ChemPubSoc Europe

DOI: 10.1002/chem.201304961

CHEMISTRY A European Journal Full Paper

Synthetic Methods

Reactivity of Hydroxy- and Aquo(hydroxy)-λ³-iodane–Crown Ether Complexes

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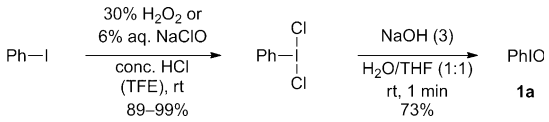
Abstract: We have designed a series of hydroxy(aryl)-λ³-iodane–[18]crown-6 complexes, prepared from the corresponding iodosylbenzene derivatives and superacids in the presence of [18]crown-6, and have investigated their reactivities in aqueous media. These activated iodosylbenzene monomers are all non-hygroscopic shelf-storable reagents, but they maintain high oxidizing ability in water. The complexes are effective for the oxidation of phenols, sulfides, olefins, silyl enol ethers, and alkyl(trifluoro)borates under mild conditions. Furthermore, hydroxy-λ³-iodane–[18]crown-6 complexes serve as efficient progenitors for the synthesis of diaryl-, vinyl-, and alkynyl-λ³-iodanes in water. Other less polar organic solvents, such as methanol, acetonitrile, and dichloromethane, are also usable in some cases.

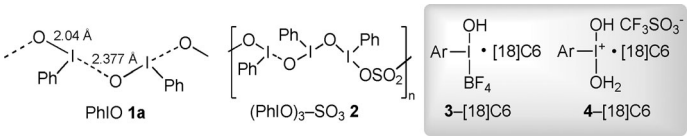
Introduction

Iodosylbenzene (PhIO) (**1a**), a non-volatile pale-yellow amorphous powder, has limited use in modern synthetic organic chemistry and in biomolecular chemistry, despite the fact that it displays potentially high oxidizing ability and chemoselectivity.[1] This is due, at least in part, to its high cost (26 US$/g, TCI America Co. Ltd.) and poor solubility (see below). Recent developments in the methodologies for the synthesis of **1a** have greatly alleviated the former hindrance: synthesis of **1a** from iodobenzene no longer requires expensive reagents or special techniques (Scheme 1).[2]



Scheme 1. Two-step convenient synthesis of iodosylbenzene **1a** from iodobenzene.

In 1994, X-ray powder diffraction and extended X-ray absorption fine structure analysis revealed that the structure of **1a** is a μ-oxo-bridged polymer with a secondary hypervalent I···O bond of 2.377(12) Å (Scheme 2).[3] Recently, Zhdankin and co-workers synthesized $(PhIO)_3{\cdot}SO_3$ (**2**), a partially clipped out analogue of iodosylbenzene, the structure of which was unequivocally confirmed by X-ray crystal structure analysis; the μ-oxo-bridged chain and the T-shaped geometry around the iodine(III) center were seen to be maintained.[4] Because of its polymeric structure, iodosylbenzene (**1a**) is essentially insoluble in most non-reactive organic solvents, a feature that limits its utility in synthetic organic chemistry. Thus, in most oxidation reactions using **1a**, activation with a Brønsted or Lewis acid is required to enhance the solubility as well as the oxidizing power.[1]



Scheme 2. Structures of iodosylbenzene and its derivatives.

Recently, we have found that some iodosylbenzene monomers, namely hydroxy(phenyl)-λ³-iodane (**3**) and aquo(hydroxy)(phenyl)-λ³-iodane (**4**), form discrete complexes with [18]crown-6 ([18]C6) through hypervalent interactions between the iodine(III) atom and the oxygen atoms of [18]C6.[5] Complexation with [18]C6 dramatically increases the thermal stabilities of **3** and **4**, yet their high reactivities in various organic solvents and water are maintained.[5,6]

We report herein the improved synthesis and reactivity of activated iodosylbenzene equivalents, namely hydroxy- and aquo(hydroxy)-λ³-iodane–[18]C6 complexes **3**–[18]C6, **4**–[18]C6,

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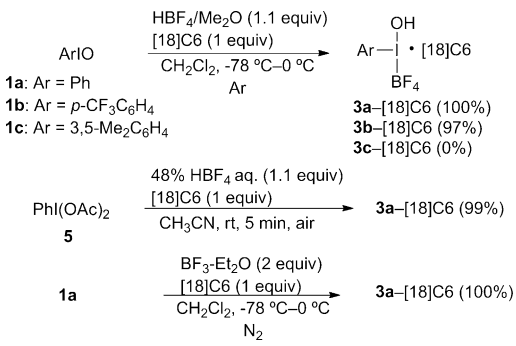
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304961.

and **8**–[18]C6. These complexes are fairly stable in the solid state at room temperature, but serve as excellent oxidants even in water. In addition, they function as pivotal progenitors for diaryl-, vinyl-, and alkynyl-λ^3-iodane–[18]C6 complexes under mild reaction conditions.

Results and Discussion

The synthetic methods for hydroxy(aryl)-λ^3-iodane–[18]C6 complexes (**3**–[18]C6) are straightforward. Thus, treatment of iodosylarenes **1a** and **1b** with HBF_4·Me_2O in the presence of 1 equivalent of [18]C6 in dichloromethane at low temperature (−78 °C to 0 °C) results in a smooth ligand-exchange reaction on the iodine(III) atom, yielding hydroxy(aryl)-λ^3-iodane–[18]C6 complexes (**3**–[18]C6) in almost quantitative yields, whereas the attempted synthesis of a hydroxy-λ^3-iodane complex with electron-donating 3,5-Me_2 groups (**3c**–[18]C6) was found to be fruitless (Scheme 3). Notably, the use of (diacetoxyiodo)benzene (**5**) and 48% aqueous tetrafluoroboric acid also produced **3a**–[18]C6 in 99% yield. This method seems to be the more practical alternative, because the reaction does not require low temperature or anhydrous conditions. Interestingly, the use of 2 equivalents of BF_3·Et_2O, instead of tetrafluoroboric acid, resulted in the formation of **3a**–[18]C6 in 100% yield. BF_3·Et_2O-catalyzed oxidation reactions employing iodosylbenzene (**1a**) have been proposed to involve the zwitterionic species [PhI^+·OBF_3^-].[1,7] In this case, ligand exchange at the iodine(III) center by external water should be a facile process, producing the hydroxy(phenyl)-λ^3-iodane complex **3a**–[18]C6.



Scheme 3. Synthesis of hydroxy(aryl)-λ^3-iodane–[18]C6 complexes.

Hydroxy(phenyl)-λ^3-iodane **3a**, with the poorly nucleophilic tetrafluoroborato ligand, has been considered to be too unstable to be isolated,[5] probably because of the high electrophilicity of the iodine(III) atom. In contrast, the complexes **3a**–[18]C6 and **3b**–[18]C6 can be kept indefinitely at −20 °C and no decomposition was detected even when they were left to stand in air at ambient temperature for more than a week. Complexes **3a**–[18]C6 and **3b**–[18]C6 are soluble in acetone, acetonitrile, and methanol, and sparingly soluble in dichloromethane and water, but insoluble in the less polar solvents chloroform, diethyl ether, and hexane. At room temperature, the half-life ($t_{1/2}$) of a solution of **3a**–[18]C6 in CD_3CN was found to be 25 h, whereas that of complex **3b**–[18]C6 was found to be somewhat shorter ($t_{1/2}$ = 8 h). Moreover, the complexes showed good stability in D_2O ($t_{1/2}$ = 5 days for **3a**–[18]C6; 7 days for **3b**–[18]C6). In the ^1H NMR spectra of **3a**,**b**–[18]C6 in CD_3CN, downfield shifts of the methylene singlet of [18]C6 were observed for both complexes ($\Delta\delta$ = 0.13 ppm for **3a**–[18]C6; 0.15 ppm for **3b**–[18]C6). In contrast, the ^{13}C resonance of [18]C6 at δ = 71.2 ppm is shifted to higher field (δ = 70.7 ppm for **3a**–[18]C6; 70.6 ppm for **3b**–[18]C6), probably because of the shielding effect of the aryl groups.[8] These results suggested that the hydroxy-λ^3-iodanes **3** were tightly coordinated to [18]C6 in CD_3CN. Further evidence for complexation in acetonitrile was obtained by cold-spray ionization mass spectrometry (CSI-MS).[9] Thus, CSI mass spectra of both complexes **3**–[18]C6 in MeCN clearly revealed the strong ion peaks of [(**3a** + [18]C6) − BF_4^-]$^+$ at *m/z* 485 and [(**3b** + [18]C6) − BF_4^-]$^+$ at *m/z* 553 (Figure 1).

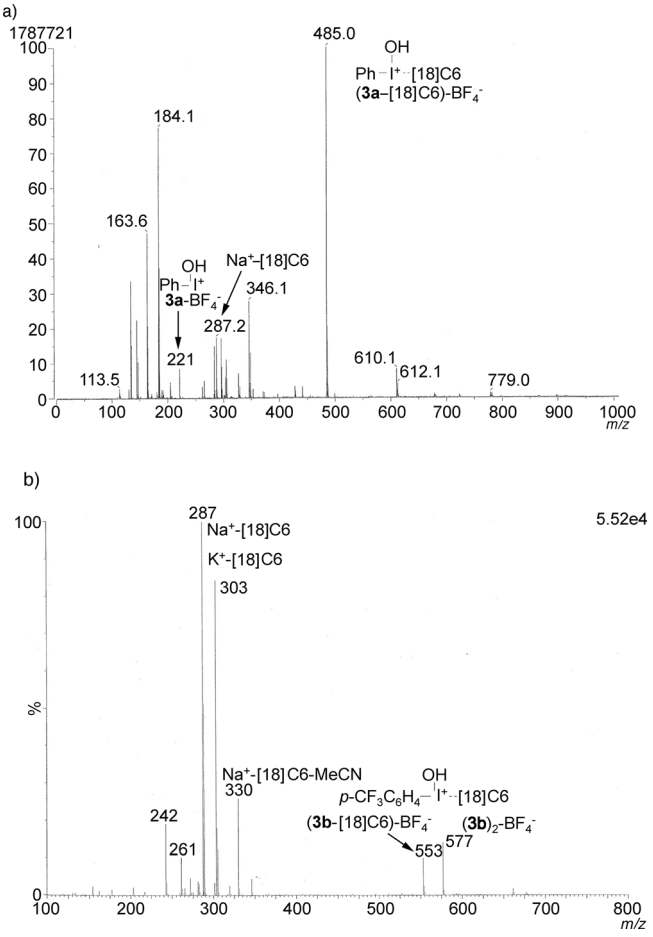
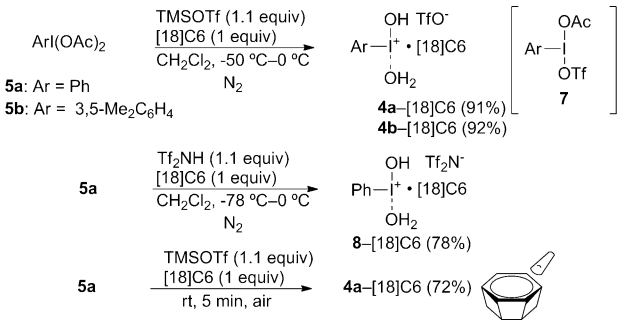


Figure 1. CSI mass spectra of complexes: a) **3a**–[18]C6 and b) **3b**–[18]C6 in MeCN.

Hydroxy-λ^3-iodane with one of the least nucleophilic of oxygen ligands, triflato, has been synthesized by the reaction of PhIO (**1a**) or $PhI(OAc)_2$ (**5**) with TfOH and is widely used for versatile oxidative transformations.[10] However, hydroxy(phenyl)(triflato)-λ^3-iodane (**6**) is a highly hygroscopic compound and hence needs to be carefully handled under anhydrous conditions.[10c] Interestingly, when **5** was treated with tri-

methylsilyl trifluoromethanesulfonate (triflate; 1.1 equiv) in the presence of [18]C6 (1 equiv) in dichloromethane at low temperature (−50 °C to 0 °C) under nitrogen, smooth ligand exchange at the iodine(III) center took place to produce aquo(hydroxy)(phenyl)(triflato)-λ^3-iodane–[18]C6 complex (**4a**–[18]C6) in high yield (91%) (Scheme 4).[5b] Complex **4b**–[18]C6



Scheme 4. Synthesis of aquo(hydroxy)-λ^3-iodane–[18]C6 complexes.

was also obtained in a similar manner from 3,5-dimethyl(diacetoxyiodo)benzene (**5b**) in 92% yield. Use of bis(trifluoromethylsulfonyl)imide (1.1 equiv), instead of trimethylsilyl triflate, resulted in a 78% yield of aquo(hydroxy)(phenyl)[bis(triflyl)imido]-λ^3-iodane–[18]C6 complex (**8**–[18]C6). It should be noted that complex **4a**–[18]C6 could also be readily prepared in good yield (72%) by a solvent-free procedure that involved grinding $PhI(OAc)_2$ (**5**) in an agate mortar with trimethylsilyl triflate and [18]C6 at ambient temperature in air[11] (Scheme 4). Neither the transient intermediate, acetoxy(phenyl)(triflato)-λ^3-iodane (**7**), nor its [18]C6 complex could be isolated. This is probably because **7** bears moderately and weakly *trans*-influencing ligands, acetoxy and triflato, at the iodine(III) center.[12] This is an unfavorable pairing, and is responsible, at least in part, for the driving force for the facile ligand exchange with the more preferable hydroxy and water ligands at the iodine(III) center.

The three complexes **4a**,**b**–[18]C6 and **8**–[18]C6 are fairly stable, non-hygroscopic solids. They can be stored at room temperature in air for at least 10 days. Complexes **4a**,**b**–[18]C6 and **8**–[18]C6 are broadly soluble in common organic solvents, including chloroform, dichloromethane, acetonitrile, ethyl acetate, acetone, and methanol, as well as in water, but are insoluble in the less polar solvents diethyl ether and hexane. Solutions of **4a**–[18]C6, **4b**–[18]C6, and **8**–[18]C6 in $CDCl_3$ at room temperature were found to have half-lives ($t_{1/2}$) of 12 days, 21 days, and 3 days, respectively. Interestingly, complexes **4a**–[18]C6 and **8**–[18]C6 were found to be more stable in D_2O ($t_{1/2}$ = 50 days for **4a**–[18]C6; 23 days for **8**–[18]C6). The increased stabilities in water are probably due to the higher electron-donor ability of the water molecule to the iodine(III) atom. In the ^{1}H NMR spectra of **4**–[18]C6 and **8**–[18]C6 in CD_3CN, small downfield shifts of the methylene singlet of [18]C6 were observed, whereas the ^{13}C NMR signals for [18]C6 were shifted to higher field (Table 1). These shifts are comparable to those observed for hydroxy-λ^3-iodane–[18]C6 complexes (**3**–[18]C6). Firm evidence for association in solution was obtained by mass spectrometry. CSI mass spectra of complexes **4**–[18]C6 and **8**–[18]C6 measured in MeCN at below room temperature revealed strong ion peaks of $[(\mathbf{4a}+[18]C6)-H_2O-TfO^-]^+$ at *m/z* 485, $[(\mathbf{4b}+[18]C6)-H_2O-TfO^-]^+$ at *m/z* 513, and $[(\mathbf{8}+[18]C6)-H_2O-TfO^-]^+$ at *m/z* 485. Interestingly, no water molecules were included in these ions. The results suggest that the coordination of a water molecule to the iodine(III) atom is less strong than that of [18]C6 in MeCN solution.

Table 1. ^{1}H and ^{13}C NMR chemical shifts of [18]C6 in complexes and *m/z* of related molecular ions observed in CSI mass spectra.

Complex	$\delta_{[18]C6}$ [ppm][a]		*m/z*[b] $[M-X]^+$
	^{1}H NMR	^{13}C NMR	
–	3.51	71.2	–
3a–[18]C6	3.64	70.7	485 ($X=BF_4^-$)
3b–[18]C6	3.66	70.6	553 ($X=BF_4^-$)
4a–[18]C6	3.69	70.8	485 ($X=TfO^-+H_2O$)
4b–[18]C6	3.58	70.9	513 ($X=TfO^-+H_2O$)
8–[18]C6	3.57	70.7	485 ($X=Tf_2N^-+H_2O$)

[a] In CD_3CN at 5–10 mM. [b] In CSI mass spectra measured in positive mode in MeCN at below room temperature.

The solid-state structure of **8**–[18]C6 (Figure 2), obtained by recrystallization from ethyl acetate/diethyl ether at −20 °C, revealed a T-shaped motif, with one molecule of water coordinated at the apical site of the iodine(III) center of the hydroxy(phenyl)iodonium ion with a near-linear O1-I1-O2 triad (174.43°).[13] There is also a close contact between one of the crown ether oxygen atoms, O3, and the iodine atom, I1. The complex adopts a square-planar geometry about the iodine atom. A root-mean-square deviation of 0.048 Å was observed for I1, O1, O2, O3, and C1 from their least-squares plane, and the sum of the iodine-centered bond angles $\Sigma^\circ I = 359.8^\circ$. The hypervalent O1-I1-O2 bonding is highly unsymmetrical, as ob-

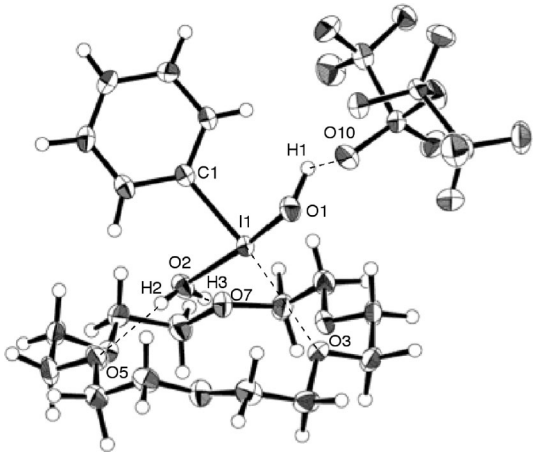
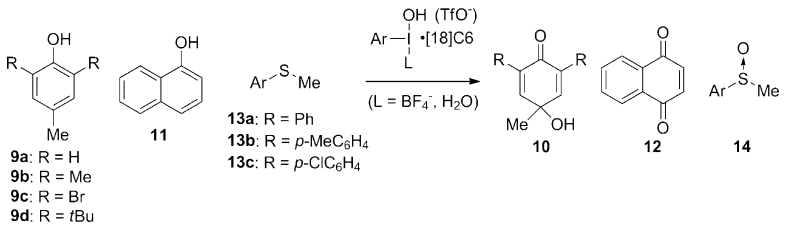


Figure 2. ORTEP drawing of **8**–[18]C6 with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: I1–C1 2.106(6), I1–O1 1.955(5), I1–O2 2.381(5), I1···O3 2.893(4), O10···H1 1.819, O5···H2 1.968, O7···H3 1.810; C1-I1-O1 92.8(2), C1-I1-O2 82.00(18), O1-I1-O2 174.43(16).

served in the structure of **4a**–[18]C6.[5b] The hydroxy ligand is engaged in strong hydrogen bonding with the bis(triflyl)imide anion (H1···O10 1.819 Å), which is probably due to its highly acidic nature ($pK_a = 4.3$).[14] In addition, the ligated water molecule also interacts with two oxygen atoms of [18]C6 through hydrogen bonds (O5···H2 and O7···H3). All of these close contacts are responsible for the enhanced thermal stability of the complexes. The coordination behavior of **4a**–[18]C6 and **8**–[18]C6 seemed to suggest that the structure of the iodosylbenzene monomer in aqueous acid should be a tetracoordinate square-planar hydroxy(phenyl)iodonium ion with two molecules of water coordinated through hypervalent bonding.[15]

Since these hydroxy- and aquo(hydroxy)-λ^3-iodane–[18]C6 complexes are fairly soluble in water, they serve as versatile oxidizing agents in aqueous media. The oxidation of phenols proceeds smoothly at below room temperature. Exposure of 4-methylphenol (**9a**) to **3a**–[18]C6 (1.2 equiv) in water at 0 °C, followed by gradual warming to room temperature, resulted in the formation of *p*-quinol **10a** in 97% yield (Table 2, entry 1).[1a,16] Use of complex **4a**–[18]C6 also proved to be effective (entry 2). Phenols *ortho*-disubstituted with methyl and bromo groups also served as good substrates. Thus, mesitol (**9b**) and 2,6-dibromo-4-methylphenol (**9c**) cleanly produced the corresponding *p*-quinols in good to high yields (entries 3–5). Because of its poor solubility in water, 2,6-di-*tert*-butylphenol (**9d**) was inert under similar conditions (entry 6). However, the use of MeCN as a co-solvent dramatically improved the yield of *p*-quinol **10d** to 79% (entry 7). 1-Naphthol (**11**) selectively afforded 1,4-naphthoquinone when treated with 2.1 equivalents of **3a**–[18]C6 (entry 8).[17] In this case, the use of acetonitrile slightly increased the yield (entry 9). The oxidation of thioanisole with **3a**–[18]C6 or **4a**–[18]C6 proceeded smoothly in water and selectively afforded methyl phenyl sulfoxide in high yields (entries 10 and 11).[18] No formation of methyl phenyl sulfone was observed. Other thioanisoles **13b** and **13c**, bearing electron-donating and electron-withdrawing groups, were also selectively oxidized to sulfoxides **14b** and **14c** in a similar manner (entries 12 and 13).

Table 2. Oxidation of phenols and sulfides with activated iodosylbenzene monomer–[18]C6 complexes.[a]



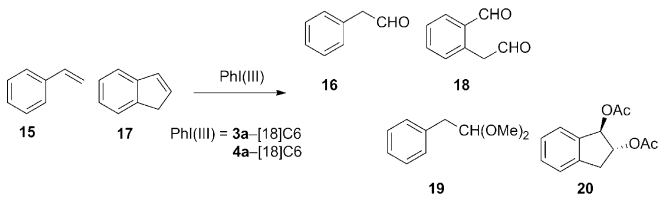
Entry	Substrate	Complex	Solvent	Product	Yield [%][b]
1	**9a**	**3a**–[18]C6	H_2O	**10a**	97
2	**9a**	**4a**–[18]C6	H_2O	**10a**	87
3	**9b**	**3a**–[18]C6	H_2O	**10b**	92
4	**9c**	**3a**–[18]C6	H_2O	**10c**	85
5	**9c**	**4b**–[18]C6	H_2O	**10c**	68
6	**9d**	**3a**–[18]C6	H_2O	**10d**	0
7	**9d**	**3a**–[18]C6	MeCN/H_2O (3:1)	**10d**	79
8[c]	**11**	**3a**–[18]C6	H_2O	**12**	68
9[c]	**11**	**3a**–[18]C6	MeCN/H_2O (2:1)	**12**	75
10[d]	**13a**	**3a**–[18]C6	H_2O	**14a**	98
11[d]	**13a**	**4a**–[18]C6	H_2O	**14a**	93
12[d]	**13b**	**3a**–[18]C6	H_2O	**14b**	90
13[d]	**13c**	**3a**–[18]C6	H_2O	**14c**	89

[a] Unless otherwise noted, the reaction was carried out using 0.02 M complex (1.2 equiv) in water or in water/MeCN at 0 °C to room temperature for 3 h. [b] Isolated yields. [c] 2.1 equiv. of **3a**–[18]C6 was used. [d] Reactions were carried out at room temperature.

It is well known that hypervalent λ^3-iodanes with two heteroatom ligands can be used for oxidative 1,2- and/or 1,1-difunctionalization of carbon-carbon double bonds.[1a,19] However, to the best of our knowledge, no reports of oxidative difunctionalization of olefins in water have appeared in the literature, probably because of poor solubility of the substrates and/or the λ^3-iodanes in water. Our complexes could serve as versatile oxidizing agents for various olefins in water (Table 3). The oxidation of styrene (**15**) with **3a**–[18]C6 or **4a**–[18]C6 produced phenylacetaldehyde (**16**) in high yields (Table 3, entries 1 and 2), and the oxidation of indene (**17**) with 2 equivalents of **3a**–[18]C6 gave homophthalaldehyde (**18**) in 76% yield (entry 3).[15] The former oxidation presumably proceeds through oxy-λ^3-iodanylation followed by 1,2-rearrangement of the phenyl group, whereas the latter oxidative cleavage of the double bond probably proceeds through 1,2-dihydroxylation of the olefin followed by glycol fission mediated by the λ^3-iodane.[1a,19] Other solvents also serve as good nucleophiles. Thus, the use of methanol as solvent afforded the rearranged acetal **19** (entries 4 and 5). In acetic acid, **17** gave *trans*-diacetate **20** with 90% stereoselectivity, probably through facile S_N2 reaction of a cyclic acetoxonium ion intermediate (entry 6).[20]

3a–[18]C6 functions as a selective oxygen atom donor toward ketones. Reaction of β-ketoester **21** with **3a**–[18]C6 in water at room temperature quantitatively afforded the corresponding α-hydroxy-β-ketoester **22** (Table 4, entry 1). Treatment of acetophenone (**23**) with **3a**–[18]C6 in acetonitrile/H_2O (3:1) at 45 °C produced α-hydroxyacetophenone (**24**) in moderate yield (entry 2). These results indicate that a keto–enol equilibrium exists under the reaction conditions, and that the in situ generated enol presumably reacts with **3a**–[18]C6 to give an α-iodanylketone intermediate,[21] which then undergoes S_N2 reaction with water. Silyl enol ether **26** was found to be a better substrate. Thus, oxidation of **26** in water with **3a**–[18]C6 afforded **24** in 58% yield, accompanied by the coupling product, 1,4-diketone **27**, in 24% yield (entry 3).[22] The use of acetonitrile as a co-solvent increased the yield of **24** (entries 4 and 5). It is interesting to note that 1,4-diketone **27** was obtained in 62% yield as the predominant product in dichloromethane (entry 6). Use of **8**–[18]C6, instead of **3a**–[18]C6, increased the yield to 88% (entry 7). Silyl enol ether **28** selectively afforded α-hydroxycy-

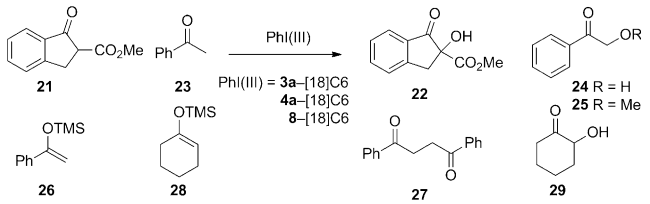
Table 3. Oxidative transformation of olefins with activated iodosylbenzene monomer–[18]C6 complexes.[a]



Entry	Olefin	Complex	Solvent	*T* [°C]	Product	Yield [%][b]
1	**15**	**3a**–[18]C6	H_2O	rt	**16**	98[c]
2	**15**	**4a**–[18]C6	H_2O	rt	**16**	85[c]
3[d]	**17**	**3a**–[18]C6	H_2O	rt	**18**	76[c]
4	**15**	**3a**–[18]C6	MeOH	0–rt	**19**	73
5	**15**	**4a**–[18]C6	MeOH	0–rt	**19**	90
6[e]	**17**	**3a**–[18]C6	AcOH	16	**20**	89[f]

[a] Unless otherwise noted, the reaction was carried out using 0.02 M complex (1.2 equiv) in water or other solvent for 1–3 h. [b] Isolated. [c] Isolated after reduction with $NaBH_4$. [d] 2.1 equiv of **3a**–[18]C6 was used. [e] Ac_2O (5 equiv) was used as an additive. [f] The *cis*-isomer of **20** was also produced as a contaminant (10%).

Table 4. Oxidative transformation of ketones and silyl enol ethers with activated iodosylbenzene monomer–[18]C6 complexes.[a]



Entry	Substrate	Complex	Solvent	*T* [°C]	Product: Yield [%][b]
1	**21**	**3a**–[18]C6	H_2O	rt	**22**: 100
2	**23**	**3a**–[18]C6	MeCN/H_2O (3:1)	45	**24**: 43
3	**26**	**3a**–[18]C6	H_2O	rt	**24**/**27**: 58/24
4	**26**	**3a**–[18]C6	MeCN/H_2O (3:1)	0	**24**: 73
5	**26**	**4a**–[18]C6	MeCN/H_2O (3:1)	0	**24**: 93
6[c]	**26**	**3a**–[18]C6	CH_2Cl_2	−78 to 0	**27**: 62
7	**26**	**8**–[18]C6	CH_2Cl_2	−78 to 0	**27**: 88
8	**28**	**3a**–[18]C6	MeCN/H_2O (3:1)	0	**29**: 63(91)
9	**26**	**3a**–[18]C6	MeOH	−70 to 0	**25**: 80
10	**26**	**4a**–[18]C6	MeOH	−70 to 0	**25**: 87

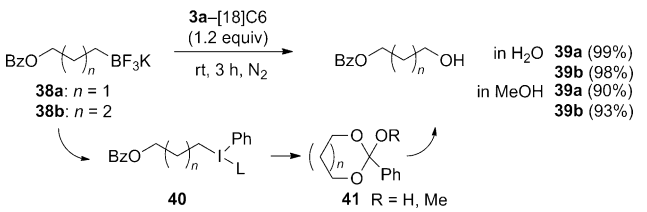
[a] Unless otherwise noted, the reaction was carried out using 0.02 M complex (1.2–1.5 equiv) in water or other solvent for 1–3 h. [b] Isolated yields. Figure in parentheses is the ^{1}H NMR yield. [c] 3 equiv of **26** was used.

clohexanone (**29**) (entry 8). In methanol, silyl enol ether **26** produced α-methoxyacetophenone (**25**) in high yields (entries 9 and 10).[16a,23]

These complexes provide convenient routes for the synthesis of diverse diaryl-, 1-alkenyl(phenyl)-, and 1-alkynyl(phenyl)-λ^3-iodanes complexed with [18]C6 (Table 5). Treatment of phenyl(trimethyl)tin (**30**) with **3a**–[18]C6 and **4a**–[18]C6 in water at room temperature resulted in ligand exchange at the iodine(III) center to afford diphenyl-λ^3-iodane–[18]C6 complexes **33** in high yields (entries 1 and 2).[1a] Phenylboronic acid (**31**) as well as potassium phenyl(trifluoro)borate (**32**) also serve as good phenyl group donors, but they require activation with 3 equivalents of BF_3·Et_2O (entries 3 and 4).[24] The boron-λ^3-iodane ligand-exchange methodology can be extended to 1-alkenyl(trifluoro)borates **34a**,**b** as well as 1-alkynyl(trifluoro)borates **36a**,**b** (entries 5–13). It is worth noting that activation with BF_3·Et_2O was not essential for these transformations: for example, ligand exchange of borate **36a** with **3a**–[18]C6 proceeded in high yield without BF_3·Et_2O (entry 8), although a slightly better yield was obtained in the presence of BF_3·Et_2O (entry 9).

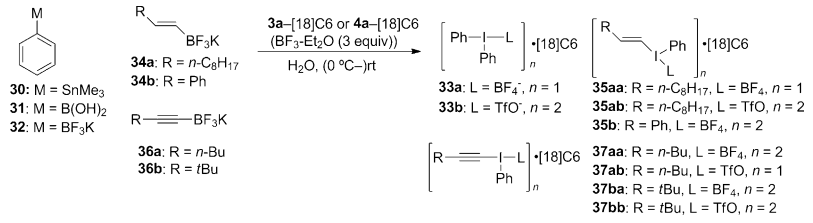
The boron-λ^3-iodane ligand exchange could be extended to potassium 1-alkyl(trifluoro)borates **38a**–**c**; thus, treatment of **38** with **3a**–[18]C6 resulted in the formation of the corresponding alcohols **39** in high yields (Scheme 5). Interestingly, when the reactions were carried out in methanol in the presence of 3 Å molecular sieves, the same products, alcohols **39**, were obtained, rather than the alkyl methyl ether. The reaction probably involves the initial formation of alkyl-λ^3-iodane **40**, which would undergo intramolecular S_N2 reaction with the ω-benzoate ester to form cyclic intermediate **41**,[25] followed by hydrolysis during the work-up process, resulting in the formation of alcohols **39**.

The reactivity of hydroxy-λ^3-iodane–[18]C6 complexes was found to be affected by the solvent nucleophilicity. Thus, 1-decynyl(trimethyl)silane **42** did not react with **3a**–[18]C6 in water, whereas a moderate yield of the 1-decynyl-λ^3-iodane–[18]C6 complex (**43**–[18]C6) was produced in acetonitrile (Scheme 6).[26] Further activation with BF_3·Et_2O increased the yield of **43**–[18]C6 to 72%. Similar results were obtained when 1-decyne **44** was used as the substrate. Thus, 1-decyne underwent direct CH-λ^3-iodanylation in the presence of HgO (4 mol%) in dichloromethane, whereas the reaction did not take place in water.[27] Reaction of propylbenzene (**45**) with **3a**–[18]C6 in the presence of BF_3·Et_2O in dichloromethane produced diaryl-λ^3-iodane–[18]C6 complex **46** in high yield.[28] Activation with BF_3·Et_2O was essential. The direct aryl-λ^3-iodanylation did not proceed in water. These differences can probably be ascribed to destabilization of the hypervalent bonds in less nucleophilic solvents.



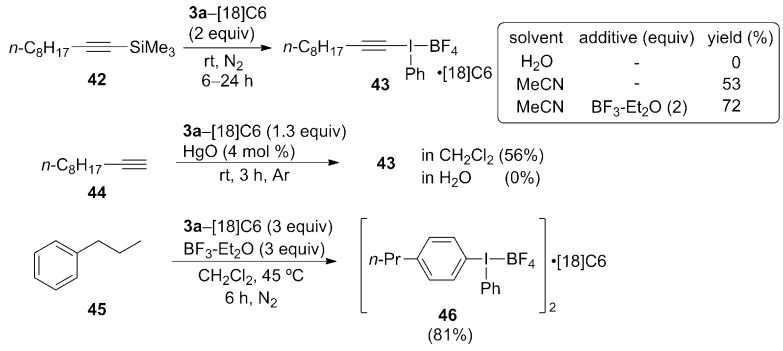
Scheme 5. Oxidation of alkyl(trifluoro)borates **38** with **3a**–[18]C6.

Table 5. Synthesis of diphenyl-, 1-alkenyl(phenyl), and 1-alkynyl(phenyl)-λ^3-iodanes with activated iodosylbenzene monomer–[18]C6 complexes.[a]



Entry	Substrate	Complex	T [°C]	Product: Yield [%][c]
1	**30**	**3a**–[18]C6	rt	**33a**: 67
2	**30**	**4a**–[18]C6	rt	**33b**: 72
3[b]	**31**	**3a**–[18]C6	rt	**33a**: 87
4[b]	**32**	**3a**–[18]C6	rt	**33a**: 85
5	**34a**	**3a**–[18]C6	rt	**35aa**: 83
6	**34a**	**4a**–[18]C6	rt	**35ab**: 90
7	**34b**	**3a**–[18]C6	rt	**35b**: 91
8	**36a**	**3a**–[18]C6	rt	**37aa**: 84
9[b]	**36a**	**3a**–[18]C6	0–rt	**37aa**: 93
10	**36a**	**4a**–[18]C6	rt	**37ab**: 81
11	**36b**	**3a**–[18]C6	rt	**37ba**: 76
12[b]	**36b**	**3a**–[18]C6	0–rt	**37ba**: 92
13	**36b**	**4a**–[18]C6	rt	**37bb**: 92

[a] Unless otherwise noted, the reaction was carried out using 0.02 M complex (1–1.2 equiv) in water for 3–8 h. [b] 3 equiv of BF_3•Et_2O was used. [c] Isolated yields. The ratios between λ^3-iodanes and [18]C6 were determined after recrystallization.



Scheme 6. Solvent effects on the reactivity of **3a**–[18]C6.

Conclusion

In conclusion, we have synthesized and characterized various iodosylbenzene monomers complexed with [18]C6, which are stable in water. These complexes have been shown to be excellent oxidizing agents for the oxidation of phenols, sulfides, olefins, silyl enol ethers, and alkyl(trifluoro)borates under mild reaction conditions. Furthermore, these complexes serve as progenitors for diverse λ^3-iodane–[18]C6 complexes with two carbon ligands. The reactivity of iodosylbenzene monomer–[18]C6 complexes has been found to be controlled by the coordination ability of the solvent. Thus, the use of less polar solvents enhances the reactivity of the complexes, which can probably be ascribed to a destabilization of the hypervalent bonds.

Experimental Section

Synthesis of 3a–[18]C6 from (diacetoxyiodo)benzene (5a) and aqueous tetrafluoroboric acid

Compound 3a–[18]C6: Aqueous 48% tetrafluoroboric acid (72 μL, 0.55 mmol) was added to a stirred solution of (diacetoxyiodo)benzene (**5a**) (162 mg, 0.5 mmol) and [18]crown-6 (133 mg, 0.5 mmol) in acetonitrile (1.5 mL) at room temperature under air, and the mixture was stirred for 5 min. After evaporation of the solvent under an aspiratory vacuum at ambient temperature, the yellow residue was washed several times with hexane and then with diethyl ether by decantation at −60 °C to −40 °C to give a pure **3a**–[18]C6 (283 mg, 99%) as a pale-yellow powder.[5a] M.p. 88–93 °C (decomposition); ^{1}H NMR (400 MHz, CD_3CN): $\delta = 8.26$ (d, $J = 8.1$ Hz, 2H), 8.01 (br s, 1H), 7.81 (t, $J = 7.3$ Hz, 1H), 7.67 (dd, $J = 8.1$, 7.3 Hz, 2H), 3.64 ppm (s, 24H); ^{13}C NMR (75 MHz, CD_3CN): $\delta = 136.4$, 134.5, 132.4, 123.1, 70.7 ppm; IR (Nujol): $\tilde{\nu} = 3533$, 2471, 1567, 1353, 1300, 1245, 1150–1000, 955, 836, 750, 611 cm^{-1}.

Solvent-free synthesis of 4–[18]C6

Compound 4–[18]C6: Trimethylsilyl triflate (122 mg, 0.55 mmol) was added to a ground mixture of (diacetoxyiodo)benzene (**5a**) (160 mg, 0.5 mmol) and [18]crown-6 (130 mg, 0.5 mmol) in an agate mortar at room temperature under air over a period of 5 min. The mixture became a yellow oil, which was washed several times with hexane and diethyl ether on the agate mortar to give **4a**–[18]C6 (240 mg, 72%) as a pale-yellow powder.[5b] M.p. 61–63 °C; ^{1}H NMR (400 MHz, CD_3CN): $\delta = 8.24$ (d, $J = 8.0$ Hz, 2H), 7.78 (t, $J = 7.3$ Hz, 1H), 7.64 (dd, $J = 8.0$, 7.3 Hz, 2H), 3.56 ppm (s, 24H); ^{13}C NMR (75 MHz, CD_3CN): $\delta = 136.3$, 134.4, 132.4, 123.3, 126.0 (q, $^1J_{CF} = 315.0$ Hz), 70.8 ppm; IR (Nujol): $\tilde{\nu} = 3564$, 3485, 1354, 1285, 1109, 1038, 965, 842, 638 cm^{-1}.

CCDC-944789 (**8**–[18]C6) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgements

This work was supported by the Japan Society for the Promotion of Science (JSPS) through a Grant-in-Aid for Scientific Research (B) and a Grant-in-Aid for Young Scientists (B). We are grateful to Dr. Motoo Shiro (Rigaku Corporation) for useful advice concerning the X-ray crystal structure analysis.

Keywords: crown ethers · hypervalent compounds · iodine · oxidation · supramolecules

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Received: December 19, 2013
Published online on March 18, 2014