Chelated Diborenes and their Inverse-Electron-Demand Diels-Alder Reactions with Dienes

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Abstract: A doubly base-stabilized diborane based on a benzylphosphine linker was prepared by a salt elimination reaction between $2\text{-}LiC_6H_4CH_2PCy_2.Et_2O$ and B_2Br_4. This compound was reduced with KC_8 to its corresponding diborene, with the benzylphosphine forming a five-membered chelate. The diborene reacts with butadiene, 2-trimethylsiloxy-1,3-butadiene and isoprene to form 4,5-diboracyclohexenes, which interconvert between their 1,1- (geminal) and 1,2- (vicinal) chelated isomers. The 1,1-chelated diborene undergoes a halide-catalysed isomerisation into its thermodynamically favoured 1,2-isomer, which undergoes Diels-Alder reactions more slowly than the kinetic product.

Cycloaddition reactions of unsaturated compounds are the most powerful tools for the synthesis of organic ring systems.[1] Almost a century has passed since the discovery of [4+2] cycloaddition reactions,[2] and a vast array of derivatives of this reaction is now known. While the majority of the research has naturally been confined to organic chemistry, inorganic chemists have often sought to extend these reactions to other main group elements (Scheme 1). In 1972, Roark et al. used anthracene and 1,4-diphenyl-1,3-butadiene to trap a proposed fleeting disilene via Diels-Alder cycloadditions.[3] Although the subsequently discovered stable disilenes typically did not undergo reactions with butadienes,[4] a tetrasilyldisilene was reported to react with 2,3-dimethyl-1,3-butadiene to afford a [4+2]-cycloaddition product.[5] Diels-Alder reactions with digermenes followed a similar path, with 1,3-dienes initially being used to trap otherwise unstable $R_2Ge=GeR_2$ species.[6] These reactions were, however, often low yielding, and hampered by the propensity of disilenes and digermenes to dissociate into R_2E: species. These inorganic Diels-Alder reactions could in some cases be reversed by pyrolysis (500-600 °C).[7] Ando and Tsumuraya then showed that the digermene $Mes_2Ge=GeMes_2$, which is stable enough to be observed in solution, reacts with 2,3-dimethyl-1,3-butadiene to give the digermacyclohexene product in good yield.[8]

The equivalent reactions for group 13 doubly-bonded compounds have been significantly limited by the instability of RE=ER compounds. To the best of our knowledge, the only examples of [4+2]-cycloadditions of isolated group 13 dimetallenes are the reactions by Power and co-workers of the isolable terphenyl-substituted digallene ArGa=GaAr (Ar = 2,6-$(2,6\text{-}^iPr_2C_6H_3)_2C_6H_3$) with cyclopentadiene and cycloheptatriene (Scheme 1).[9] The same group reported the trapping of the analogous dialumene, ArAl=AlAr, as its Diels-Alder adduct with toluene,[10] while analogous arene cycloaddition products have

also been shown to act as sources of the dialumene unit for reactions with other substrates.[11] Related reactions of boron-boron doubly-bonded compounds have never been reported.
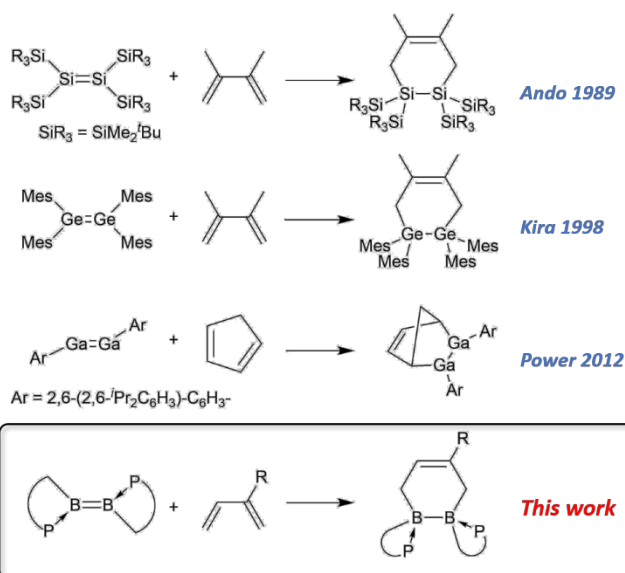
**Scheme 1.** Examples of Diels-Alder reactions of homoatomic main-group alkene derivatives.

The free diborene unit, RB=BR, has only been isolated under low-temperature matrix conditions[12] or in the coordination sphere of a transition metal.[13] However, in the last decade, several compounds containing B=B double bonds have been reported, in which coordination of neutral Lewis bases to the boron atoms allows their isolation.[14] The advent of these stable diborenes offered a unique opportunity to extend main group Diels-Alder reactions to boron. In this work, we report the synthesis of new sterically unencumbered diborenes, and their reactions with dienes to produce diboracyclohexenes.

Initially, the previously reported[14a] diborene, Dur(IMe)B=B(IMe)Dur (Dur = duryl = 2,3,5,6-tetramethylphenyl, IMe = N,N'-dimethylimidazol-2-ylidene) was treated with an excess of 1,3-butadiene in benzene solution. Disappointingly, no reaction was observed, even after heating to 80 °C for one week. We ascribed the lack of reactivity to the large steric demand of the duryl groups, and that a less encumbered diborene may be necessary. We recently reported cyclic diborenes containing a chelating benzylphosphine linker.[15] In these compounds, in contrast to other homoarene-substituted diborenes, the aryl group is held coplanar to the boron-boron bond. This configuration reduces the steric crowding around the central diborene unit, which we anticipated could facilitate the approach of small molecules.

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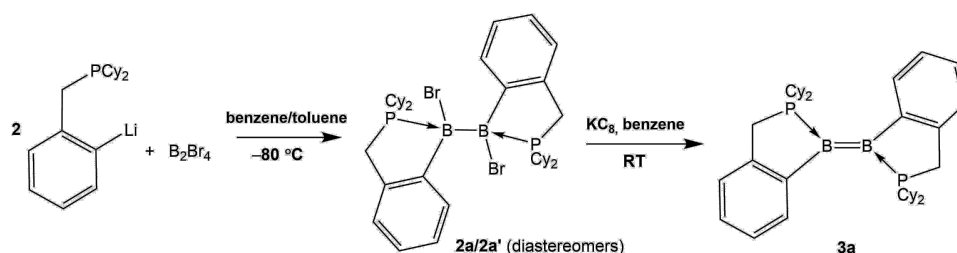
Scheme 2. Synthesis of *gem*-chelated diborene **3a** via **2a/2a'**.

Whereas B_2Br_4 only reacts with a single equivalent of the silylated benzylphosphine 2-Me$_3$SiC$_6$H$_4$CH$_2$PCy$_2$, producing unsymmetrical sp^2-sp^3 diboranes, treatment with two equivalents of the corresponding lithiated benzylphosphine species, 2-LiC$_6$H$_4$CH$_2$PCy$_2$.Et$_2$O (**1**), resulted in a double salt elimination. While the crude product displays a single ^{11}B NMR signal at –3.5 ppm, close inspection of the ^{31}P NMR spectrum revealed the presence of two species with adjacent resonances (32.7, 32.2 ppm), the ratio of which varied across multiple syntheses. Recrystallisation from toluene/hexane yielded solely the species giving rise to the signal at 32.7 ppm, allowing full characterisation by NMR spectroscopy, and X-ray diffraction on a single crystal confirmed the identity of the compound as the sp^3-sp^3 hybridised diborane(6), **2a**. The B-B bond length of 1.749(7) Å falls in the expected range for an sp^3-sp^3 diborane. Over the course of several hours at room temperature in C$_6$D$_6$ solution, the signals for the second compound reappeared, albeit never exceeding a ratio of 2.2:1. Elemental analysis of the mixture, the lack of a separate ^{11}B NMR signal and its reactivity (see below) implied that the second compound was an isomer of **2a**. Geometry optimisation of **2a** and its hypothetical 1,2-substituted isomer (**2b**) within density functional theory (DFT) at the OLYP/TZ2P level revealed **2b** to be considerably higher in energy (10.2 kcal·mol^{-1}), and we therefore assigned the compound as the *meso* diastereomer of **2a** (**2a'**). The isomerisation of **2a** presumably occurs by dissociation and reassociation of the phosphine ligands; it is noteworthy in this regard that diaryldihalodiboranes(4) only bind a single equivalent of PMe$_3$ or PEt$_3$.[14d, 16] Treatment of either pure **2a** or the crude **2a/2a'** mixture with KC$_8$ in benzene led to an intensely red solution with an ^{11}B NMR resonance at 21.3 ppm, in the expected range for diborenes. The ^{31}P NMR spectrum of the reaction mixture showed a major signal at 28.6 ppm alongside small quantities (typically 5-10%) of a second compound at 7.8 ppm. Recrystallisation provided the major species in pure form in reasonable yield (59%). Crystals suitable for X-ray diffraction were obtained from benzene/hexane solution, and the structure was confirmed as diborene **3a**, in which the benzylphosphine groups chelate in a geminal fashion with respect to the diboron unit. The boron-boron bond distance of 1.585(3) Å is in the expected range for a double bond. The most striking feature of the structure of **3a** is the alignment of the aryl substituent with the plane of the B=B π-bond, as reflected by the B1'-B1-C1-C2 torsion angle of 173.6(2)°.

The lack of a distinct second ^{11}B NMR signal during the reduction led us to suspect that the minor compound may also be a diborene, with its NMR signal obscured by that of **3a**. Optimisation of the corresponding 1,2-chelated isomer, **3b** (Figure 1), using DFT calculations (OLYP/TZ2P) showed that **3b** should be more stable by 0.8 kcal·mol^{-1}. The calculated ^{31}P NMR

chemical shifts at the same level of theory of 1.8/2.0 ppm for **3b** also correlated reasonably well with the second observed species.

Heating a sample of **3a** to 80 °C in benzene for four days resulted in approximately 30% conversion to the species responsible for the signal at 7.8 ppm in the ^{31}P NMR spectrum, but the reaction was accompanied by slow decomposition of **3a**. However, addition of a halide source was found to promote the reaction. Addition of a substoichiometric amount (7 mol%) of InBr$_3$ led to rapid precipitation of a grey solid, presumed to be indium metal, and reappearance of the ^{31}P NMR signals for **2a/2a'**, thus a partial oxidation of the diborene product to its precursor diborane(4) had occurred. Heating the resulting mixture for 24 h at 80 °C resulted in a colour change from red to orange, and complete conversion of **3a** to the second species by NMR spectroscopy.[17] The ^{11}B NMR signal of the compound at 22.8 ppm suggested diborene formation, and X-ray diffraction on single crystals grown from benzene/hexane confirmed the structure as **3b** (Figure 2).
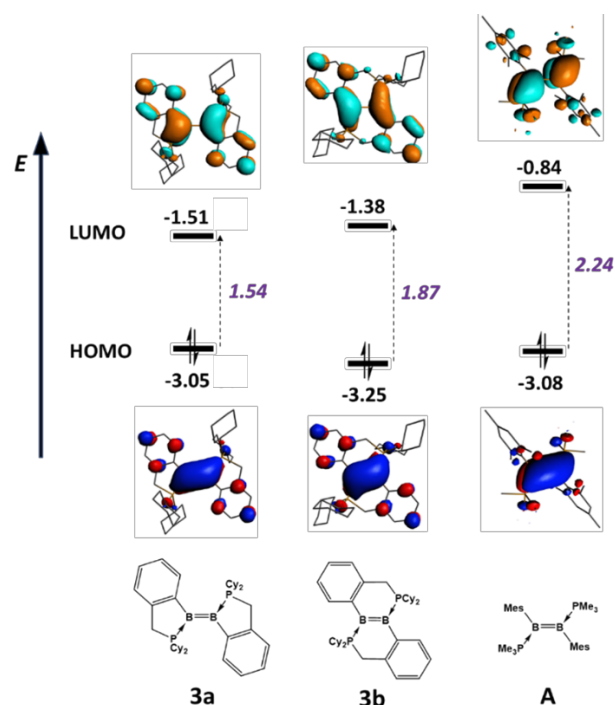

Figure 1. Frontier orbitals of (from left to right) **3a**, **3b** and **A** (OLYP/TZ2P) with orbital energies in eV.
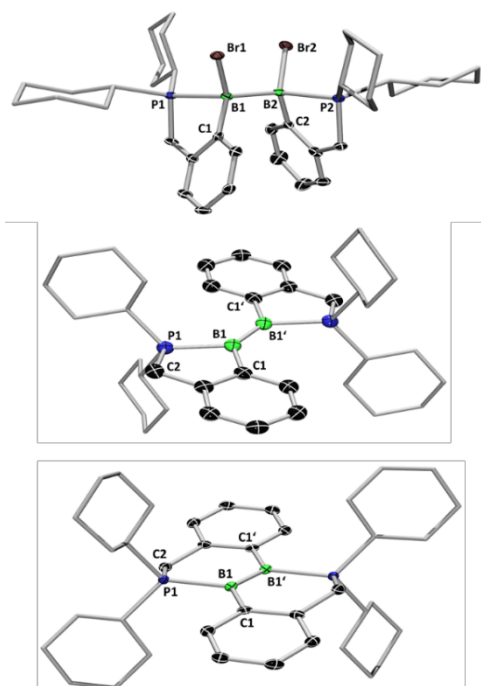
Figure 2. Molecular structures of **2a** (top), **3a** (middle) and **3b** (bottom) with selected atomic displacement parameters at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): **2a**: B1-B2 1.749(7), B1-P1 1.974(5), B2-P2 1.979(5), B1-C1 1.628(6), B2-C2 1.624(6); **3a**: B1-B1' 1.585(3), B1-P1 1.939(2), B1-C1 1.594(4), C1-B1-P1 98.7(1), C1-B1-B1' 134.0(2), P1-B1-B1' 127.3(2), B1-P1-C2 98.4(1); **3b**: B1-B1' 1.587(3), B1-P1 1.914(2), B1-C1 1.577(2), C1-B1-P1 120.8(1), C1-B1-B1' 130.1(2), P1-B1-B1' 108.9(1), B1-P1-C2 108.54(9).

The B-B bond of **3b** is the same length as that in **3a** (1.587(3) Å), whereas the B1-C1 and B1-P1 bonds are both slightly contracted. The switch from a five- to a six-membered ring does, however, have a significant effect on the bond angles around boron. Whereas the C1-B1-P1 angle in **3a** is significantly distorted from the ideal 120°, at 98.7(1)°, the value in **3b** of 120.8(1)° suggests a relaxed and thus preferential geometry. At 168.2(2)°, the B1'-B1-C1-C2 torsion angle indicates poorer alignment of the aryl groups with the π-system compared to **3a**.

The frontier molecular orbitals of **3a** and **3b** are displayed in Figure 1 alongside those of the previously published diborene $B_2Mes_2(PMe_3)_2$ (**A**).[18] The HOMOs of all three compounds largely represent the B=B π-bond, with additional bonding B-P interactions, while the LUMOs represent the B=B antibonding π* orbital. The major difference between the new compounds and **A** is that both the HOMO and LUMO have significant contributions from the aryl group. The LUMO in particular reveals the presence of an extended π-system across the whole ArB=BAr framework in **3a** and **3b**, which significantly stabilises these orbitals, whereas the HOMO energies are very similar to that of **A**. The resulting smaller HOMO-LUMO gaps correlate well with the UV-vis absorption maxima of the diborenes, which are red-shifted for **3a** (λ_{max} = 514 nm) and **3b** (483 nm) compared to **A** (365 nm). Compounds **3a** and **3b** differ in the nature of the HOMO-1 (see supporting information), which in **3a** is primarily localised on the aryl substituents, but in **3b** represents the B-B sigma bond, suggesting that the boron-boron bond in **3b** is slightly more electron rich. This is probably due to the higher ring strain in **3a** (demonstrated by the angle B1-P1-C2 = 98.4(1)° vs. 108.54(9)° for **3b**), resulting in poorer overlap of the phosphorus lone pair with the vacant σ-symmetry orbital on boron.

The possibility that an indium-catalysed process was responsible for the conversion of **3a** to **3b** was ruled out by the observation that adding a small quantity (10 mol%) of dibromodiborane **2a** to a solution of **3a** resulted in complete conversion of **3a** to **3b** after two days at 80 °C. The process is also promoted by adding substoichiometric amounts of $GeCl_2$ and $CoCl_2$; in these cases, ^{31}P NMR signals at 34.7 and 34.4 ppm and an ^{11}B NMR signal at –0.8 ppm correspond to the dichlorodiboranes **4a/4a'**. In the $CoCl_2$ case, a single crystal of the 1,2-isomer of the dichlorodiborane, **4b**, was obtained (see supporting information), proving the accessibility of the bridged isomer under the reaction conditions. We thus propose a tentative mechanism for the conversion (Scheme 3) whereby the diboranes **2a/2b** (or **4a/4b** in the case of chloride) catalyse the isomerisation of the diborenes. Compound **2b** is formed in low concentration via the aforementioned facile dissociation of the phosphine ligands, and reduced by **3a**, forming diborene **3b**, which is the thermodynamic product. The 1,1-substituted diborane **2a** is regenerated, providing more **2b** via the equilibrium rearrangement.
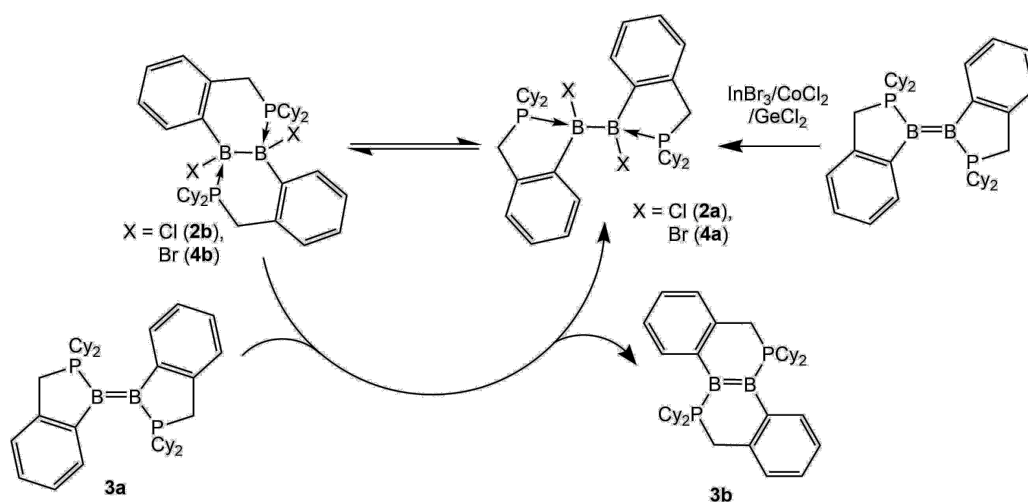
Scheme 3. Proposed mechanism for the catalytic conversion of **3a** into **3b**.
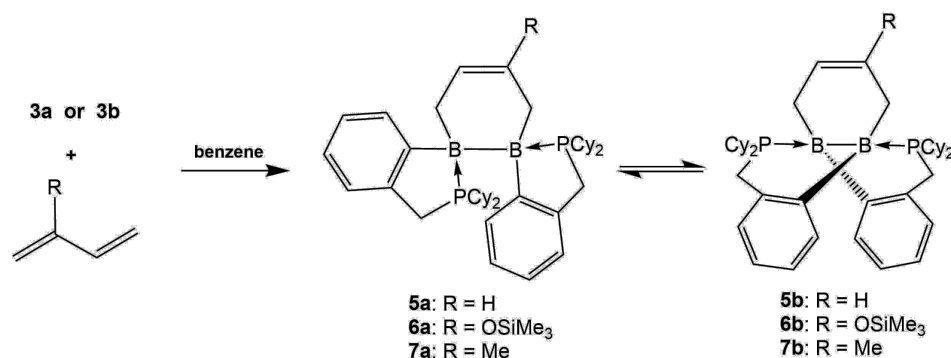
Scheme 4. Diels-Alder reactions of diborenes **3a** and **3b** with dienes.

Hoping to take advantage of its relatively unhindered double bond, we treated compound **3a** with butadiene (Scheme 4). After 16 h at room temperature, roughly 20% conversion to two new species was observed by NMR spectroscopy. The ^{11}B NMR signals were observed at –11.5 (minor) and –18 ppm (major), with ^{31}P NMR resonances at 42.0 (minor) and 3.5 ppm (major). Heating the mixture to 60 °C for a further 16 h gave complete conversion to these two species alongside traces of side products. Recrystallisation from Et$_2$O produced X-ray quality crystals of both compounds, which were confirmed to be cycloaddition products **5a** and **5b** (Figure 3). In both cases, the bond lengths and angles point to 4,5-dibora-1-cyclohexene structures; the boron-boron bond distances (**5a**: 1.815(3) Å, **5b**: 1.814(3), 1.816(3) Å) are at the upper end for B-B single bonds and considerably longer than that in **2a**, while the C1-C2 distances (**5a**: 1.325(3) Å, **5b**: 1.335(3), 1.332(3) Å) indicate clear double bonds. An interesting difference between the two structures is that the newly formed six-membered ring in **5a** is twisted to allow the diborane substituents to assume the favoured staggered conformation. In **5b**, the bridgehead positions of the B4 and B5 in the tricyclic system force an eclipsed geometry, giving the diboracyclohexene ring a boat-type conformation. Reaction of **3b** with butadiene led to the same products, albeit at a much slower rate; four days at 80 °C were required for complete conversion.

The identity of the isomers was established by recrystallisation of a mixture of **5a** and **5b** from pentane and recording NMR spectra directly after solvation in C$_6$D$_6$. The resulting crystalline solid was a single compound, confirmed as **5b** by X-ray diffraction. After just 45 min in solution at room temperature, the ratio of **5a**:**5b** was 15:85, and after 16 h the equilibrium mixture of 40:60 had been reached. Further calculations were carried out, which reproduced the highly divergent ^{31}P NMR shifts of the isomers with reasonable accuracy (**5a**: 41.4, 44.7 ppm; **5b**: 8.9, 11.3 ppm), further confirming the assignment of the compounds. For **5a**, the HOMO represents the B-B σ bond (see supporting information), whereas for **5b** this orbital has a large contribution from the newly formed alkene. The slightly lower energy of the HOMO of **5b** suggests that the bridging conformation results in better stabilisation of the B-B bond. The LUMO and LUMO+1 of both compounds are almost exclusively located on the aryl substituents.
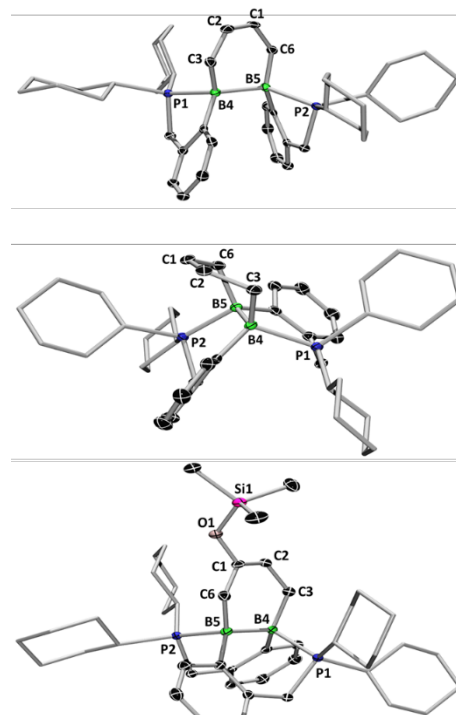

Figure 3. Molecular structures of **5a** (top), **5b** (middle) and **6b** (bottom) with selected atomic displacement parameters at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): **5a** B4-B5 1.815(3), C1-C2 1.325(3), B4-P1 2.000(2), B5-P2 1.988(2); **5b** (avg. of two molecules in asym. unit) B4-B5 1.815, C1-C2 1.334, B-P 1.978; **6b** B4-B5 1.826(3), C1-C2 1.322(3), B5-P2 1.966(2), B4-P1 1.962(3).

The well-established electron-rich nature of diborenes suggests that the formation of **5a**/**5b** can be considered an inverse-electron-demand Diels-Alder reaction, in which a relatively electron-poor diene reacts with an electron-rich dienophile. Although 1,3-butadiene is not considered an especially electron-poor diene, the considerably destabilised HOMO of diborenes compared to alkenes allows the alignment of the frontier orbitals. We were therefore keen to investigate the scope of the reaction with more electron-rich dienes. Treatment of a benzene solution of **3a** with 2-trimethylsiloxy-1,3-butadiene, a slightly more nucleophilic compound than its parent butadiene,[19] also leads to the formation of two products, as observed by ^{31}P and ^{11}B NMR spectroscopy, with conversion complete after 16 h at 60 °C. The ^{31}P NMR spectrum reveals two AB systems at 41.6/42.1 ppm ($^3J_{PP}$ = 134 Hz) and 1.5/1.7 ppm ($^3J_{PP}$ = 68 Hz), consistent with the Diels-Alder products **6a** and **6b**, in which the symmetry is disrupted due to the OSiMe$_3$ group. The ^{11}B NMR signals at –11.5 (**6a**) and –18.5 ppm (**6b**) correlate well to those of **5a** and **5b**; in this case, the inequivalent boron signals within one isomer are not sufficiently resolved due to the large

linewidth. Single crystals of **6b** suitable for X-ray diffraction were grown from hexane solution, and the structure (Figure 3) resembles that of **5b**, with the exception that the tipping of the diboracyclohexene ring is less pronounced as a result of the steric demand of the SiMe$_3$ substituent. The equivalent reaction with isoprene for 16 h at 60 °C gave the products **7a** and **7b**, with observations and NMR parameters very similar to those for **6a/6b** (**7a**: δ(^{31}P) = 41.9 ppm, δ(^{11}B) = −11.5 ppm; **7b**: δ(^{31}P) = 3.0, 3.2 ($^3J_{PP}$ = 72 Hz), δ(^{11}B) = −18.5 ppm). The highly electron-rich diene 2,3-dimethoxy-1,3-butadiene did not react with **3a**, even after four days at 80 °C, suggesting that an electrophilic diene is required for successful Diels-Alder reactions with diborenes.

In conclusion, we have isolated and characterized sterically unhindered diborenes based on chelating benzylphosphine substituents. Experimental and computational studies of the diborenes and their diborane precursors provided insight into the preferred configurations of chelated diboron systems. The diborenes **3a** and **3b** undergo the first reported examples of Diels-Alder reactions of boron-boron multiple bonds with dienes. We are now focused on expanding the scope of this reaction and on exploring the reactivity of the 4,5-diboracyclohexene products.

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