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Dibora[2]ferrocenophane: A Carbene-Stabilized Diborene in a Strained *cis*-Configuration

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Abstract: Unsaturated bridges that link the two cyclopentadienyl ligands together in strained *ansa* metallocenes are rare and limited to carbon-carbon double bonds. The synthesis and isolation of a strained ferrocenophane containing an unsaturated two-boron bridge, isoelectronic with a C=C double bond, was achieved by reduction of a carbene-stabilized 1,1'-bis(dihaloboryl)ferrocene. A combination of spectroscopic and electrochemical measurements as well as density functional theory (DFT) calculations was used to assess the influence of the unprecedented strained *cis* configuration on the optical and electrochemical properties of the carbene-stabilized diborene unit. Initial reactivity studies show that the dibora[2]ferrocenophane is prone to boron-boron double bond cleavage reactions.

Metallocenes with bridged cyclopentadienyl ligands, commonly named *ansa* metallocenes or metallocenophanes, have emerged as a class of organometallic compounds with an exceptionally wide and diverse range of applications.^[1] Among other applications, *ansa* metallocenes are employed as catalyst precursors in the industrial production of polyolefins^[2] and as monomers for ring-opening polymerization to form functional metallopolymers.^[3] Their versatility and usefulness stems largely

from the fact that their physical properties, and hence reactivity, can be tuned through structural modifications of the ligand framework. For instance, unsaturated two-atom bridges have been developed to increase the configurational rigidity^[4] as well as the molecular strain of metallocenophanes, but also to add additional functionality to the metallocene fragment. In part due to difficulties encountered in their synthesis, these types of bridges are relatively rare and only a handful of these have been successfully incorporated into the ferrocene structure, as shown in Figure 1 (I-V). The first examples involved bridging aromatic rings, such as an *ortho*-phenylene (I),^[5,6] a cyclobutadiene cobalt (II)^[6] and a ruthenacyclopentadiene fragment (III).^[7] Whereas the focus of the initial studies was on synthesis and structural features, the vinylene-bridged dicarba[2]ferrocenophanes IV and V have been developed as candidates for ring-opening metathesis polymerization (ROMP) to produce conjugated metal-containing polymers.^[8-10] As shown by the groups of Tilley and Manners, such strained ferrocenophanes can indeed undergo ROMP with Schrock- and Grubbs-type catalysts to form conjugated metallopolymers.^[9,10]

Although homo- and heteronuclear multiple bonding is common for other p-block elements, especially the second-period elements,^[11] unsaturated *ansa* bridges in metallocenophanes are to date restricted to carbon. By capitalizing on the isoelectronic relationship between Lewis base-stabilized diborenes, [(L)RB=BR(L)] (L = Lewis base),^[12,13] and olefins, R₂C=CR₂, we sought to prepare the first *ansa* metallocene with a heteroatom-containing multiple bond in the bridge. Herein, we describe the successful synthesis of a strained dibora[2]ferrocenophane (VI), in which the bridging diborene moiety is forced to adopt a *cis* rather than the prevailing *trans* configuration. The effects of changing the regiochemistry, as well as the interrelationship between the strain and properties of the diborene are addressed.

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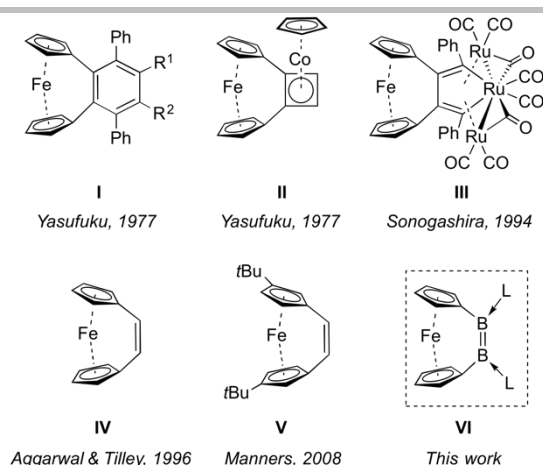
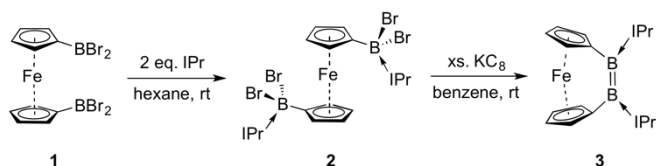


Figure 1. Examples of ferrocenophanes containing an unsaturated two-atom bridge (R^1 , R^2 = Ph or CO_2CH_3 , L = Lewis base).

For the synthesis of the title compound we have made use of our recently-established procedure for the synthesis of diborenes, namely the reduction of base-stabilized aryldihaloboranes.^[13] To this end, 1,1'-bis(dibromoboryl)ferrocene (**1**) was reacted with two equivalents of the N-heterocyclic carbene (NHC) 1,3-bis(diisopropyl)imidazol-2-ylidene (IPr) to give adduct **2**, which was isolated as an off-white solid in 94% yield (Scheme 1). It was found that **2** could be successfully reduced in benzene solution with potassium graphite (KC_8) to induce ring closure and formation of the diborene bridging unit. It is important to note, however, that the choice of carbene is critical for this transformation, as NHCs with a different steric demand failed to produce the desired unsaturated two-boron bridge.^[14] Following workup by recrystallization from benzene, dibora[2]ferrocenophane **3** was obtained as air-sensitive, purple crystals in 71% yield. The diborene moiety in **3** was readily identified by its characteristic ^{11}B NMR signal at $\delta = 28.4$ ppm and its lowest energy UV/vis absorption at 571 nm.^[15-21] Furthermore, the 0.53 ppm chemical shift difference between the α and β protons of the Cp ring, which has been shown to provide a qualitative correlation with the degree of molecular distortion in *ansa* metallocenes,^[22] indicates notable ring strain (cf. **2**: $\Delta\delta = 0.21$ ppm).



Scheme 1. Synthesis of dibora[2]ferrocenophane **3**.

An X-ray diffraction analysis of suitable single crystals of **3** confirmed the bent sandwich geometry with formation of the two-boron bridge. The molecular structure, as shown in Figure 2, revealed a noticeable distortion of the Cp ligands from coplanarity ($\alpha = 16.1^\circ$), which is significantly increased relative to the corresponding dibora[2]ferrocenophanes containing a B_2Mes_2 ($\alpha = 10.5^\circ$)^[23] and $\text{B}_2(\text{NMe}_2)_2$ ($\alpha = 12.8^\circ$)^[24] bridging moiety. This can be attributed to the decrease in the length of the boron-boron bond (**3**: 1.602(2) Å) which falls in the normal range of B=B double bonds in base-stabilized diborenes.^[15-21] As a result of the increase in bond order in the *ansa* bridge, the Ct-Fe-Ct angle ($\delta = 165.4^\circ$, Ct = centroid of the Cp ligand) in **3** is more distorted from the ideal of 180° than in both $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{BMes})_2]$ ($\delta = 173.4^\circ$) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{BNMe}_2)_2]$ ($\delta = 170.1^\circ$). The B-B bond is almost parallel to the metal-centroid axis, resulting in a nearly eclipsed conformation of the Cp rings. The geometry of the double bond is appreciably distorted, as illustrated by the small B=B-C_{Cp} angles which average 113.2° and by the C1-B1=B2-C4 torsion angle of 154.2° , indicating pyramidalization of the diborene. The boron atoms remain in an approximately trigonal-planar coordination, with angular sums of 359.4° and 358.0° at B1 and B2, respectively.

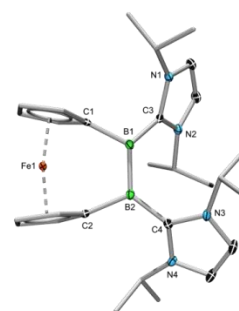


Figure 2. Molecular structure of **3**. Hydrogen atoms and some thermal ellipsoids are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: B1-B2 1.602(2), B1-C1 1.627(2), B1-C3 1.559(2), B2-C2 1.616(2), B2-C4 1.574(2); B2-B1-C1 111.7(1), B1-B2-C2 114.8(1).

To elucidate the effect of both the *cis*-configuration and the molecular strain on the physical properties of diborene **3**, we carried out a series of analytical and computational studies. The unstrained *trans*-diborenes of the general formula $[(\text{L})\text{RB}=\text{BR}(\text{L})]$ (L = Lewis base) were used as a reference to which the properties and reactivity of the cyclic diborene **3** were compared.

Electrochemical measurements in THF solution revealed that **3** has a remarkably low oxidation potential of $E_{\text{pa}} = -1.56$ V vs. ferrocene/ferrocenium,^[19] corresponding to the one-electron oxidation of the diborene unit. The value is comparable with other N-heterocyclic carbene (NHC)-stabilized diborenes such as $[(\text{Ime})\text{DurB}=\text{BDur}(\text{Ime})]$ ($E_{1/2} = -1.55$ V; Dur = 2,3,5,6-tetramethylphenyl; Ime = 1,3-dimethylimidazol-2-ylidene).^[19] Although the strained *cis* configuration seems to have no

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apparent influence on the HOMO energy of the diborene, it might be accountable for the observed electrochemical irreversibility of the first oxidation process.

The solution UV/vis absorption spectrum of the purple dibora[2]ferrocenophane **3** showed, besides the previously mentioned lowest energy absorption at $\lambda_{\text{max}} = 571$ nm, an additional absorption band at $\lambda = 382$ nm. In comparison to the related *trans*-diborene [(Ime)DurB=BDur(Ime)] ($\lambda_{\text{max}} = 538$ nm),^[19] the lowest energy transition of **3** is shifted to lower wavelengths by about 33 nm, indicating a considerably smaller HOMO-LUMO band gap for the cyclic diborene **3**. This, combined with the voltammetric measurements, suggests that the smaller band gap is mainly a result of an energetically lower-lying LUMO.

In order to gain more insight into the shape and relative ordering of the molecular orbitals, we performed density functional theory (DFT) calculations at the B3LYP*/TZP level of theory. Similar to the frontier orbitals of the related *trans*-configured diborene [(Ime)DurB=BDur(Ime)],^[17-19] the HOMO (-3.20 eV) of **3** is mainly composed of π orbitals centered on the B-B core, whereas the LUMO (-1.09 eV), though similarly composed of C(Ar)-B-C(carbene) π interactions, presents a more overall bonding character due to the *cis* configuration, hence rationalizing the observed stabilization of the LUMO. This is one of the rare occasions where a LUMO has a non anti-bonding character, which immediately suggests some very interesting reactivity patterns and property tuning possibilities. A comparison with the orbital energy levels of *trans*-diborene [(Ime)DurB=BDur(Ime)] (HOMO: -3.15 eV and LUMO: -0.48 eV) shows that the LUMO of **3** lies about 0.61 eV lower in energy, whereas the HOMO energies are very similar. Mainly due to the stabilization of the LUMO, the HOMO-LUMO gap in **3** ($\Delta E = 2.11$ eV) is significantly lower than that of [(Ime)DurB=BDur(Ime)] ($\Delta E = 2.67$ eV), consistent with the smaller optical band gap observed in the UV/vis spectrum. A similar effect has been observed for the phosphine-stabilized *cis*-diborene [B₂Mes₂(dppm)] (dppm = bis(diphenylphosphino)methane), in which the B=B double bond is incorporated into a five-membered ring system.^[25] In this case, the decrease of the LUMO energy seems, to a large extent, to originate from extended electron delocalization into the phenyl groups.

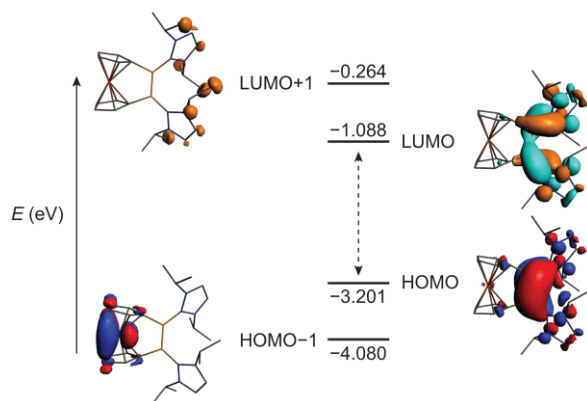


Figure 3. Representation of the frontier orbitals of **3**.

With the help of time-dependent DFT calculations at the same level of theory, the two main absorption bands in the UV/vis spectrum could be assigned to specific electronic transitions. The lowest energy absorption can be attributed to a HOMO \rightarrow LUMO transition, whereas the other major electronic excitation is due to a metal-to-ligand charge transfer transition between the HOMO-1, which is predominantly a mixture of the iron $d_{x^2-y^2}$ and d_{xy} orbitals, and the LUMO (see SI for details).

The presence of ring strain in saturated dibora[2]ferrocenophanes has previously been shown to enhance the reactivity of the B-B single bond, facilitating new reactivity modes of diboranes(4) including diboration reactions of substrates with non-activated multiple bonds.^[26] We were therefore curious to see how strain affects the reactivity of the B=B double bond. As previously established, carbene-stabilized diborenes are capable of providing all four B=B bonding electrons in reduction reactions with suitable oxidants (e.g. elemental chalcogens).^[27] We envisioned that dibora[2]ferrocenophane **3** might be especially prone to such reactivity due to the presumed strain energy that would be released by cleavage of the B=B bond. Given our previous success with chalcogens in the elucidation of the reactivity of boron-boron multiple bonds,^[27,28] we chose a diorganyl diselenide to test this validity.

The reaction of **3** with an excess of 1,2-diphenyldiselenide in THF led to the emergence of a new signal at $\delta = -8.1$ ppm in the ¹¹B NMR spectrum, indicating quaternization of both boron atoms (Figure 4). Integration of the aromatic protons in the ¹H NMR spectrum revealed that the product (**4**) consists of four [SePh] groups, tantamount to the consumption of two equivalents of [SePh]₂. Using only one equivalent of 1,2-diphenyldiselenide led to conversion of about half of **3**, indicating that the reaction does not stop after initial 1,2-addition. The NMR data thus supports formation of a ring-opened product with cleavage of the boron-boron double bond. After work-up and recrystallization, ferrocene complex **4** was obtained as an analytically pure yellow solid in 55% yield. The molecular structure, as determined by single-crystal X-ray crystallographic analysis, confirmed the double addition of [SePh]₂ across the B=B bond and revealed the formation of a base-stabilized 1,1'-bis(boryl)ferrocene (**4**). Due to steric repulsions between the two boryl substituents, they adopt an *anti*-periplanar conformation (dihedral angle = 154°). The B-C bonds in **4** (avg. 1.704(6) Å) are longer than the boron-NHC bond in diborene **3** (avg. 1.567(4) Å), consistent with a change in hybridization of the boron atoms from sp² to sp³.

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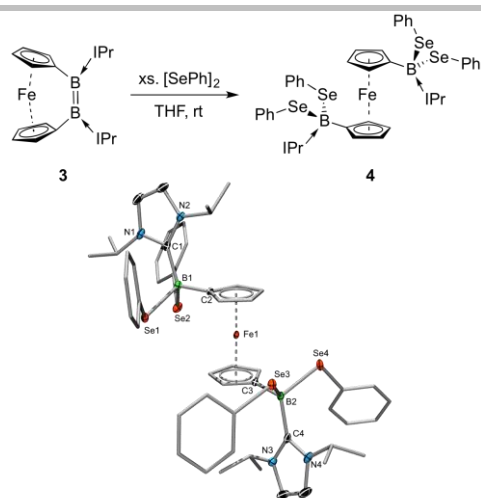


Figure 4. Top: Double addition reaction of diborene **3** with 1,2-diphenyldiselenide. Bottom: Molecular structure of **4**. Hydrogen atoms and some thermal ellipsoids are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Se1–B1 2.130(3), B1–Se2 2.099(2), B1–C1 1.710(3), C2–B1 1.511(3), B2–C3 1.507(3), B2–C4 1.697(3), B2–Se3 2.133(3), B2–Se4 2.135(3).

The B–B bond cleavage product (**4**) is reminiscent of the reductive insertion of elemental sulfur into the boron-boron double bond of an NHC-stabilized diborene with thienyl groups, which resulted (after activation through ultrasound) in the formation of a 1,2,4-trithia-3,5-diborolane.^[27] Given that sulfur is a much more powerful oxidant than 1,2-diphenyldiselenide, the ease of the boron-boron bond scission in **3** is quite remarkable and likely due to release of ring-strain energy upon cleavage of the boron-boron bond. Furthermore, the observed ring-opening reactivity of **3** also bodes well for future polymerization studies.

In summary, we have synthesized and structurally characterized a diborene-bridged ferrocenophane, which is to our knowledge the first strained *ansa* metallocene with a multiply-bonded bridge not based on carbon. Comparisons of the optical and electrochemical properties of the strained *cis*-diborene **3** to related acyclic *trans*-diborenes showed that it has a smaller HOMO-LUMO gap, mainly due to a substantial stabilization of the LUMO. Initial reactivity studies with 1,2-diphenyldiselenide led to ring opening of the ferrocenophane by cleavage of the B=B double bond, indicating that the cyclic *cis*-diborene **3** is highly reactive as a result of ring strain. We are currently further exploring its reactivity, including its ability to undergo ring-opening polymerization.

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Keywords: metallocenes • boron • strained molecules • density functional calculations • diborenes

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