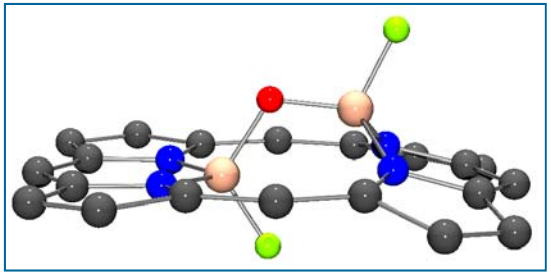
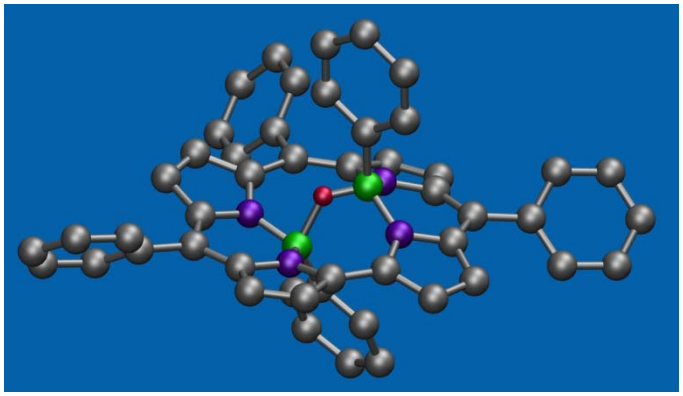
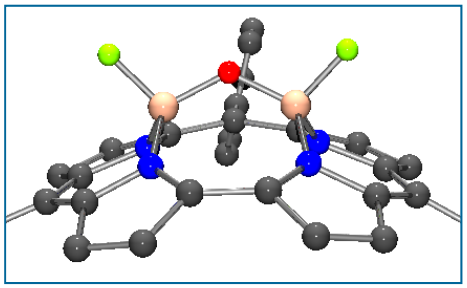
Diboron porphyrins and corroles: using computational chemistry to untangle experimental results

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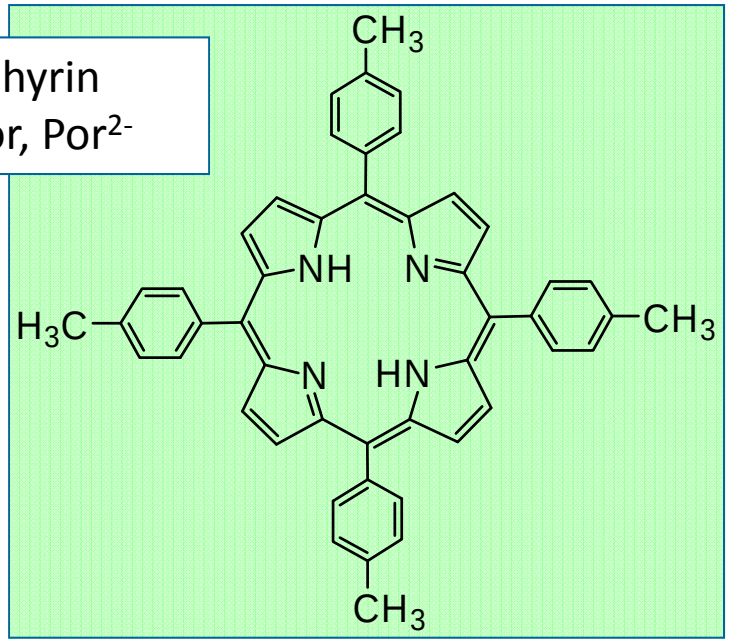
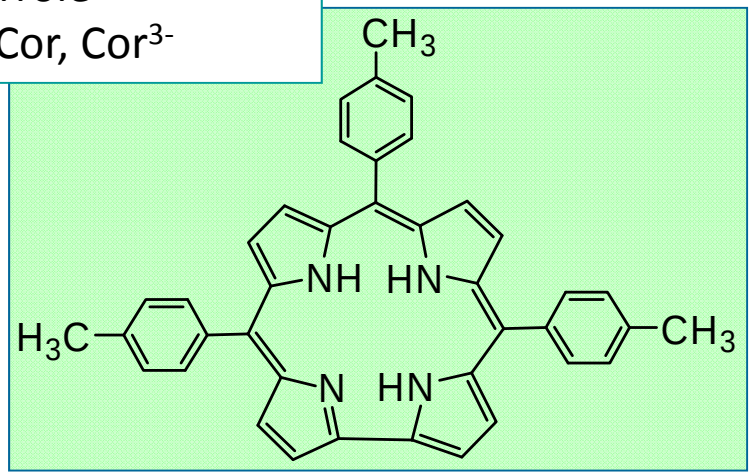
Ligands

Porphyrin
H_2Por, Por^{2-}



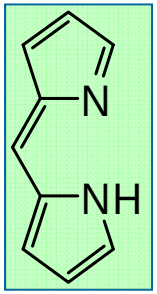
Tetra-*p*-tolylporphyrin, H_2TTP

Corrole
H_3Cor, Cor^{3-}



Tri-*p*-tolylcorrole, H_3TTC

Dipyrrin
H(dipyr), $dipyr^-$



Why study boron porphyrins and corroles?

Anticipate unusual features

- Incommensurate size of boron atom and coordination site in porphyrin
- Porphyrin complexes typically square planar, square pyramidal, octahedral
- But boron prefers trigonal planar or tetrahedral geometry

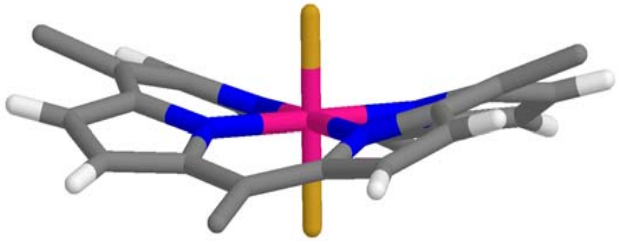
Potential applications

- Sugar sensors (boronic acids)
- Boron Neutron Capture Therapy (BNCT)

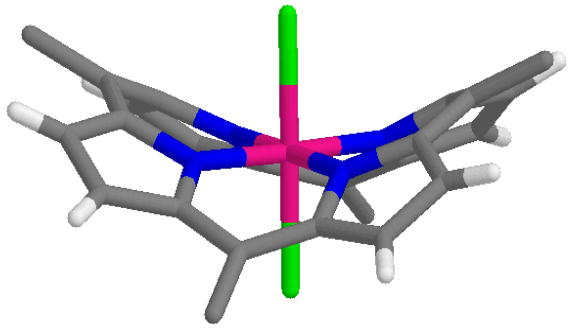
  (porphyrin to localise, neutron capture by boron)
- Laser and fluorescent dyes (difluoroboron dipyrromethene, BODIPY)

Main group porphyrin complexes

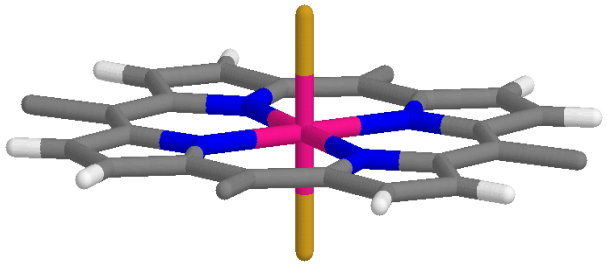
$r_{cov}(B) = 0.90$ Å



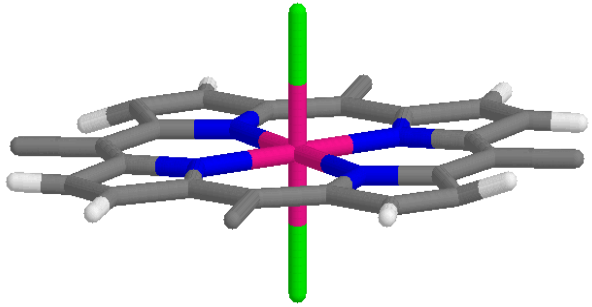
$Si(TTP)F_2$ $r_{cov}(Si) = 1.18$ Å



$[P(TPP)Cl_2]^+$ $r_{cov}(P) = 1.10$ Å



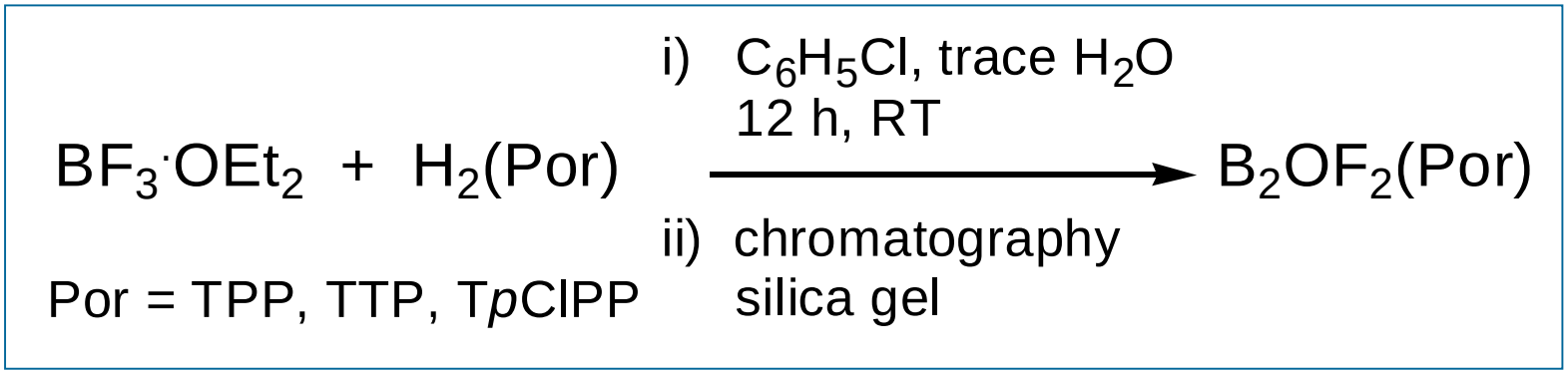
$Sn(TPP)F_2$ $r_{cov}(Sn) = 1.40$ Å



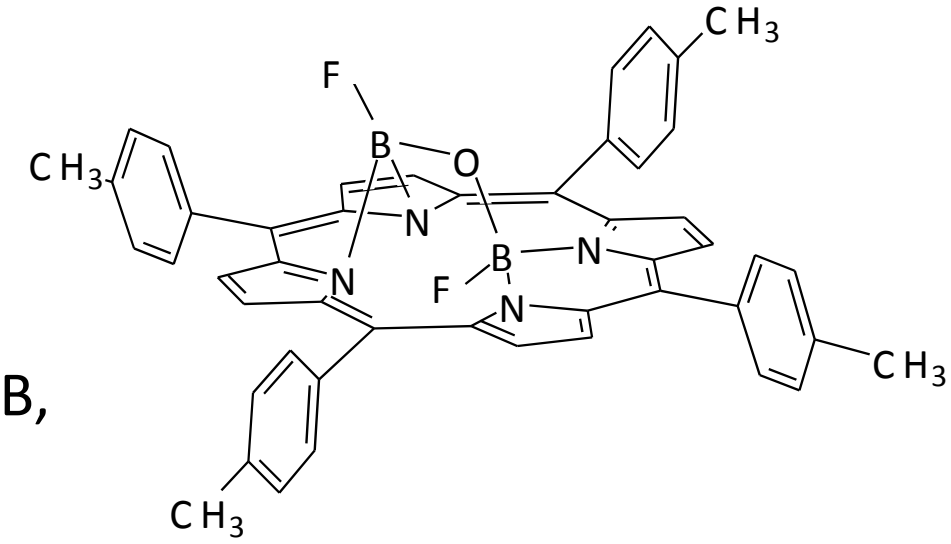
$[Sb(TAP)Cl_2]^+$ $r_{cov}(Sb) = 1.43$ Å

$Si(TTP)F_2$	Kane, K. M.; Lemke, F. R.; Petersen, J. L. *Inorg. Chem.* **1997**, *36*, 1354.
$[P(TPP)Cl_2]^+$	Guo, J. L.; Sun, F.; Li, Y.; Azuma, N. *Polyhedron* **1995**, *14*, 1471.
$Sn(TPP)F_2$	Arnold, D. P.; Tiekink, E. R. T. *Polyhedron* **1995**, *14*, 1785.
$[Sb(TAP)Cl_2]^+$	Liu, I. C.; Chen, J. H.; Wang, S. S.; Wang, J. C. *Polyhedron* **1996**, *15*, 3947.

Synthesis of a boron porphyrin complex



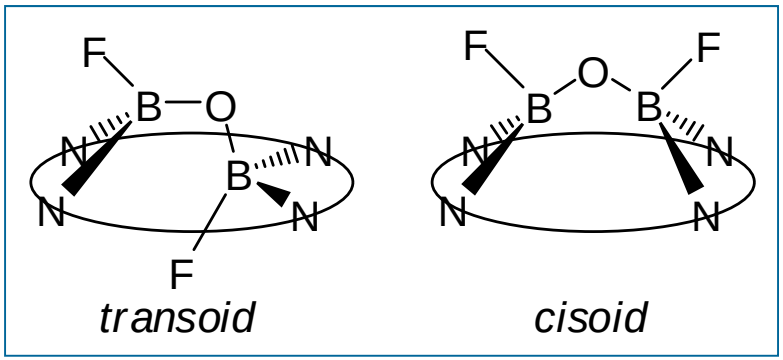
- Partial hydrolysis during reaction
- FBOBF group threaded through porphyrin cavity
- Asymmetric: one in-plane B, one out-of-plane B

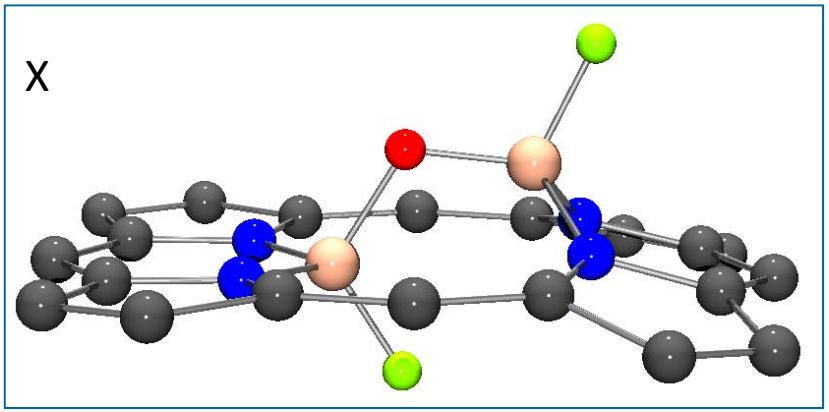


Belcher, W.J.; Boyd, P.D.W.; Brothers, P.J.; Liddell, M.J.; Rickard, C.E.F. *J. Am. Chem. Soc.* **1994**, *13*, 8416.

Cisoid versus *transoid* geometry

- Calculations show that the *transoid* geometry is *ca.* 16 kcal mol^{-1} more stable than the *cisoid* geometry





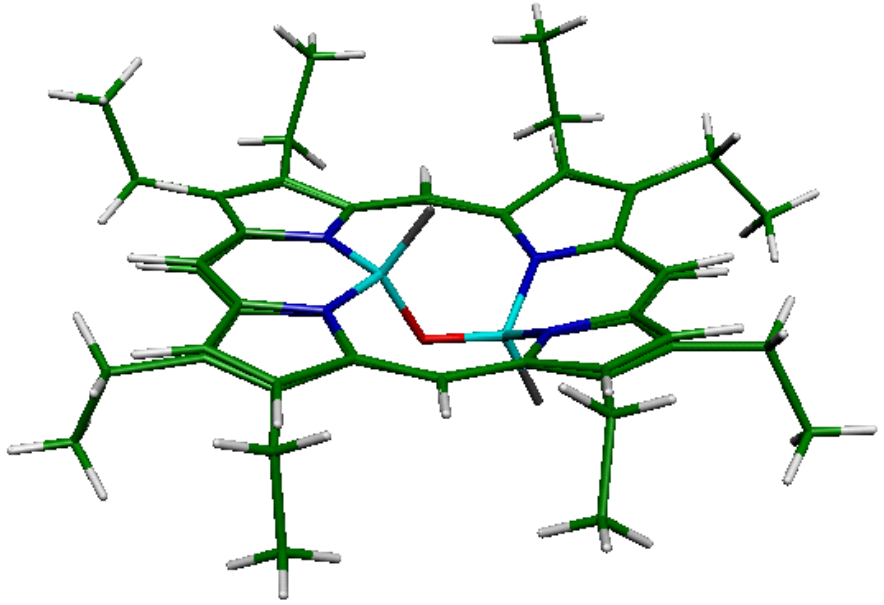
$[B_2OF_2(OEP)]$

X = molecular structure (X-ray crystallography)

DFT computations have been essential

- Structure of B_2OF_2(TTP) determined first by computation, then subsequently confirmed by X-ray crystallography on B_2OF_2(TpClPP) and B_2OF_2(OEP)
- Excellent structural agreement with DFT calculated structure of B_2OF_2(porphine) (B3LYP/6-311(d,p))

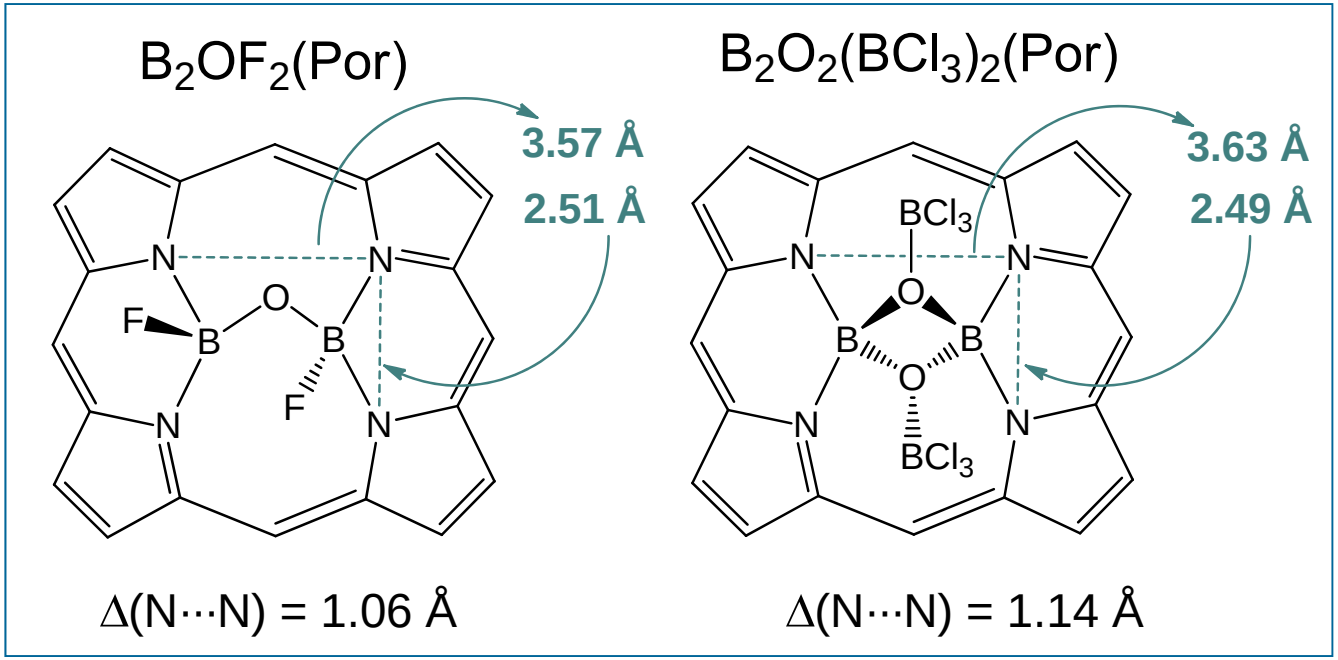
	Calc/Å	X-ray/Å
B-O-B	117.9°	116.4°
B-O(ip)	1.41	1.45
B-O(oop)	1.37	1.38
B-N(ip)	1.54	1.52
B-N(oop)	1.59	1.55



T.Köhler, M.C. Hodgson, D. Seidel, J.M. Veauthier, S. Meyer, V. Lynch, P.D.W. Boyd, P.J. Brothers and J.L. Sessler, *Chem. Commun.* **2004**, 1060-1061

Rectangular distortions in the porphyrin plane

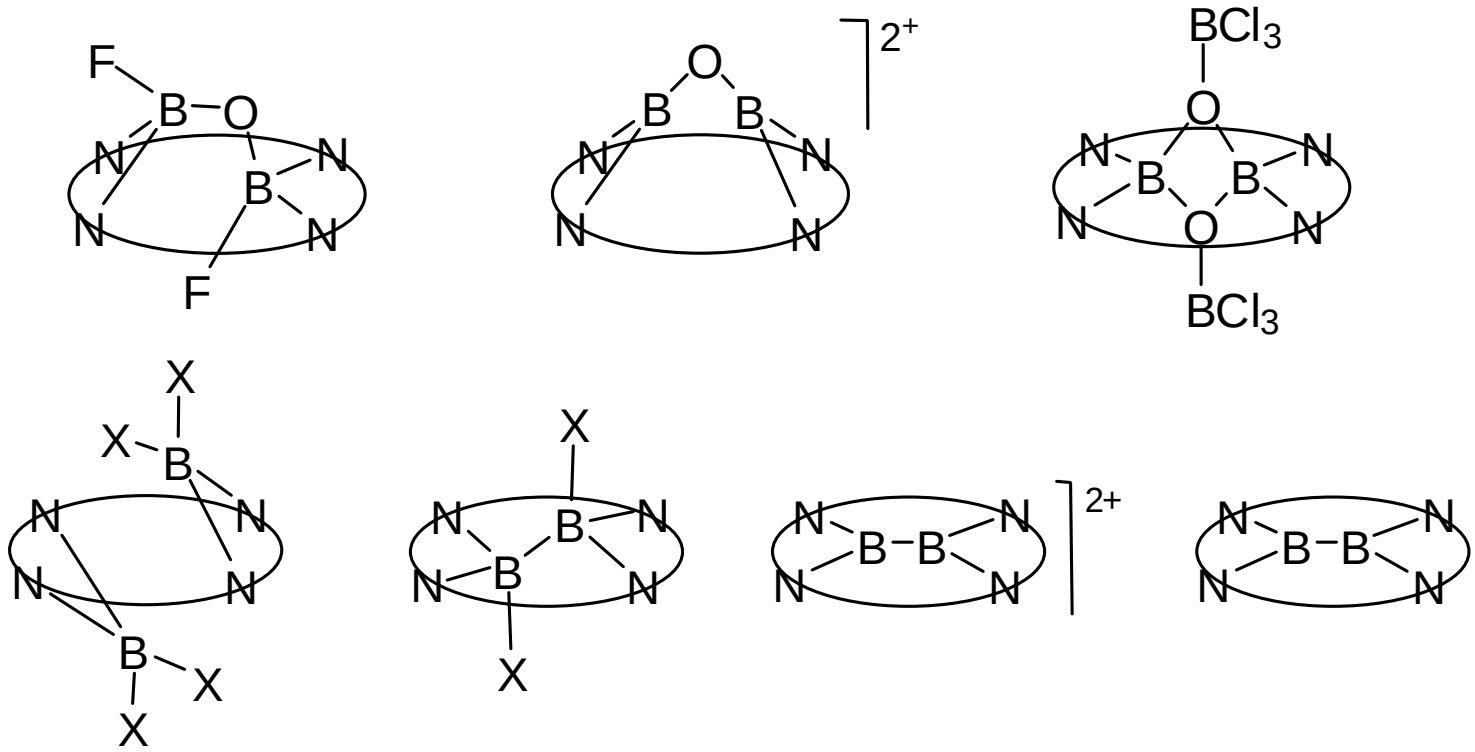
- Rectangular distortions in the porphyrin plane:
- Δ(N···N) is the difference between the non-bonded N···N distances parallel and perpendicular to B···B axis
- For boron porphyrins Δ(N···N) ranges from 0.84 to 1.28 Å



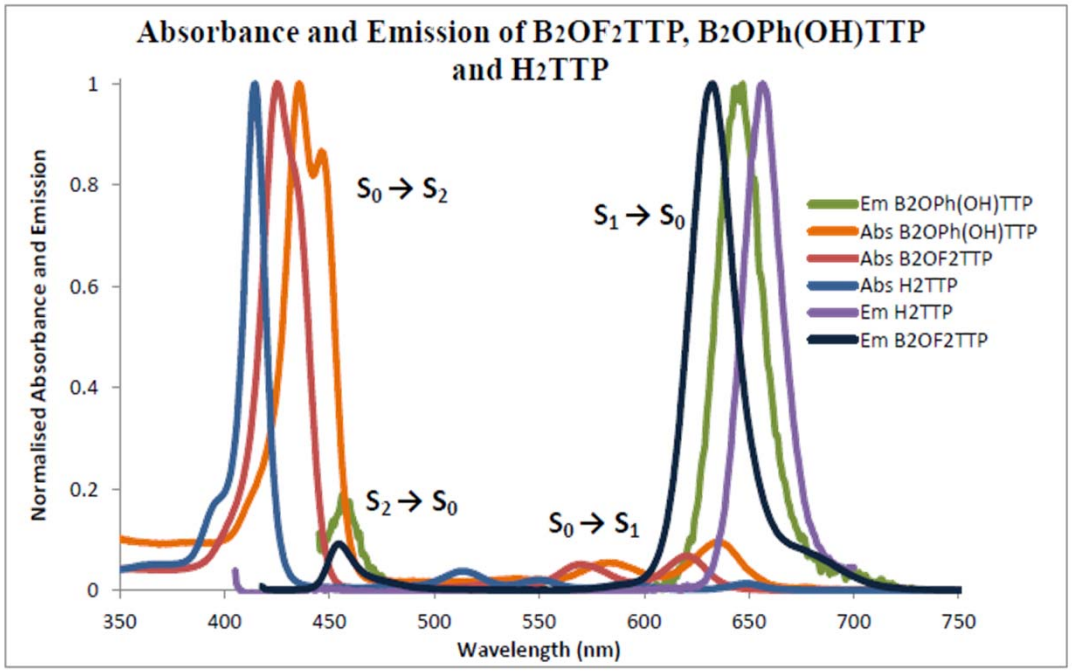
Belcher, W. J.; Hodgson, M. C.; Sumida, K.; Torvisco, A.; Ruhlandt-Senge, K.; Ware, D. C.; Boyd, P. D. W.; Brothers, P. J. *Dalton Trans*. **2008**, 1602-1614.

Boron porphyins – structural features

- Two borons per porphyrin
- Boron is four coordinate (tetrahedral) or three coordinate (trigonal planar)
- Many stereochemical possibilities
- Rectangular distortions in the porphyrin plane



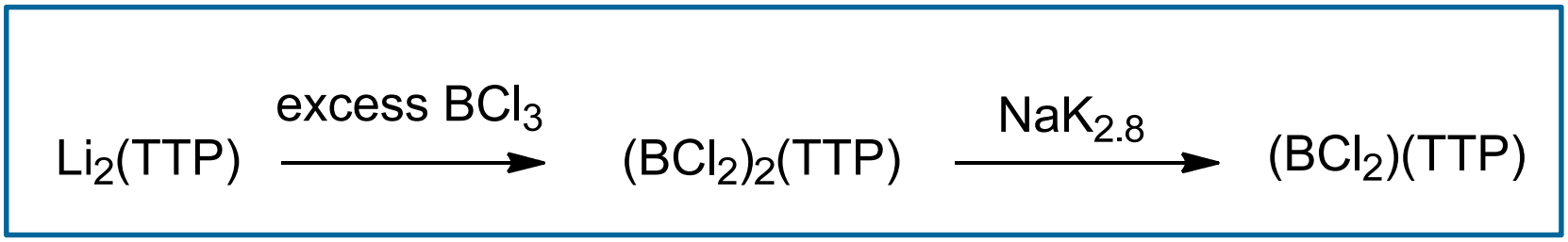
Absorption and Emission



- High molar extinction coefficient
- Large Stokes shifts
- Sharp emission profile
- Broadening of Soret band
- Fluorescence from S_2 state
- $B_2OF_2(TTP)$ – highest fluorescence quantum yield, high brightness factor

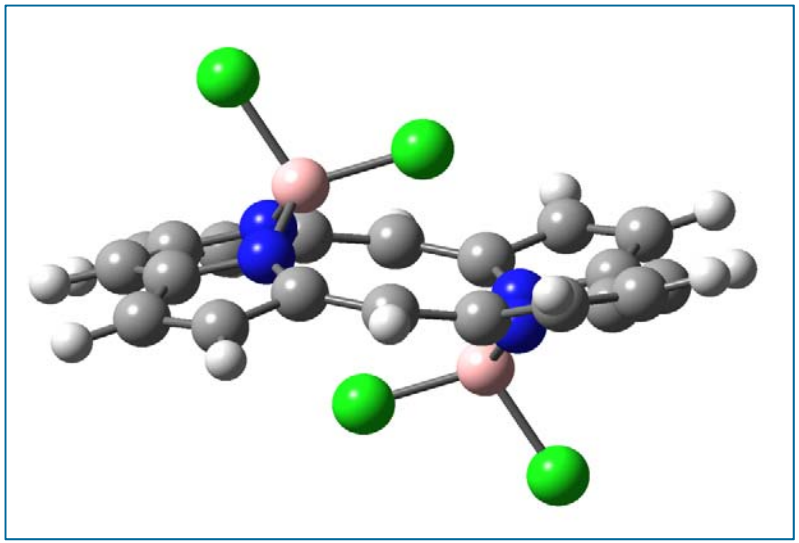
	λ_{abs} [nm]	λ_{em} [nm]	$\Delta\lambda$ [nm]	ϕ_f	ε [M^{-1} cm^{-1}]	Brightness [M^{-1}cm-1]
H_2TTP	415	655	245	0.11	360,000	39.6
B_2OF_2TTP	425	630	205	0.28	350,000	98
B_2O Ph(OH)TTP	435	645	210	0.13	160,000	20.8

Diboryl and diboranyl porphyrins



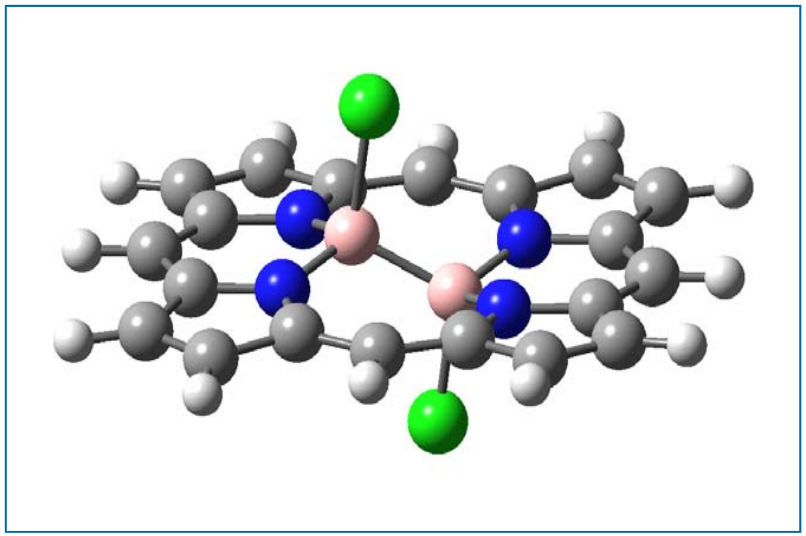
$(BCl_2)_2(TTP)$

Diboryl porphyin



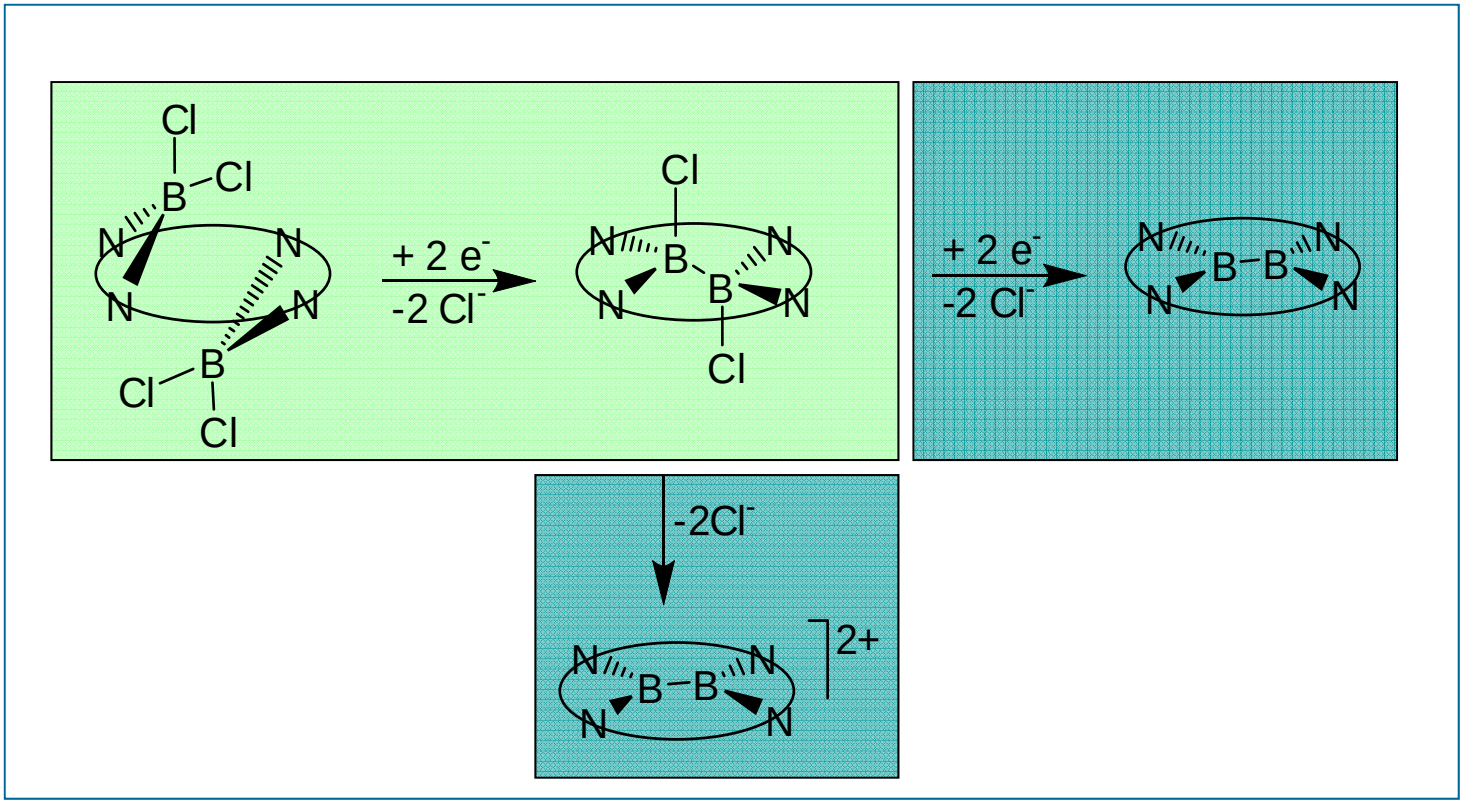
$(BCl_2)(TTP)$

Diboranyl porphyin

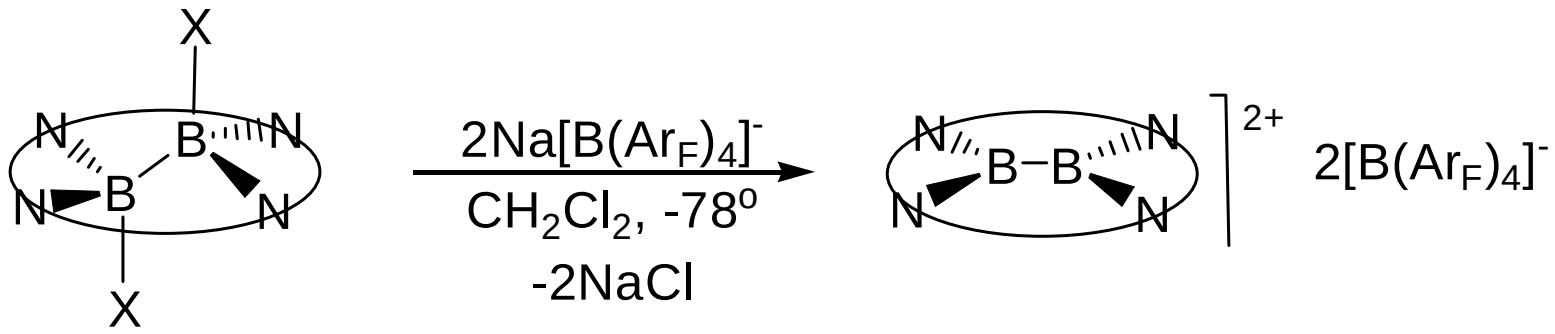


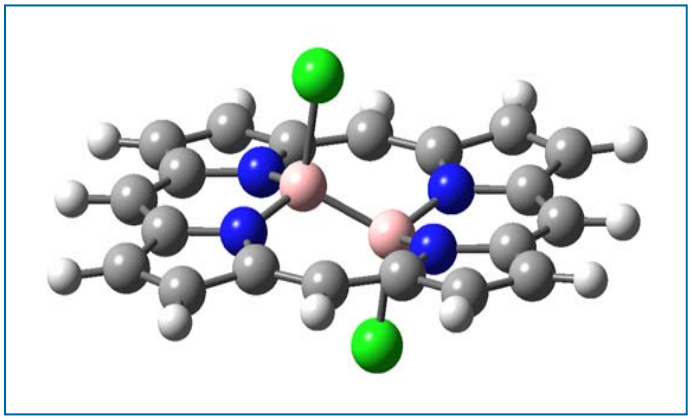
Redox chemistry

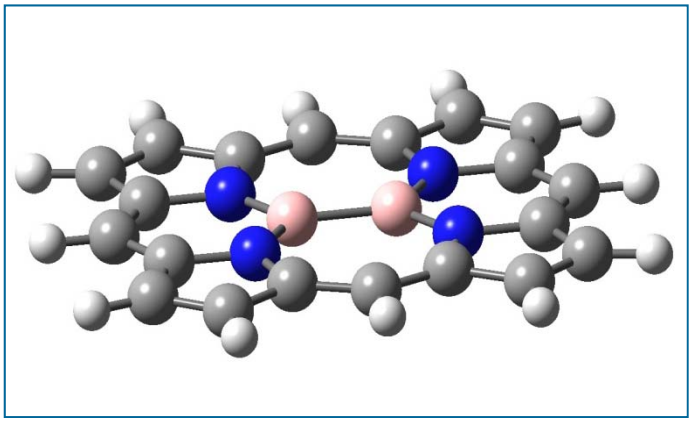
- All the complexes so far contain B(+3)
- Can envisage reduction to B(+2) or even B(+1)
- Is this possible?



Halide abstraction to form a cationic complex





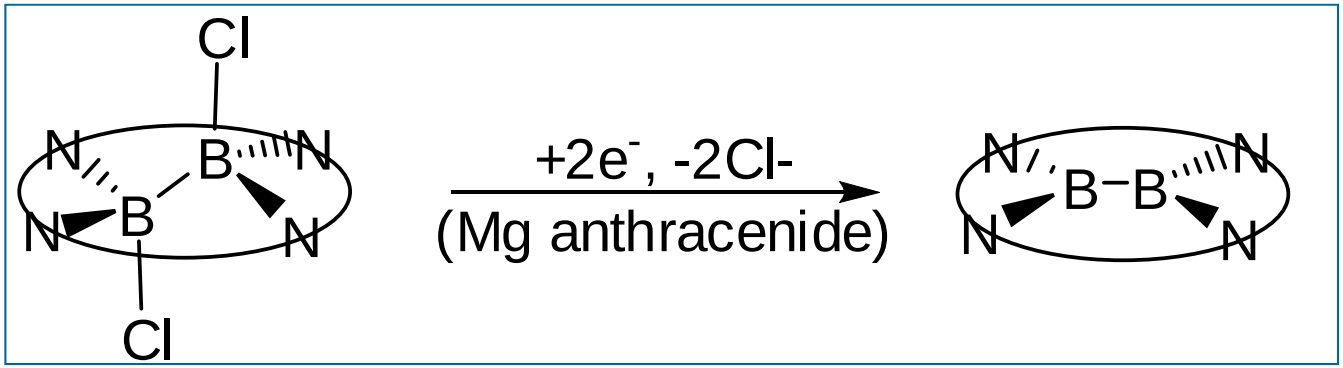


B-B	1.737 Å	1.70
B-N	1.557 Å	1.45 Å
N-B-N	105.6°	113.0°
Δ(N···N)	0.84 Å	0.89 Å

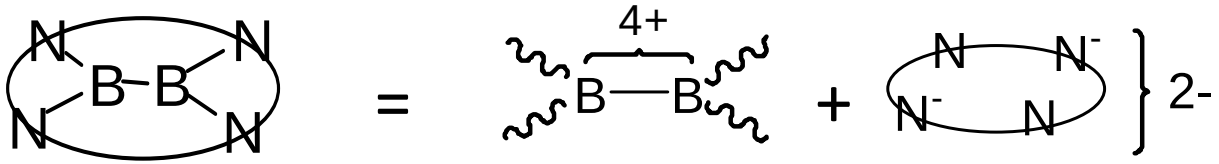
B3LYP/6-31G(d)

D_{2h} symmetry

Chemical reduction of $(BCl)_2(TTP)$

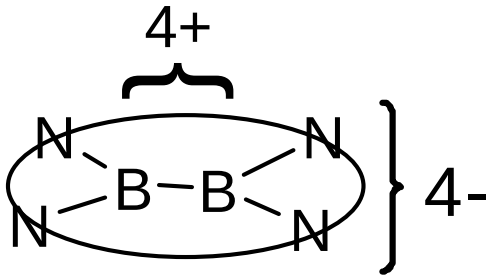


- The reduced species may be described as:
  - either a diborene, containing boron(I) and a –B=B– moiety coordinated to the porphyrin dianion
  - or a diborane in which the diboranyl unit contains boron(II), a –B–B– single bond and a porphyrin ligand reduced by two electrons to form the 20 π-electron isophlorin tetraanion



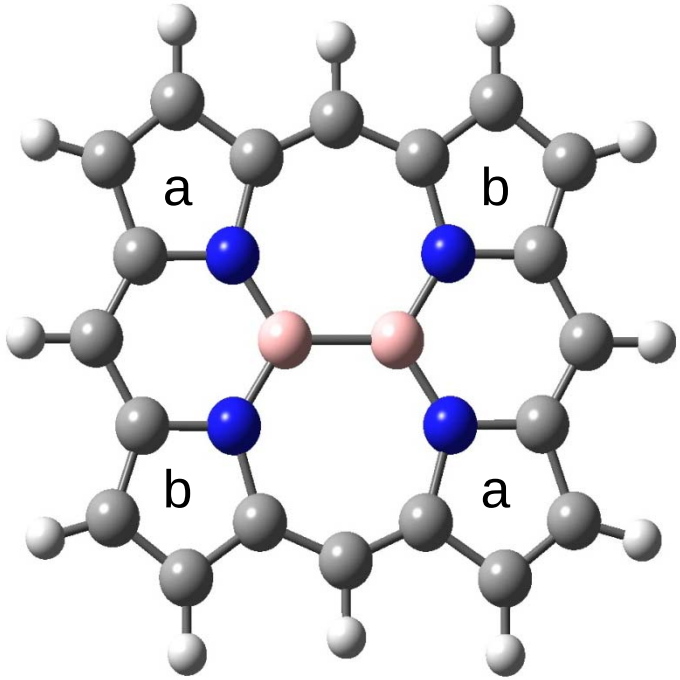
Optimised structure of B_2(Por)

- Product is *neutral* B_2(Por)
- Computation shows alternation of bond lengths/angles
- Porphyrin undergoes distortion from D_{2h} to C_{2h} symmetry



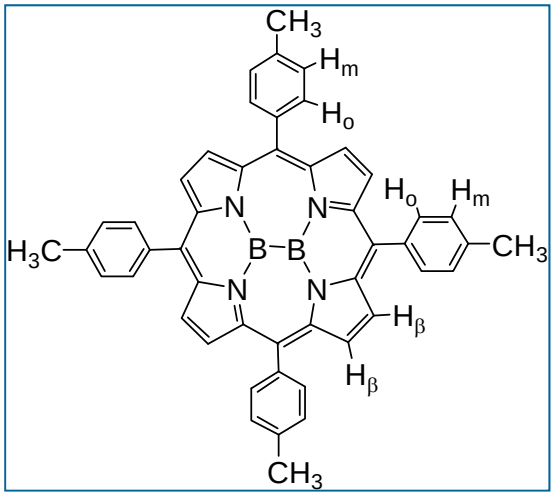
B-B	1.73 Å	
B-N	(a) 1.44 Å	(b) 1.46 Å
C_β-C_β	(a) 1.35 Å	(b) 1.40

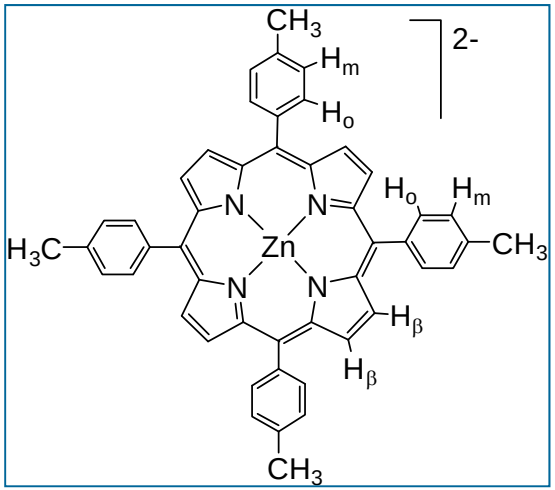
B3LYP/6-31G(d)



Compare ^{1}H NMR of B_2(TTP) and $[Zn(TTP)]^{2-}$

	$[B_2(TTP)]^{2+}$	$B_2(TTP)$	$[Zn(TTP)]^{2-}$
H_β	9.16	1.05, 0.51	-0.9 (s)
H_o	8.20	5.84, 5.69	4.95 (d)
H_m	7.73, 7.65	6.38, 6.27	6.05 (d)
CH_3	2.75, 2.70	1.64, 1.62	1.50 (s)

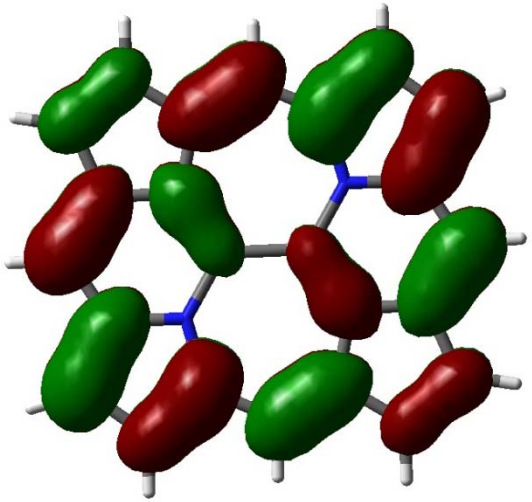


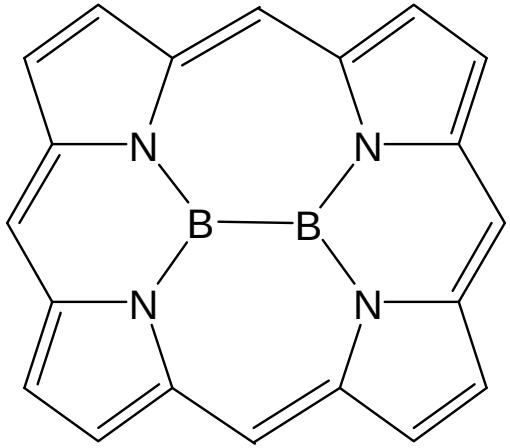


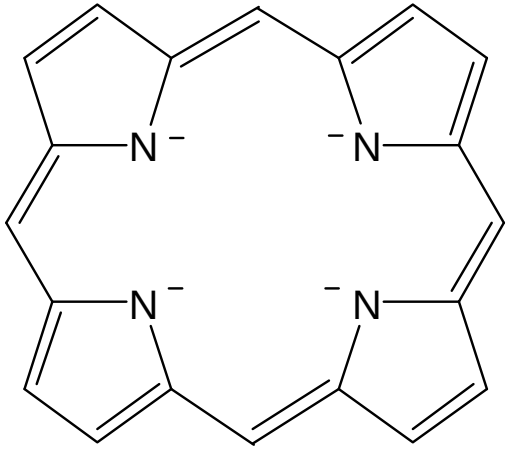
- Chemical shifts consistent with 20 π electron perimeter
- Shifts comparable with $[Zn(TTP)]^{2-}$, taking into account differences in symmetry

$[Zn(TTP)]^{2-}$ Cosmo, R.; Kautz, C.; Meerholz, K.; Heinze, J.; Müllen, K. *Agnew. Chem., Int. Ed. Engl.* **1989**, *28*, 604.

Reduced 20e$^-$ macrocycle formed by reduction

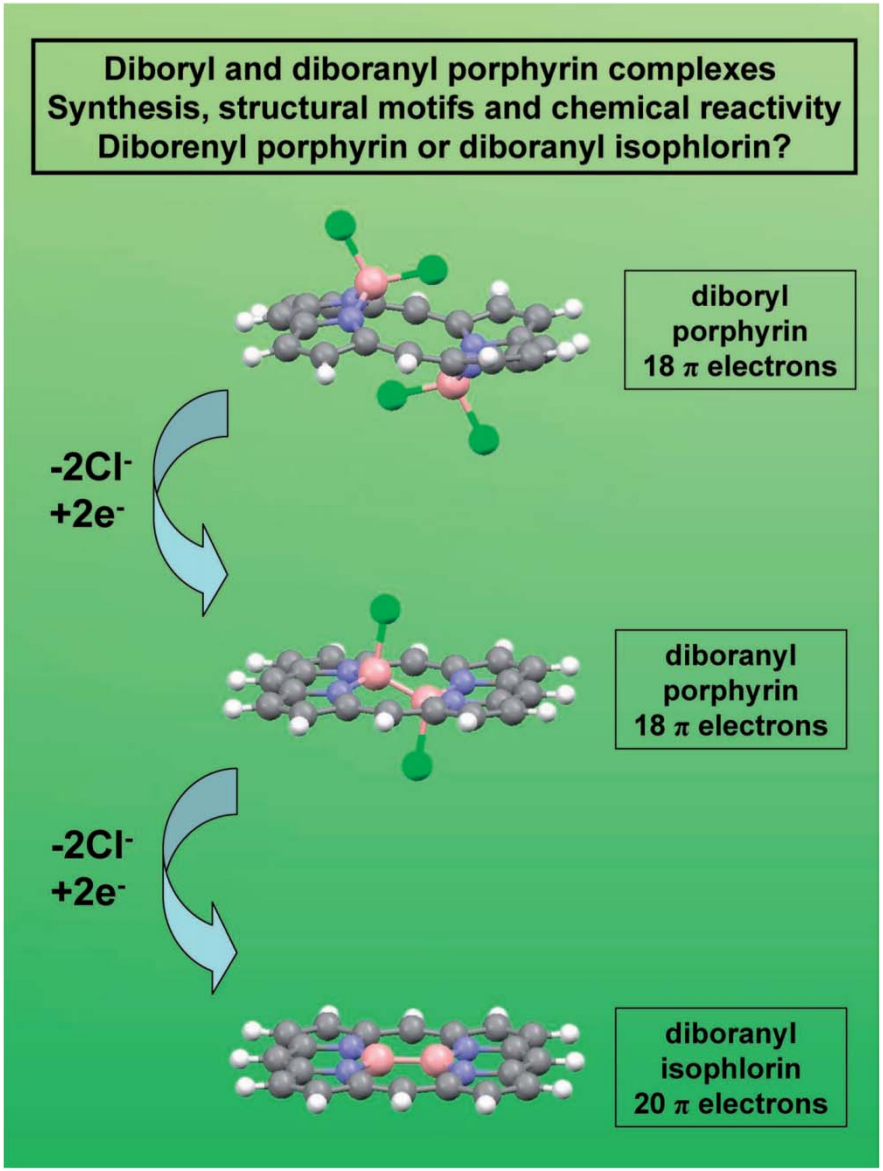






- 20-electron π system, antiaromatic, isophlorin
- HOMO calculated by DFT consistent with isophlorin (B3LYP/6-31G(d), NBO analysis)
- Antiaromatic, partially localised π electrons
- Alternating pyrrole rings also observed in calculated complex

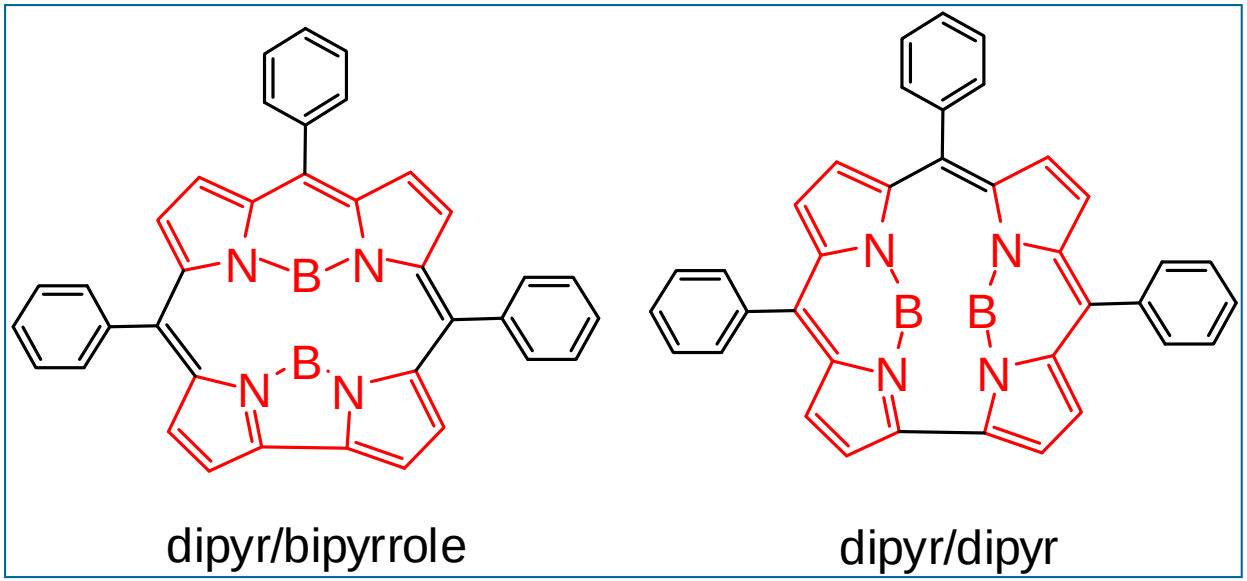
Weiss, A.; Hodgson, M. C.; Boyd, P. D. W.; Pritzkow, H.; Brothers. P. J.; Siebert, W. *Chem. Eur. J.* **2007**, *13*, 5982 – 5993.



Boron corroles: regioisomers and stereoisomers

- Regioisomers: dipyrrin site
  bipyrrole site

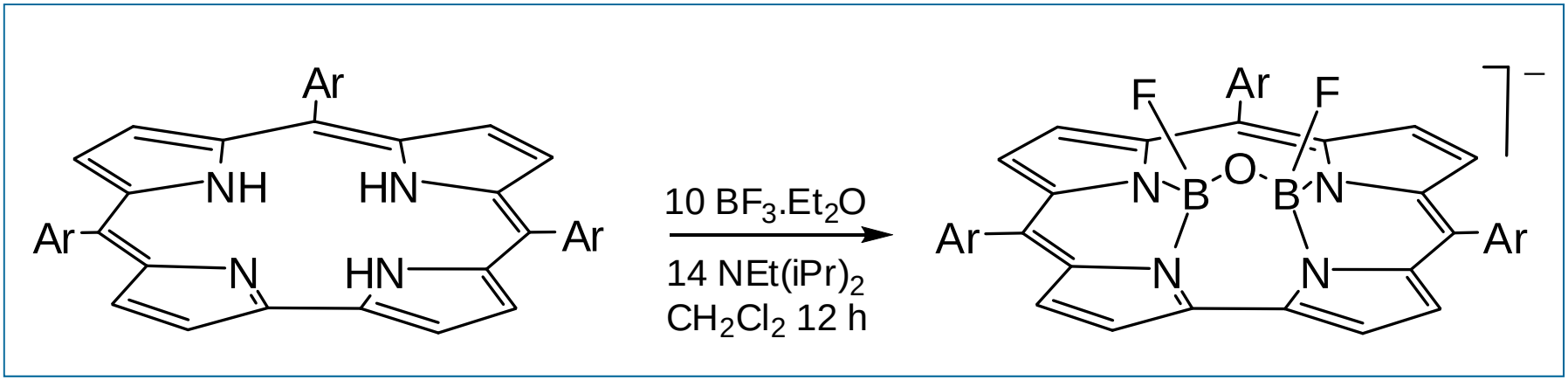
Diboron corroles



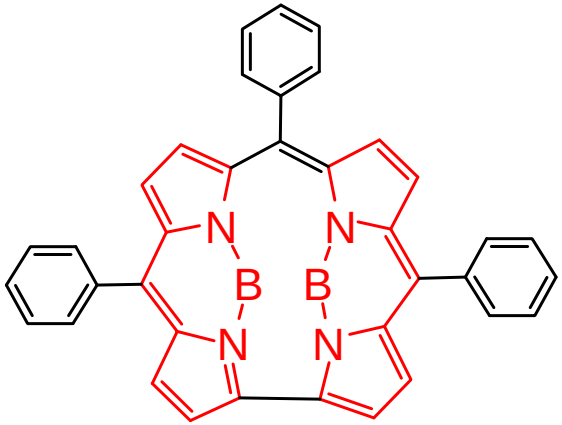
dipyr/bipyrrole dipyr/dipyr

- Stereoisomers: B in-plane, out-of-plane
  Two B atoms cisoid, transoid

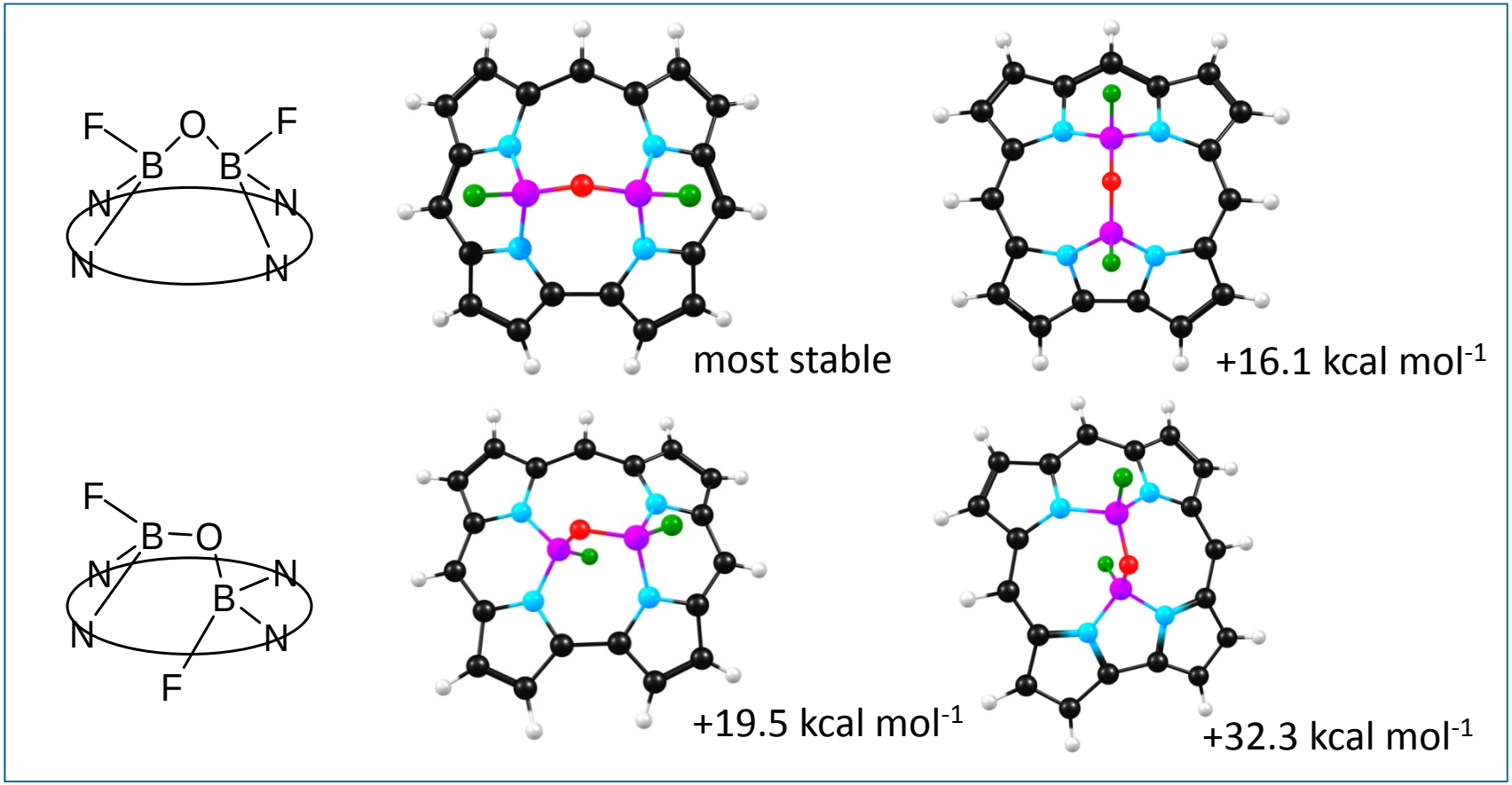
Preparation of a boron corrole complex



- Ar = C_6H_5, $C_6H_4CH_3$, C_6H_4F, $C_6H_4CF_3$
- Boron atoms coordinate in dipyrrin sites, not the bipyrrole site
- FBOBF group is on one face of corrole (cisoid)



$[B_2OF_2(Cor)]^-$ (OLYP/TZ2P)

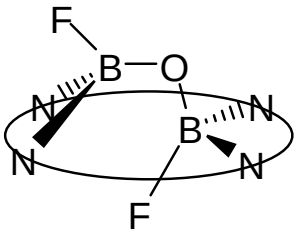


- Four possible regio/stereoisomers
- Good agreement between computation experimental data

Reaction of $BF_3 \cdot OEt_2$ with H_2Por or H_3Cor

- $B_2OF_2(Por)$

  Transoid more stable than *cisoid* by 16 kcal mol^{-1}

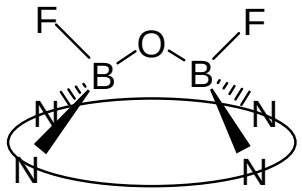


transoid

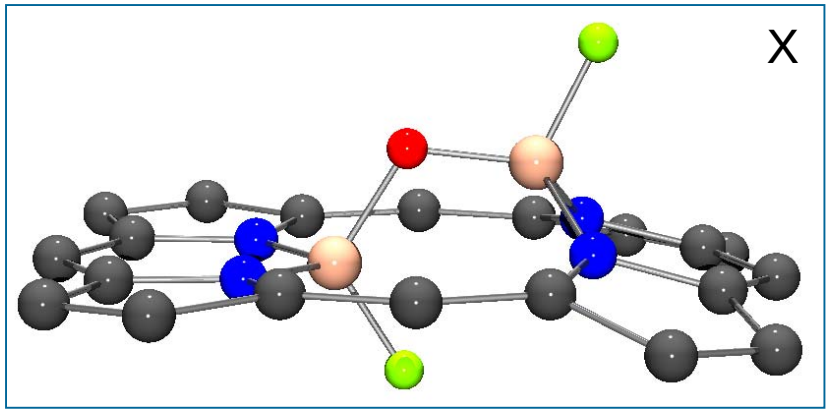
- $[B_2OF_2(Cor)]^-$

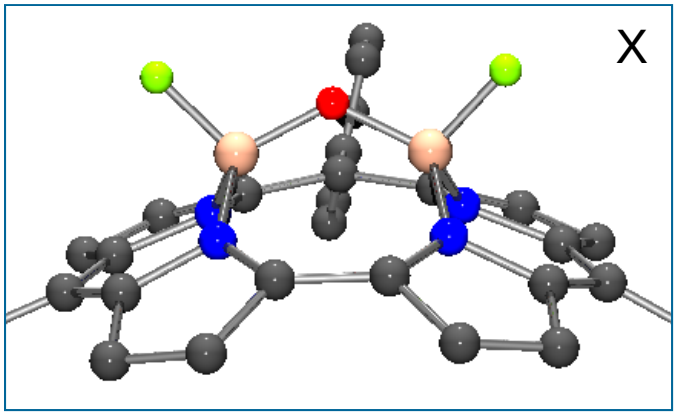
  Dipyr/dipyr regioisomer

  Cisoid more stable than *transoid* by 19.5 kcal mol^{-1}



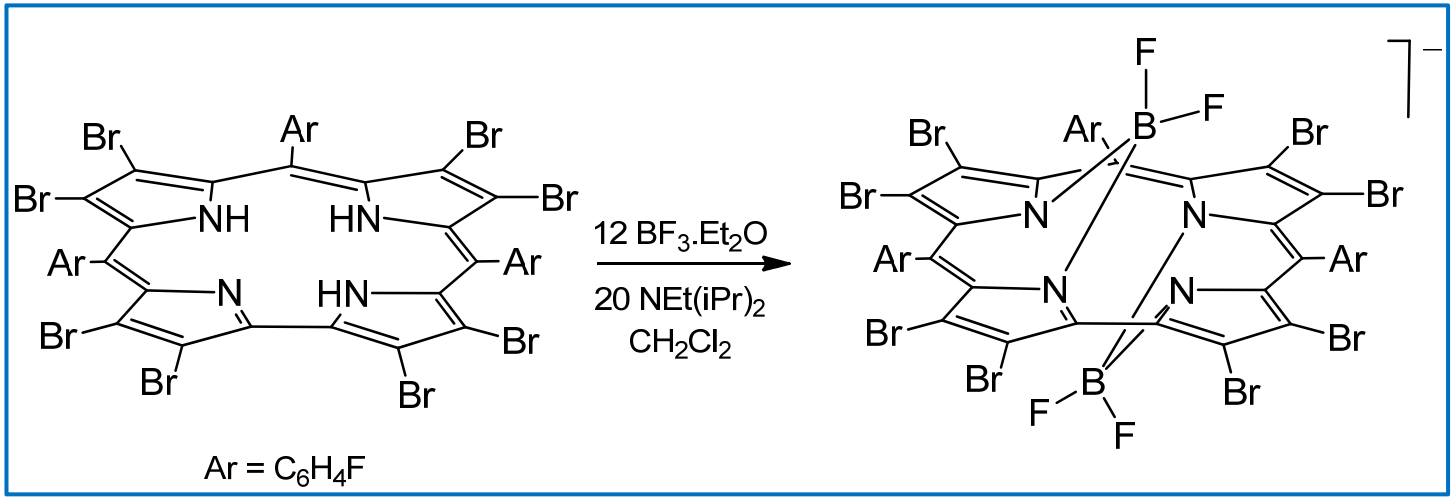
cisoid



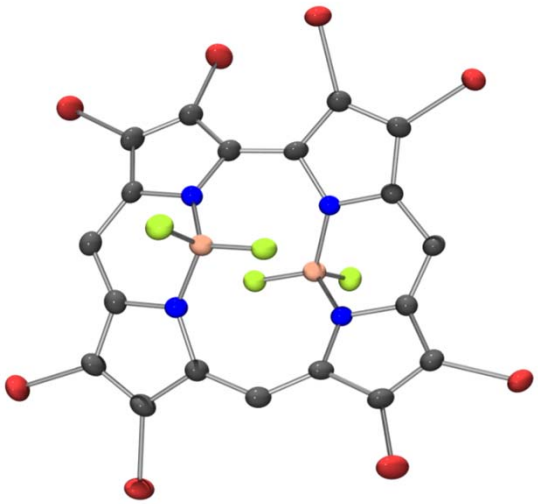


Belcher, W.J.; Boyd, P.D.W.; Brothers, P.J.; Liddell, M.J.; Rickard, C.E.F. *J. Am. Chem. Soc.* **1994**, *116*, 8416.

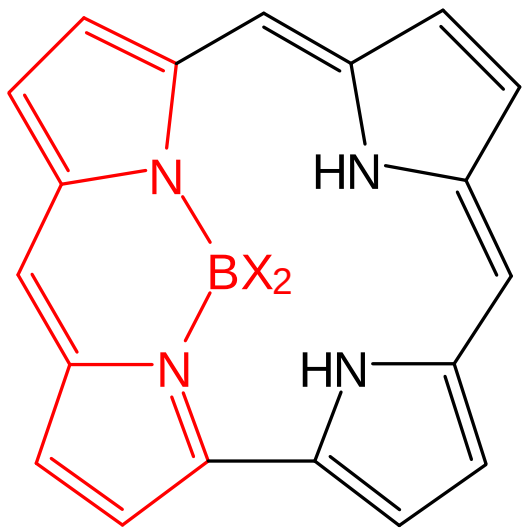
A diboryl corrole



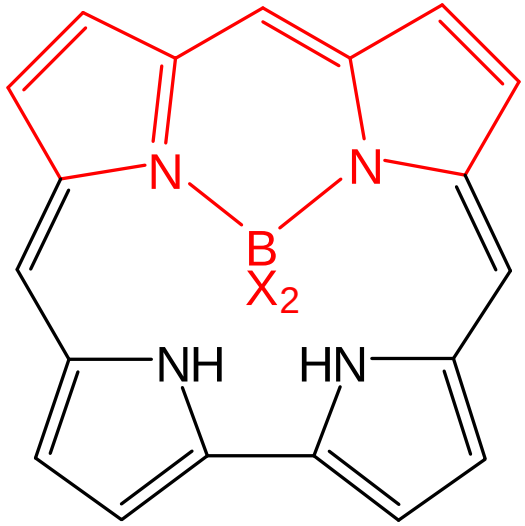
- No hydrolysis to F-B-O-B-F compound
- Relates to difficulty of doming the sterically crowded octabromo corrole – required for F-B-O-B-F compound



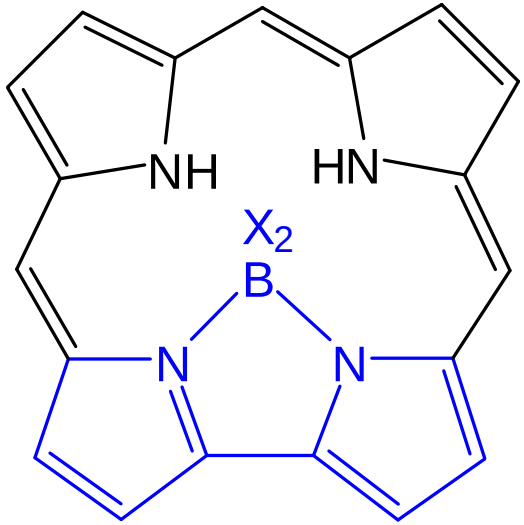
Monoboron corroles: regio- and stereoisomers



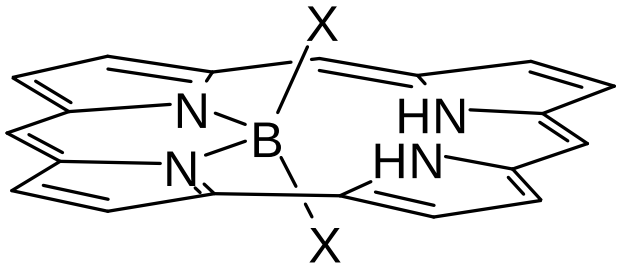
dipyrromethene-A



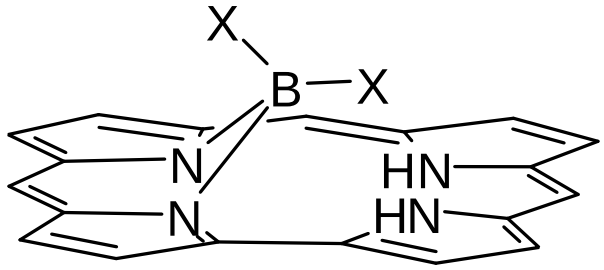
dipyrromethene-B



bipyrrole

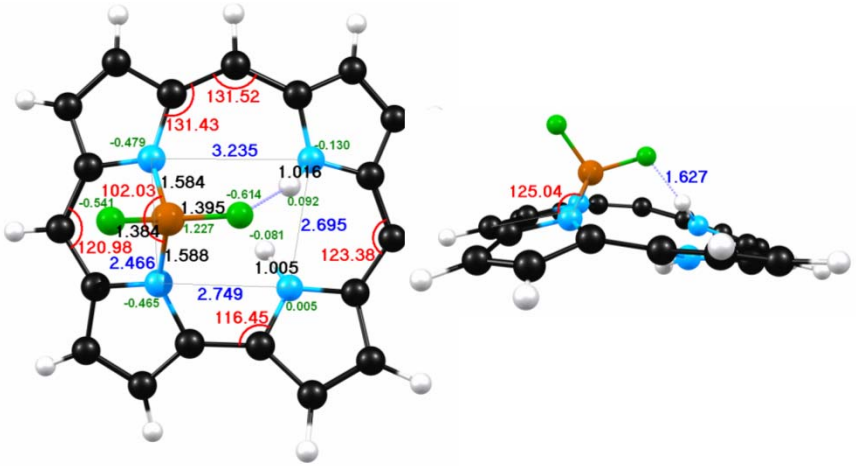


in-plane

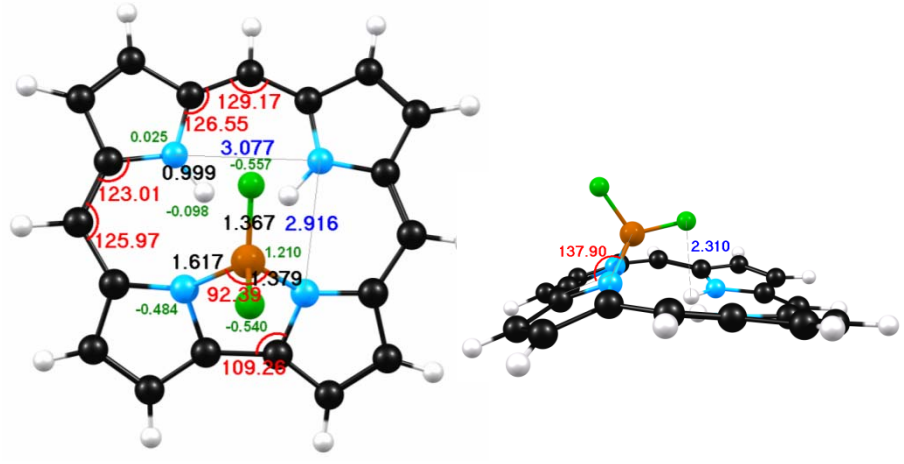


out-of-plane

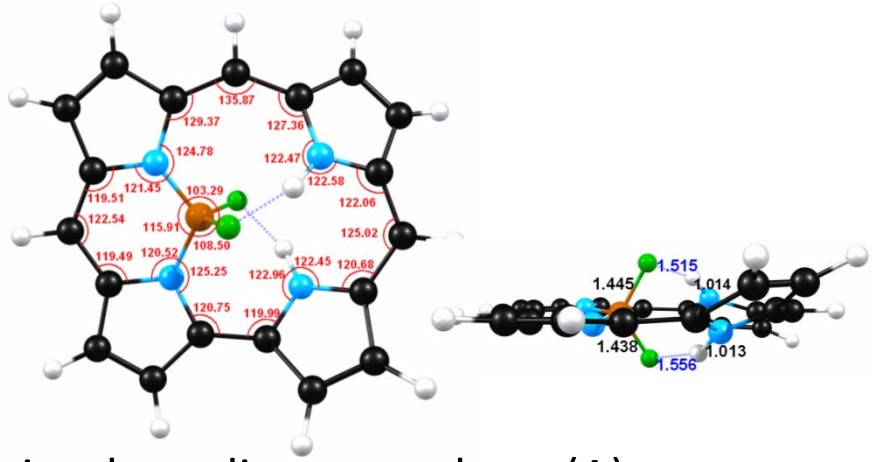
$BF_2(H_2Cor)$ optimisations (OLYP/TZ2P)



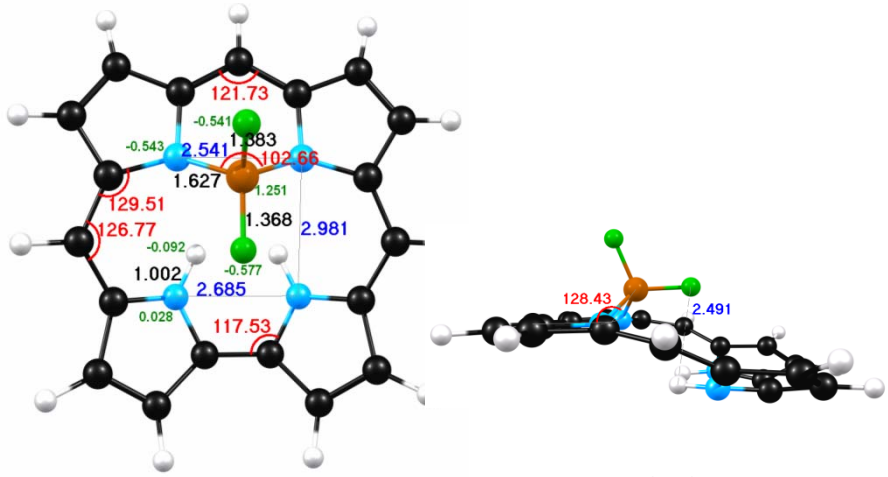
out-of-plane dipyrromethene(A)
(0 kcal mol^{-1})



out-of-plane bipyrrole
(+7.4 kcal mol^{-1})



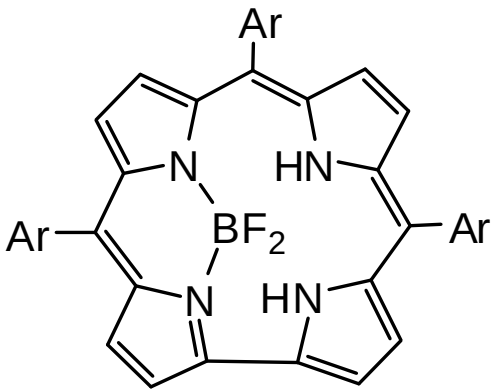
in-plane dipyrromethene(A)
(+16.6 kcal mol^{-1})

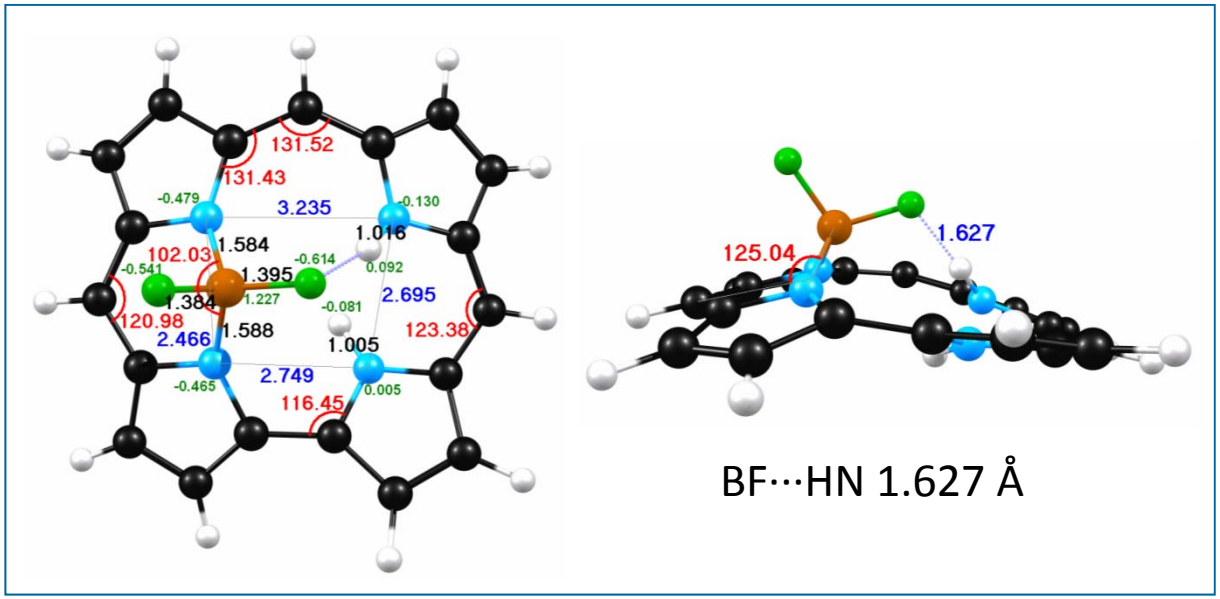


out-of-plane dipyrromethene(B)
(+10.6 kcal mol^{-1})

Monoboron BF_2 corrole complex: $BF_2(H_2Cor)$

- Monoboron BF_2 complex also isolated from reaction of $BF_3{\cdot}OEt_2$ + H_3Cor, product retains two corrole NH protons
- NMR data and DFT (OLYP/TZ2P) consistent with the lower symmetry dipyrromethene regioisomer, out-of-plane stereochemistry
- Most stable optimised structure minimises corrole distortions, maximises intramolecular B-F···H-N hydrogen bonding



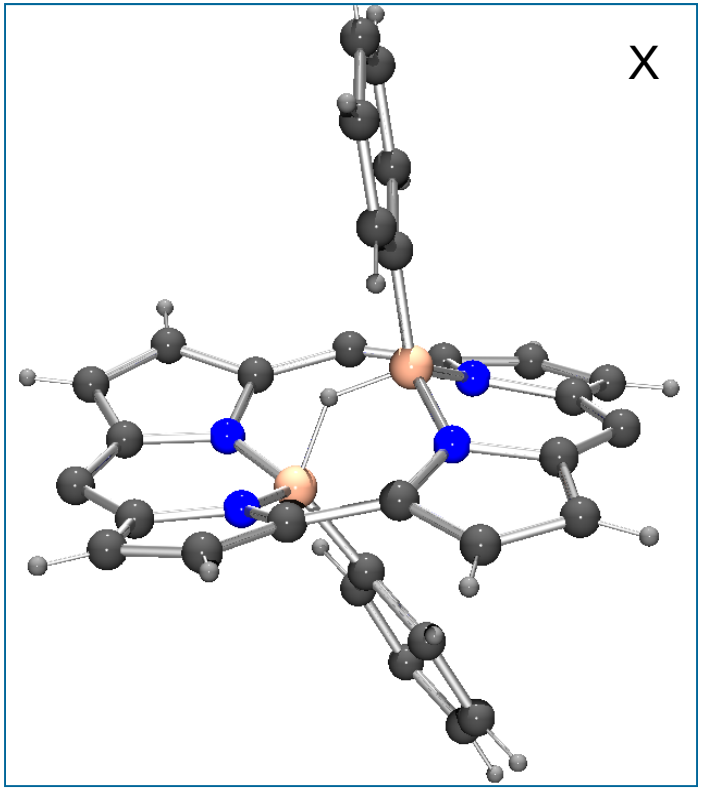


Reaction of $PhBCl_2$ with H_3Cor

$$PhBCl_2 + H_3Cor \longrightarrow PhBHBPh(Cor)$$

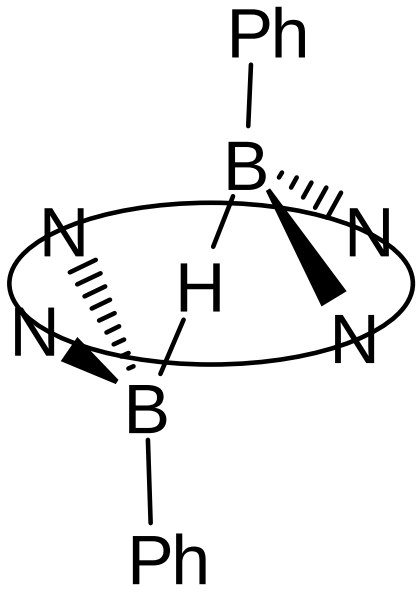
Diboron corrole $B_2Ph_2H(TPC)$:

- B-H-B bridging hydrogen located in two X-ray crystal structures
- Observed at -6.35 ppm in ^1H NMR spectrum (calc -9 ppm)
- B-H distances 1.194, 1.327 Å
- B···B distance 2.309 Å
- BHB angle 133°



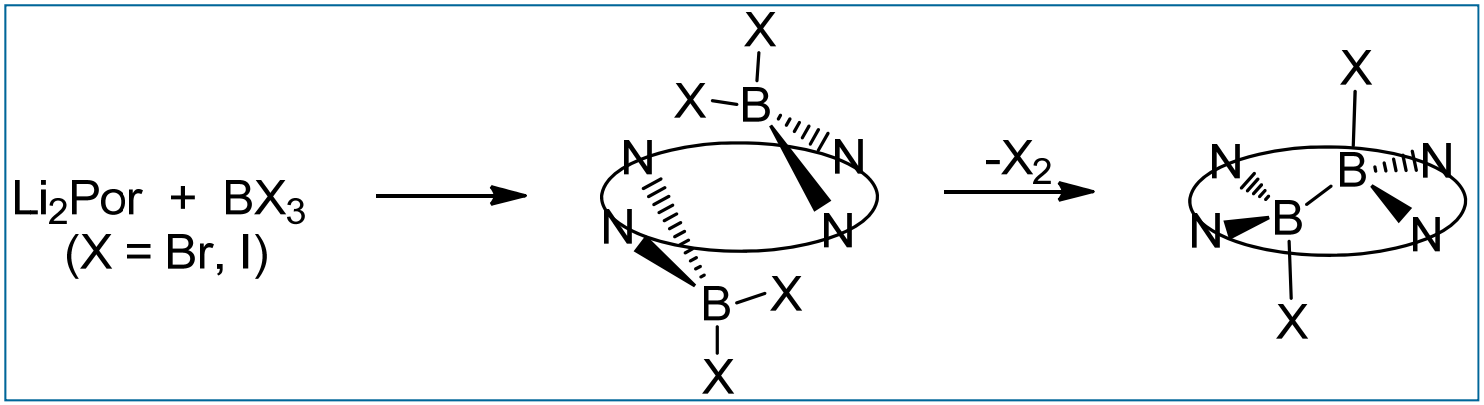
Formation of PhBHBPh(Cor)

- The formation of this product requires a net chemical reduction
- What is being oxidised?
- Is there precedent for this type of reaction?



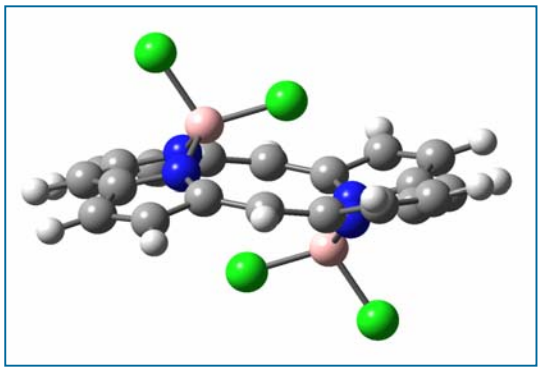
$$2PhBCl_2 + H_3(TTC) + 2e^- \longrightarrow B_2Ph_2H(TTC) + 2HCl + 2Cl^-$$

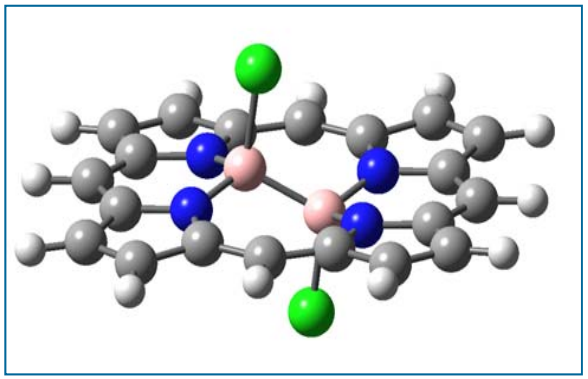
Spontaneous reductive coupling in boron porphyrins



BF_3, BCl_3 + Li_2Por gives $(BX_2)_2(Por)$

BBr_3, BI_3 + Li_2Por gives $(BX)_2(Por)$

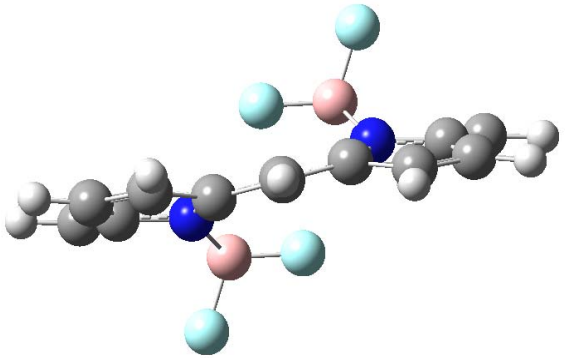




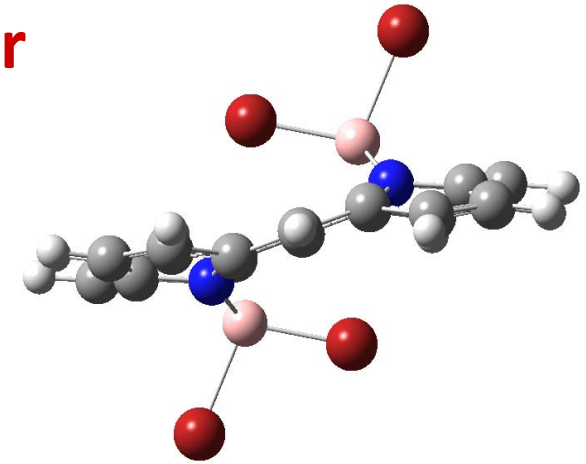
- Driving force linked to strongly distorted, crowded molecule in $(BX_2)_2(Por)$

$(BX_2)_2$(Por) for all X = F, Cl, Br, I

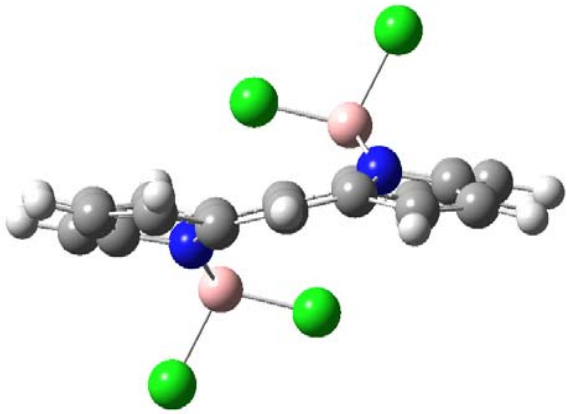
F



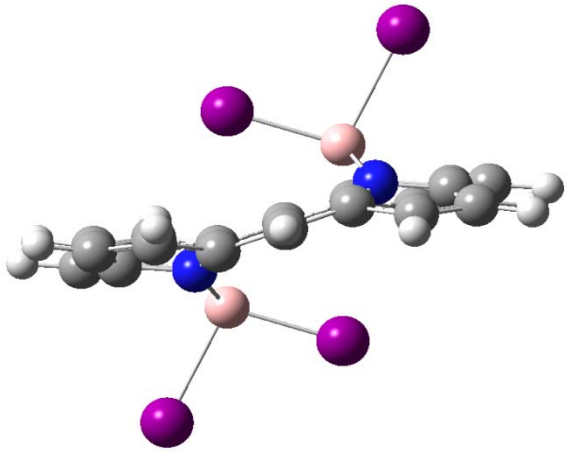
Br



Cl



I

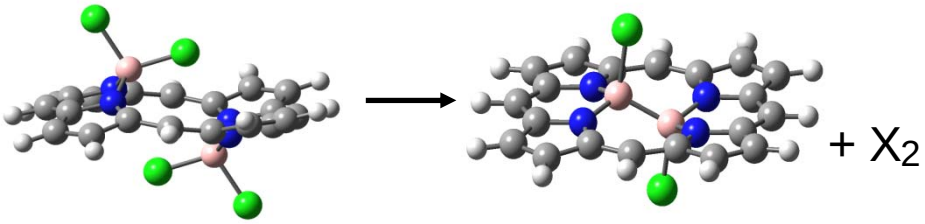


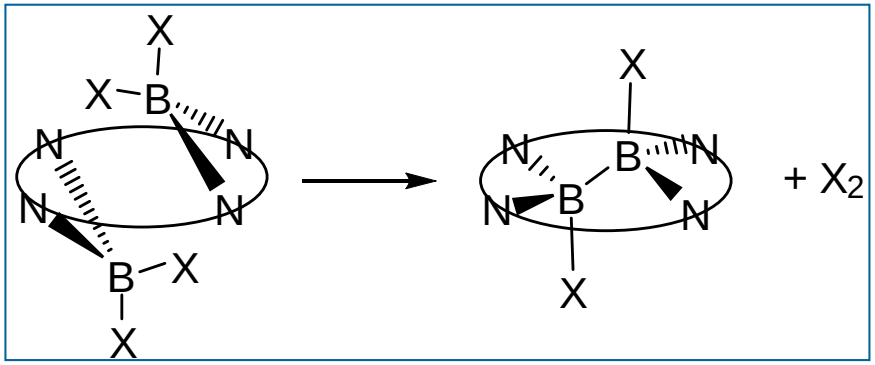
B3LYP/6-311G(d,p)

Thermochemical calculations

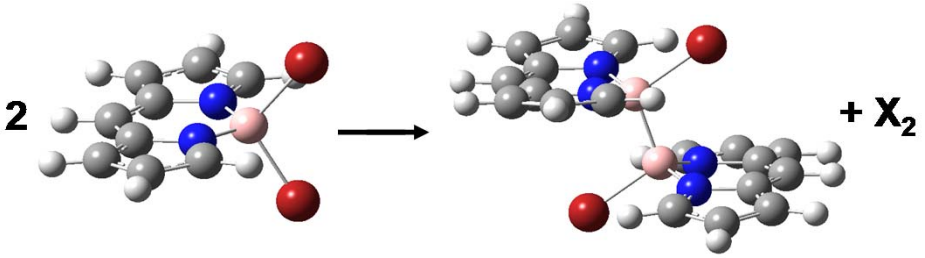
- ΔH and ΔG calculated for the reductive elimination reaction for porphyrin and dipyrromethene reactions:

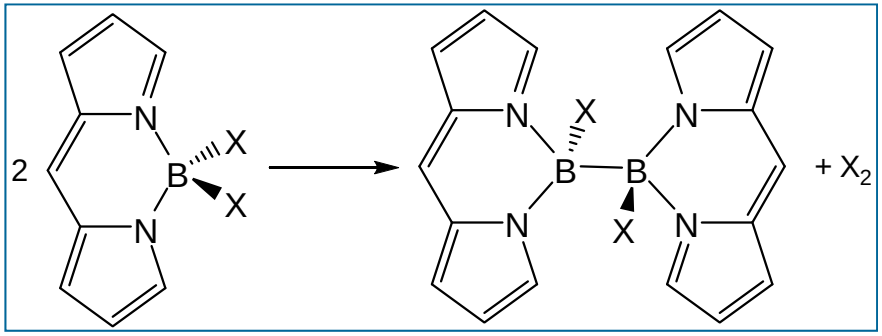
Porphyrin:





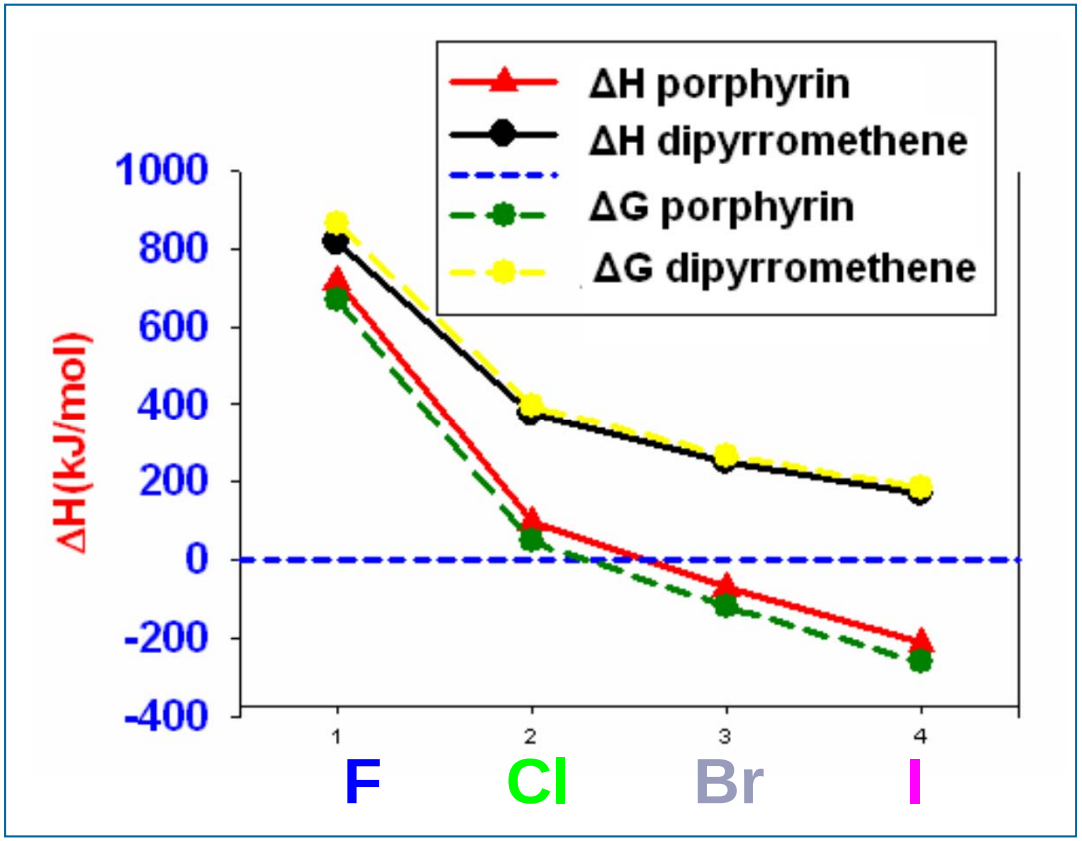
Dipyrromethene:





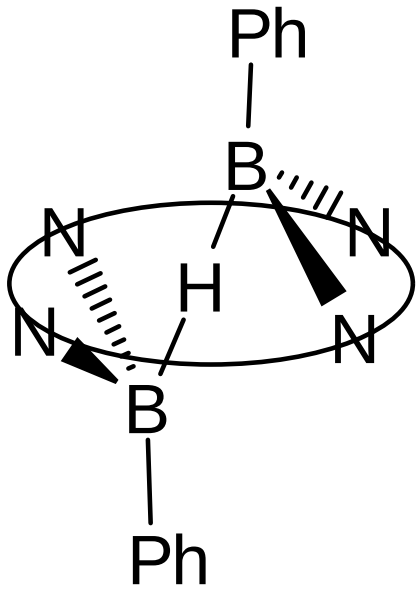
ΔH, ΔG for reductive coupling in diboryl porphyrins

- Porphyrin: ΔH and ΔG **negative for Br, I**
  ΔH and ΔG positive for F, Cl
- Dipyrrin: ΔH and ΔG positive for F, Cl, Br, I



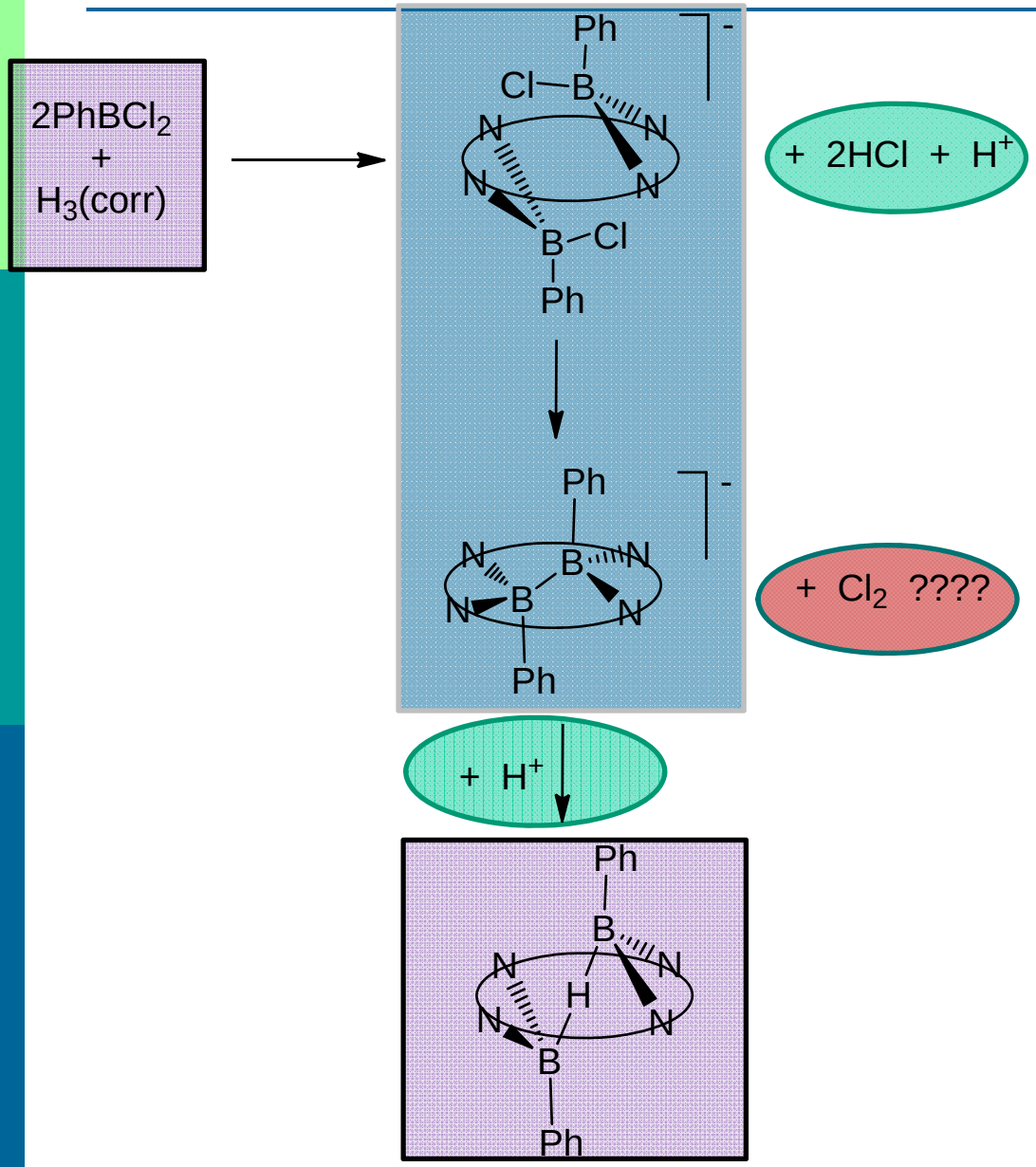
Formation of PhBHBPh(Cor)

- The formation of this product requires a net chemical reduction
- What is being oxidised?
- Is there precedent for this type of reaction?



$$2PhBCl_2 + H_3(TTC) + 2e^- \longrightarrow B_2Ph_2H(TTC) + 2HCl + 2Cl^-$$

Another example of reductive coupling?



Start and end points known

Propose reductive coupling, similar to porphyrin example

Known from boron cluster chemistry

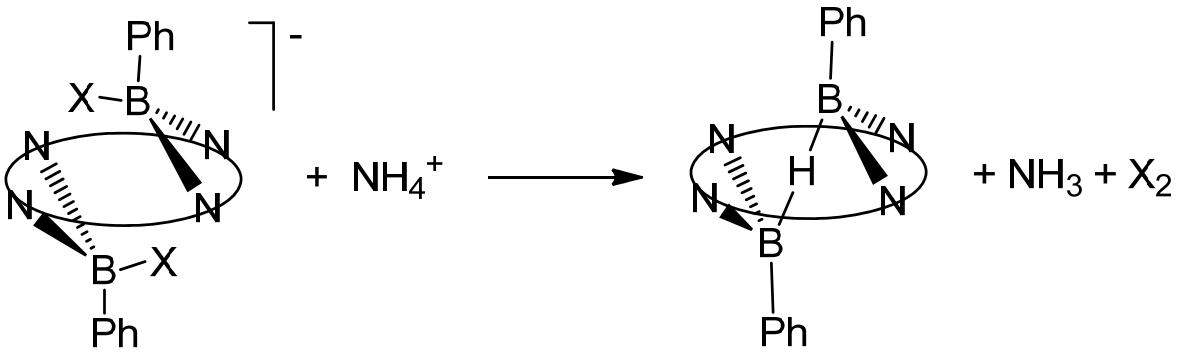
Is this really occurring?

Test by modelling

Model the reaction of $PhBX_2$ with corrole for X = F, Cl, Br, I using computational chemistry

Negative values of ΔG indicate the B-H-B product **should be** observed when **X = Cl, Br and I**

Positive value of ΔG indicates the B-H-B product **should NOT be** observed when **X = F**

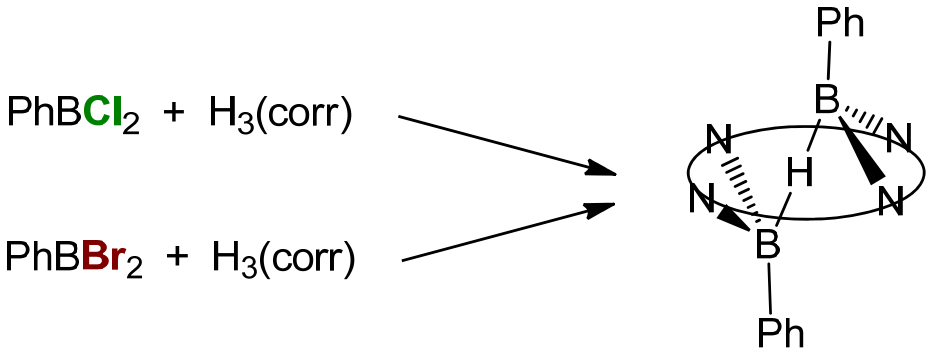


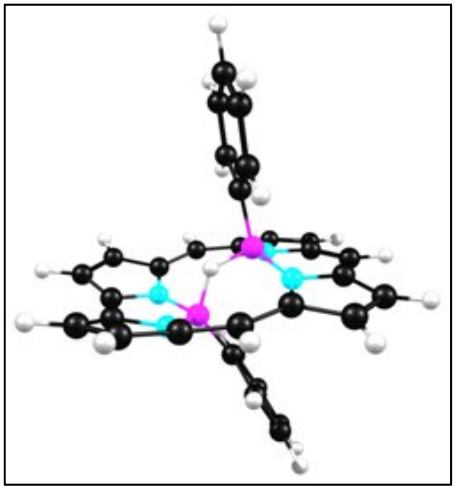
	ΔG / kcal mol^{-1}
F	+32.0
Cl	-90.3
Br	-121.7
I	-153.9

OLYP-TZ2P

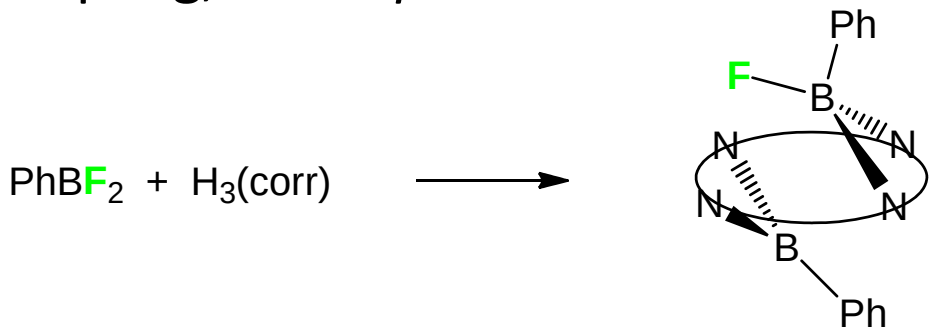
Test by experiment

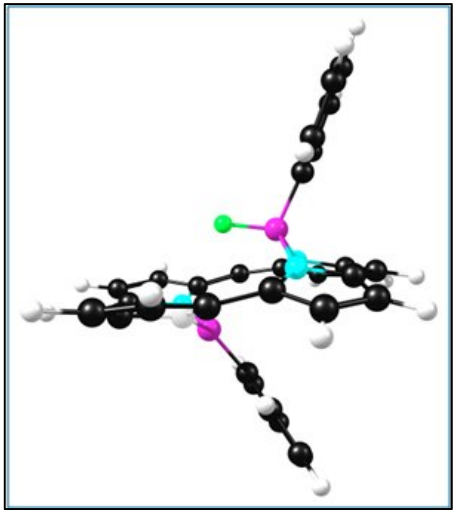
Reaction of $PhBCl_2$ and $PhBBr_2$ with corrole **both** give the B-H-B product, *as we predicted*





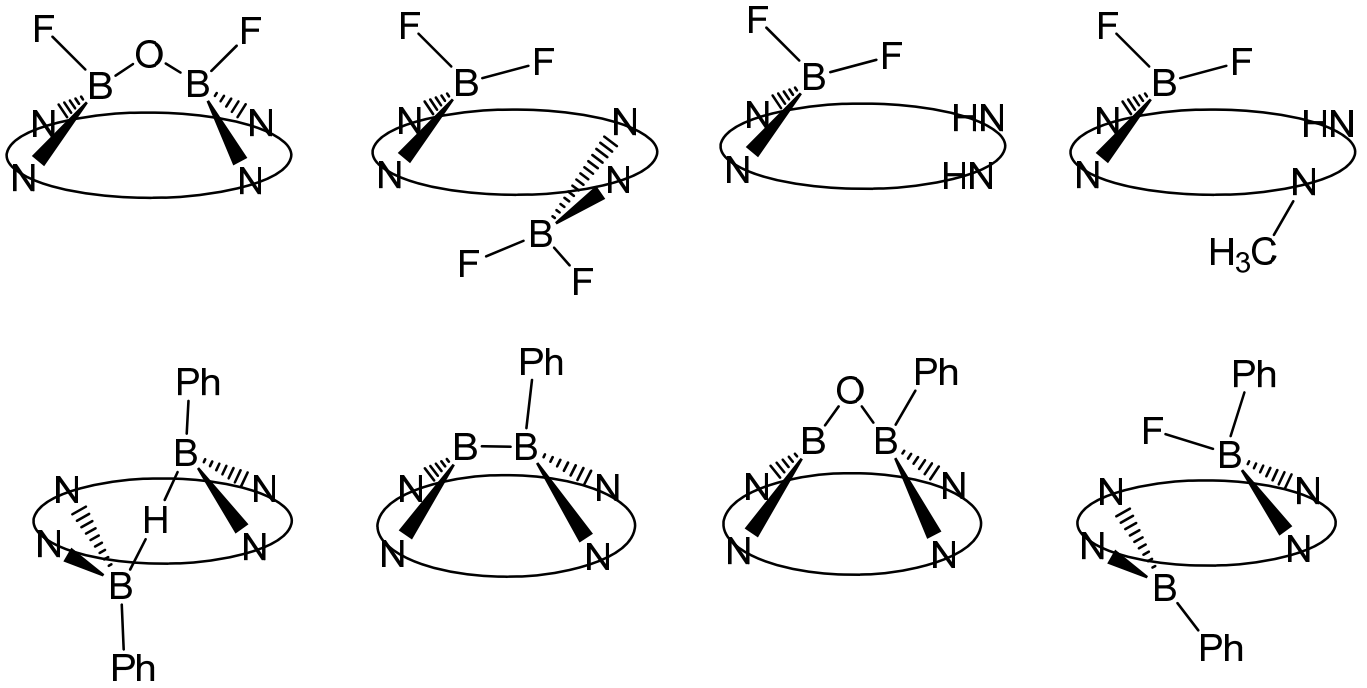
Reaction of $PhBF_2$ with corrole gives a **different** product which does **not** involve reductive coupling, *as we predicted*





Albrett, A.M.; Boyd, P. D. W.; Clark, G. R.; Gonzalez, E.; Brothers, P. J., *Dalton Trans*. **2010**, *39*, 4032

Mono and diboron corroles



- New compounds and structural types
- Sterically induced reductive coupling

Feature article: Brothers, P. J. *Chem. Commun.* **2008**, 2090–2102

Forum: Brothers, P.J. *Inorg. Chem.* **2011**, *50*, 12374-12386.

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Dr Kolle Thomas
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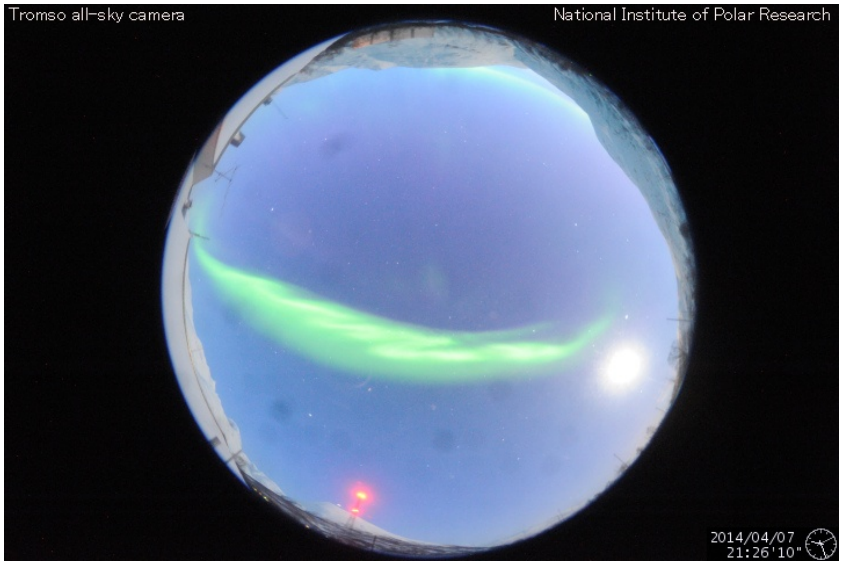

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