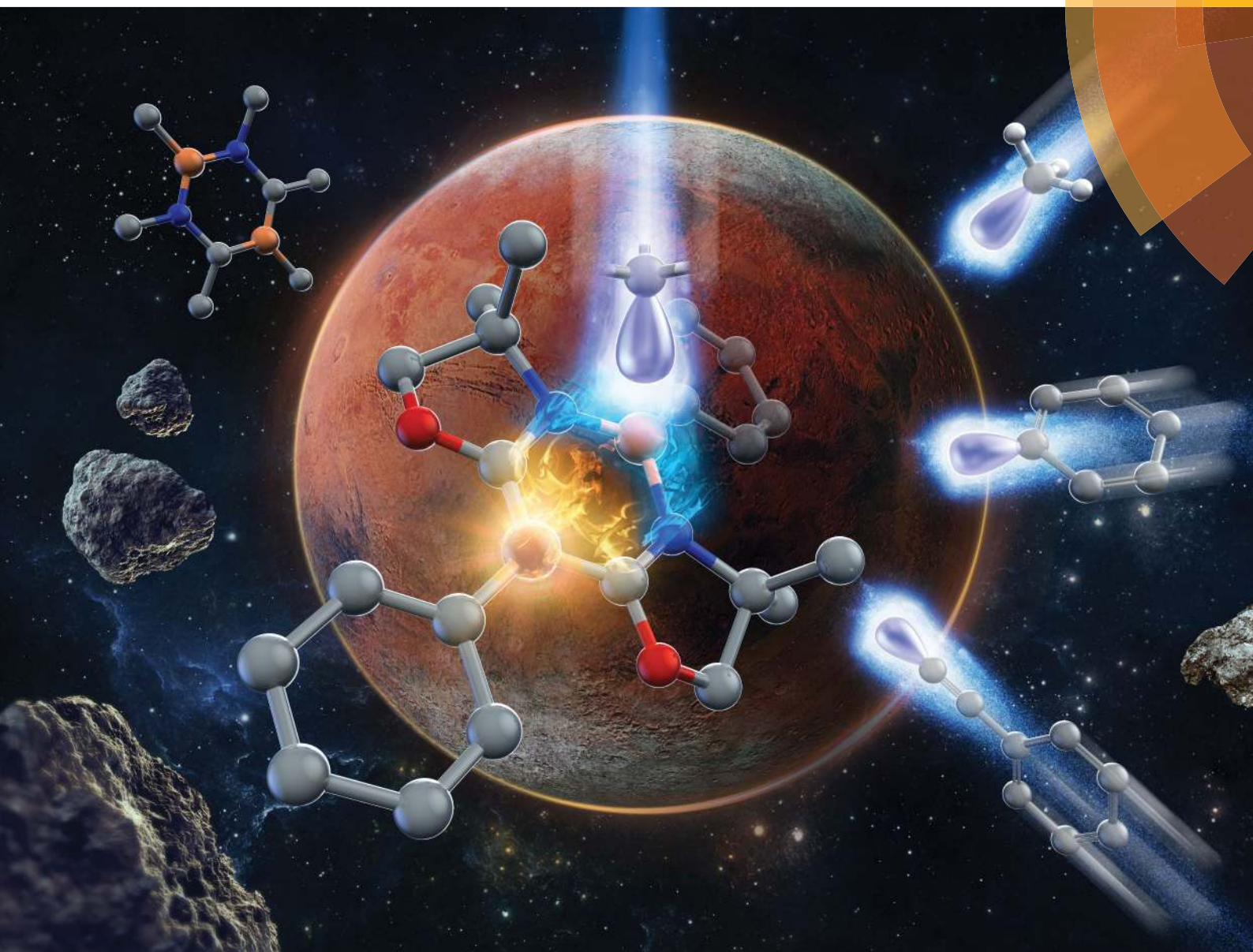


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A snapshot of inorganic Janovsky complex analogues featuring a nucleophilic boron center†

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The addition of phenyl lithium (PhLi) to an aromatic 1,3,2,5-diazadiborinine (**1**) afforded isolable ionic species **2**, which can be deemed as an inorganic analogue of a Janovsky complex. X-ray diffraction analysis and DFT studies of **2** indicate the delocalization of π -type electrons mainly over the C–B–C unit in the central B₂C₂N₂ six-membered ring. The reactions of **2** with methyl iodide (MeI) and chloro(tricyclohexylphosphine)gold(I) (Cy₃PAuCl) gave **3** bearing a B–Me bond and **4** featuring a B–Au bond, respectively, demonstrating the nucleophilic properties of the tricoordinate boron center in **2**.

Functionalization of an electron deficient aromatic ring by the addition of a nucleophile, namely nucleophilic aromatic substitution (S_NAr), is one of the most significant reactions in the modern organic chemistry arsenal.¹ The reaction pathway involves (i) the addition of a nucleophile (Nu[−]) to an aromatic ring (**I**) bearing an electron withdrawing group (X) to generate an anionic intermediate, called σ -complex **A** (Meisenheimer² or Jackson–Meisenheimer complexes³ for O/N-nucleophiles, Janovsky complexes⁴ for C-nucleophiles) involving a sp³-carbon in the six-membered ring,⁵ (ii) elimination of the leaving group (X) from complex **A** concomitant with rearomatization to afford substituted aromatic ring **II** (Fig. 1a). Significantly, when the carbon attacked by the nucleophile does not possess a good leaving group, the Janovsky complex may be trapped by an appropriate electrophile, which leads to the dearomatization of the ring.⁶ In general, Janovsky complexes are highly unstable and hence considered as transient species; however, several methodologies for the isolation of such species have been

described,⁷ which has significantly contributed to a deep comprehension of the chemical nature of Janovsky complexes.

Because of the isoelectronic and isosteric relationship between the C=C and B–N units, borazine (B₃N₃R₆) is referred to as inorganic benzene.⁸ When borazine possesses appropriate leaving groups on the B atom, nucleophilic substitution readily takes place via a similar route to the S_NAr mechanism, thus involving a Janovsky complex.⁹ Indeed, it has been reported that the reaction of nucleophiles with borazine without the leaving groups on the B atom affords isolable ionic species corresponding to the Janovsky complex.¹⁰ Very recently, Szymczak *et al.* reported that the reaction of hexamethylborazine **III** and a trifluoromethyl anion, which was generated *in situ* from HCF₃ and a base, led to the formation of complex **B** as an isolable species (Fig. 1b).¹¹ Significantly, complex **B** serves as a CF₃ group transfer reagent, and various CF₃-containing compounds **IV** were obtained after the treatment of **B** with electrophiles (E⁺), demonstrating the potential utility of inorganic Janovsky complexes in applications. Meanwhile, although the preparation of a plethora of aromatic azaborinine (BNC₄) and diazadiborinine (B₂N₂C₂) derivatives, as well as their functionalization

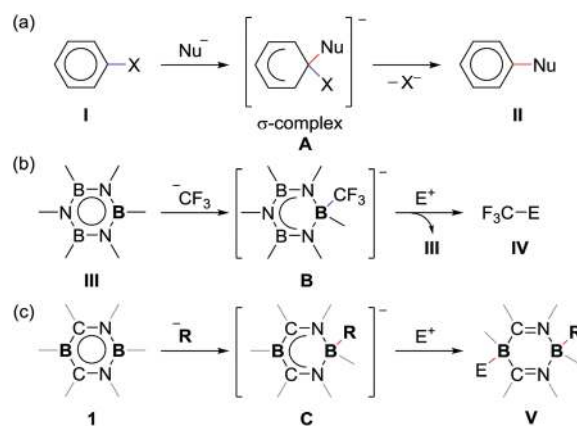


Fig. 1 (a) σ -Complex **A** in a classical nucleophilic aromatic substitution reaction. (b) Inorganic Janovsky complex **B** as a CF₃ transfer reagent. (c) This work.

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by nucleophilic substitution reactions at the B atom, has been reported,^{9,12} to the best of our knowledge, the corresponding Janovsky-complex analogues have never been isolated thus far. Recently, we have reported the synthesis of an aromatic 1,3,2,5-diazadiborinine (**1**) featuring both Lewis acidic (between two nitrogen atoms) and Lewis basic (between two carbon atoms) boron centers, which can cooperatively activate neutral small molecules such as carbon dioxide, carbonyls, alkenes, and alkynes.^{13,14} We reasoned that the Lewis acidic boron center in **1** may accept anionic nucleophiles, which could lead to the formation of Janovsky-complex analogues **C** (Fig. 1c). Moreover, because of the absence of a leaving group on the tetracoordinate boron atom, while the Lewis basic boron center remains in **C**, the reaction with electrophiles (E^+) will afford **V** to achieve a nucleophilic dearomatization (D_NAr) reaction.⁶ Herein, we show that indeed the synthesis of complex **C** from 1,3,2,5-diazadiborinine **1** is feasible. We also present single-crystal X-ray diffraction analysis, computational studies and the reactivity of **C** toward electrophiles.

Reacting **1** with phenyl lithium (PhLi) in a deuterated tetrahydrofuran (THF- d_6) solution at room temperature led to a red solution, which displays two signals at -0.5 ppm and -3.2 ppm in the ^{11}B NMR spectrum (Fig. S1, ESI †). Both signals are shifted upfield compared with those (7.3 ppm and 24.9 ppm) of **1**.¹³ After work up with 12-crown-4 ether, **2'** was isolated as a red powder in 70% yield. Single crystals of **2** were obtained from a concentrated solution of THF at -10 °C, and the solid-state structure determined by X-ray diffraction analysis reveals the separated ionic structure of **2** including a cationic lithium coordinated by four THF molecules. The closest distance between the cationic and anionic fragments is 5.471 Å, indicating no interaction between them (Scheme 1).

Fig. 2a shows the structure of the anionic moiety of **2**, in which the central $B_2C_2N_2$ six-membered ring is nearly co-planar. The B1 atom is tetra-coordinated with two nitrogen atoms (N1, N2) and two Ph groups, confirming that the B center was attacked by PhLi, which is in agreement with the Lewis acidic nature of the B center.^{13,14} Meanwhile, the B2 atom is tri-coordinated by three carbon atoms (C17, C18, C23) with the sum of the bond angles being 359.9° , indicative of a characteristic sp^2 hybridization. Both the B1–N1 (1.574(6) Å) and B1–N2 (1.564(5) Å) distances are longer than that (1.443(3) Å) in **1**, whereas the distances of the N1–C17 (1.358(5) Å) and N2–C18 (1.356(5) Å) bonds are shorter than that (1.374(3) Å) in **1**. Significantly, the B2–C17 (1.492(6) Å) and B2–C18 (1.485(7) Å) distances are close to the corresponding bond (1.483(3) Å) of **1** and lie between the typical boron–carbon single and double

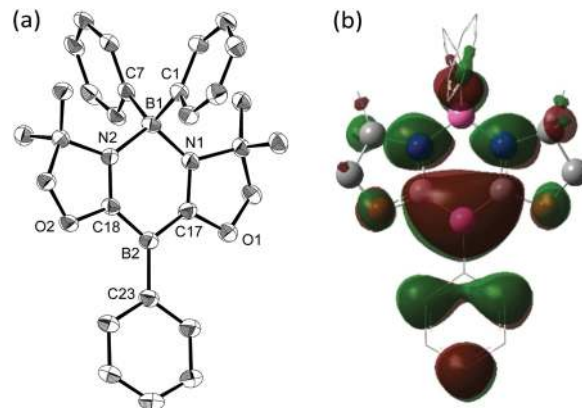
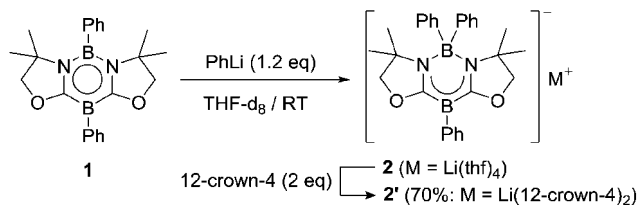


Fig. 2 (a) The solid-state structure of **2** (all hydrogen atoms and the counterion are omitted for clarity). (b) The plot of the HOMO of **2**.

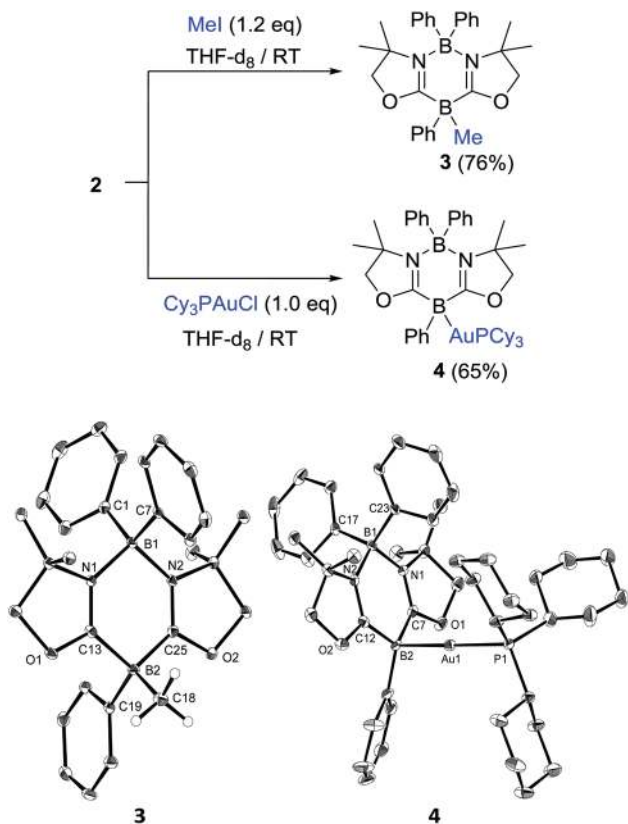
bonds, suggesting delocalization of π -electrons over the C18–B2–C17 moiety. In line with the experimental results, DFT calculations performed at the B3LYP/6-311+(d,p) level of theory confirm that the HOMO of **2** is mainly a π -type orbital over the C18–B2–C17 moiety with some contribution from the N and O lone pairs (Fig. 2b). Wiberg bond index values larger than 1 for the B2–C17 bond (1.21) and the B2–C18 bond (1.21) support the partial double-bond character of these bonds. As far as we are aware, the structure of **2** represents the first structural authentication of a Janovsky complex analogue derived from diazadiborinine.

The electronic properties of **2**, in particular around the C18–B2–C17 moiety, are reminiscent of that around the B center in the recently reported borylenes (L_2RB),^{15,16} many of which exhibit nucleophilic nature owing to their electron richness.^{15b,16c,e,i} To examine the reactivity of **2** toward electrophiles, we carried out the reaction with methyl iodide (MeI). The treatment of **2** with a slight excess amount of MeI in deuterated tetrahydrofuran solution afforded **3** in 76% yield (Scheme 2). The X-ray diffraction study of **3** confirmed that the methyl group is bound to the B2 atom demonstrating the nucleophilic nature of **2**, which is in sharp contrast to the CF_3 -transfer reactivity of **B** (Fig. 1). Note that the electron-transfer mechanism involving the radical intermediate cannot be ruled out for the formation of **3**.¹⁷

Moreover, when one equivalent of phosphine-gold chloride Cy_3PAuCl was added to a deuterated tetrahydrofuran solution of **2** at room temperature, gold complex **4** was obtained in 65% yield after work up (Scheme 2). The ^{11}B NMR spectrum of **4** shows two singlets at -0.4 ppm and -11.6 ppm that are assigned to the B atom between two nitrogen atoms and the B atom bound to the Au atom, respectively. The crystallographic study demonstrates the formation of the B2–Au bond with the bond distance of 2.204(5) Å which is nearly identical to that (2.166(14) Å) in $L_2PhB: \rightarrow AuCl$ ($L = \text{oxazol-2-ylidene}$).^{18,19} These results, thus, confirm that the addition of PhLi to 1,3,2,5-diazadiborinine leads to the formation of nucleophilic boron species, formally by transferring the anionic charge from the carbon (PhLi) to the boron in **1**. Note that the conventional synthetic method for isolable nucleophilic boron-metal species is limited to the reduction of haloboranes,^{17b,20,21} and other approaches remain relatively elusive.²²

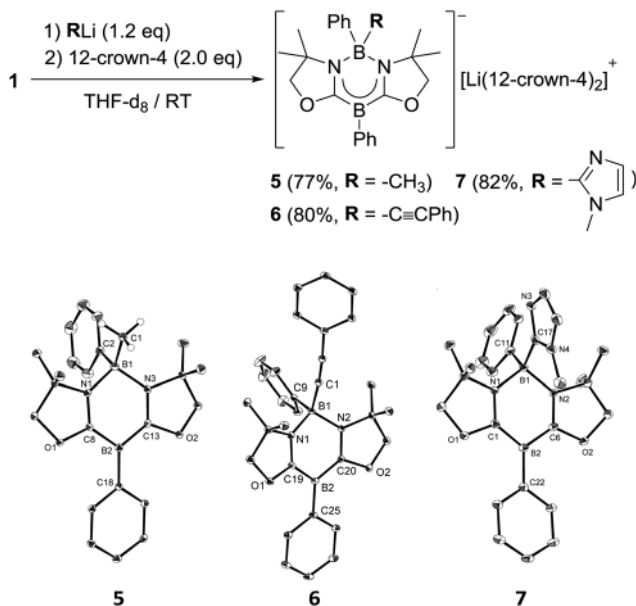


Scheme 1 Synthesis of **2/2'**.



Scheme 2 Reactions of **2** with MeI or Cy₃PAuCl, and the solid-state structures of **3** and **4**.

To examine the scope of nucleophiles, we further explored the addition reactions of **1** by employing sp³ and sp hybridized carbanions (Scheme 3). The addition of methyl lithium (MeLi)



Scheme 3 Synthesis and the solid-state structures of **5–7** (all hydrogen atoms except for those on C1 in **5** and counterions are omitted for clarity).

to a tetrahydrofuran solution of **1** led to a red solution. Subsequent addition of two equivalents of 12-crown-4 ether afforded **5** as red crystals in 77% yield. Using the same synthetic procedure with (phenylethynyl)lithium (PhCCLi), **6** was isolated in 80% yield. Note that this result is in stark contrast to the previously reported [4+2] cycloaddition reaction between **1** and alkyne.¹³ Moreover, the nucleophile is not limited to the hydrocarbon-based substrate. Thus, 2-lithio-1-methylimidazole was also readily reacted with **1**, and the corresponding adduct **7** was obtained in 82% yield. Meanwhile, MeMgI, Me₂NLi, NaN₃, CsF, ^tBuLi, and ^tBuONa did not react with **1** under ambient conditions, probably due to the weak nucleophilicity and/or steric factor.

In summary, we have demonstrated that the addition of nucleophiles to aromatic diazadiborinine **1** affords isolable ionic species corresponding to a Janovsky-type complex. A series of nucleophiles based on sp, sp², and sp³-carbanions (PhLi, MeLi, PhC≡CLi, and 2-lithio-1-methylimidazole) are compatible with the addition reaction to furnish the respective adducts **2** and **5–7**. Compound **2** was allowed to react with MeI and Cy₃PAuCl to afford **3** and **4**, respectively. Thus, the π-system over the B₂C₂N₂ six-membered ring in **1** is activated by the sole nucleophilic addition of an anionic group, providing a range of well-defined and isolable boryl anions that appear to undergo nucleophilic reactions. Subsequent reactions present a regioselective nucleophilic dearomatization (D_NAr) reaction⁶ through stepwise functionalization of the two boron atoms of **1**.

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Conflicts of interest

There are no conflicts to declare.

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