2,2'-Bipyridyl as a Redox-Active Borylene Abstraction Agent

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Abstract: 2,2'-Bipyridyl is shown to spontaneously abstract a borylene fragment (R-B:) from various hypovalent boron compounds. This process is a redox reaction in which the bipyridine is

reduced and becomes a dianionic substituent bound to boron through its two nitrogen atoms. Various transition metal borylene complexes and diboranes, as a well as a diborene, take part in this reaction. In the latter case, our results show an intriguing example of the homolytic cleavage of a B=B double bond.

Introduction

+3 is the ubiquitous and overwhelmingly prominent oxidation state of boron, both in natural and synthetic materials. In neutral, tricoordinate boron compounds, this common state corresponds to a partially filled valence shell, thus it is unsurprising that these boron compounds are associated with Lewis acidity, electrophilicity and electron-accepting properties.[1] The tantalizing prospect of utilizing boron compounds in transition metal-free catalysis has prompted considerable interest in redox chemistry centred on this classically redox-static element. As a result, recent years have seen the emergence of a growing number of molecular compounds that feature boron atoms in hypovalent states (i.e. less than +3).[2] The most representative examples of neutral hypovalent boron compounds include diboranes(4) (B(II)),[2a-c,3] diborenes (B(I)),[2a-c,4] diborynes (B(0)),[2a-c,5] and borylenes (B(I)).[2d,6] These fascinating species exhibit starkly different reactivity to that of their B(III) counterparts and have led to the observation of nucleophilic,[7] reductive,[8] and metallomimetic[9] behavior for boron.

In transition metal chemistry, the use of redox-active ligands – i.e. ligands that can participate in redox events – has shown tremendous potential in unlocking redox reactivity in complexes of base metal complexes and in giving rise to inexpensive catalysts that contain only elements of

low toxicity.[10] A typical example of a redox-active ligand, 2,2'-bipyridyl, (**1**) is known to readily accept two electrons and form a stable dianion (Fig. 1).[11] In its coordination to transition metals, **1** can adopt its dianionic form through metal-to-ligand charge transfer, in the process transforming from a L_2 to an X_2-type ligand (Fig. 1).[12] In the chemistry of the main group elements, analogous redox behavior has also been observed in the reaction of **1** with transient silylene complexes or other hypovalent silicon sources.[13] By contrast, the few known examples of boron or aluminium complexes featuring a reduced bipyridine ligand are generally synthesized by salt elimination of bipyridine reagents that are already in their anionic form.[14]
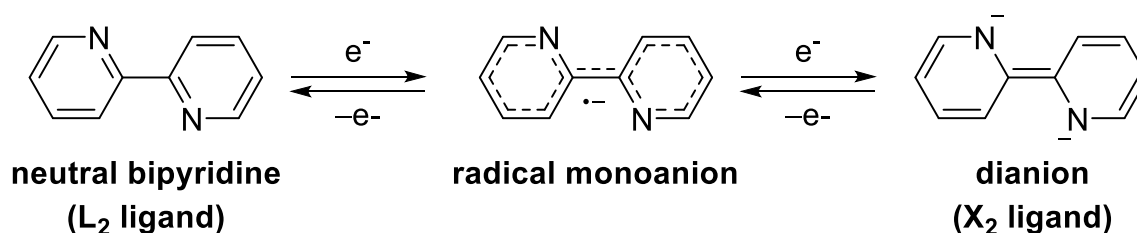

neutral bipyridine
(L_2 ligand)

radical monoanion

dianion
(X_2 ligand)

Figure 1. Reduction states of 2,2'-bipyridyl (**1**).

In order to probe the potential redox reactions of such ligands with hypovalent boron compounds, we became interested in the reactivity of redox-active 2,2'-bipyridyl with B(I) and B(II) species. In this contribution, we report the unusual reactivity of 2,2'-bipyridyl with various diborene, borylene and diborane compounds, showing that the redox-activity of the ligand indeed leads to a change of oxidation state in these boron compounds in the absence of external oxidants or reductants.

Results and Discussion

Terminal transition-metal borylene complexes (of the form [L_nM=B-R]) are a well-studied class of reactive B(I) compounds.[15] Our group and others have previously reported the synthesis and reactivity of a wide range of borylene complexes, notably of the group 6 metals[16] and of iron.[17] These complexes display a rich reactivity in which the boron atom can couple with various substrates,[18] notably Lewis acids,[18a] Lewis bases,[9d] alkynes,[18b,c] CO[9e] and transition metal complexes.[18d,e,g] Several of these reactions can be seen as borylene transfer reactions, in which the M=B bond of the borylene complex is cleaved and the B-R fragment is delivered to a substrate.

The rich and varied reactivity of terminal metal-borylene complexes inspired us to investigate their reaction with 2,2'-bipyridyl (**1**). Treating [(OC)$_5$Mo=BN(SiMe$_3$)$_2$] (**2**) with 1 equiv. of **1** in benzene led to a rapid color change in the reaction mixture from yellow to deep red (Scheme 1). The complete conversion of **2** to a single new boron-containing compound was confirmed within six hours by the appearance of a new resonance at $\delta = 20$ in the ^{11}B NMR spectrum and the complete disappearance of that associated with **2**. Although the new boron-containing product can be isolated by crystallizing out the molybdenum-containing by-products (thought to be [Mo(CO)$_6$] or bipyridine adducts of molybdenum carbonyls and elemental Mo),[18g] its crystallization eluded all of our attempts and **3a** could only be recovered as a bright red oil, thus precluding its crystallographic characterization. ^{1}H and ^{13}C{[1]H] NMR spectroscopy allowed us to identify **3a** as a symmetrical 1:1 complex of the [(Me$_3$Si)$_2$N-B:] borylene fragment with bipyridyl **1**. Interestingly, in this new compound, the aromatic proton resonances are found at considerably higher field ($\delta = 7.51, 7.11, 6.11, 5.99$) than those of the free bipyridine ($\delta = 8.75, 8.54, 7.20, 6.68$).
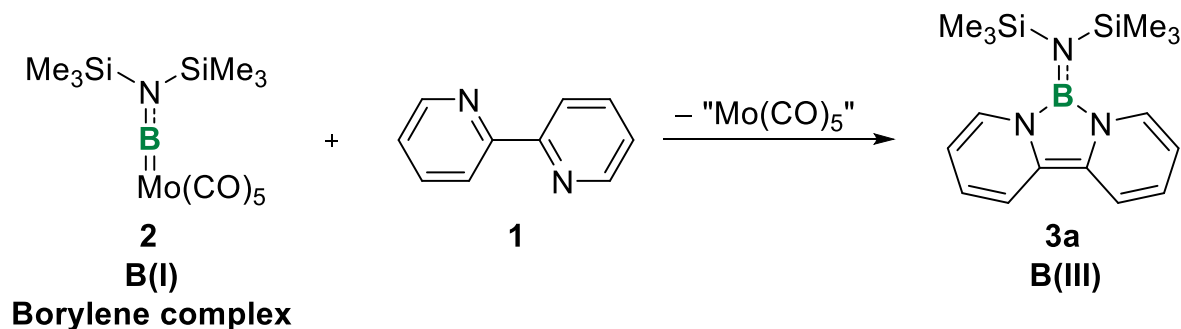
Scheme 1. Reaction of [(OC)$_5$Mo=BN(SiMe$_3$)$_2$] with **1**.

A similar compound was obtained by reacting the iron borylene adduct [(Me$_3$P)(OC)$_3$Fe=BDur] (Dur = 2,3,5,6-tetramethylphenyl) (**4**) with **1** (Scheme 2). Within 12 hours, a benzene solution containing equimolar amounts of **1** and **4** became dark red. The ^{11}B NMR spectrum of the reaction mixture showed a new resonance at δ = 23. This time, the resulting product could be recrystallized from cold pentane to give **3b** as red crystals (43% yield) that were suitable for X-ray diffraction analysis. As in the case of **3a**, ^{1}H and ^{13}C NMR spectra showed that **3b** is a 1:1 adduct of 2,2'-bipyridyl and the borylene fragment [Dur-B:]. The solid-state structure of **3b** confirmed this characterization, showing that the complex is a tricyclic diazaborafluorene-like compound (Fig. 2).
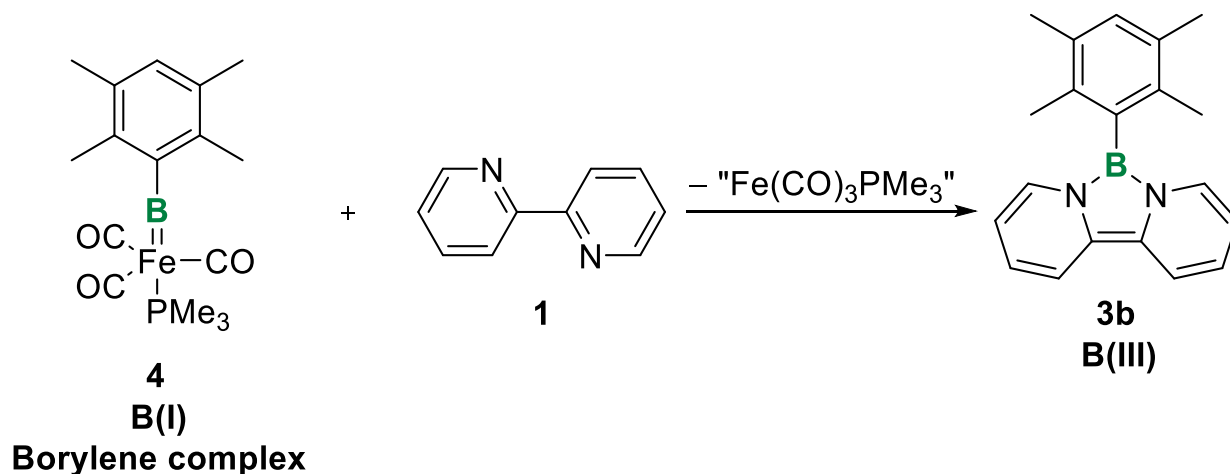
Scheme 2. Reaction of [(Me$_3$P)(OC)$_3$Fe=BDur] with **1**.

The solid-state structure of **3b** also reveals B-N bond lengths (1.436(3) and 1.435(3) Å) that are in the range of covalent bonds with π-bond character.[19] Furthermore, the bipyridyl C2-C2' bond distance (linking the two pyridine rings) is significantly shorter (1.387(3) Å) than the corresponding bond in free **1** (1.488 Å),[20] suggesting double bond character. The C-C bond lengths within the pyridine rings in **3b** are also consistent with alternating single and double bonds. Thus, **3b** appears to feature reduced aromaticity in its pyridine rings, the bipyridine unit having been reduced and to form covalent bonds with the borylene fragment. Indeed, **3b** is structurally similar to previously reported analogues that were prepared by non-redox salt elimination reactions from the reduced dianion of 2,2'-bipyridyl and haloboranes, the products of which also feature B(III) centers, a reduced bipyridine ligand and an aromatic C$_2$N$_2$B ring.[14a] Thus, in the present case, the borylene ligand undergoes a spontaneous two-electron redox reaction with 2,2'-bipyridyl, which oxidizes the boron atom from B(I) to B(III), with concomitant reduction of the bipyridine. This assignment is consistent with the ^{1}H NMR spectrum of **3b**, in which aromatic proton resonances are found at considerably higher field (δ = 7.28, 7.19, 6.20, 5.93) than in free bipyridine, suggesting reduced aromaticity. Furthermore, on the basis of ^{1}H NMR spectroscopy, a similar bonding situation is expected for **3a** (see above). Interestingly, this process is reminiscent of the [4+1] cycloaddition of an anionic borylene complex with a strongly oxidizing benzoquinone reported by Aldridge and Jones.[21]
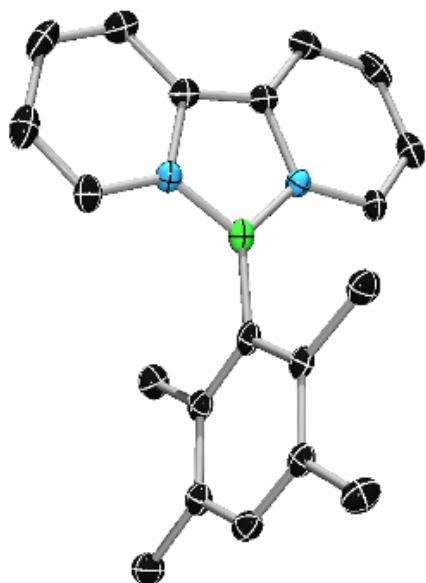
Figure 2. Crystallographically determined solid-state structure of **3b**. Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms omitted for clarity. Black: carbon, green: boron, cyan: nitrogen).

It is interesting to note that steric bulk does not seem to hamper this redox borylene transfer reaction: similar results were obtained in the reaction of 2,2'-bipyridine with the chromium borylene complex [(OC)$_5$Cr=BTp] (**5**; Tp = 2,6-dimesitylphenyl), which bears a very bulky terphenyl group bound to boron (Scheme 3).
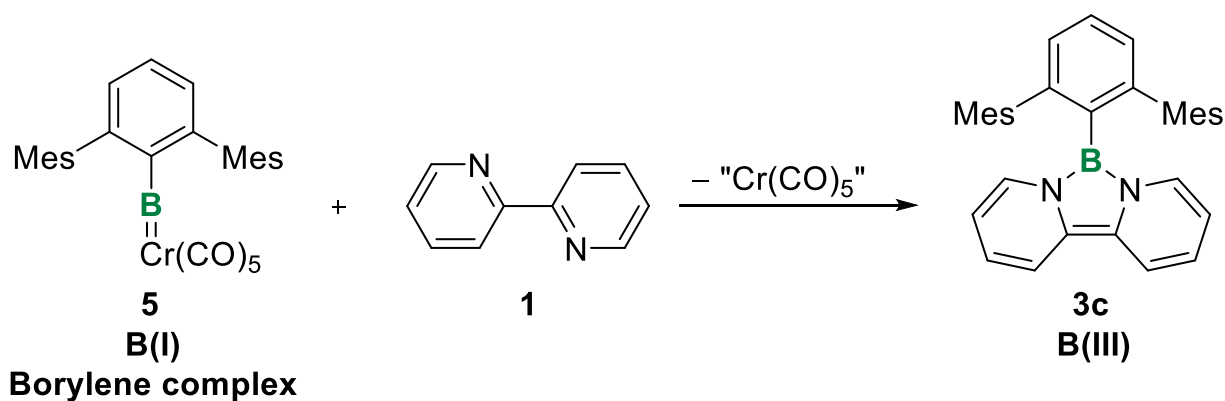
Scheme 3. Reaction of [(OC)$_5$Cr=BTp] with **1**.

Indeed, the reaction of **5** with **1** (2 equiv) in toluene afforded product **3c** after 20 hours at room temperature. Isolated **3c** could be obtained as a red crystalline solid by fractional recrystallization of the reaction mixture in hexanes (yield: 39%). The structure of **3c** was found to be analogous to that of **3a** and **3b** by NMR spectroscopy (^{1}H, ^{13}C{^{1}H} and ^{11}B), an assignment that was supported by low-quality crystallographic data (see ESI). Once again, high-field resonance signals were found for the bipyridine protons (δ = 7.39, 6.79, 5.94, 5.84), indicating the reduction of the ligand. Indeed, repeated crystallization of **3c** yielded only single crystals of poor quality, providing diffraction data suitable only for confirmation of connectivity and not detailed discussion of structural details (Fig. 3).


Figure 3 Crystallographically determined solid-state structure of 3c. Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms omitted for clarity. Black: carbon, green: boron, cyan: nitrogen).

The intriguing redox nature of the borylene transfer reaction to bipyridine prompted us to investigate whether other hypovalent boron compounds could undergo a similar process. With boron atoms in the formal +2 oxidation state, diborane(4) compounds also have the potential to

undergo redox reactions with 2,2'-bipyridine. We thus reacted the symmetrical $B_2Br_2Dur_2$ (**6**) with 2.2 equivalents of **1** in benzene (Scheme 4). After 24 hours of stirring at room temperature, the reaction mixture was found to consist of a deep-red solution and a white precipitate. ^{11}B and ^1H NMR spectra revealed **3b** to be the only soluble species in the mixture. **3b** could be isolated by filtration and recrystallization in hexanes (yield: 78%). While the nature of the white precipitate in this reaction remains unknown due to its complete insolubility, it plausibly corresponds of a complex of Br_2BDur (the expected byproduct of the reaction according to stoichiometry) and **1**.[22] Similarly, the unsymmetrical diborane BF_2BMes_2 reacted with **1** to yield **3d** after isolation (yield: 50%). This new compound is structurally and spectroscopically analogous to **3a-c** (Fig. 4).

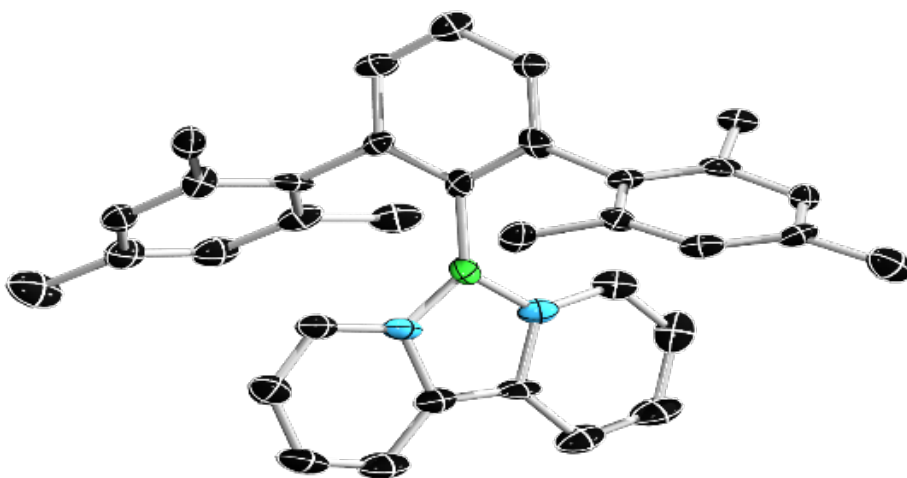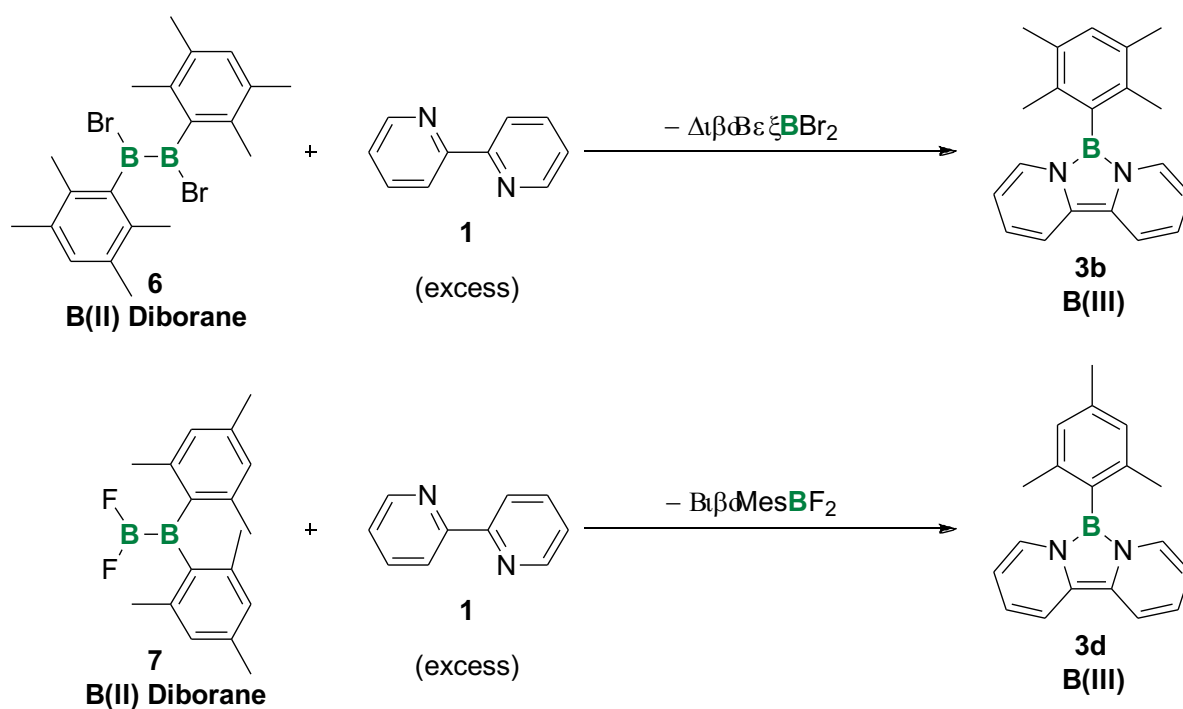**Scheme 4.** Reactions of diboranes **6** and **7** with **1**.
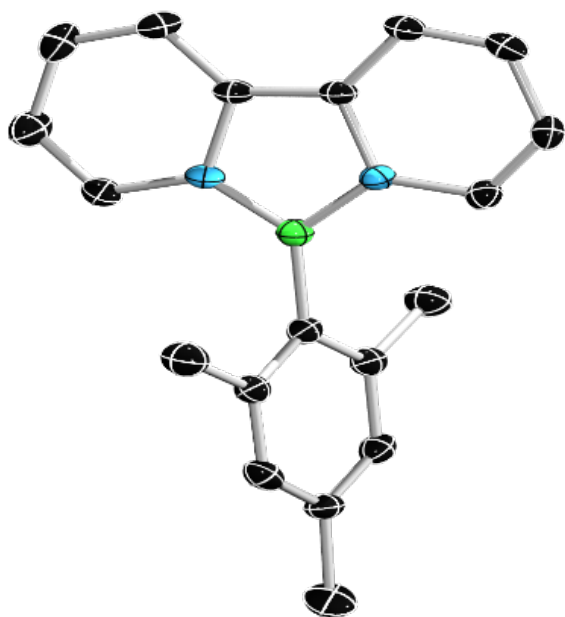
Figure 4 Crystallographically determined solid-state structure of **3d**. Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms omitted for clarity. Black: carbon, green: boron, cyan: nitrogen).

The reactions of **1** with dihalodiboranes **6** and **7** are also redox processes: from diborane starting materials that possess two B(II) atoms ($R_2B_2X_2$; R = Mes or Dur, X = Br or (f), two B(III) products are formed ($C_{10}H_8N_2BR$ (**3b** and **3d**)) and presumably X_2BR). Concomitantly, one equivalent of bipyridine ligand is reduced by two electrons in the formation of **3b** (R = Dur, X = Br) or **3d** (R = Mes, X = (f). This process is related to the reactions of the redox-active 1,4-pyrazine,[23] 4,4'-bipyridine,[24] 4-cyanopyridine[25] and 4-Mes$_2$B-pyridine[26] with diboron(4) reagents, which effect the homolytic cleavage of the B-B bond in a formal redox process.

Finally, we also became interested in studying redox reactions using a diborene complex as the hypovalent boron component. In addition to featuring boron in the formal +1 oxidation state,

diborenes are particularly intriguing as the conceptual dimers of borylene fragments, being potentially related to the latter through a Wanzlick-type equilibrium,[27] which has thus far not been observed[27f] but that is conceptually close to the fact that diborane(4) dianions can react like two equivalents of boryl anion.[28] Thus, [(Me$_3$P)MesB=BMes(PMe$_3$)] (**8**)[29] was treated with one equivalent of **1** in benzene (Scheme 5). After six days at 80 °C, the ^{11}B NMR spectrum of the reaction mixture showed the complete disappearance of the signal for 8, which correlated with the liberation of free PMe$_3$ according to ^{31}P NMR spectroscopy. Two new signals (δ = 23 and 46) were observed in the [11]B spectrum, the first of which indicated the formation of the previously characterized **3d**, arising from the displacement of PMe$_3$ from the diborene and oxidative cleavage of the B=B bond. Thus, in this reaction, diborene **8** can act as a source of monomeric borylene fragments through a redox process that leads to B(III) atoms. This reaction reiterates the relationship between diborenes and borylenes as conceptual dimers and monomers.

Scheme 5. Reaction of [(Me$_3$P)MesB=BMes(PMe$_3$)] with **1**.

Unfortunately, repeating the reaction several times led to formation of the two boron-containing products **3b** and **9** (^{11}B NMR resonances at δ = 23 (**3b**) and 46 (**9**)) in different ratios (even when more than two equivalents of **1** were used), along with thermal decomposition products of **8** the quantitative separation of these species from each other and from residual **1**

was unsuccessful. We were able to isolate small amounts of crystalline material, which allowed us to characterize the new complex (**9**) by X-ray diffraction analysis (Fig. 5). Interestingly, product **9** arises from the displacement of PMe$_3$ in **8** by **1** without cleavage of the B=B bond. Furthermore, ^{1}H NMR chemical shifts of the bipyridine protons (δ = 7.80, 7.49, 6.20, 5.84), as well as the bond distances are consistent once more with a structure in which the bipyridine ligand in **9** is reduced and exhibits low aromaticity in its C$_5$N cycles (B-N d = 1.442(2) and 1.452(2) Å; C2-C2' (bipyridine) d = 1.395(2) Å). At the same time, the long B-B bond distance observed (1.639(3) Å) is consistent with the assignment of **9** as a diborane(4) in which the boron atoms are formally in the +2 oxidation state. This assignment is also supported by the observed ^{11}B NMR chemical shift. **9** is thus an analogue of phenanthrene, but features reduced aromaticity in the terminal cycles with significantly localized double bonds.
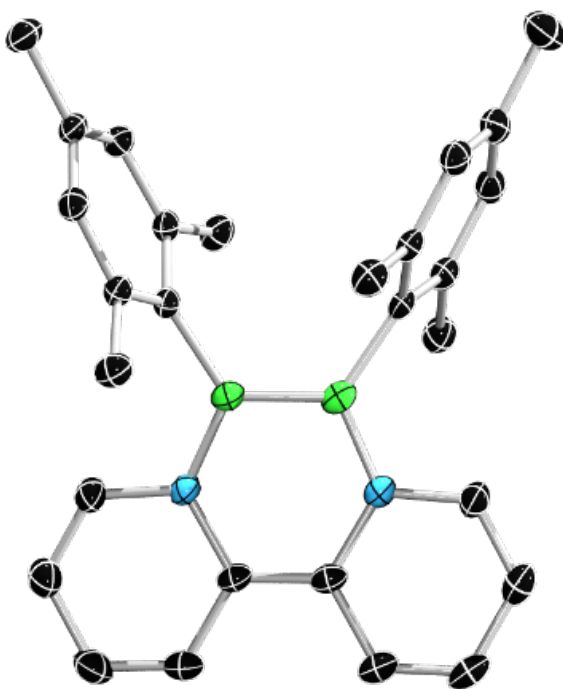
Figure 5. Crystallographically determined solid-state structure of **9**. Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms omitted for clarity. Black: carbon, green: boron, cyan: nitrogen.

Conclusion

In summary, we find that 2,2'-bipyridyl readily reacts with a variety of hypovalent boron species in formal two-electron redox processes. These reactions allow for the facile and mild formation of B-N aromatic tricyclic building blocks, without the need for external reducing agents. Consequently, we believe that this reaction has tremendous potential for the synthesis of materials-relevant units that are not compatible with harsher synthetic methods.

Experimental Section

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Solvents (both deuterated and non-deuterated) were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired on a Bruker Avance 400 NMR spectrometer and a Bruker Avance 500 NMR spectrometer. Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei ($^{13}C\{^1H\}$) or residual protons (^1H) of the solvent. ^{11}B spectra are referenced to external standards [$BF_3 \cdot OEt_2$]. High-resolution mass spectrometry was obtained from a Thermo Scientific Exactive Plus spectrometer. Compounds **2**,[30] **4**,[17a] **5**,[9e] **6**,[31] **7**[32] and **8**[29] were synthesized according to literature procedures.

Reaction of [(OC)₅Mo=BN(SiMe₃)₂] (2) with 2,2'-bipyridyl (1): To a solid mixture of **2** (41 mg, 0.10 mmol) and **1** (16 mg, 0.10 mmol) was added benzene (5 mL). The mixture was stirred

at room temperature for 6 hours and the resulting red solution was filtered through a cotton plug. The solvent of the filtrate was then evaporated under reduced pressure. The red oil was dissolved in pentane (3 mL) and recrystallized by slow evaporation at –30 ºC. The crystals that were formed during the evaporation were filtered off and the filtrate was dried under reduced pressure to give a red oil which was similarly recrystallized three more times. **3a** was obtained in this way as red oil. ^{1}H NMR (500 MHz, C_6D_6) δ = 7.51 (dt, J = 7.2, 1.2 Hz, 2H, C*H*-bipyridine), 7.11 (dt, J = 9.2, 1.3 Hz, 2H, C*H*-bipyridine), 6.11 (ddd, J = 9.2, 6.0, 1.1 Hz, 2H, C*H*-bipyridine), 5.99 (ddd, J = 7.2, 6.0, 1.2 Hz, 2H, C*H*-bipyridine), 0.07 (s, 18H, Si(C*H*$_3$)$_3$); ^{11}B NMR (160 MHz, C_6D_6) δ = 20 (s); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ = 126.4 (s, CH-bipyridine), 118.7 (s, C*H*-bipyridine), 117.1 (s, C*H*-bipyridine), 114.0 (s, C*H*-bipyridine), 3.0 (s, Si(C*H*$_3$)$_3$); El. Anal. [%]: calc. C 54.70, H 8.01, N 12.84; found: C 54.53, H 7.83, N 11.50.

Reaction of [(Me$_3$P)(OC)$_3$Fe=BDur] (4) with 2,2'-bipyridyl (1): To a solid mixture of **4** (36 mg, 0.10 mmol) and **1** (16 mg, 0.10 mmol) was added benzene (5 mL). The reaction mixture was kept at room temperature for 12 hours and the dark red solution was filtered through a cotton plug. The solvent of the filtrate was evaporated at reduced pressure and the red solid was dissolved in 3 mL of pentane. The solution of the crude product was filtered and stored at –30 ºC. After 12 h, the filtrate yielded red crystals of **3b** (13 mg, 43%). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.28 (dt, J = 9.2, 1.2 Hz, 1H, C*H*-bipyridine), 7.19 (dt, J = 7.2, 1.1 Hz, 1H, C*H*-bipyridine), 7.04 (s, 1H, C*H*-Dur), 6.20 (ddd, J = 9.2, 6.1, 1.0 Hz, 1H), 5.93 (ddd, J = 7.2, 6.1, 1.2 Hz, 1H, C*H*-bipyridine, 2.16 (s, 6H, C*H*$_3$-Dur), 1.95 (s, 6H, C*H*$_3$-Dur); ^{11}B NMR (160 MHz, C_6D_6) δ = 23; ^{13}C{^{1}H] NMR (126 MHz, C_6D_6) δ = 138.7 (s, CH-Dur), 133.5 (s, C*H*-Dur), 133.0 (s, C*H*-Dur), 118.7 (s, C*H*-bipyridine), 114.5 (s, C*H*-bipyridine), 110.7 (s, C*H*-bipyridine), 20.1 (s, C*H*$_3$-

Dur), 19.2 (s, *CH$_3$*-Dur); El. Anal. [%]: calc. C 80.02, H 7.05, N 9.33; found: C 79.73, H 7.69, N 8.90.

Reaction of [(OC)$_5$Cr=BTp] (5) with 2,2'-bipyridyl (1): A mixture of **5** (100 mg, 0.19 mmol) and **1** (60.5 mg, 0.39 mmol) was dissolved in toluene (5 mL) and stirred for 20 hours. The solution was filtered, and the filtrate was dried *in vacuo*. The resulting red residue was taken up in hexane and stored at –30 °C, leading to precipitation. The resulting precipitate was removed by filtration and storage of the solution at –30 °C afforded **3c** as a red solid (36 mg, 39%). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 7.39 (dt, J = 7.2, 1.1 Hz, 2H C*H*-bipyridine), 7.39 (t, J = 7.6 Hz, 1H C*H* (para B-Ar)), 7.19 (d, J = 7.6, 2H, C*H* (meta B-Ar)), 6.79 (dt, J = 9.2, 1.2 Hz, 2H, C*H*-bipyridine), 6.57 (s, 4H C*H* Mes), 5.95 (dd, J = 9.2, 0.9 Hz, 1H, C*H*-bipyridine), 5.94 (dd, J = 9.2, 0.9 Hz, 1H, C*H*-bipyridine), 5.86 (ddd, J = 7.3, 6.1, 1.2 Hz, 2H, C*H*-bipyridine), 2.16 (s, 12H, C*H$_3$*), 1.89 (s, 6H, C*H$_3$*); ^{11}B NMR (128 MHz, C$_6$D$_6$): δ = 22; ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ = 147.4 (s, Ar), 139.6 (s, Mes), 135.9 (s, Mes), 135.5 (s, *C* Mes), 129.2 (s, *C*H Ar), 129.1 (s, *C*H Ar), 128.9 (s, *C*H Mes), 118.8 (s, *C* bipyridine), 118.4 (s, *C*H bipyridine), 114.0 (s, *C*H bipyridine), 109.5 (s, *C*H bipyridine), 21.3 (s, *C*H$_3$-Mes), 20.9 (s, *C*H$_3$-Mes); El. Anal. [%]: calc. C 85.00, H 6.92, N 5.83; found: C 84.67, H 6.85, N 5.89.

Reaction of [B$_2$Dur$_2$Br$_2$] (6) with 2,2'-bipyridyl (1): A mixture of [B$_2$Br$_2$Dur$_2$] (**6**) (30.0 mg, 0.07 mmol) and **1** (23.0 mg, 0.15 mmol, 2.2 equiv) was dissolved in benzene (0.7 mL) and stirred at room temperature for 24 hours. After filtration, all volatiles were removed from the filtrate under reduced pressure and the resulting deep red residue was dissolved in hexane (0.6 mL). Slow evaporation of this solution at –30 °C afforded red crystals, which were isolated and dried *in vacuo* to yield **3b** as red crystals (7.8 mg) contaminated with approx. 35% of free **1**

which we were not able to separate. **3b** isolated in this way is spectroscopically similar to **3b** prepared from the reaction of **1** with [(Me$_3$P)(OC)$_3$Fe=BDur] (**4**) (see above).

Reaction of [F$_2$B$_2$Mes$_2$] (7) with 2,2'-bipyridyl (1): A mixture of F$_2$BB(Mes)$_2$ (**7**) (50.0 mg, 0.17 mmol) and **1** (26.2 mg, 0.17 mmol) was dissolved in benzene (1 mL) and left to stand for 5 hours whereupon a color change to deep red occurred. A precipitate formed, which was filtered off and the benzene solution was dried under reduced pressure. The residue was dissolved in hexane. Slow evaporation of this solution at ambient temperatures yielded red crystals which were washed with a small amount of cold pentane (2 x 0.3 mL) to yield **3d** as red crystals (12.3 mg, 0.04 mmol, 50%). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 7.26 (dt, J = 9.3, 1.3 Hz, 2H, C*H*-bipyridine), 7.18 (dt, J = 7.2, 1.1 Hz, 2H, C*H*-bipyridine), 6.90 (s, 2H, C*H*-Mes), 6.19 (dd, J = 6.0, 1.0 Hz, 2H C*H*-bipyridine), 5.92 (td, J = 6.0, 1.0 Hz, 2H, C*H*-bipyridine), 2.25 (s, 3H, C*H*$_3$), 2.04 (s, 6H, C*H*$_3$); ^{11}B NMR (160 MHz, C$_6$D$_6$): δ = 23; ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ = 143.0 (s, *C*$_{quat}$-Ar), 138.9 (s, *C*$_{quat}$-Ar), 127.6 (s, *C*H-Ar), 119.0 (s, *C*H-Ar), 118.7 (s, *C*H-Ar), 114.5 (s, *C*H-Ar), 110.8 (s, *C*H-Ar), 22.1 (s, *C*H$_3$), 21.4 (s, *C*H$_3$); El. Anal. [%]: calc**.** C 79.74, H 6.69, N 9.79; found: C 79.79, H 7.47, N 9.68.

Reaction of [(Me$_3$P)MesB=BMes(PMe$_3$)] (8) with 2,2'-bipyridyl (1): [(Me$_3$P)MesB=BMes(PMe$_3$)] (**8**) (30 mg, 72.8 μmol) and **1** (11.4 mg, 72.8 μmol) were dissolved in 0.6 mL C$_6$D$_6$ and heated to 80 °C for 6 days. After removal of all volatiles *in vacuo*, the resulting red solid could be ascertained to contain **3d** by comparison of its NMR spectrum with that of previously characterized **3d** (see above), as well as a new product (**9**) and thermal decomposition products of **8**. While all attempts to quantitatively isolate both products were unsuccessful, we were able to obtain a few crystals of **9** from a pentane solution of the mixture, which allowed us to characterize it by XRD. Characterization of 3b and 9 was thus done on a

freshly prepared crude reaction mixture. HRMS analysis of the reaction mixture confirmed the composition of both **3d** and **9**.

Characterization of **9**: ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.80 (dt, J = 7.5, 1.1 Hz, 2H, C*H*-bipyridine), 7.18 (dt, J = 9.6, 1.1 Hz, 2H, C*H*-bipyridine), 6.78 (s, 4H, C*H*-Mes), 6.20 (overlap, 2H, C*H*-bipyridine), 5.84 (ddd, J = 7.5, 6.0, 1.3 Hz, 2H C*H*-bipyridine), 2.15 (s, 6H, C*H*$_3$-Mes), 2.04 (s, 12H, C*H*$_3$-Mes); ^{11}B NMR (126 MHz, C$_6$D$_6$): δ = 46; HRMS (LIFDI, toluene): [M]$^+$ = 416. 2587 (calc. 416. 2590)

Additional characterization of **3b**: HRMS (LIFDI, toluene): [M]$^+$ = 286. 1634 (calc. 286. 1636)

ASSOCIATED CONTENT

Supporting Information. Full characterization of new compounds and crystallographic data. The following files are available free of charge.

Characterization of new compounds (PDF)

Crystallographic data (.cif)

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Author Contributions

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TOC text and graphic:

2,2'-Bipyridyl reacts similarly with several sources of low-oxidation-state boron in a redox

borylene abstraction process