The redox reaction between a bulky BODIPY and a magnesium(I) reducing agent leads to the formal one-electron reduction of the BODIPY, initially generating a dipyrrromethene-centred radical compound that dimerises via C–C bond formation. In contrast, reduction with magnesium anthracene leads to the formal two-electron reduction of the BODIPY, resulting in the formation of the corresponding anion.

4,4-Difluoro-4-bora-3a,4a-diaza-s-indacenes, more commonly known as BODIPYs, are typically strongly UV-absorbing molecules that fluoresce at visible wavelengths with high quantum yields.1 Due to these excellent photophysical properties along with their easy synthesis, low toxicity, and high stability, BODIPYs have found wide applications in biological imaging,2 optoelectronics3 and sensing.4

The redox chemistry of BODIPYs has recently attracted interest,5 with several studies showing that BODIPY compounds can undergo reversible redox processes.6 Moreover, subtle variations of substituents at the α-, β-, and γ-pyrrole and meso positions of the BODIPY core (Figure 1) have been found to have a pronounced effect on the redox potentials of the compounds.7 One-electron reduction of BODIPYs often leads to the BODIPY radical anions, typically generated electrochemically and characterised in situ.5-8 Isolation of the radical anion or other reduction product is rare due to the high sensitivity of these species. An exception to this is a recent report by Heiden and co-workers of a one-electron reduction of a BODIPY bearing a 1,1,3,3-tetramethylguanidine fragment in the meso-position (Figure 1).9 They were successful in isolating the BODIPY radical anion as the potassium salt and characterised the compound in the solid state using X-ray crystallography. Consistent with previous calculations for BODIPY radical anions,5 the spin density was calculated to reside mainly on the meso-carbon atom, but with minor contributions on the α- and γ-carbon atoms. This is consistent with its reactivity, as upon protonation of the guanidine group, the protonated radical comproportionates leading to the reduction of the meso-carbon.9 In 2018, Hu, Trofimov, Yang and co-workers reported that the reduction of an α,β,γ-substituted BODIPY with hydrazine also formed the radical anion, but this species rapidly dimerised through the meso-positions of two BODIPY moieties via C–C bond formation (Figure 1), once again showing reactivity through the meso-C of the BODIPY core.10

As these examples of BODIPY one-electron reduction chemistry exhibit subsequent reactivity at the meso-carbon,9,10 we were keen to investigate the reduction of a bulky BODIPY compound in which the meso-carbon is sterically protected from further reactivity. Recently, Harder and co-workers reported the synthesis of the extremely sterically demanding ligand in the isolation of a terminal zinc hydride complex (DippDPM)ZnH.11 In this work, we have employed H(DippDPM)BF3 (1-F) as a highly soluble, highly fluorescent powder in near quantitative yield (Scheme 1). An attempt to prepare the analogous boron dibromide (DippDPM)BBR3 compound halide (1-Br) was investigated by exchange between 1-F and BBr3 (Scheme 1). Addition of excess

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One- and two-electron reductions of a bulky BODIPY compound

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The synthesis of the corresponding BODIPY compound and explored its reduction chemistry.
BBr$_3$ to a solution of 1-F at room temperature resulted in an instant and dramatic colour change from bright orange to deep purple. Subsequent analysis of the reaction solution by $^1$H NMR spectroscopy showed considerable shifts in the $^{3}$PDM resonances from 1-F, suggesting that the product was not simply the result of halide exchange. The purple compound was found by X-ray crystallography (see below) to be the charge-separated species [Dipp$^{3}$PDM]BBr[BBr$_3$] (2), proposed to have formed by bromide extraction from the target 1-Br by the Lewis acidic BB$_3$F. Fortunately, 1-Br could be isolated in turn by simply placing the charged-separated species 2 under high vacuum (<0.05 mbar) for 30 minutes, which removed BB$_3$F and formed 1-Br in high yield. This reaction was found to be reversible, with addition of stoichiometric BB$_3$F to a toluene solution 1-Br quickly reforming compound 2 (Scheme 1). The synthesis of 1-Br was also attempted directly by various metathesis reactions between H$^{3}$PDM and BB$_3$F, but these typically led to complex mixtures of products.

Compounds 1-F, 1-Br and 2 were characterised by X-ray crystallography, and their solid-state structures are shown in Figure 2. Even though bromide analogues of BODIPY compounds (Br-BODIPYs) have previously been reported, 1-Br is the first example to be crystallographically characterised. 1-F and 1-Br are essentially isostructural in the solid-state, with 4-coordinate boron centres, bound to the two nitrogen atoms of DPM and two halides. However, in 1-F the BODIPY core is almost perfectly planar (common for BODIPY compounds), whereas in 1-Br the boron centre sits slightly above the plane of the BODIPY core, possibly to maintain a tetrahedral boron centre whilst minimising steric repulsion between the larger bromides and flanking Dipp groups. In contrast, the boron centre in the ([Dipp$^{3}$PDM]BBr)$^+$ cation of 2 is 3-coordinate, and lies in the plane of the BODIPY core. The 3-coordinate boron cation in 2 exhibits significant shorting of the B–N and B–Br bonds compared with those in 1-Br (B–N = 1.539(2), 1.546(2) Å in 1-Br, 1.439(5), 1.440(5) Å in 2; B–Br = 1.994(2), 2.060(2) Å in 1-Br, 1.874(4) Å in 2).

With 1-F and 1-Br in hand, the reduction of both compounds was investigated. Addition of 0.5 equivalents (or excess) of the magnesium(I) reducing agent ([MesNacNac]Mg)$_2$ (MesNacNac = [HC(C(Me)NMes)$_2$])$^{14}$ to hexane solutions of 1-F and 1-Br at room temperature gave similar results (Scheme 2). Both solutions quickly turned an intense blue colour accompanied by the formation of a colourless precipitate. $^1$H NMR spectra recorded of the reaction solutions collected at this point showed very broad peaks characteristic of open shell species. Stirring the reactions overnight at room temperature resulted in further colour changes to a less intense green colour. Interestingly, $^1$H NMR spectra of the reaction mixtures at this point were consistent with the presence of a single new diamagnetic product in each case, but with considerable loss of symmetry compared with the starting materials (e.g. 4 seceptets observed for the Dipp isopropyl groups). After filtration and concentration of the reaction mixtures, colourless crystals were isolated from each, allowing for structural determination of the major products 3-F and 3-Br by X-ray crystallography (Figure 3).

Compounds 3-F and 3-Br are isostructural in the solid state, with the structure of 3-F shown in Figure 3 (see SI for 3-Br). The structure of 3-F comprises two ([Dipp$^{3}$PDM]BF moieties that have coupled through one γ-pyrrrole ring via C–C bond formation. This has resulted in the loss of aromaticity of the two, newly coupled pyrrole rings and the formation of two stereogenic centres. In Figure 3, the S,S’ enantiomer of 3-F is shown, but the reaction gives a racemic mixture of the $R,R’$ and $S,S’$ enantiomers, with the product crystallising in the
centrosymmetric space group \((P2_1/\text{c})\). Compound 3-F is the result of dimerisation following a formal one-electron reduction of the BODIPY derivative \([\text{DippDPM}]BF_3\) (1-F). The magnesium(I) reducing agent is oxidised to give \([([\text{MesNacNac}])\text{Mg}[\mu-\text{F}])_2\), accepting a fluoride from the boron centre, producing the 3-coordinate boron centres in 3-F. This, along with the loss of aromaticity in one of the pyrrole rings results in two amido donors and more localised double and single bonds in the delocalised starting material. The bromide congener 3-Br is formed similarly.

It is proposed that the C–C bond formation in 3-F and 3-Br occurs via the reductive coupling of two neutral \([\text{DippDPM}]\text{BX})^+\) radical intermediates \((\text{INT})\), Scheme 2). This mechanism would account for the initially observed deep blue reaction solutions and broad \(^1\text{H}\) NMR spectra in the syntheses of 3-F and 3-Br. A similar mechanism is proposed in the formation of the meso-C–C bond-coupled dimeric dianion shown in Figure 1,\(^{10}\) although in this case the product was a result of coupling between two anionic BODIPY radicals.

To gain further evidence for this radical coupling mechanism, the reaction between 1-F and \([([\text{MesNacNac}])\text{Mg})_2\] was repeated, and the initial blue reaction solution was analysed by Electron Paramagnetic Resonance (EPR) spectroscopy. A sharp, narrow was observed at \(g = 2.005\) confirming the \(S = \frac{1}{2}\) nature of the radical (see SI for further details). Furthermore, analysis of the reaction solution after standing at room temperature overnight showed a significant decrease in the intensity of the EPR signal, consistent with the proposed radical coupling mechanism. To the best of our knowledge, this is the first time that the reductive coupling of two BODIPY units through the \(\gamma\)-position of the pyrrole has been reported. Several attempts were made to crystallise the radicals \(\text{INT}\) to verify their structure by X-ray crystallography, but to no avail. Concentrating solutions of the radicals appeared to speed up their rate of dimerisation, which meant that only crystals of 3-F and 3-Br were ever isolated from these attempts.

The reductions of 1-F and 1-Br were also investigated with magnesium anthracene \(\text{Mg(C}_{14}\text{H}_{10})\text{(THF)}_2\) as the reductant. The addition of various equivalents of magnesium anthracene to solutions of 1-Br gave only complex mixtures of products by \(^1\text{H}\) NMR spectroscopy, with no single product ever isolated. However, addition of one equivalent (or excess) magnesium anthracene to a benzene solution of 1-F produced an instant colour change from bright orange to deep blue, similar to that seen in the formation of 3-F and 3-Br (Scheme 3). However, within a few seconds this blue solution turned deep red accompanied by a colourless precipitate. Inspection of this red solution by \(^1\text{H}\) NMR spectroscopy showed that a single new diamagnetic \(\text{DippDPM}\)-containing product had formed. Similar to the reductions with \([([\text{MesNacNac}])\text{Mg})_2\], the product appears to have lost symmetry of the \(\text{DippDPM}\) (compared to 1-F), with 4 septets once again observed for the Dipp isopropyl groups. Work up of the reaction, followed by crystallisation of the orange/red product from benzene saw single crystals of the product \([\text{Mg(THF)}_2([\text{DippDPM}]\text{BF})_2])\) isolated and characterised by X-ray crystallography (Figure 4).

Compound 4 is the result of a formal two-electron reduction of the BODIPY 1-F. The compound bears two anionic \([\text{DippDPM}]\text{BF})^+\) fragments bound to a single \(\text{Mg}^{2+}\) cation. Similar to 3-F and 3-Br, the \(\gamma\)-position of one of the pyrrole rings has been reduced, but in this case by two electrons to give the corresponding carbanion. Inspection of the solid-state structure of 4 (Figure 4) reveals that the C–C bonds associated with the carbanion at the \(\gamma\)-position (1.465(5) and 1.469(5) Å) are significantly longer than those in neutral 1-F (1.380(2) and 1.413(2) Å), consistent with loss of aromaticity in the pyrrole ring. As far as we are aware, this is the first isolated product from a two-electron reduction of a BODIPY compound. Organometallic magnesium complexes are well known carbon nucleophiles (e.g. Grignard reagents), therefore this two-electron reduction route could be used to post-functionalise BODIPYs in the \(\gamma\)-position.

![Scheme 2. One-electron reduction of 1-F and 1-Br to give 3-F and 3-Br, proceeding through the radical intermediate INT.](image)

![Figure 3. Solid-state structure 3-F as determined by X-ray crystallography. Displacement ellipsoids set at the 50% probability level. Most hydrogen atoms have been omitted, and the Dipp-Pr and Mes-Me groups have been displayed in wireframe for clarity.](image)
In summary, the reduction of a bulky substituted BODIPY 1-F and its bromine derivative 1-Br have been investigated. Reduction with the magnesium(I) reducing agent [(DippNacNac)Mg]₂ results in one-electron reduction of both compounds to give a radical intermediate, which upon standing overnight, dimerises through the γ-position of the Dipp-DPM via C–C bond formation to produce 3-F and 3-Br. Reduction of 1-F with magnesium anthracene leads to a formal two electron reduction of the compound to give the anion [(Dipp-DPM)BF]⁻ as the magnesium salt 4.

Conflicts of interest
There are no conflicts to declare.

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