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# Solid state structures of pentacoordinated $\lambda^3$-iodanes with a trigonal bipyramidal geometry: synthesis of diphenyl- and alkynyl(phenyl)-$\lambda^3$-iodane complexes with 1,10-phenanthroline

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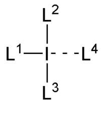
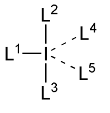
**The single crystal X-ray structure of the supramolecular complex formed between diphenyl-$\lambda^3$-iodane ($Ph_2IBF_4$) or 1-alkynyl(phenyl)-$\lambda^3$-iodane [$Bu^tCCI(Ph)BF_4$] and 1,10-phenanthroline indicates a hitherto unknown distorted trigonal bipyramidal geometry around iodine(III), in which 1,10-phenanthroline acts as a bidentate ligand and occupies equatorial sites.**

Hypervalent $\lambda^3$-iodanes exhibit a T-shaped geometry and are regarded as pseudotrigonal bipyramidal structures with two lone pairs at the iodine(III).[1] In the solid state, most $\lambda^3$-iodanes exist as tetra- or penta-coordinated species through intra- and/or inter-molecular secondary contacts. Tetracoordinated $\lambda^3$-iodanes, **1**, adopt a virtually square planar arrangement[2] as a result of hypervalent secondary interactions; the fourth ligand, $L^4$, interacts with the I–$L^1$ antibonding orbital of the $\lambda^3$-iodanes and donates an electron pair into the σ* orbital forming a nearly linear $L^1$–I···$L^4$ triad irrespective of whether it is a neutral or anionic species.[3]



**1**



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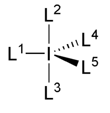

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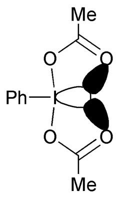

**4**

Pentacoordinated $\lambda^3$-iodanes generally exist in a pentagonal planar geometry, **2**, in the solid state.[4] For instance, the crystal structure of (diacetoxyiodo)benzene 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 and co-workers proposed the three-centre secondary bonding model, **4**, *i.e.* 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).[4a] We report herein that the coplanarity of all the ligands on iodine(III) is not a crucial requirement in the solid state structures of pentacoorinated $\lambda^3$-iodanes; single crystal X-ray structures of pentacoordinated $\lambda^3$-iodane complexes **5** and **6**, prepared from diphenyl- and 1-alkynyl(phenyl)-$\lambda^3$-iodanes by the reaction with 1,10-phenanthroline, exhibit a distorted trigonal bipyramidal geometry, **3**.

Synthesis and characterization of $\lambda^3$-iodanes coordinated by neutral nitrogen ligands are very limited, probably because of the facile oxidation of amino groups with $\lambda^3$-iodanes.[1] [Bis(trifluoromethanesulfonyloxy)iodo]benzene·(pyridine)$_2$[5] and 1-trifluoromethanesulfonyloxy-1*H*-1$\lambda^3$-benzo[*d*][1,2]iodoxol-3-one·2,2′-bipyridyl complexes[6] are known but no solid state structures of these interesting pyridine complexes are available.

Slow evaporation of a dichloromethane–*n*-hexane (3 : 1) solution of a 1 : 2 mixture of diphenyl-$\lambda^3$-iodane **7** ($Ph_2IBF_4$) and 1,10-phenanthroline in a refrigerator (*ca.* 4 °C) afforded a 94% yield of single crystals of 1 : 1 complex **5**† that were suitable for X-ray crystallography (Fig. 1).[7] Pyridine-based ligands, 2,2′-bipyridyl and 2,2′:6′2″-terpyridine, did not afford crystalline complexes with **7** under the same conditions.

As indicated in Fig. 1, the 1 : 1 complex **5** adopts a distorted trigonal bipyramidal geometry with a phenyl group and $BF_4$ occupying apical positions, and with the other phenyl group and 1,10-phenanthroline in equatorial sites. As observed in the solid state structures of organotransition metal compounds,[8] 1,10-phenanthroline acts as a bidentate ligand on the trivalent iodine.[9] The equatorial ligands are nearly planar; the RMS deviation of the four atoms (iodine, two nitrogens and *ipso* carbon of an equatorial phenyl group) from their least squares planes is 0.090(1) Å and the sum of the iodine centered bond angles is $\Sigma°I = 358.6(3)°$.

The I1···N1 and I1···N2 distances in **5** are 3.164(4) and 2.925(4) Å, respectively, and considerably longer 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).[10,11] Cooperative donation of electron density from the nitrogen lone pairs to the vacant I1–C1 σ* orbital, originally proposed by Alcock,[4a] will be responsible for these secondary I···N contacts. These intermolecular secondary contacts, however, are not in the same plane as both primary bonds, but the plane of these contacts is nearly perpendicular to the linear C7–I1···F3 triads. This is probably due to the negligibly small repulsion between 1,10-phenanthroline and the lone pairs on iodine(III).

The crystal structure of **5** involves a half-molecule of dichloromethane, being disordered at the two locations related

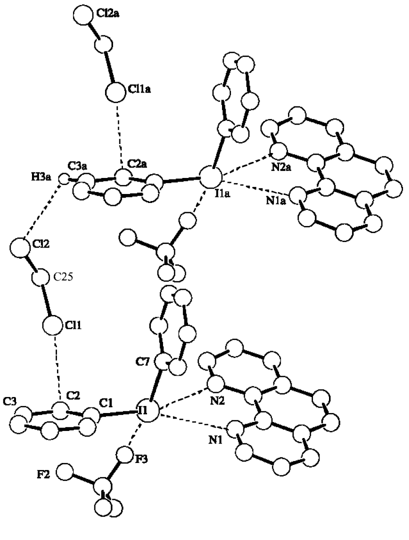

**Fig. 1** X-Ray structure of $Ph_2IBF_4$·1,10-phenanthroline·$\frac{1}{2}CH_2Cl_2$, **5**. Selected bond lengths (Å) and angles (°): I1–C1 2.120(5), I1–C7 2.098(5), I1···F3 3.012(8), I1···N1 3.164(4), I1···N2 2.925(4), Cl1···C2 3.04(1), Cl2···H3a 2.86; C1–I1–C7 96.4(2), C1–I1···N1 140.8(2), C1–I1···N2 164.4(2), C7–I1···F3 156.1(2).

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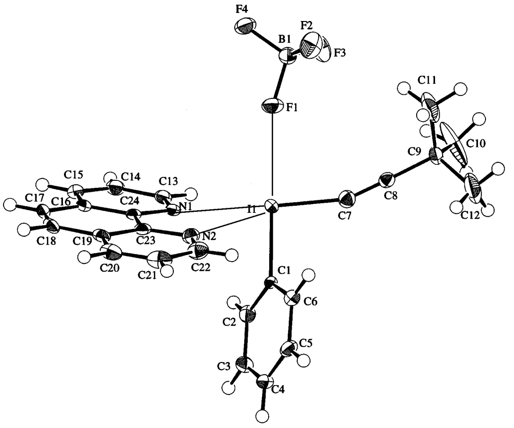
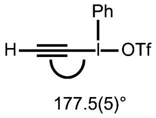


**Fig. 2** ORTEP drawing of Bu$^t$CCI(Ph)BF$_4$·1,10-phenanthroline, **6**. Selected bond lengths (Å) and angles (°): I1–C1 2.112(2), I1–C7 2.032(3), C7–C8 1.189(3), I1···N1 2.661(2), I1···N2 3.263(2), I1···F1 2.882(1); C1–I1–C7 95.23(9), I1–C7–C8 159.8(2), C7–I1···N1 174.9(1), C7–I1···N2 130.0(1), C1–I1···F1 172.3(1).

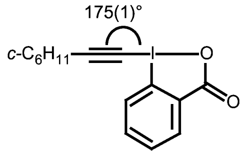
by a 2-fold axis, and each 1 : 1 complex **5** is probably connected through close contacts with dichloromethane. Both the Cl1···C2 and Cl2···H3a distances of 3.04(1) and 2.86 Å are shorter than the sums of the van der Waal's radii, 3.45 Å (Cl–C) and 2.95 Å (Cl–H).

1-Alkynyl(phenyl)-$\lambda^3$-iodane also binds with 1,10-phenanthroline; single crystals of 1 : 1 complex **6** for X-ray analysis were grown from a dichloromethane–diethyl ether solution of a 1 : 1 mixture of 3,3-dimethyl-1-butynyl(phenyl)-$\lambda^3$-iodane **8** and 1,10-phenanthroline (Fig. 2).[12] The iodine(III) in the 1 : 1 complex **6** adopts a highly distorted trigonal bipyramidal geometry with the alkynyl group and 1,10-phenanthroline occupying equatorial sites. The RMS deviation of I1, C7, N1 and N2 atoms from planarity is 0.029(1) Å and the sum of the iodine centered bond angles is $\Sigma°\text{I} = 359.6(1)°$.

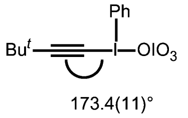
Very interestingly, the ethynyl ligand is not bound linearly to the iodine(III) with the I1–C7–C8 angle of 159.8(2)°. The observed bending is in marked contrast with those of the simple ethynyl-$\lambda^3$-iodane **9**[13] and the cyclic $\lambda^3$-iodane **10**,[4c] both of which show good linearity with angles of 177.5(5) and 175(1)°. The large bending is not due to the presence of the sterically demanding β-*tert*-butyl group in **6**; a nearly linear bonding was shown in a solid state structure of (3,3-dimethyl-1-butynyl)-$\lambda^3$-iodane **11**.[14] The I1–C7 and C7–C8 lengths are comparable to the reported values for $\lambda^3$-iodanes **9–11**.



**9**



**10**



**11**

A similar unusual bending was found by Ruhlandt-Senge and co-workers in the X-ray structures of heavy alkaline earth metal (triphenylsilyl)ethynyl derivatives [M(18-crown-6)(CCSiPh$_3$)$_2$] [M = Ca (**12a**), Sr (**12b**) and Ba (**12c**)]:[15] the M–C–C angles reported were 162.4(5) and 164.0(5)° (**12a**), 158.9(3) and 159.7(3)° (**12b**), and 126.6(3) and 141.3(3)° (**12c**). They suggested that the unusual geometry in **12** can be interpreted in terms of the high s-character of the sp-hybridized carbon atom of the ethynyl group causing a low directionality of the ligand orbitals, and the resulting very low energy barrier is responsible for the bending at the C atom.

In conclusion, we have synthesized diphenyl- and 3,3-dimethyl-1-butynyl(phenyl)-$\lambda^3$-iodane complexes with a bidentate nitrogen ligand, 1,10-phenanthroline. Solid state structures of both complexes with pentacoordinated iodine(III) indicated a hitherto unknown distorted trigonal bipyramidal geometry, instead of the common pentagonal planar arrangement. Interestingly, 3,3-dimethyl-1-butynyl ligand in the complex is not bound linearly to the iodine(III), the I–C–C angle being 159.8(2)°.

## Notes and references

† *Selected data* for **5**: colorless needles; mp 144–144.5 °C; $\delta_H$ (400 MHz, CD$_2$Cl$_2$, *J*/Hz, 0.01 M, 24 °C): 7.53 (dd, *J* 7.5 and 7.3, 4H), 7.66 (dd, *J* 8.1 and 4.3, 2H), 7.70 (t, *J* 7.5, 2H), 7.85 (s, 2H), 8.03 (d, *J* 7.3, 4H), 8.31 (dd, *J* 8.1 and 1.6, 2H), 9.07 (dd, *J* 4.3 and 1.6, 2H); $\delta_C$ (75 MHz, CD$_2$Cl$_2$, 0.04 M, 24 °C): 113.8, 123.7, 127.1, 129.3, 132.9, 133.3, 135.6, 136.9, 145.9, 149.9; $\nu_{max}$(KBr)/cm$^{-1}$: 3063, 1564, 1508, 1443, 1422, 1100—1000, 842, 733; CSI-MS (CH$_2$Cl$_2$, 0.005 M): *m*/*z* 461 [(M − BF$_4$)$^+$]. Anal. calc. for C$_{24}$H$_{18}$BF$_4$IN$_2$·$\frac{1}{2}$CH$_2$Cl$_2$: C 49.83, H 3.24, N 4.74. Found: C 49.84, H 3.29, N 4.69%.

1 (*a*) G. F. Koser, in *The Chemistry of Functional Groups, Supplement D*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1983, ch. 18; (*b*) A. Varvoglis, *The Organic Chemistry of Polycoordinated Iodine*, VCH, New York, 1992; (*c*) P. J. Stang and V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123; (*d*) M. Ochiai, in *Topics in Current Chemistry*, ed. T. Wirth, **vol. 224**, Springer, Berlin, 2003, p. 5.

2 For tetracoordinated square planar $\lambda^3$-iodanes, see: (*a*) A. J. Edwards, *J. Chem. Soc., Dalton Trans.*, 1978, 1723; (*b*) M. Ochiai, Y. Kitagawa, N. Takayama, Y. Takaoka and M. Shiro, *J. Am. Chem. Soc.*, 1999, **121**, 9233; (*c*) G. F. Koser, D. B. McConville, G. A. Rabah and W. J. Youngs, *J. Chem. Crystallogr.*, 1995, **25**, 857; (*d*) V. Montanari, D. D. DesMarteau and W. T. Pennington, *J. Mol. Struct.*, 2000, **550–551**, 337.

3 (*a*) N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1; (*b*) J. Starbuck, N. C. Norman and A. G. Orpen, *New J. Chem.*, 1999, **23**, 969.

4 For pentacoordinated pentagonal planar $\lambda^3$-iodanes, see: (*a*) N. W. Alcock, R. M. Countryman, S. Esperas and J. F. Sawyer, *J. Chem. Soc., Dalton Trans.*, 1979, 854; (*b*) N. W. Alcock and R. M. Countryman, *J. Chem. Soc., Dalton Trans.*, 1979, 851; (*c*) M. Ochiai, Y. Masaki and M. Shiro, *J. Org. Chem.*, 1991, **56**, 5511; (*d*) V. V. Zhdankin, A. E. Koposov, J. T. Smart, R. R. Tykwinski, R. McDonald and A. Morales-Izquierdo, *J. Am. Chem. Soc.*, 2001, **123**, 4095.

5 R. Weiss and J. Seubert, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 891.

6 V. V. Zhdankin, A. Y. Koposov and N. V. Yashin, *Tetrahedron Lett.*, 2002, **43**, 5735.

7 Crystal data for **5**: C$_{24.50}$H$_{19}$BF$_4$IN$_2$Cl, *M* = 590.59, monoclinic, space group *C*2/*c* (no. 15), *a* = 13.230(4), *b* = 10.440(3), *c* = 34.25(1) Å, *β* = 97.60 (3)°, *V* = 4688(2) Å$^3$, *T* = 93 K, *Z* = 8, Mo-K$\alpha$ radiation ($\lambda$ = 0.71075 Å), 27719 reflections measured, 6837 unique [$I > 3.00\sigma(I)$, $R_{int}$ = 0.054], $\mu$ = 15.28 cm$^{-1}$, *R* = 0.070, $R_w$ = 0.196. Dichloromethane and BF$_4$ are disordered at the two locations related by a 2-fold axis. Non-hydrogen atoms, excluding those of the disordered molecules, were refined anisotropically. CCDC reference number 198725.

8 T. Mizuno, W.-H. Wei, L. R. Eller and J. L. Sessler, *J. Am. Chem. Soc.*, 2002, **124**, 1134.

9 It has been reported that, in the 1-trifluoromethanesulfonyloxy-1*H*-1$\lambda^3$-benzo[*d*][1,2]iodoxol-3-one·2,2′-bipyridyl complex, 2,2′-bipyridyl serves as a monodentate but not bidentate ligand, probably because of the restrictive pseudotrigonal bipyramidal geometry of trivalent iodine with the most electronegative ligands occupying the apical positions.[6] Our results, however, clearly indicate that 1,10-phenanthroline can act as a bidentate equatorial ligand on iodine(III). For a $\lambda^5$-iodane·2,2′-bipyridyl complex, see also ref. 6.

10 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

11 For I···N secondary contacts in iodonium ylides, see: (*a*) A. K. Mishra, M. M. Olmstead, J. J. Ellison and P. P. Power, *Inorg. Chem.*, 1995, **34**, 3210; (*b*) M. Boucher, D. Macikenas, T. Ren and J. D. Protasiewicz, *J. Am. Chem. Soc.*, 1997, **119**, 9366.

12 Crystal data for **6**: C$_{24}$H$_{22}$BF$_4$IN$_2$, *M* = 552.16, monoclinic, space group *P*2$_1$/*c* (no. 14), *a* = 7.183(2), *b* = 17.257(5), *c* = 18.711(5) Å, *β* = 102.80 (3)°, *V* = 2261(1) Å$^3$, *T* = 93 K, *Z* = 4, Mo-K$\alpha$ radiation ($\lambda$ = 0.71075 Å), 25941 reflections measured, 6445 unique [$I > 3.00\sigma(I)$, $R_{int}$ = 0.039], $\mu$ = 14.63 cm$^{-1}$, *R* = 0.029, $R_w$ = 0.049. CCDC reference number 198779. See http://www.rsc.org/suppdata/cc/b3/b302579a/ for crystallographic data in CIF or other electronic format.

13 P. J. Stang, A. M. Arif and C. M. Crittell, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 287.

14 M. Ochiai, M. Kunishima, K. Fuji, Y. Nagao and M. Shiro, *Chem. Pharm. Bull.*, 1989, **37**, 1948.

15 D. C. Green, U. Englich and K. Ruhlandt-Senge, *Angew. Chem., Int. Ed.*, 1999, **38**, 354.