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Reluctance of 4-Chloro-5-metalla-1,3,2-diazaborolines To Undergo Metal Halide *β*-Elimination: An Opportunity for C-Functionalization of 1,3,2-Diazaborolines

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N,N′-Bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene reacts with dichlorophenylborane, affording the *N,N′*-bis(2,6-diisopropylphenyl)-2-phenyl-4-chloro-1,3,2-diazaboroline in a one-step process. The addition of lithium diisopropylamide gives rise to the 4-chloro-5-lithio-1,3,2-diazaboroline derivative, which cleanly undergoes a transmetalation reaction with $TiCl_4 \cdot 2THF$. Both the lithium and titanium complexes are stable with respect to metal chloride elimination and have been characterized by multinuclear NMR spectroscopy and by single-crystal X-ray diffraction studies. These findings open an avenue for the C-functionalization of 1,3,2-diazaborolines.

We have recently shown that it is possible to polarize the p system of allenes up to the breaking point, which led to the discovery of stable bent allenes **A**,[1,2] also called carbodicarbenes after Frenking's computational studies[3] (Figure 1). An obvious extension of this work is to attempt to polarize a C≡C triple bond, in the hope of bending the usually very rigid linear skeleton of alkynes, without significant destabilization.[4] By analogy with the approach used in the case of allenes, one option is to attach amino groups at both ends of the C≡C triple bond and to incorporate the alkyne moiety into a five-membered ring, as shown in **B**. Bent allenes **A** can easily be synthesized by deprotonation of the conjugate acids. For preparing alkynes, one of the simplest approaches is to perform a 1,2-elimination from a suitable unsaturated precursor. It is well-known that acyclic alkenes with an alkali metal and a halogen on neighboring carbon atoms are unstable with respect to metal halogen salt elimination and readily give rise to alkynes. In contrast, their cyclic versions are often more stable,[5] except when aromatic compounds are involved;[6,7] for instance, 1-fluoro-2-lithiobenzene decomposes at −60 °C.[6d]

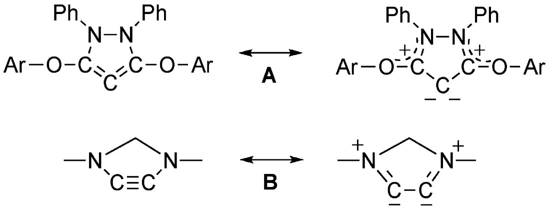

Figure 1

On the basis of this analysis, we chose to target 4,5-dehydro-1,3,2-diazaborolines **3**, which feature, as desired, two nitrogen atoms bonded to the unsaturation and a 6π-electron system. Here we report the synthesis, spectroscopic investigation, and single-crystal X-ray diffraction studies of

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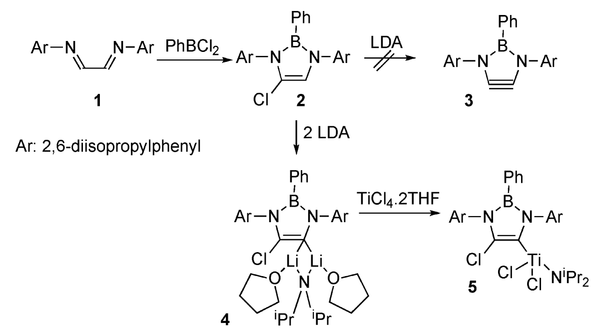
Scheme 1



a novel 4-chloro-1,3,2-diazaboroline, as well as its 5-lithio derivative. We also describe the transmetalation reaction of the latter with titanium.

Heterocycles containing boron and nitrogen are an important class of compounds owing to their wide applications in industry and academia.[8] Among them, 1,3,2-diazaborolines have gained increasing attention[9] because recent physicochemical studies point to possible applications, especially for optoelectronic devices.[10] Therefore, several synthetic routes are available.[8] Of particular interest, it has recently been shown that *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (**1**)[11] reacts with boron trichloride in methylene chloride to afford the corresponding *N*,*N*′-bis(2,6-diisopropylphenyl)-2,4-dichloro-1,3,2-diazaboroline.[12] Although this compound features a proton next to a halogen-substituted carbon, the presence of the chlorine on the boron atom was not desirable for our purpose. Thus, we extended this synthetic methodology to dichlorophenylborane. Indeed, the reaction of **1** with 1 equiv of dichlorophenylborane in CH_2Cl_2 cleanly afforded *N*,*N*′-bis(2,6-diisopropylphenyl)-2-phenyl-4-chloro-1,3,2-diazaboroline (**2**; Scheme 1), which was isolated after crystallization from hexanes at −30 °C in 78% yield, as air-stable colorless crystals.[12]

Surprisingly, according to NMR spectroscopy, the reaction of **2** with 1 equiv of lithium diisopropylamide (LDA) in a tetrahydrofuran (THF) solution at −78 °C gave rise to a 1:1 mixture of the starting material **2** and a new compound **4**. After the addition of a second 1 equiv of LDA, the conversion of **2** to **4** was completed, and the latter compound was isolated after crystallization from a hexane solution at −30 °C as air-sensitive pink crystals (87% yield). Interestingly, the ^1H and ^{13}C NMR spectra showed the presence of a *i*-Pr_2N group and two THF molecules, ruling out the formation of the desired 4,5-dehydro-1,3,2-diazaboroline **3**.

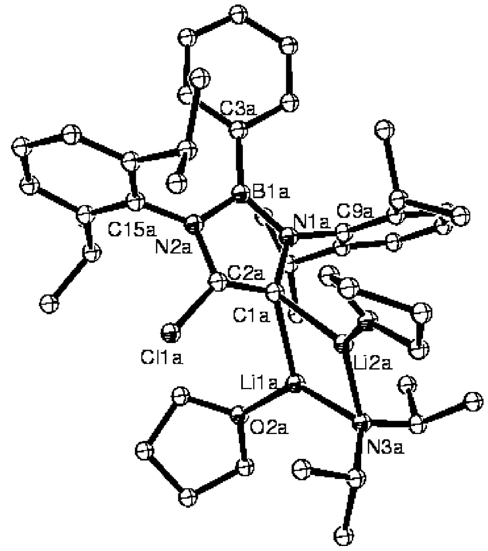


Figure 2. Molecular structure of **4** in the solid state (hydrogen atoms are omitted for clarity; ellipsoids are drawn at 30% probability). Selected bond lengths [Å] and angles [deg]: B1A−N1A 1.432(13), B1A−N2A 1.430(13), N1A−C1A 1.436(12), N2A−C2A 1.411(12), C1A−C2A 1.338(13), Cl1A−C2A 1.721(9), Li1A−C1A 2.226(18), Li2A−C1A 2.195(19), Li1A−N3A 1.974(19), Li2A−N3A 2.005(19), Li1A−O2A 1.914(19); N2A−B1A−N1A 103.3(8), B1A−N1A−C1A 113.0(7), C2A−N2A−B1A 106.3(7),C2A−C1A−N1A102.0(7),C1A−C2A−N2A115.3(8),Li2A−C1A−Li1A 65.9(7), Li1A−N3A−Li2A 74.4(7).

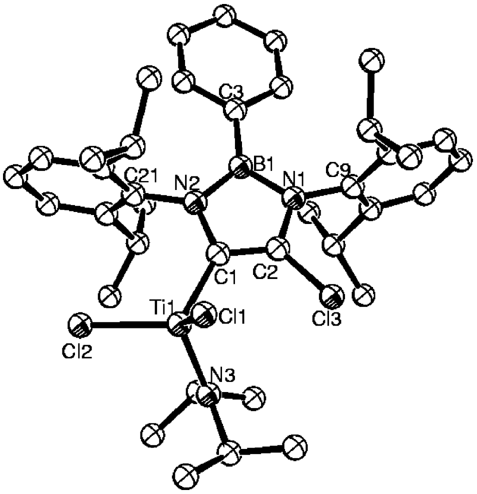


Figure 3. Molecular structure of **5** in the solid state (hydrogen atoms are omitted for clarity; ellipsoids are drawn at 30% probability). Selected bond lengths [Å] and angles [deg]: B1−N1 1.459(3), B1−N2 1.434(2), N1−C2 1.380(2), N2−C1 1.419(2), C1−C2 1.366(3), Cl3−C2 1.7178(18), Ti1−C1 2.0716(19), Ti1−N3 1.8411(17); N2−B1−N1 103.43(16), C1−N2−B1 111.30(15), C2−N1−B1 107.44(15), C2−C1−N2104.79(15), C1−C2−N1 113.03(16).

A single-crystal X-ray diffraction study[13] unambiguously demonstrated that **4** was 4-chloro-5,5-dilithio-1,3,2-diazaboroline, with the two lithium atoms sharing a disopropylamino moiety and each being further coordinated by a THF molecule (Figure 2). Complex **4** is reminiscent of 3-bromo-2-lithiobenzofuran and 3-iodo-2-lithioindole, prepared and crystallographically characterized by Boche et al.[7]

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(13) CCDC 696763 (**2**), 696764 (**4**), and 696765 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

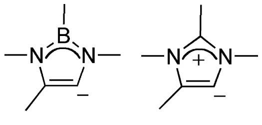

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Figure 4

Derivative **4** appeared to be stable at room temperature, in solution, and in the solid state under an argon atmosphere, for at least 2 weeks. All attempts to induce the β-elimination of lithium chloride failed. Therefore, in the hope of favoring the elimination reaction, transmetalation of **4** was attempted.

When the lithium complex **4** was treated at room temperature with 1 equiv of $TiCl_4 \cdot 2THF$ in benzene, a clean reaction occurred. After workup, the resulting solid was recrystallized from a hexanes solution at −30 °C. Complex **5** was isolated in 28% yield, as extremely air-sensitive red crystals, and its structure ascertained by a single-crystal X-ray diffraction study (Figure 3).[13] All of our attempts to induce the β-elimination reaction failed again.

The reactivity and functionalization of 1,3,2-diazaborolines typically occur at boron, less frequently at nitrogen, but not at carbon.[9] Therefore, although we have not as yet been able to prepare our targeted bent alkyne, this work shows that the unsaturated carbon atoms of the ring can also be functionalized, opening up a new avenue in 1,3,2-diazaboroline chemistry. Moreover, the boron heterocycle of type **6**, which is present in complexes **4** and **5**, can be regarded as an anionic version of the so-called abnormal N-heterocyclic carbenes **7**,[14] which have found numerous applications as strong donor ligands for transition-metal-based catalysts (Figure 4). The use of these anionic boron heterocycles **6** in organometallic catalysis is under active investigation.

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Supporting Information Available: Crystallographic data including CIF files as well as synthetic and spectroscopic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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