affords a high yield of the 1:1 complex $HCCI(Ph)BF_4 \cdot 18C6$ **7**. The complexation with 18C6 significantly changed the solubility in organic solvents as well as the stability. The λ^3-iodane **6a** is sparingly soluble in less polar solvents such as dichloromethane and chloroform, while the complex **7** is highly soluble in these solvents. Furthermore, the complexation with 18C6 markedly increased the stability of **6a** and almost no decomposition of **7** was observed on standing under ambient conditions over 1 month.

X-ray analysis of the complex **7**, shown in Fig. 5, illustrates a structure closely related to the $Ph_2IBF_4 \cdot 18C6$ complex **5a**. The positively charged iodine(III) atom contacts with three adjacent oxygen atoms O2–O4 of 18C6 and the complex **7** adopts a distorted pentagonal planar geometry about the iodine. The I1···O2 and I1···O4 distances are shorter than the van der Waal's distance (3.50 Å), and both C2–I1···O2 and C3–I1···O4 are near-linear. Therefore, these close contacts are indicative of hypervalent secondary interactions.

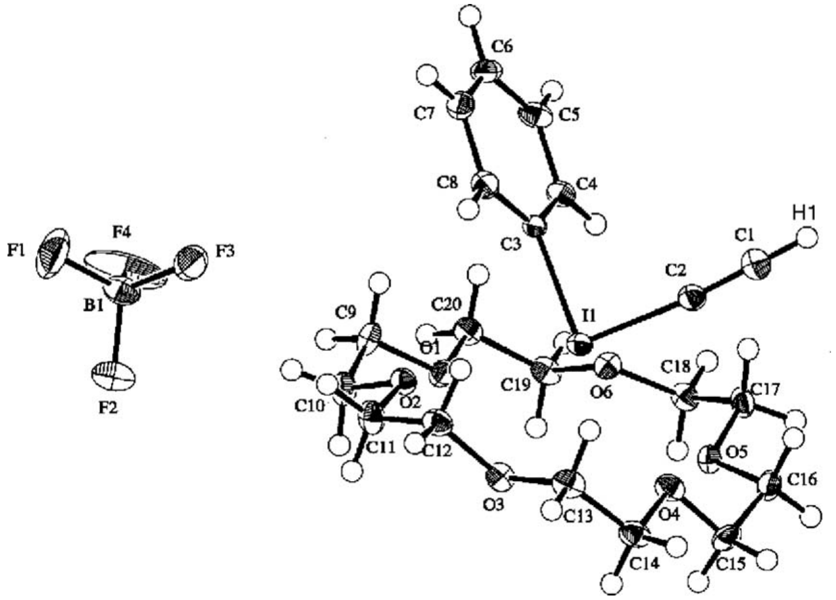
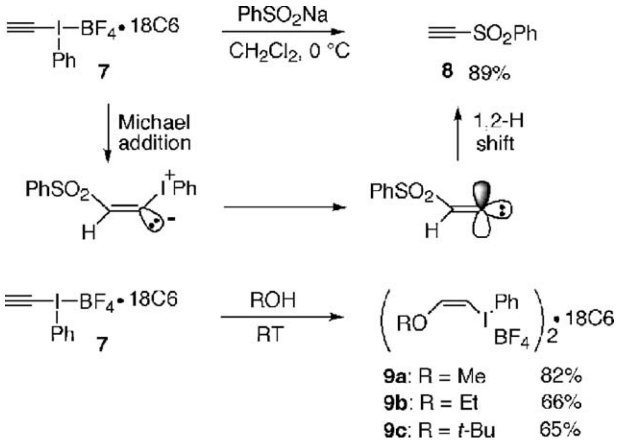


Fig. 5. ORTEP drawing of $HCCI(Ph)BF_4 \cdot 18C6$ complex **7**.

The heteroatom ligand BF_4 shows a close contact with the acetylenic hydrogen atom via hydrogen bonding, which was suggested by a short $H1 \cdots F2$ distance (2.34(5) Å), a nearly linear $C1–H1 \cdots F2$ bond, the ratio of isotropic displacement parameters ($U(C1)/U(C2) = 1.23$) [27], a small isotropic displacement parameter of F2 ($U = 0.0377(8)$) compared to those of the other fluorine atoms (U(F1), 0.068(1); U(F3), 0.047(1); U(F4), 0.084(l)) [28], and the C_{sp}–H stretching frequency (3208 cm^{-1}) of **7**. Highly acidic nature of H1 in **7** will be responsible for the $C–H \cdots F$ hydrogen bonding [29].

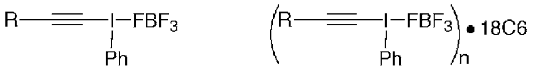
In solution, ethynyl-λ^3-iodane **6a** forms 1:1 complex with 18C6. ^1H NMR analyses showed that a solution of 18C6 in $CDCl_3$ solubilizes 0.9 equiv. of the solid λ^3-iodane **6a** at 23 °C. CSI-MS spectrum for the complex **7** in dichloromethane showed the most prominent ion peak of 1:1 complex $[\mathbf{7}–BF_4]^+$. A binding constant (K_a) value of $1.92 \times 10^3\ M^{-1}$ was obtained by ^1H NMR titrations of $CDCl_3$ solutions of 18C6 with **6a** at 23 °C.

The 1:1 complex **7** holds for the high reactivity of **6a** toward the attack of nucleophiles and serves as a good Michael acceptor. Reaction of **7** with sodium benzenesulfinate undergoes tandem Michael addition–alkylidene carbene rearrangement to give the ethynyl sulfone **8** under mild conditions (Scheme 2) [30]. Interestingly, it is possible to synthesize the highly labile (Z)-(β-methoxyvinyl)-λ^3-iodane as a crown ether complex **9a** via *anti* Michael addition of methanol to the complex **7**. Ethanol and *tert*-butanol similarly undergo the Michael addition to give the analogous 2:1 complexes. In these reactions, 18C6 functions as a stabilizing ligand not only for the reactant ethynyl-λ^3-iodane **6a** but also for the products (Z)-(β-alkoxyvinyl)-λ^3-iodanes, which have never been synthesized. Without use of 18C6, the isolation and purification of these (Z)-(β-alkoxyvinyl)-λ^3-iodanes are very difficult, probably because of the facile anti-β-elimination [31] of the phenyl-λ^3-iodanyl group with remarkable nucleofugality [32].



Scheme 2. Reaction of the 1:1 complex **7** with nucleophiles.

1-Alkynyl(phenyl)-λ^3-iodanes **10a–c** also form a 1:1 complex **11a** or 2:1 complexes **11b** and **11c** with 18C6 [33]. Phenylethynyl(tetrafluoroborato)-λ^3-iodane **10c** is thermally labile and gradually decomposes even when it was preserved at −30 °C. Complexation with 18C6 dramatically increased the stability of phenylethynyl-λ^3-iodane **10c** in the solid state. Thus, no decomposition was observed when the 2:1 complex **11c** was left standing under ambient conditions for more than 10 days. The 1:1 **11a** and 2:1 complex **11b** are more stable and can be kept for over 1 month under ambient conditions without decomposition.



10a: R = n-C_8H_{17}
10b: R = t-Bu
10c: R = Ph

11a: **10a**·18C6
11b: $(\mathbf{10b})_2$·18C6
11c: $(\mathbf{10c})_2$·18C6

The X-ray crystal structure of the 2:1 complex **11b** (Fig. 6) illustrates that the iodine(III) contacts with three adjacent oxy-

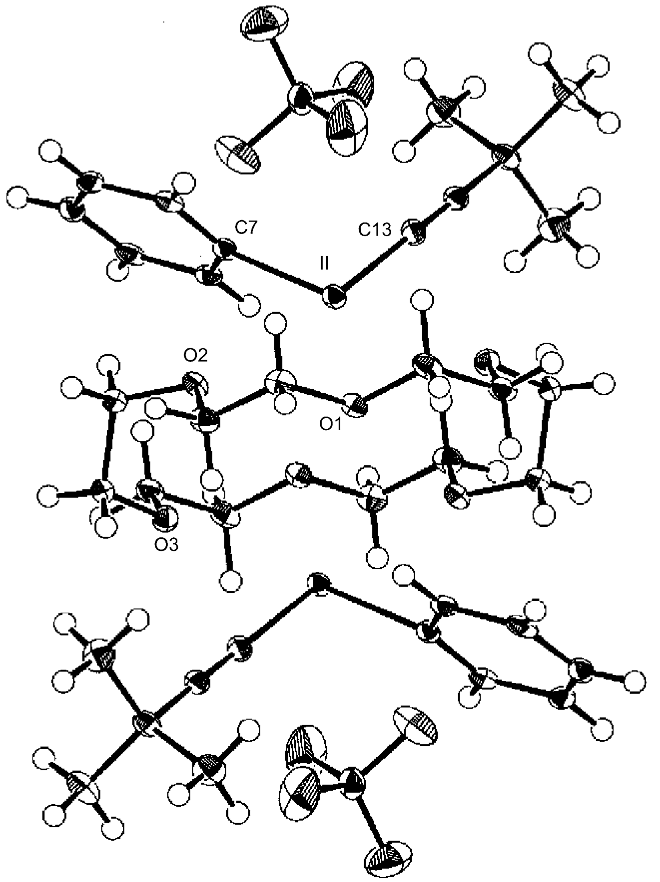


Fig. 6. ORTEP drawing of **11b**.

gen atoms (O1, O2, and O3*) of 18C6. The short I1···O2 and I1···O3* distances as well as the near-linear C7–I1···O3* and C13–I1···O2 triads are compatible with the hypervalent interactions. The other I1···O1 contact is weak and considerably deviates from linearity.

The CSI-MS spectrum for a 1:1 mixture of the λ^3-iodane **10a** and 18C6 in dichloromethane showed the most prominent ion peak of the 1:1 complex **11a**. The 1:1 stoichiometry for the complexation of **10a** in CD_2Cl_2 solution was confirmed from the Job plots by the ^{1}H NMR experiments. In contrast to the solid state structure of **11b**, showing the formation of 2:1 complex, Job plots for **10b** indicate the formation of 1:1 complex in solution. Similar results were observed for complexation of diphenyl(tetrafluoroborato)-λ^3-iodane (**4a**) with 18C6 [14]. The facile formation of the crystalline 2:1 complex **11b** is due to the limited solubility.

Compared to the binding efficacy of 18C6 to diphenyl-λ^3-iodane **4a** (Table 1, entry 1), both alkylethynyl-λ^3-iodanes **10a** (K_a: 2.40×10^4 M^{-1}) and **10b** (K_a: 1.38×10^4 M^{-1}) form more stable supramolecular complexes in CD_2Cl_2 and afford the binding constants of one order of magnitude greater. Because alkylethynyl groups are more efficient electron-withdrawing groups compared to phenyl group [34], the positive charge on the iodine(III) in alkylethynyl-λ^3-iodanes **10a** and **10b** seems to be greater than that in the diphenyl-λ^3-iodane **4a**, which in turn increases the binding constants between **10a** and **10b** and 18C6. Compared with phenyl group, the less sterically demanding nature of alkylethynyl groups will be also responsible for the increased stability of alkylethynyl-λ^3-iodane complex.

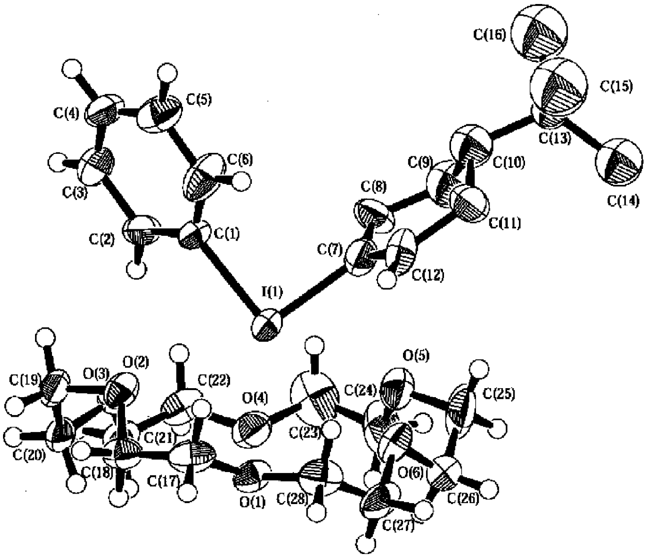
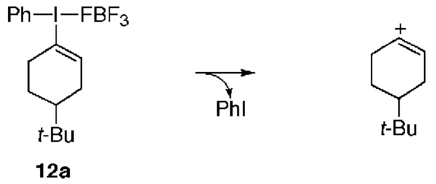


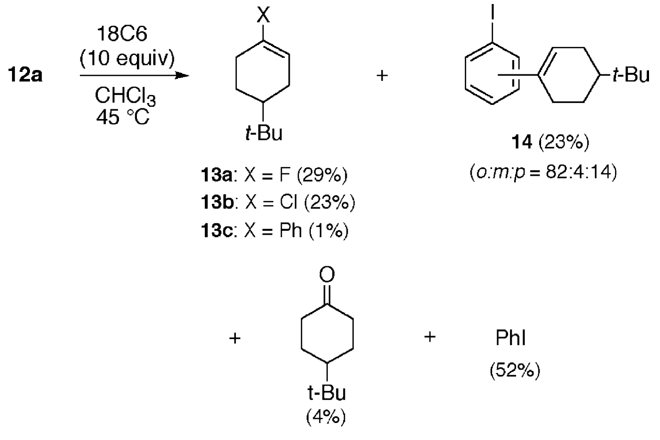
Fig. 7. ORTEP drawing of a 1:1 complex **12a**·18C6. BF_4 was omitted for clarity.

4-*tert*-Butyl-1-cyclohexenyl(phenyl)(tetrafluoroborato)-λ^3-iodane **12a** also forms a 1:1 supramolecular complex by the reaction with 18C6 through the hypervalent I(III)···O interactions in the solid state as well as in solution (Fig. 7) [35].

Solvolysis of λ^3-iodane **12a** in alcohol and aqueous solutions proceeds under mild conditions and generates a reactive 1-cyclohexenyl cation with the concomitant reductive elimination of iodobenzene (Scheme 3) [32]. The phenyl-λ^3-iodanyl group is an excellent nucleofuge with a leaving group ability of 10^6 times greater than the superleaving group triflate (TfO). The origin of this high nucleofugality of the phenyl-λ^3-iodanyl group is attributed to the involvement of an energetically favorable reduction of the hypervalent iodine(III) to the normal valency with octet structure during the leaving process [23a]. This process is also associated with an increase in entropy. Therefore, the phenyl-λ^3-iodanyl group is termed a hypernucleofuge [9d]. The phenyl-λ^3-iodanyl groups are the most efficient leaving groups that have been evaluated quantitatively. The high nucleofugality of phenyl-λ^3-iodanyl groups makes possible the unusual vinylic S_N2 displacement of β-alkylvinyl(phenyl)-λ^3-iodanes by the reaction with a wide range of nucleophiles [36]. Nucleophiles that undergo vinylic S_N2 reactions with (*E*)-(β-alkylvinyl)phenyl-λ^3-iodanes involve halides, dialkyl sulfides and selenides, phosphoroselenoates, dithiocarbamates, carboxylic acids, amides, and thioamides.



Scheme 3.



Scheme 4.

Thermolysis of **12a** in the presence of a large excess of 18C6 in chloroform at 45 °C resulted in a product profile shown in Scheme 4. Nucleophilic attack of tetrafluoroborate ion, chloroform, and iodobenzene to the initially generated 1-cyclohexenyl cation produces vinyl fluoride **13a** (29%), vinyl chloride **13b** (23%), and a mixture of vinylated iodobenzenes **14** (23%), respectively. Predominant formation of the *ortho* isomer of **14** indicates the intervention of an intimate ion–molecule pair of 1-cyclohexenyl cation and iodobenzene during the thermal decomposition [32].

The pseudo-first order rate constants k_{obsd} for the thermal decomposition of 1-cyclohexenyl-λ^3-iodane **12a** in the absence and presence of 18C6 at varying concentrations in chloroform are shown in Fig. 8. Interestingly, both acceleration and retardation of the rates were observed in the decomposition, depending upon the concentrations of added 18C6. At low concentrations of 18C6, a slight increase in the rates of decomposition of **12a** was detected as shown in the inset of Fig. 8; however, increased concentrations of 18C6 decreased the rates. A similar concentration dependence of the rates was also observed in the thermal decomposition of *p*-methylphenyl- (**12b**) and *p*-chlorophenyl(4-*tert*-butyl-1-cyclohexenyl)(tetrafluoroborato)-λ^3-iodane (**12c**).

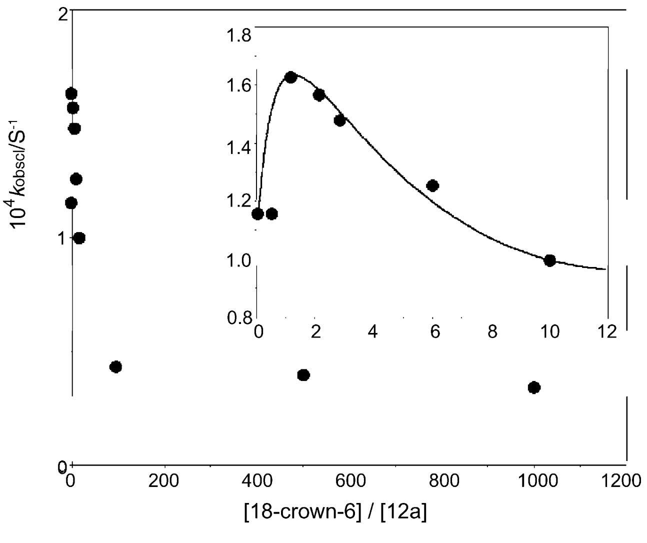
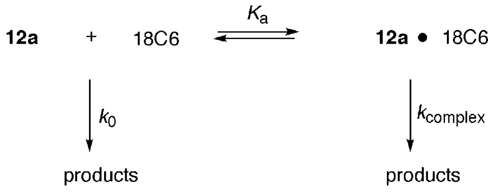


Fig. 8. Observed rate constants for thermal decomposition of **12a** (1×10^{-4} M) in the presence of 18C6 in $CHCl_3$ at 45 °C. The inset shows details at low concentrations of 18C6.



Scheme 5.

The association constant (K_a = ca. $3.3 \times 10^2\,\mathrm{M}^{-1}$) and the rate constant (k_{complex} = ca. $3.1 \times 10^2\,\mathrm{M}^{-5}\,\mathrm{s}^{-1}$) for the decomposition of the 1:1 complex in $CHCl_3$ were estimated according to the equation shown in Scheme 5. Comparison of k_{complex} with k_0 ($1.15 \times 10^{-4}\,\mathrm{s}^{-1}$) indicates that the leaving group ability of the phenyl-λ^3-iodanyl group was decreased by the complexation with 18C6 to about one-fourth.

The estimated association constant (K_a) is rather small and, therefore, at low concentrations of 18C6 the proportion of the 1:1 complex is quite small, which suggests that the effect of complexation with 18C6 on the decomposition rates would be negligible at the low concentrations of 18C6. It seems reasonable to assume that initial increase in the decomposition rates in Fig. 8 is presumably due to the increased polarity of the medium by the addition of 18C6.

Recently, we reported the first synthesis and characterization of 1-alkynyl(aryl)-λ^3-bromanes, which serve as excellent Michael acceptors and undergo tandem Michael-carbene rearrangements and/or tandem Michael-carbene insertions by the reaction with a variety of nucleophiles [37]. Alkynyl-λ^3-bromanes also form stable complexes with 18C6 and structure of the 2:1 complex **15** of *tert*-butylethynyl(phenyl)(tetrafluoroborato)-λ^3-bromane with 18C6 is shown in Fig. 9 [37a]. The complex adopts a distorted pen-

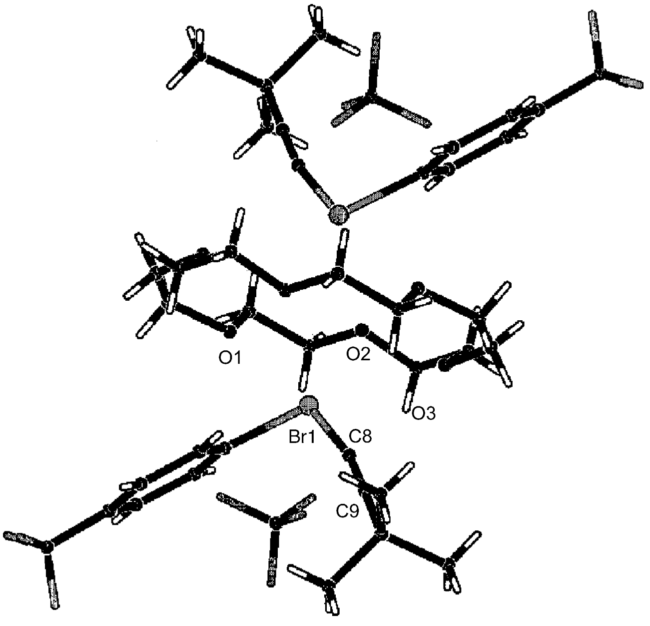
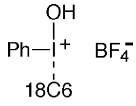


Fig. 9. Structure of the 2:1 complex **15**.

tagonal planar coordination about the bromine(III), in which the bromine atom contacts with the three adjacent oxygen atoms (O1–O3) of 18C6. Interestingly, the *tert*-butylethynyl ligand is not bound linearly to the bromine(III) with the Br1–C8–C9 angle of 167.3(4)°. The C8–C9 distance (1.211(6) Å) in **15** is considerably longer than the average triple bond length (1.181 Å) [15], which probably reflects an effective polarization of π-electrons of the triple bond caused by the positive partial charge on bromine(III). This long carbon–carbon triple bond length, combined with the strong electron-withdrawing nature of phenyl-λ^3-bromanyl group with a large Hammett substituent constant ($\sigma_p = 1.63$ for $PhBrBF_4$), makes the 1-alkynyl(aryl)-λ^3-bromanes highly efficient Michael acceptors.

4. Activated iodosylbenzene monomer complex

Iodosylbenzene (ISB), a versatile oxidizing agent, is a polymer bridged by hypervalent I(III)···O interactions [38], and hence essentially insoluble in all nonreactive organic solvents. In most of the oxidations with ISB, addition of Brønsted or Lewis acids is required to increase the activity through its depolymerization and/or its coordination to its oxygen atom. For instance, HBF_4-catalyzed reactions using ISB are believed to involve as a reactive species the generation of protonated iodosylbenzene monomer PhI^+OH [39]. Detailed structure of this reactive species, however, is unknown, because its isolation appears to be very difficult owing to the lack of the thermal stability. In fact, hydroxy(phenyl)(tetrafluoroborato)-λ^3-iodane $PhI(OH)BF_4$, generated from ISB by the reaction with HBF_4–Me_2O at −50 to 0 °C in dichloromethane, decomposes at room temperature within a few minutes to give a black tar.



$$\begin{array}{c} OH \\ | \\ Ph{-}I^{+} \quad BF_4^- \\ | \\ 18C6 \end{array}$$

16

Complexation with 18C6 dramatically increased the stability of the hydroxy-λ^3-iodane $PhI(OH)BF_4$. Reaction of ISB with HBF_4–Me_2O in the presence of equimolar 18C6 in dichloromethane afforded quantitatively the crystalline crown ether complex **16**, which is soluble in MeCN, MeOH, water, and dichloromethane, but not in less polar solvents (chloroform and diethyl ether). No decomposition of the complex **16** was detected when it was left standing under ambient conditions over 10 days. In solution, however, it gradually decomposes at room temperature with half-life times ($t_{1/2}$) of 6 h in CD_2Cl_2 and 25 h in CD_3CN. Interestingly, the complex is more stable in water ($t_{1/2} = 5$ days).

The characteristic IR absorption at 2471 cm^{-1} suggests the presence of a OH ligand on iodine(III) involved in strong hydrogen bonding [40]. CSI-MS taken in positive mode in MeCN at −20 °C revealed the prominent peak of the molecular ion $[PhIOH{\cdot}18C6]^+$. A base peak corresponding to $[PhIOMe{\cdot}18C6]^+$ observed in MeOH indicates the intervention of a facile ligand exchange of the hydroxy group on the iodine(III) by the solvent MeOH. X-ray analysis reveals a protonated ISB monomer structure **16**, which was stabilized by a close hypervalent interaction I1···O2, two weak contacts I1···O3 and I1···O4, and a strong intramolecular hydrogen bonding H1O···O5 of the hydroxy ligand on the iodine(III) (Fig. 10). The presumed highly acidic nature of H1O will be responsible for the pronounced hydrogen bonding [41].

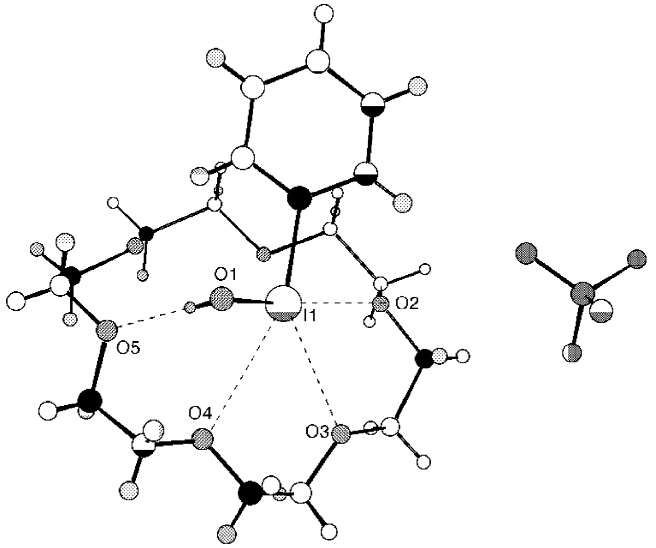
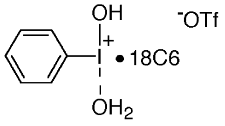


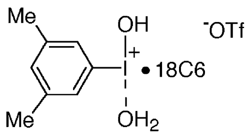
Fig. 10. ORTEP drawing of the complex **16**.

Upon dissolution in water, the Koser reagent [hydroxy(tosyloxy)iodo]benzene (**18**) undergoes ionization to give the hydroxy(phenyl)iodonium cation PhI^+OH [41], which was presumed to be ligated with at least one water molecule at an apical site of the iodine(III) atom. Iodosylbenzene is highly soluble in water at pH < 2.3, in which the aqua(hydroxy)iodonium ion $PhI^+(OH){\cdot}H_2O$ was also assumed to be a primary monomeric species [41].

Aqua complexes of λ^3-iodanes with a water molecule coordinated to iodine(III) are very unique and there are no well established precedents. We found that the reaction of (diacetoxyiodo)benzene (**3**) with TMSOTf in the presence of 18C6 in dichloromethane affords the aqua crown ether complex **17a** in high yield [42]. The aqua complex **17b** was also prepared from 3,5-dimethyl(diacetoxyiodo)benzene. The complex **17a** is stable in the solid state as well as in solution: no decomposition was detected when it was left standing under ambient conditions over 10 days. In water, the half-life time ($t_{1/2}$) at room temperature was found to be over 50 days.



17a



17b

X-ray analysis of **17a** (Fig. 11) illustrates a T-shaped structure, ligated with one water molecule at the apical site of the iodine(III) of hydroxy(phenyl)iodonium ion, with a near-linear O1–I1–O2 triad (173.96°). Including a close contact with one of the crown ether oxygens, O7, the complex adopts a distorted square planar geometry around the iodine.

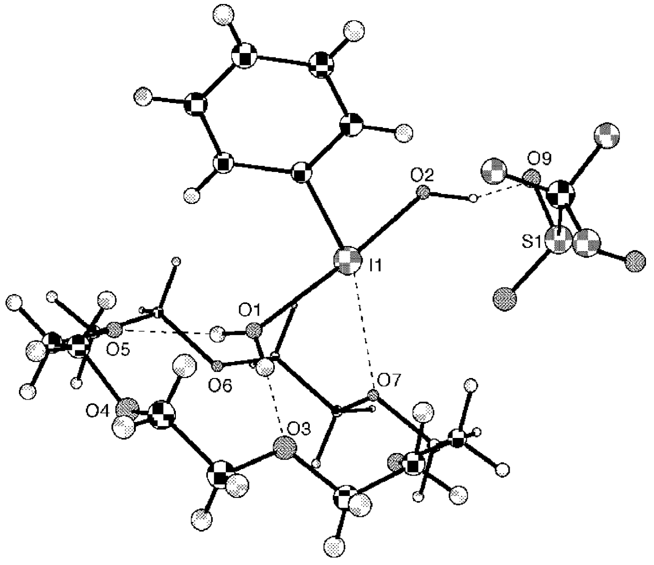
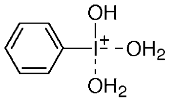


Fig. 11. Structure of the aqua complex **17a**.

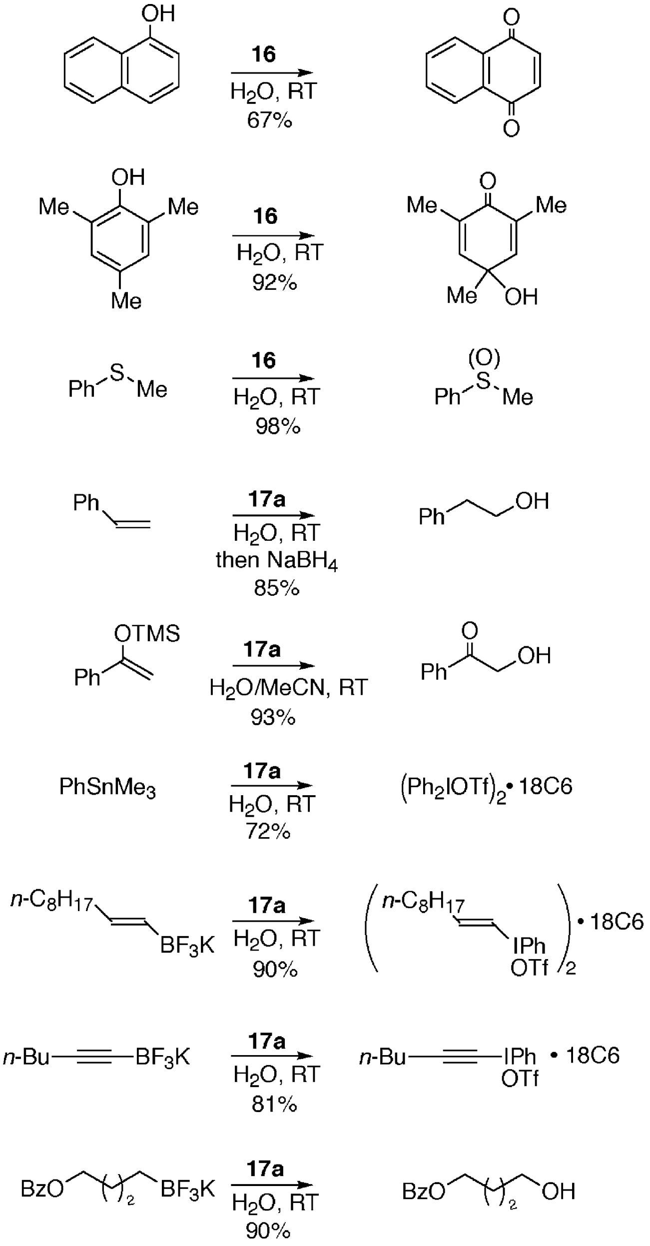
The linear O1–I1–O2 hypervalent bonding in **17a** is highly unsymmetrical, as observed in polymeric ISB (2.04 and 2.38 Å) [38]: the hydroxy ligand in **17a** is tightly bound to the iodine(III), while the water ligand is loosely bound. Scheme 6 depicts the degrees of unsymmetrical nature of the hypervalent bonding in the hydroxy-λ^3-iodanes, in which HO–I bond distances (a) increase in this order: interestingly, the other I–O distances (b) inversely decrease in the order.



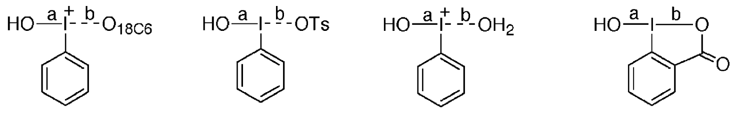
20

Based on the structure of **17a** (Fig. 11), a monomeric species of ISB in an aqueous acidic solution is assumed to be a tetracoordinated square planar iodonium ion **20**, in which each water molecule coordinates to the iodine(III) through hypervalent contacts.

Both the hydroxy-λ^3-iodane complex **16** and the aqua complex **17** serve as versatile oxidizing agents. The reactions shown in Scheme 7 illustrate a broad range of their utility. It is noted that these complexes function as efficient oxidizing agents especially in water, because of both the moderate solubility and the excellent stability in water. Thus, oxidation of 1-naphthol and 2,4,6-trimethylphenol with **16** in water afforded naphthoquinone and *p*-quinol in good yields. Thioanisole gave the corresponding sulfoxide with no evidences for formation of methyl phenyl sulfone. Oxidation of styrene with the aqua complex **17** in water produced phenylacetaldehyde and after reduction with $NaBH_4$ 2-phenylethanol was obtained in 85% yield. Reac-



Scheme 7. Reaction of the hydroxy-λ^3-iodane complexes **16** and **17a** in water under nitrogen.



	16		**18**		**17a**		**19**
bond a (Å):	1.937(2)	<	1.940(4)	<	1.967(2)	<	2.00
bond b (Å):	2.598(2)	>	2.473(3)	>	2.392(2)	>	2.30

Scheme 6. Distances of hypervalent HO–I· · ·O bondings in hydroxyiodanes.

tion of a silyl enol ether in MeCN–water afforded α-hydroxy ketone. Exposure of phenyl(trimethyl)stannane to **17a** in water at room temperature resulted in the facile ligand exchange on iodine(III) and afforded the diphenyl-λ^3-iodane·18C6 complex [14]. Similarly, borate-λ^3-iodane exchange of 1-alkenyl- and 1-alkynyl(trifluoro)borates produced the corresponding 1-alkenyl-λ^3-iodane and 1-alkynyl-λ^3-iodane·18C6 complexes in high yields [33,43]. On the other hand, the reaction with alkyl(trifluoro)borates resulted in the introduction of a hydroxyl group yielding a primary alcohol. All of these reactions proceed smoothly without further activation of the complexes **16** and **17a** by adding an external acid catalyst.

5. Conclusions

Crown ethers bind metal cations through ion–dipole electrostatic interactions, while hydrogen bonding is a driving force for the complexation with a variety of organic molecules with acidic hydrogens, such as onium ions (ammonium, sulfonium, phosphonium, and hydronium ions) and neutral molecules (MeCN, $MeNO_2$, Me_2SO_2, and $CHCl_3$ having polar C–H bonds). In addition to these well-known driving forces for the complexation, we found that, as a new binding force, the hypervalent interaction plays an essential role in the complexation between crown ethers and hypervalent compounds. As in the case of hydrogen bonding, the hypervalent interaction is highly directional in nature with a preferred linear orientation.

In general, the complexation of hypervalent organo-λ^3-iodanes and λ^3-bromanes with crown ethers through hypervalent interactions increases in their thermal stability as well as in solubility toward water, which makes the environmentally friendly organo-λ^3-iodanes more useful oxidizing agents. Thus, complexation with 18-crown-6 makes it possible to synthesize and to isolate the activated iodosylbenzene monomers PhI^+OH and $PhI^+(H_2O)OH$, which serve as versatile oxidizing agents especially in water. We expect that this new methodology will provide us an enough chance to develop a new type of hypervalent organo-λ^3-iodane.

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