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COMPLEXATION OF DIPHENYL(TETRAFLUOROBORATO)-λ^3-IODANE WITH PYRIDINES

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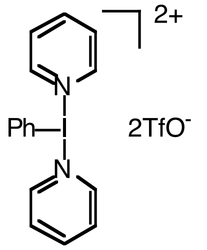
Abstract – Diphenyl(tetrafluoroborato)-λ^3-iodane forms 1:1 complexes with pyridine-derived ligands in CD_2Cl_2 solution and the binding constants decrease in the order: 1,10-phenanthroline > 2,2':6',2"-terpyridine > 2,2'-bipyridyl ≈ pyridine. The 1:1 complex of the λ^3-iodane with pyridine adopts a distorted square-planar geometry around the iodine atom.

Recently we found that crown ethers serve as efficient ligands for organo-λ^3-iodanes. 18-Crown-6 (18C6) forms a discrete complex with diphenyl(tetrafluoroborato)- and ethynyl(phenyl)(tetrafluoroborato)-λ^3-iodanes, in which the iodine(III) atoms contact with the three adjacent oxygen atoms of 18C6 through two hypervalent secondary bonding and a weak interaction.[1] The complexation with 18C6 increases the stability of labile λ^3-iodanes. Thus, the thermally unstable hydroxy(phenyl)(tetrafluoroborato)-λ^3-iodane[2] that decomposes at room temperature within a few minutes forms a stable crystalline crown ether complex.[3]

By contrast, synthesis and characterization of λ^3-iodane complexes coordinated by neutral nitrogen ligands are very limited, probably because of the facile oxidation of amino groups by λ^3-iodanes.[4] Weiss and Seubert prepared [bis(trifluoromethanesulfonyloxy)iodo]benzene·(pyridine)$_2$ complex (**1**) with highly increased oxidation power by the reaction of (diacetoxyiodo)benzene with pyridine in the presence of trimethylsilyl trifluoromethanesulfonate.[5] Stable 1:1 complex (**2**) of benziodoxole with pyridine was synthesized by Zhdankin and co-workers.[6] Detailed structures of these interesting pyridine complexes, however, are not available, because of the lack of the solid state structure analyses. We have reported the synthesis and solid state structure of 1:1 complex (**3**) of diphenyl(tetrafluoroborato)-λ^3-iodane with 1,10-

phenanthroline, in which the iodine atom adopts a distorted trigonal bipyramidal geometry with a phenyl group and BF_4 occupying apical positions, and 1,10-phenanthroline acts as a bidentate equatorial ligand on the trivalent iodine.[7] We now found that monodentate pyridine also binds to the iodine(III) of diphenyl(tetrafluoroborato)-□^{3}-iodane to give a 1:1 complex (**4**). Binding constants with 1,10-phenanthroline, 2,2':6',2"-terpyridine, 2,2'-bipyridyl, and pyridine were also measured.



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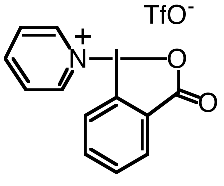

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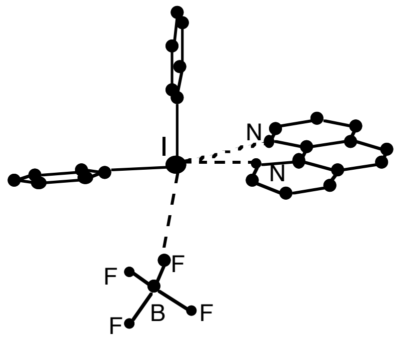

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Slow evaporation of a dichloromethane□ether (2:1) solution of a 1:2 mixture of diphenyl(tetrafluoroborato)-□^{3}-iodane and pyridine in a refrigerator (*ca.* 4 °C) afforded an 83% yield of single crystals of 1:1 complex (**4**) that were suitable for X-Ray crystallography (Figure 1). The iodine(III) in **4** adopts a tetracoordinated square planar arrangement, ligated with pyridine. The RMS deviation of the five atoms (I(1), C(1), C(7), N(1), and F(1)) from their least squares planes is 0.141(5) Å, and the sum of the iodine-centered these bond angles is □°I = 360.4(2)°. The I(1)···N(1) distance 2.864(2) Å is considerably longer

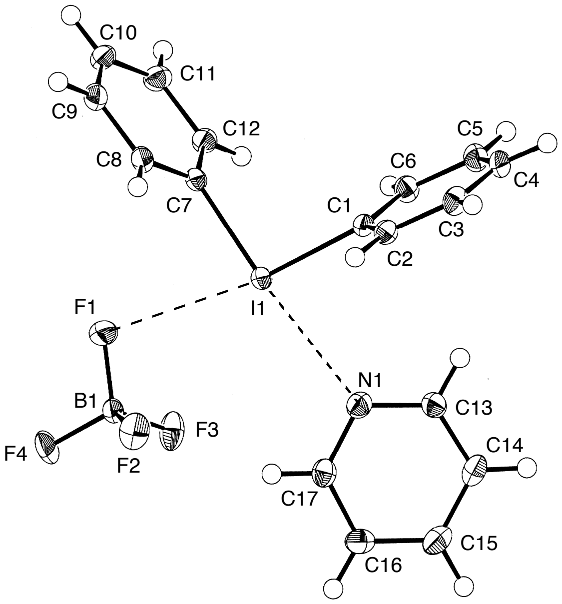

Figure 1. ORTEP drawing of Ph_2IBF_4·pyridine complex (4). Selected bond lengths (Å) and angles (°): I(1)-C(1) 2.110(2), I(1)-C(7) 2.118(2), I(1)···N(1) 2.864(2), I(1)···F(1) 2.976(2), C(1)-I(1)-C(7) 98.45(8), C(7)-I(1)···N(1) 175.75(7), C(1)-I(1)···F(1) 167.73(7).

than the computed covalent single bond length of 2.03 Å, but definitively shorter than the sums of the van der Waal's radii of N (1.55 Å) and I (1.98 Å).[8] Because both the C(7)-I(1)···N(1) and C(1)-I(1)···F(1) triads are near-linear (175.75(7)° and 167.73(7)°), these close contacts are indicative of secondary hypervalent interactions, in which the nitrogen and fluorine atoms donate an electron pair into the I-C σ^* orbital.[1] Interestingly, the C(1)-I(1)-C(7) angle of 98.45(8)° is greater than those of the crown ether complexes $Ph_2IBF_4\cdot 18C6\cdot 1.5\ H_2O$ (91.6(1)°) and $(Ph_2IBF_4)_2\cdot 18C6$ (92.18(7)°).[1]

The complex formation of diphenyl-λ^3-iodane with pyridine and 1,10-phenanthroline in solution is clearly evident in ^1H and ^{13}C NMR spectral experiments. For instance, the resonance of H2 and H9 of 1,10-phenanthroline in CD_2Cl_2 (0.01 M) exhibits an upfield shift of 0.06 ppm by the addition of one equivalent of diphenyl-λ^3-iodane, probably because of the shielding effects of the phenyl group.[9] Similar upfield shifts of 0.6 ppm (for C2, C9) and 0.8 ppm (for C10a, C10b) observed in the ^{13}C NMR spectrum (0.04 M in CD_2Cl_2) are also attributed to the anisotropic effects of the phenyl group. In addition, irradiation of the H2 and H9 of 1,10-phenanthroline gives rise to nuclear Overhauser effects (NOEs) for the *ortho* protons of diphenyl-λ^3-iodane, but not for the *meta* and *para* protons. These results probably suggest the formation of a stable complex similar to the solid state structure in CD_2Cl_2 solution.[7] The pyridine complex showed a similar upfield shift of 0.02 ppm (H2 and H6) in CD_2Cl_2 (0.01 M).

The 1:1 stoichiometry between the diphenyl-λ^3-iodane and 1,10-phenanthroline in CD_2Cl_2 solution was indicated from the Job plots by the ^1H NMR spectral experiments (Figure 2):[10] the complexation-induced shifts of H2 and H9 of 1,10-phenanthroline were reproducible and a plot of complex concentration versus

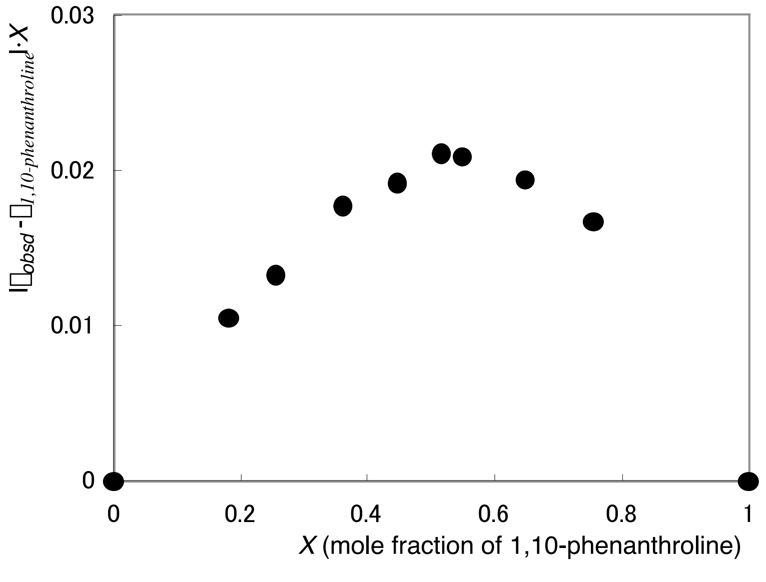

Figure 2. Job plot for complexation between Ph_2IBF_4 and 1,10-phenanthroline in CD_2Cl_2 at 24 °C. Concentration: $[Ph_2IBF_4] + [1,10\text{-phenanthroline}] = 0.01$ M.

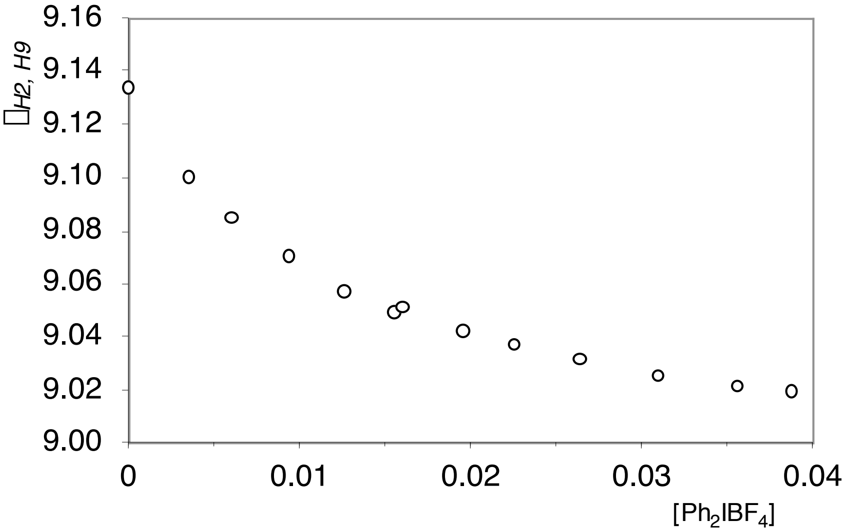

Figure 3. Observed ^{1}H NMR chemical shifts of H2 and H9 of 1,10-phenanthroline (0.01 M) when titrated with Ph_2IBF_4 in CD_2Cl_2 at 24 °C.

[λ^3-iodane]/([λ^3-iodane] + [1,10-phenanthroline]) showed a maximum at near 0.5. Coldspray ionization (CSI) MS spectrum[11] for the 1:1 complex (**3**) in dichloromethane showed the most prominent ion peak of [**3** - BF_4]$^+$ at *m/z* 461, which further illustrates formation of the 1:1 complex in solution.

The binding efficiency was measured by ^{1}H NMR spectral titrations of CD_2Cl_2 solutions of 1,10-phenanthroline with the diphenyl-λ^3-iodane at 24 °C (Figure 3). The resulting binding curve gave an excellent fit with a 1:1 binding model and was analyzed by nonlinear least-squares method to give a binding constant (K_a) value of 2.00×10^2 M^{-1} (correlation coefficient 0.99). Changing the bidentate ligand from 1,10-phenanthroline to the more flexible 2,2'-bipyridyl decreased the binding constant to one-eighth ($K_a = 2.50 \times 10$ M^{-1}). Monodentate pyridine gave a comparable binding constant ($K_a = 2.02 \times 10$ M^{-1}), while the increased binding was observed with tridentate 2,2':6',2"-terpyridine ($K_a = 6.35 \times 10$ M^{-1}).

In contrast to the pentacoordinated 1,10-phenanthroline complex of diphenyl(tetrafluoroborato)-λ^3-iodane that shows a distorted trigonal bipyramidal geometry, the pyridine complex is tetracoordinated and the iodine(III) in solid state structure adopts a square planar arrangement. In CD_2Cl_2 solution, the diphenyl-λ^3-iodane forms a 1:1 complex with pyridine-derived ligands and the binding constants decrease in the order: 1,10-phenanthroline > 2,2':6',2"-terpyridine > 2,2'-bipyridyl □ pyridine.

EXPERIMENTAL

Melting points were determined using a Yanaco micro melting points apparatus and are uncorrected. IR spectra were recorded on JASCO IRA-1 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on

JEOL JNM-AL400 spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from internal Me_4Si. CSI-MS spectra measurements were performed with a four-sector (BE/BE) tandem mass spectrometer (JMS-700T, JEOL) equipped with the CSI source.

Diphenyl(tetrafluoroborato)-λ^3-iodane·Pyridine Complex (4)

Diphenyl(tetrafluoroborato)-λ^3-iodane (61 mg, 0.17 mmol) and pyridine (26 mg, 0.33 mmol) were dissolved in dichloromethane (2.5 mL), and the solution was stirred for 1 h at rt. After addition of ether (1.3 mL), a slow evaporation at 4 °C of the solvent with exposure to the atmosphere yielded Ph_2IBF_4·pyridine (**4**) (61.7 mg, 83%) as colorless plates: mp 129.5–131 °C (recrystallized from CH_2Cl_2-Et_2O); IR (KBr) 3090, 3064, 1589, 1566, 1472, 1441, 1150-950, 735, 708, 681 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 0.01 M) δ 8.56 (d, J = 4.4 Hz, 2H), 8.01 (d, J = 7.5 Hz, 4H), 7.72 (t, J = 7.3 Hz, 2H), 7.69 (tt, J = 7.7, 1.8 Hz, 1H), 7.55 (dd, J = 7.5, 7.3 Hz, 4H), 7.29 (dd, J = 7.7, 4.4 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2, 0.04 M) δ 149.9, 136.5, 135.6, 133.5, 133.1, 124.3, 112.9. Anal. Calcd for $C_{17}H_{15}BF_4IN$: C, 45.68; H, 3.38; N, 3.13. Found: C, 45.38; H, 3.36; N, 2.99.

Job Plot. Equimolar solutions (0.01 M) of diphenyl(tetrafluoroborato)-λ^3-iodane and 1,10-phenanthroline were prepared and mixed in various amounts. ^1H NMR spectra of the mixtures were recorded at 24 °C, and the complexation-induced chemical shifts of a doublet (H2 and H9) of 1,10-phennathroline were analyzed by the method developed by Newcomb and co-workers.[12]

^1H NMR Spectral Titration. A solution of pyridines (0.01 M) was prepared. Ten to fifteen NMR tubes were each filled with the solution and with an adequate amount of diphenyl(tetrafluoroborato)-λ^3-iodane (i.e., 0–4 equiv). ^1H NMR spectra of the mixtures were recorded at 24 °C. The curve fittings of the chemical shift data of a signal of pyridines were carried out by a nonlinear least-squares method (Marquardt–Levenberg Algorithm) according to the reported equation[13] with use of SigmaPlot (Jandel Scientific, San Rafael, CA).

Crystal Data for Ph_2IBF_4·Pyridine Complex (4). $C_{17}H_{15}NBF_4I$, colorless block of dimensions of 0.20 x 0.20 x 0.20 mm^3, monoclinic, $P2_1/n$ (#14), a = 11.933(2), b = 9.946(1), c = 14.546(2) Å, β = 95.32(1)°, V = 1719.1(5) $Å^3$, Z = 4, ρ_{calcd} = 1.727 g cm^{-3}. Data collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71075 Å) at T = 93 K, $2\theta_{max}$ = 60.1°, 18823 reflections measured, of which 4991 unique (R_{int} = 0.033), μ = 19.01 cm^{-1}. Structure was solved by heavy-atom Patterson methods[14] and expanded using Fourier techniques,[15] R = 0.050, R_w = 0.060. Hydrogen atoms were included but not refined. CCDC-198780 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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