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Synthesis and structure of supramolecular complexes between 1-alkynyl(phenyl)(tetrafluoroborato)-λ^3-iodanes and 18-crown-6

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Abstract—Slow evaporation of a solution of 1-decynyl(phenyl)(tetrafluoroborato)-λ^3-iodane and 18-crown-6 in dichloromethane–diethyl ether–hexane gave a supramolecular 1:1 complex, while 3,3-dimethyl-1-butynyl- and phenylethynyl(phenyl)(tetrafluoroborato)-λ^3-iodanes afforded 2:1 complexes. Complexation with 18-crown-6 increased the thermal stability of the phenylethynyl-λ^3-iodane. Solid state and solution structures of these complexes were examined by single crystal X-ray analyses, ^{1}H and ^{13}C NMR spectra, and cold-spray ionization MS. Binding constants were measured by ^{1}H NMR titrations.

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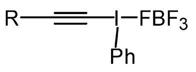
1. Introduction

Metal ions form crystalline complexes with crown ethers through ion-dipole electrostatic interactions,[1] while a variety of organic molecules with acidic hydrogens bind to crown ethers via hydrogen bonding.[2] Recently, we reported a new type of interaction for forming supramolecular complexes, i.e. hypervalent secondary bonding involving crown ether oxygens.[3] X-Ray crystal structures of 1:1 and 2:1 complexes between diphenyl(tetrafluoroborato)-λ^3-iodane and 18-crown-6 (18C6), obtained by slow evaporation of solvents (dichloromethane–diethyl ether or –hexane) at 4°C, indicated that each iodine atom contacts with the three adjacent oxygen atoms of 18C6 through two hypervalent secondary bonding and a weak interaction. Simple ethynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**1a**) also forms a 1:1 complex **2a** with 18C6.[4] The complexation with 18C6 not only stabilizes **1a** but also holds its high reactivity toward nucleophiles. We report herein synthesis and characterization of supramolecular complexes formed between substituted ethynyl(phenyl)-λ^3-iodanes **1b–d** and 18C6.

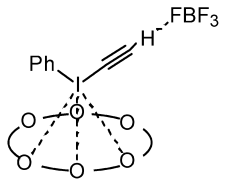
2. Results and discussion

Slow evaporation of a dichloromethane–diethyl ether–hexane solution of a 1:1 mixture of 1-decynyl(phenyl)-(tetrafluoroborato)-λ^3-iodane (**1b**) and 18C6 in a refrigerator (ca. 4°C) afforded a 93% yield of white powder of 1:1 complex **2b**. In contrast, 3,3-dimethyl-1-butynyl(phenyl)-(tetrafluoroborato)-λ^3-iodane (**1c**) afforded colorless prisms of 2:1 complex **2c** by evaporation of a dichloromethane–diethyl ether solution. Similarly, 2:1 complex **2d** was prepared from phenylethynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**1d**).



1a: R = H
1b: R = n-C_8H_{17}
1c: R = t-Bu
1d: R = Ph

$R{-}C{\equiv}C{-}I(Ph){-}FBF_3$



2a

Ligand exchange on iodine(III) of phenyl(hydroxy)-λ^3-iodane·18C6 complex **4**[5] with 1-alkynyl(trimethyl)silanes **3** provides an alternative method for the synthesis of 1-alkynyl(phenyl)-λ^3-iodane·18C6 complexes **2**. Thus, exposure of 1-trimethylsilyl-1-decyne (**3a**) to phenyl-(hydroxy)-λ^3-iodane·18C6 complex **4** (2 equiv.) in the presence of BF_3–Et_2O in MeCN at room temperature resulted in silicon-λ^3-iodane exchange and directly afforded the 1:1 1-decynyl-λ^3-iodane·18C6 complex **2b** in 72% yield. The reaction with bis(trimethylsilyl)acetylene **3b** gave the 2:1 complex **2e**, which was contaminated with a small amount of the desilylated complex **2a** (Scheme 1).

Keywords: supramolecular complex; alkynyl-λ^3-iodane; crown ether; hypervalent bonding.

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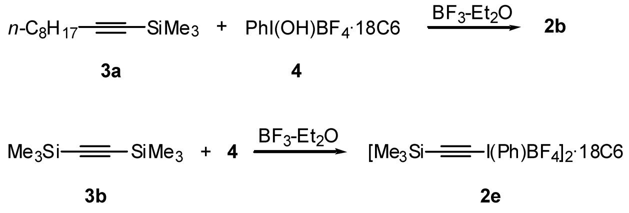

Scheme 1.

Compared to alkylethynyl-λ^3-iodanes **1b** and **1c**, phenylethynyl(tetrafluoroborato)-λ^3-iodane **1d** is thermally labile and gradually decomposes even when it was preserved at −30°C. Complexation with 18C6 dramatically increased the stability of 1-alkynyl(phenyl)-λ^3-iodanes in the solid state. Thus, no decomposition was observed when the pale yellow plates of the 2:1 phenylethynyl-λ^3-iodane·18C6 complex **2d** was left standing under ambient conditions for more than 10 days. The 1:1 (**2b**) and 2:1 complex (**2c**) are more stable and can be kept for over one month under ambient conditions without decomposition (Table 1).

The X-ray crystal structure of the 2:1 complex **2c** (Fig. 1) illustrates that each 1-alkynyl(phenyl)-λ^3-iodanyl group protrudes above both faces of 18C6. The iodine(III) contacts with three adjacent oxygen atoms (O(1), O(2), and O(3*)) of 18C6. The complex **2c** adopts a distorted pentagonal planar geometry about the iodine, with RMS deviation (0.1874(4) Å for I(1), C(7), C(13), O(1), O(2), and O(3*)) from their least squares plane and the sum of the iodine centered bond angles ($\sum°I$=361.93(3)°).

Table 1. Synthesis of 1-alkynyl-λ^3-iodane·18-crown-6 complexes **2** from 1-alkynyl-λ^3-iodanes **1**

λ^3-iodane·18C6 complex		Ratio[a]	Yield (%)	Mp (°C)
2b	**1b**·18C6	1:1	93	91–92
2c	**1c**·18C6	2:1	91	147–147.5
2d	**1d**·18C6	2:1	65	106–107

[a] Ratios of 1-alkynyl-λ^3-iodane/18-crown-6.

The I(1)···O(2) and I(1)···O(3*) distances are considerably shorter than the van der Waal's distance (3.50 Å). Both C(7)–I(1)···O(3*) and C(13)–I(1)···O(2) are near-linear and therefore these close contacts are indicative of hypervalent secondary interactions, in which each oxygen atom donates an electron pair into an I–C σ* orbital. The other I(1)···O(1) contact is weak and considerably deviates from the linearity of 3c–4e σ bonding.[6]

A similar perching type of host–guest relationship was observed in the solid state structure of the 2:1 complex **2d** (Fig. 2). The iodine(III) again contacts with three adjacent oxygen atoms (O(1), O(2*), and O(3*)) of 18C6 and the complex **2c** adopts a distorted pentagonal planar geometry about the iodine, with RMS deviation (0.2079(4) Å for I(1), C(1), C(9), O(1), O(2*), and O(3*)) and the sum of the iodine centered bond angles ($\sum°I$=361.99(2)°). The short I(1)···O(1) and I(1)···O(2*) distances as well as the near-linear C(1)–I(1)···O(1) and C(9)–I(1)···O(2*) triads are indicative of hypervalent contacts. The other I(1)···O(3*) contact is weak and considerably deviates from linearity.

In solution, the complex formation between **1b–d** and 18C6 is suggested by ^{1}H NMR experiments: a methylene singlet of 18C6 exhibits an upfield shift of about 0.03 ppm (in $CDCl_3$ for **2b–d**) and 0.02 ppm (in CD_2Cl_2 for **2b** and **2c**),

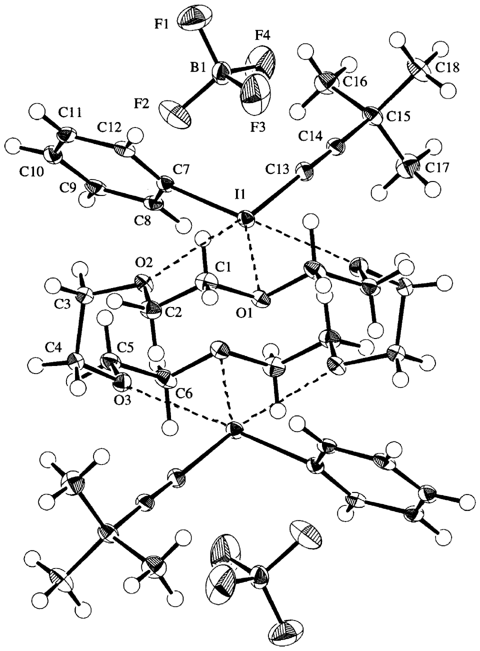

Figure 1. ORTEP drawing of [(*t*-BuCC)PhIBF$_4$]$_2$·18C6 complex **2c**. Secondary interactions are shown in dashed lines. Selected bond lengths (Å) and angles (deg): I(1)–C(7), 2.108(2); I(1)–C(13), 2.007(2); I(1)···O(1), 3.063(1); I(1)···O(2), 2.893(1); I(1)···O(3*), 2.773(1); C(7)–I(1)–C(13), 93.96(8); I(1)–C(13)–C(14), 172.0(2); C(7)–I(1)···O(3*), 171.48(7); C(13)–I(1)···O(2), 168.32(6).

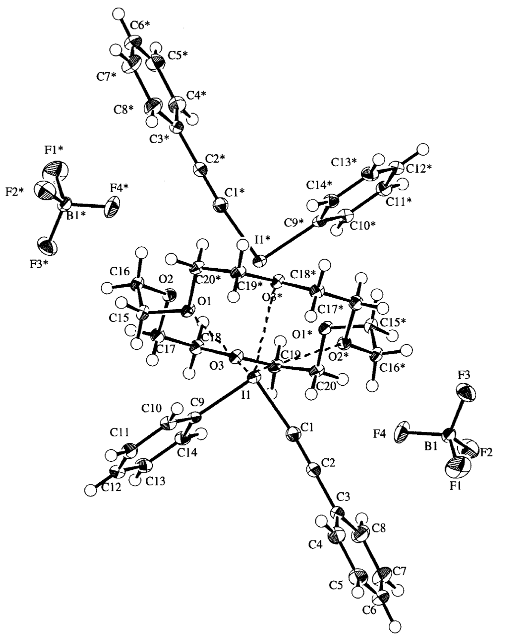

Figure 2. ORTEP drawing of [(PhCC)PhIBF$_4$]$_2$·18C6 complex **2d**. Secondary interactions are shown in dashed lines. Selected bond lengths (Å) and angles (deg): I(1)–C(1), 2.009(1); I(1)–C(9), 2.111(1); I(1)···O(1), 2.7497(8); I(1)···O(2*), 2.8197(9); I(1)···O(3*), 3.0199(9); C(1)–I(1)–C(9), 90.67(5); I(1)–C(1)–C(2), 173.7(1); C(1)–I(1)···O(1), 170.16(4); C(9)–I(1)···O(2*), 166.85(4).

probably because of the shielding effects of the phenyl group attached to iodine(III).[3,7] The ^{13}C resonance of 18C6 at δ 70.7 ppm in $CDCl_3$ is shifted to higher field (δ 69.7–69.9 ppm) in **2b–d**.

Alkylethynyl-λ^3-iodane **1b** forms a 1:1 complex with 18C6 in solution as well as in the solid state. Cold-spray ionization (CSI) MS,[8] a variant of electrospray (ESI) MS[9] operating at low temperature, allows facile characterization of labile organic species in solution. The CSI-MS spectrum for a 1:1 mixture of the λ^3-iodane **1b** and 18C6 [each 0.1 mM] in dichloromethane showed the most prominent ion peak of the 1:1 complex [**2b**$-BF_4$]$^+$ at *m*/*z* 605 in addition to the uncomplexed ion peak of [**1b**$-BF_4$]$^+$, but a peak corresponding to 2:1 complex was not detected at all (Fig. 3).

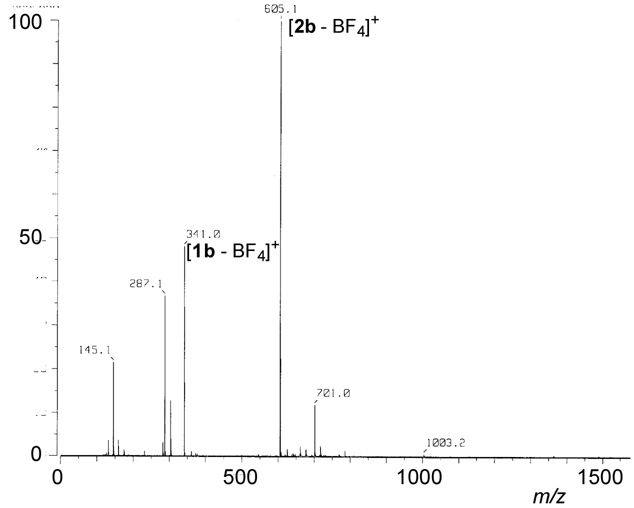

Figure 3. CSI-MS spectrum of a 1:1 mixture of the λ^3-iodane **1b** and 18C6 [each 0.1 mM] in dichloromethane.

The 1:1 stoichiometry for complexation between **1b** and 18C6 in CD_2Cl_2 solution was confirmed from the Job plots by the ^{1}H NMR experiments.[10] The ^{1}H NMR shifts of a methylene singlet of 18C6 induced by the complexation with **1b** were small but reproducible. A plot of complex concentration versus [**1b**]/([**1b**]+[18C6]) shows a maximum at near 0.5 (Fig. 4), which indicates that the λ^3-iodane **1b** exclusively forms a 1:1 complex with 18C6 in dichloromethane solution. In contrast to the solid state structure of **2c**, showing the formation of 2:1 complex, Job plots for **1c** in Figure 4 indicate the formation of 1:1 complex in dichloromethane solution. Similar results were observed for complexation of diphenyl(tetrafluoroborato)-λ^3-iodane with 18C6.[3] Thus, the facile formation of the crystalline 2:1 complex **2c** from a dichloromethane–diethyl ether solution is probably due to the limited solubility.

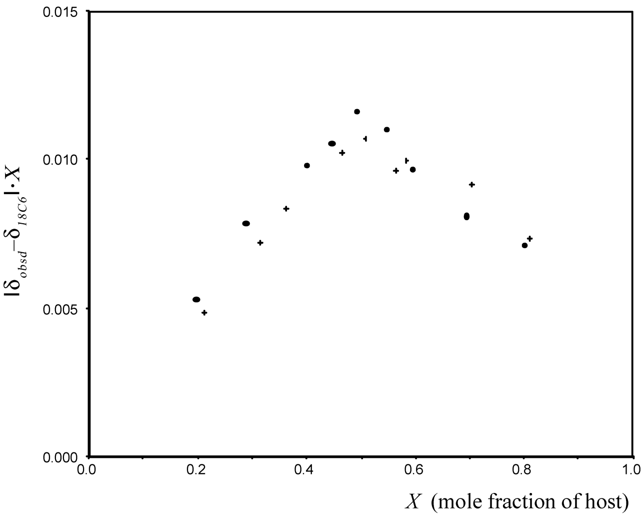

Figure 4. Job plot for complexation between the λ^3-iodane **1b** (●) or **1c** (+) and 18C6 in CD_2Cl_2 at 24°C. Concentration: [1]+[18C6]=0.01 M.

Binding constants were measured by ^{1}H NMR titrations of CD_2Cl_2 solutions of 18C6 with **1b** and **1c** at 24°C (Fig. 5). The resulting binding curves gave an excellent fit with a 1:1 binding model and were analyzed by nonlinear least-squares method. The results are shown in Table 2. Compared to the reported binding efficacy of 18C6 to

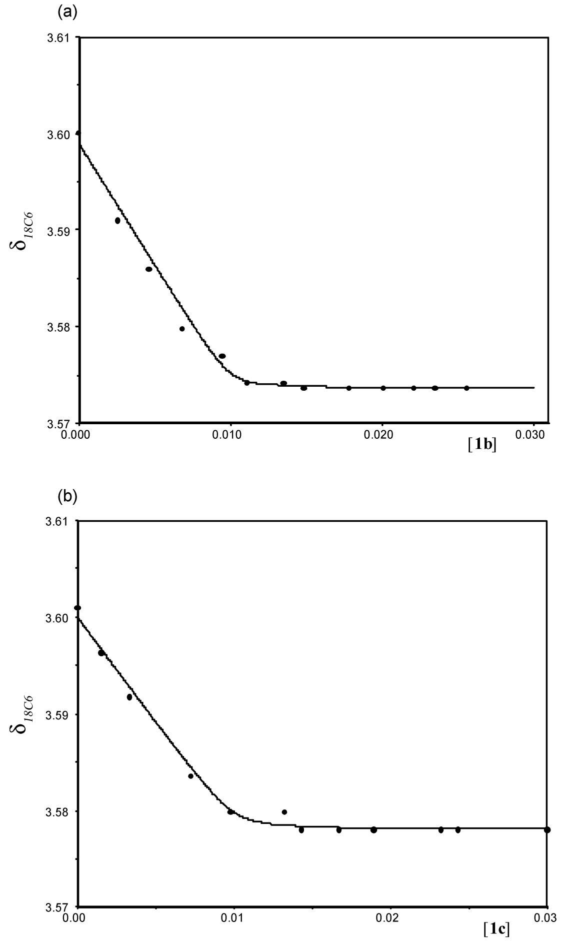

Figure 5. Observed ^{1}H NMR chemical shifts of 18C6 (0.01 M) when titrated with **1** in CD_2Cl_2 at 24°C. (a) **1b**. (b) **1c**. The solid line is calculated as described in text.

Table 2. Binding constants (K_a) obtained from ^{1}H NMR titration at 24°C

Entry	λ^3-iodane·18C6 complex	Solvent	K_a (M^{-1})
1	**2b**	CD_2Cl_2	2.40×10^4
2	**2c**	CD_2Cl_2	1.38×10^4
3[a]	Ph_2IBF_4·18C6	CD_2Cl_2	1.02×10^3

[a] Ref. 3.

diphenyl(tetrafluoroborato)-λ^3-iodane (Table 2, entry 3), both alkylethynyl-(phenyl)-λ^3-iodanes **1b** and **1c** form more stable supramolecular complexes and afford the binding constants of one order of magnitude greater.

It has been shown that substitution of an electron-withdrawing group onto the *para* position of diphenyl(tetrafluoroborato)-λ^3-iodane tends to increase in the complex stability.[3] Thus, the λ^3-iodanes with a greater positive charge on the iodine(III) interact more efficiently with 18C6. Because alkylethynyl groups are more efficient electron-withdrawing groups compared to phenyl group,[11] the positive charge on the iodine(III) in alkylethynyl(phenyl)-λ^3-iodanes **1b** and **1c** seems to be greater than that in the diphenyl-λ^3-iodane, which in turn increases the binding constants between **1b**,**c** 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.

Thus, we have synthesized supramolecular complexes of 1-alkynyl(phenyl)(tetrafluoroborato)-λ^3-iodanes with 18C6. Complexation with 18C6 increased the thermal stability of 1-alkynyl(phenyl)-λ^3-iodanes. Solid state structures of 3,3-dimethyl-1-butynyl-λ^3-iodane-18C6 and phenylethynyl-λ^3-iodane-18C6 complexes were determined by single crystal X-ray analyses. Structures of these complexes in solution were examined by ^{1}H and ^{13}C NMR spectra, and cold-spray ionization MS. Binding constants were measured by ^{1}H NMR titrations.

3. Experimental

IR spectra were recorded on Perkin–Elmer 1720 FT-IR spectrometers. ^{1}H and ^{13}C NMR were recorded on a JEOL JNM-GX 400 spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from internal Me_4Si. Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected. CSI-MS measurements were performed with a four-sector (BE/BE) tandem mass spectrometer (JEOL JMS-700T) equipped with the CSI source.

1-Alkynyl(phenyl)(tetrafluoroborato)-λ^3-iodanes **1b–d** were prepared by the silicon–iodine(III) exchange reaction.[12]

3.1. Preparation of 1-alkynyl-λ^3-iodane·18-crown-6 complexes 2b–d

3.1.1. 1-Decynyl(phenyl)(tetrafluoroborato)-λ^3-iodane·18-crown-6 (2b). 1-Decynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**1b**) (23 mg, 0.053 mmol) and 18C6 (14 mg, 0.054 mmol) were dissolved in dichloromethane (1 mL) and the solution was stirred for 0.5 h at room temperature. After addition of diethyl ether and hexane, a slow evaporation at 4°C of the solvent with exposure to the atmosphere yielded the 1:1 complex **2b** (33.9 mg, 93%) as white powder: mp 91–92°C; IR (KBr) 3083, 2921, 2181, 1562, 1468, 1354, 1250, 1200–990, 957, 838, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J=8.4 Hz, 2H), 7.70 (t, J=7.7 Hz, 1H), 7.58 (dd, J=8.4, 7.7 Hz, 2H), 3.66 (s, 24H), 2.64 (t, J=7.3 Hz, 2H), 1.62–1.54 (quint, J=7.3 Hz, 2H), 1.39–1.21(m, 10H), 0.88 (t, J=7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 132.8, 132.1, 115.6, 109.8, 69.9, 31.7, 29.1, 28.9, 28.7, 27.7, 22.6, 20.6, 20.4, 14.1. Anal. calcd for $C_{28}H_{46}BF_4IO_6$: C, 48.57; H, 6.70. Found: C, 48.17; H, 6.56.

3.1.2. [3,3-Dimethyl-1-butynyl(phenyl)(tetrafluoroborato)-λ^3-iodane]$_2$·18-crown-6 (2c). 3,3-Dimethyl-1-butynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**1c**) (29 mg, 0.078 mmol) and 18C6 (10 mg, 0.039 mmol) were dissolved in dichloromethane (0.5 mL) and the solution was stirred for 0.5 h at room temperature. After addition of diethyl ether, a slow evaporation at 4°C of the solvent with exposure to the atmosphere yielded the 2:1 complex **2c** (35.8 mg, 91%) as colorless prisms: mp 147–147.5°C; IR (KBr) 3066, 2873, 2170, 2139, 1560, 1466, 1357, 1247, 1200–990, 836, 761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J=8.4 Hz, 4H), 7.70 (t, J=7.7 Hz, 2H), 7.58 (dd, J=8.4, 7.7 Hz, 4H), 3.65 (s, 24H), 1.31 (s, 18H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 134.8, 133.4, 132.8, 119.6, 115.8, 70.2, 30.4, 30.1, 18.0. Anal. calcd for $C_{36}H_{52}B_2F_8I_2O_6$: C, 42.89; H, 5.16. Found: C, 42.64; H, 4.99.

3.1.3. [Phenyl(phenylethynyl)(tetrafluoroborato)-λ^3-iodane]$_2$·18-crown-6 (2d). Phenyl(phenylethynyl)(tetrafluoroborato)-λ^3-iodane (**1d**) (59 mg, 0.15 mmol) and 18C6 (20 mg, 0.076 mmol) were dissolved in dichloromethane (0.6 mL) and the solution was stirred for 0.5 h at room temperature. After addition of diethyl ether, a slow evaporation at −20°C of the solvent with exposure to the atmosphere yielded the 2:1 complex **2d** (51.4 mg, 65%) as pale yellow prisms: mp 106–107°C; IR (KBr) 3083, 2867, 2166, 1560, 1447, 1288, 1200–990, 808, 758, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J=8.3 Hz, 4H), 7.71 (t, J=7.7 Hz, 2H), 7.60 (dd, J=8.3, 7.7 Hz, 4H), 7.56 (d, J=7.6 Hz, 4H), 7.52 (t, J=7.3 Hz, 2H), 7.44 (dd, J=7.6, 7.3 Hz, 4H), 3.66 (s, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.9, 133.2, 133.0, 132.6, 131.6, 128.8, 119.5, 116.1, 107.7, 69.8, 29.8. Anal. calcd for $C_{40}H_{44}B_2F_8I_2O_6$: C, 45.83; H, 4.23. Found: C, 46.03; H, 4.28.

3.1.4. Reaction of 1-trimethylsilyl-1-decyne (3a) with phenyl(hydroxy)(tetrafluoroborato)-λ^3-iodane·18C6 complex (4). To a solution of $PhI(OH)BF_4$·18C6 complex **4** (56 mg, 0.098 mmol) in 1 mL of acetonitrile were added 1-decynylsilane **3a** (11 mg, 0.051 mmol) and boron trifluoride-diethyl ether complex (14 mg, 0.095 mmol) at room temperature under nitrogen and the mixture was stirred for 5.5 h. The solvent was evaporated under reduced pressure. After addition of water (1 mL), the mixture was extracted with dichloromethane four times. Filtration and concentration under reduced pressure gave a yellow oil, which was washed several times with hexane and then with diethyl ether by decantation at 0°C to give the 1:1 complex **2b** (25 mg, 72%) as white powder.

3.1.5. Reaction of bis(trimethylsilyl)acetylene (3b) with phenyl(hydroxy)(tetrafluoroborato)-λ^3-iodane·18C6 complex (4). To a solution of $PhI(OH)BF_4$·18C6 complex **4** (68 mg, 0.12 mmol) in 1 mL of acetonitrile was added bis(trimethylsilyl)acetylene (**3b**) (10 mg, 0.06 mmol) and boron trifluoride–diethyl ether complex (17 mg, 0.12 mmol) at room temperature under nitrogen and the mixture was stirred for 36 h. The solvent was evaporated under reduced pressure. After addition of an ice-cooled 50% aqueous tetrafluoroboric acid solution, the mixture was extracted with dichloromethane five times. Filtration and concentration under reduced pressure to give an oil, which was washed several times with hexane and then with diethyl ether by decantation at 0°C gave a 1:1.4 mixture (32.2 mg, 69%) of phenyl(trimethylsilylethynyl)(tetra-fluoroborato)-λ^3-iodane and 18C6. The mixture was contaminated with a 4% of ethynyl(phenyl)(tetrafluoro-borato)-λ^3-iodane (**1a**). Recrystallization from dichloromethane–hexane at 4°C gave the 2:1 complex **2e**, contaminated with a 10% of the desilylated complex **2a**.

Compound **2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J=8.1 Hz, 4H), 7.71 (t, J=7.3 Hz, 2H), 7.60 (dd, J=8.1, 7.3 Hz, 4H), 3.62 (s, 24H), 0.26 (s, 9H).

3.2. Job plot

Equimolar solutions (0.01 M) of 1-decynyl(phenyl)-λ^3-iodane **1b** or 3,3-dimethyl-1-butynyl(phenyl)-λ^3-iodane **1c** and 18C6 were prepared and mixed in various amounts. ^{1}H NMR spectra of the mixtures were recorded at 24°C, and the complexation-induced chemical shifts of a methylene singlet of 18C6 were analyzed by the method developed by Newcomb and his coworkers.[13]

3.3. ^{1}H NMR titration

A solution of 18C6 (0.01 M) in CD_2Cl_2 was prepared. Ten to fifteen NMR tubes were each filled with the solution and with an adequate amount of 1-alkynyl(phenyl)-λ^3-iodanes **1** (i.e. 0–3 equiv.). ^{1}H NMR spectra of the mixtures were recorded at 24°C. The curve fittings of the chemical shift data of a methylene singlet of 18C6 were carried out by a nonlinear least-squares method (Marquardt-Levenberg Algorithm) according to the reported equation[14] with use of SigmaPlot (Jandel Scientific, San Rafael, CA).

3.4. Crystallographic study

Crystallographic data were recorded on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[15] or heavy-atom Patterson methods[16] and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[18] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[19] All calculations were performed using the teXsan[20] crystallographic software package of Molecular Structure Corp.

X-Ray data for **2c**: $[(t\text{-BuCC})PhIBF_4]_2\cdot 18C6$: $C_{36}H_{52}B_2F_8I_2O_6$, M=1008.22, T=113 K, monoclinic space group $P2_1/n$ (No. 14), a=9.5949(2) Å, b=14.1248(3) Å, c=15.3543(3) Å, β=102.689(1)°, V=2030.09(7) Å^3, Z=2, D_c=1.649 g cm^{-3}, μ (Mo Kα)=16.29 cm^{-1}. 24211 Reflections were collected; 5910 were unique. R=0.047, R_w=0.054. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 220516.

X-Ray data for **2d**: $[(PhCC)PhIBF_4]_2\cdot 18C6$: $C_{40}H_{44}B_2F_8I_2O_6$, M=1048.20, T=93 K, monoclinic space group $P2_1/n$ (No. 14), a=10.2100(2) Å, b=13.8772(2) Å, c=15.3433(3) Å, β=99.1844(6)°, V=2146.06(7) Å^3, Z=2, D_c=1.622 g cm^{-3}, μ (Mo Kα)=15.44 cm^{-1}. 25890 Reflections were collected; 6265 were unique. R=0.029, R_w=0.036. CCDC registration number 220515.

Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc. cam.ac.uk).

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