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Cyclopropanation and Isomerization Reactions of β-Diketiminato Boron Complexes

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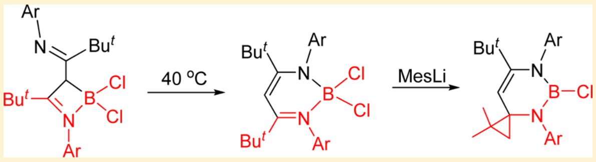
Supporting Information

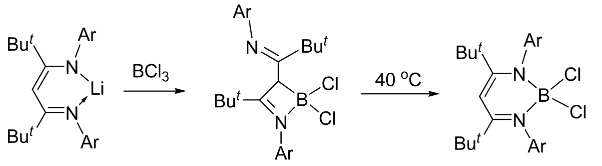
ABSTRACT: The reaction of $HC[(CBu^t)(NAr)]_2Li$ with BCl_3 yielded the azaallyl boron dichloride $[ArN{=}C(Bu^t)C(H)C(Bu^t)N(Ar)]BCl_2$ (**1**), which can be converted to the β-diketiminato boron dichloride $HC[(CBu^t)(NAr)]_2BCl_2$ (**2**) upon heating at 40 °C. Reaction of **1** with the bulky lithium salts $LiN(SiMe_3)_2$ and MesLi (Mes = $2,4,6\text{-}Me_3C_6H_2$) resulted in the cyclopropanation of the CBu^t group via the deprotonation of the methyl group, while reactions with PhLi and $LiNEt_2$ gave substitution products.



β-Diketiminato ligands are some of the most versatile supporting ligands in organometallic chemistry and homogeneous catalysis.[1] The employment of this type of ligand in boron chemistry has allowed the isolation of unique stable cationic, dicationic, and multiply bonded boron species.[2] In addition, the ligands have proved to be excellent for the stabilization of low-valent heavier group 13 carbene analogues[3] and other interesting group 13 species.[1a,4] The unusual stabilization effects can be attributed to the electron delocalization of the monoanionic ligand backbone, steric protection of the N substituents, and high stability of the ligand framework. However, recent studies have shown that the ligands may undergo C–N bond rupture and C–H bond activation of the β-methyl groups under reducing conditions.[5] Our previous studies on the boron compounds supported by the monoanionic ligand $HC[C(Me)(NAr)]_2$ (Ar = $2,6\text{-}Me_2C_6H_3$) indicated that the C–H bond of the β-methyl group may take part in chemical transformations.[2d] Current great interest in the preparation of stable borylenes[6] prompted us to investigate boron compounds incorporating this type of ligand with the expectation of generating the elusive N-heterocyclic borylenes. Herein, we report on the synthesis and reactions of boron compounds containing the $\{HC[C(Bu^t)(NAr)]_2\}^-$ framework. Interestingly, the ligand not only exhibits two types of bonding modes but also undergoes a cyclopropanation reaction upon treatment with bulky lithium salts, demonstrating the unique behavior of the ligand in boron chemistry.

The boron dichloride **1** was prepared in high yield by the reaction of $HC[C(Bu^t)(NAr)]_2Li$[7] with BCl_3 in diethyl ether (Scheme 1). Compound **1** has been fully characterized by ^1H, ^{11}B, and ^{13}C NMR and EI mass spectroscopy, elemental analysis, and an X-ray single-crystal analysis. The ^{13}C NMR spectrum of **1** exhibits two signals at δ 176.0 and 209.9 ppm for the imino carbon atoms, indicating their different chemical environments. The ^{11}B resonance observed at δ 8.17 ppm corresponds to a four-coordinate boron atom. The structure has been confirmed by an X-ray single-crystal analysis.

Scheme 1. Synthesis and Isomerization of 1



1

2

Ar = $2,6\text{-}Me_2C_6H_3$

Single crystals suitable for X-ray diffraction studies were obtained from THF/*n*-hexane at −40 °C. The structure of **1** is shown in Figure 1, along with selected bond parameters. The most noticeable structural feature of **1** is the coordination mode of the ligand, in which, unlike the normally observed N,N coordination in group 13 compounds,[4] the boron atom is coordinated to one of the nitrogen atoms and to the γ-carbon

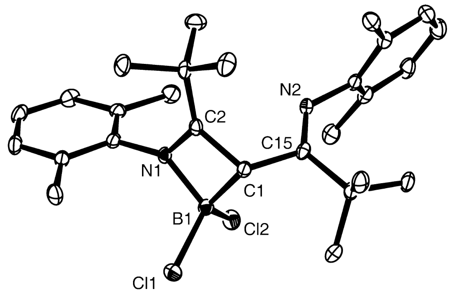


Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (deg): B1–C1 = 1.665(3), B1–N1 = 1.593(3), B1–Cl1 = 1.859(3), B1–Cl2 = 1.527(3), C1–C2 = 1.527(3), N1–C2 = 1.303(3), C1–C15 = 1.519(3), N2–C15 = 1.280(3); C1–B1–N1 = 83.16(16), C1–C2–N1 = 99.42(19), B1–N1–C2 = 93.97(18), B1–C1–C2 = 83.44(17).

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atom. The B−C bond length (1.665(3) Å) is significantly longer than those found in the reported amidinate boranes (1.613(3)−1.628(2) Å), while the B−N bond (1.593(3) Å) is comparable to those observed in the reported aminoboranes (1.583(3)−1.606(2) Å).[8] The coordination of the boron to the C1−C2−N1 aza-allylic fragment leads to the slightly lengthened C2−N1 bond length of 1.303(3) Å, in comparison to the uncoordinated C15−N2 double-bond length of 1.280(3) Å. However, the C1−C2 bond length of 1.527(3) Å is in the typical range for a C−C single bond and is even slightly longer than the C1−C15 single-bond length of 1.519(3) Å. These data indicate a very small degree of electron delocalization over the C1−C2−N1 framework. Several examples of *β*-diketiminato complexes with this type of bonding mode have also been reported.[9]

Interestingly, compound **1** is subject to isomerization to **2** under thermal conditions. Heating a solution of **1** in toluene at 40 °C for 24 h resulted in the clean formation of **2**, indicating that **2** is the thermodynamically stable isomer. The ^{11}B NMR spectrum of **2** exhibits a signal at *δ* 6.74 ppm, which is shifted upfield relative to that observed for **1** (*δ* 8.17 ppm). Furthermore, the ^{1}H and ^{13}C NMR spectra of **2** only show one set of signals for the N−C−C−C−N backbone and their substituents, indicating the normal N,N coordination of the *β*-diketiminato ligand. The molecular structure of **2** has been determined by X-ray single-crystal analysis, which is shown in Figure 2. Unlike the *β*-diketiminato boron dichloride HC[C(Me)(NC$_6$F$_5$)]$_2$BCl$_2$[10] reported by Cowley and co-workers, in which the C$_3$N$_2$B six-membered ring is planar, the boron atom in **2** is out of the C$_3$N$_2$ plane, probably due to the steric hindrance of the Ar and Bu^t groups. In addition, the Cl1 atom is nearly perpendicular to the C$_3$N$_2$ plane with a long B1−Cl1 bond distance of 1.9099(18) Å.

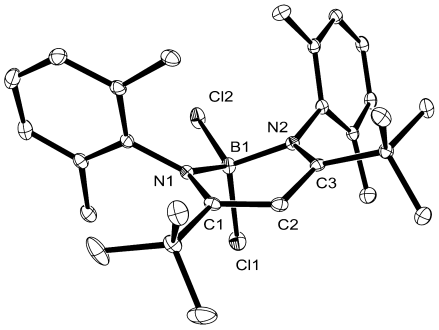
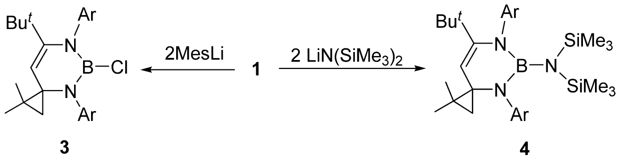


Figure 2. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): B1−N1 = 1.5297(19), B1−N2 = 1.569(2), B1−Cl1 = 1.9099(18), B1−Cl2 = 1.8416(18), C1−N1 = 1.3579(18), C1−C2 = 1.390(2), C2−C3 = 1.4124(19), N2−C3 = 1.3353(17); N1−B1−N2 = 109.79(12), B1−N1−C1 = 114.72(11), N1−C1−C2 = 117.93(13), C1−C2−C3 = 124.17(13), C2−C3−N2 = 117.63(13), B1−N2−C3 = 116.90(12).

Treatment of **1** and **2** with 2 equiv of MesLi (Mes = 2,4,6-Me$_3$C$_6$H$_2$) in toluene at 40 °C resulted in the cyclopropanation of one of the CBu^t groups to yield compound **3** instead of substitution of the chloride ligand (Scheme 2). Reaction of **1** with LiN(SiMe$_3$)$_2$ also led to a similar cyclopropanation reaction with an additional substitution reaction by the lithium salt to yield **4**. Reaction of **3** with MesLi in hot toluene led to the formation of a complicated mixture, which could not be characterized. Compound **3** and **4** have been fully characterized by ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy, elemental analysis, and X-ray single-crystal analysis. The ^{11}B NMR spectra of **3** and **4** display similar resonances at *δ* 28.7 and 28.5 ppm, respectively, which are very close to those reported for cyclic diaminoboranes.[11] The ^{1}H NMR spectra of the two compounds show that one hydrogen atom in the CBu^t group is missing with the formation of a CH$_2$ fragment, identified by the unique resonances at *δ* 0.19 and 0.41 ppm, respectively. The structures of **3** and **4** have been finally determined by X-ray single-crystal analysis.

Scheme 2. Cyclopropanation of 1



The structures of **3** and **4** are shown in Figures 3 and 4, respectively. The two structures both contain a C1−C2−C3

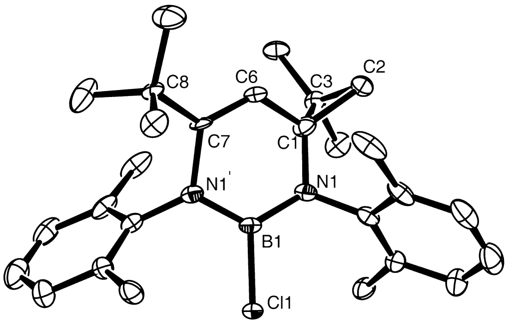


Figure 3. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): B1−N1 = 1.412(3), B1−Cl1 = 1.799(5), N1−C1 = 1.426(13), C1−C2 = 1.541(9), C2−C3 = 1.506(8), C1−C3 = 1.520(9), C1−C6 = 1.496(9), C6−C7 = 1.348(11), C7−N1′ = 1.517(11); N1−B1−N1′ = 122.7(4), N1−B1−Cl1 = 118.7(2), N1′−B1−Cl1 = 118.7(2), C1−C2−C3 = 59.8(5), C2−C1−C3 = 58.9(4), C1−C3−C2 = 61.3(5).

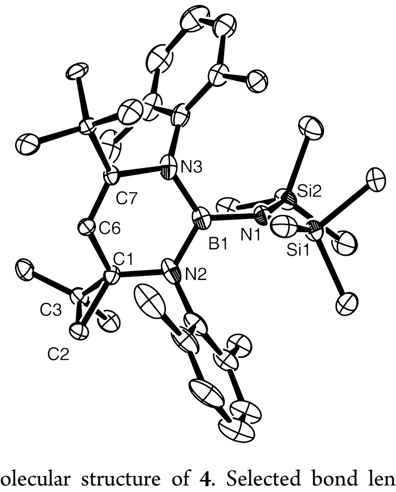
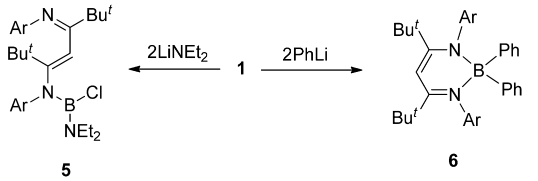


Figure 4. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): B1−N1 = 1.483(3), B1−N2 = 1.454(3), B1−N3 = 1.457(3), N2−C1 = 1.410(7), C1−C2 = 1.538(7), C2−C3 = 1.496(6), C1−C3 = 1.536(6), C1−C6 = 1.476(6), C6−C7 = 1.343(6), C7−N3 = 1.505(6); N2−B1−N3 = 116.2(2), N1−B1−N2 = 122.5(2), N1−B1−N3 = 121.3(2), C1−C2−C3 = 60.8(3), C2−C1−C3 = 58.3(3), C1−C3−C2 = 60.9(4).

cyclopropane framework with C−C bond lengths in the range of 1.496(6)−1.541(9) Å and C−C−C bond angles in the range of 58.3(3)−61.3(5)°. The three-coordinate boron atoms in **3** and **4** are planar (the sums of the angles around the boron atom are 360.1 and 360.0°, respectively, in **3** and **4**). The B−N bond distances in **3** (1.412(3) Å) are noticeably shorter than the corresponding distances in **4** (1.454(3) and 1.457(3) Å) because the existence of the exocyclic B1−N1 bond in **4** leads to reduced B−N π interactions in the six-membered ring. The C1−N1 and C1−N2 bond distances in **3** (1.426(13) Å) and **4** (1.410(7) Å) are much shorter than C7−N1′ (1.517(11) Å) in **3** and C7−N3 (1.505(6) Å) in **4**, probably due to the nitrogen lone pair interactions with the C1−C2−C3 three-membered rings.

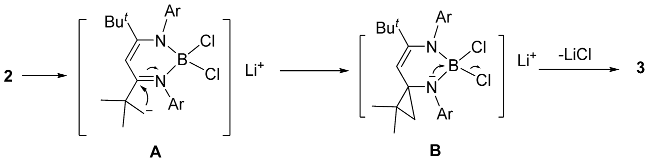
In contrast, reactions of **1** and **2** with the less hindered PhLi (Ph = C_6H_5) and $LiNEt_2$, under the same conditions as for the formation of **3** and **4**, resulted in nucleophilic substitution on the boron atom instead of cyclopropanation. Reaction of **1** with 2 equiv of $LiNEt_2$ afforded the monoamino-substituted product **5**, while the reaction with PhLi gave the diphenyl-substituted borane **6** (Scheme 3). Compounds **5** and **6** have been characterized by ^1H, ^{11}B, and ^{13}C NMR and EI mass spectroscopy and elemental analysis. The NMR spectra of **6** show only one set of signals for the substituents on the C_3N_2B backbone, indicating that its structure is similar to that of **2**. However, the ^1H NMR spectrum of **5** displays one set of resonances for the NEt_2 group and two singlets at δ 1.11 and 1.48 ppm for the Bu^t groups. X-ray single-crystal analysis shows an open ligand structure of **5** with only one nitrogen atom in the ligand being coordinated to the boron atom (see the Supporting Information, Figure S1). The three-coordinate boron atom in **5** adopts a planar geometry with the sum of the angles being 360°. The B1−N1 and B1−N2 bond distances are 1.3980(17) and 1.4480(18) Å, indicating a noticeable π interaction of the boron atom with the N1 atom.

Scheme 3. Reaction of 1 with PhLi and $LiNEt_2$



The formation of **3** and **4** might involve the initial deprotonation of one CBu^t group by the bulky lithium salt followed by the nucleophilic addition of the $Me_2CCH_2^-$ anion to the adjacent C═N double bond and the elimination of LiCl (Scheme 4). The deprotonation reaction very likely results from the bulkiness of the Mes^- and $[N(SiMe_3)_2]^-$ anions, which prevent their nucleophilic attack at the boron atom. This type of cyclopropanation reaction has not been reported for bulky β-diketiminato ligands with β-Bu^t groups.

Scheme 4. Proposed Mechanism of the Cyclopropanation Reaction



In summary, the initial formed azaallyl boron dichloride **1** undergoes an isomerization reaction to give the corresponding β-diketiminato compound **2**. The bulky Lewis bases MesLi and $LiN(SiMe_3)_2$ deprotonate one of the β-Bu^t groups of **2** to yield the cyclopropanation products **3** and **4**, while the less sterically hindered bases $LiNEt_2$ and PhLi lead to the formation of the normal substitution products **5** and **6**. These types of isomerization and cyclopropanation reactions have not been reported for other elemental and metal complexes supported by β-diketiminato ligands, indicating the unique bonding and chemical properties of this class of boron compounds. The investigation of the reduction chemistry of **1** and **2** with various reducing reagents is currently in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, a figure, and a table giving synthetic procedures and characterization data for the new compounds reported in this paper and CIF files giving crystallographic data for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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