

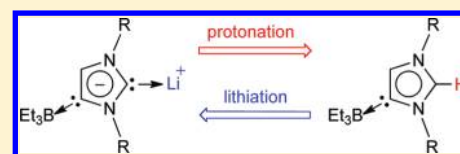
From Anionic N-Heterocyclic Dicarbenes to Abnormal Carbene–Borane Complexes: A Logical Synthetic Route

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S Supporting Information

ABSTRACT: The anionic N-heterocyclic dicarbenes (NHDCs) **I** are demonstrated to be a convenient platform from which abnormal NHC (*a*NHC)–borane complexes **V–VII** may be prepared. The anionic NHDC binuclear complex **II** and the *a*NHC mononuclear adduct **VII** can be interconverted through lithiation and protonation, respectively, of the C2 carbon atom of the imidazole ring.

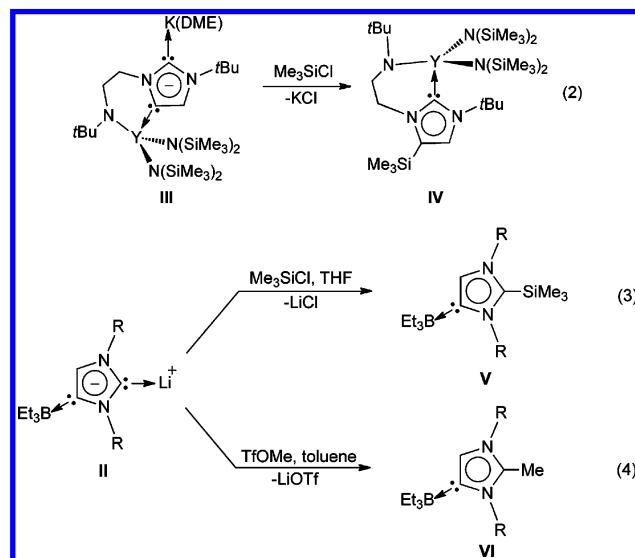
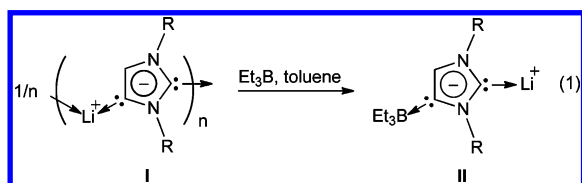


The considerable impact of carbenes on synthetic and catalytic chemistry is all the more impressive considering that the first crystalline N-heterocyclic carbene (NHC), 1,3-di-1-adamantylimidazol-2-ylidene, was reported merely two decades ago.¹ While their utility in transition-metal catalysis is well documented,² these ubiquitous ligands are attracting increasing attention in main-group chemistry.^{3–5} Indeed, recent reports detailing the role of NHCs in the stabilization of highly reactive main-group molecules^{6–11} are noteworthy.

Imidazole-based abnormal N-heterocyclic carbenes (*a*NHCs), moieties in which the carbene center resides at the C4 (or C5) position, have begun to play a role in the synthesis of transition-metal complexes.^{12–14} This is attributed to the fact that *a*NHCs possess stronger electron-donating capabilities than (normal) NHCs.¹⁵ Bertrand's significant isolation of a metal-free *a*NHC^{16–18} followed Crabtree's observation of transition-metal–*a*NHC complexes a decade earlier.¹⁹ Although synthetic and catalytic applications of transition-metal–*a*NHC complexes are increasing,^{12–14} the literature reveals a paucity of studies concerning main-group-element–*a*NHC complexes. While Carty synthesized *a*NHC-stabilized phosphinidenes²⁰ and Tamm prepared an *a*NHC–borane and *a*NHC–P₄–borane complexes,^{21,22} it would be desirable to prepare and study a variety of *a*NHC–main-group complexes. To this end, the development of facile synthetic routes in this area is necessary.

This laboratory recently reported that lithiation of NHCs afforded the first examples of anionic N-heterocyclic dicarbenes (NHDC; **I**, R = 2,6-Prⁱ₂C₆H₃).²³ Corresponding NHDC–borane binuclear complexes were subsequently prepared (eq 1).²⁴

Herein, we report that **I** may also be conveniently utilized to prepare various *a*NHC–borane complexes (**V–VII**)²⁵ through simple transformations of the (normal) carbene center (C2) of



II that was synthesized by combining **I** with BEt₃ (eq 1): silylation for **V**, alkylation for **VI**, and protonation for **VII**.²³ Moreover, **VII** may readily be converted back to the starting material, **II**, via lithiation. This interconversion between **II** and **VII** is particularly interesting, since it provides new synthetic routes for both anionic NHDC binuclear complexes and *a*NHC mononuclear adducts.

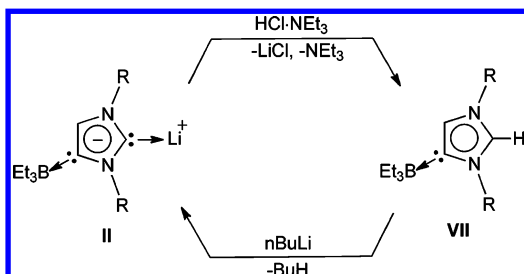
In notable contrast to the reaction of the C4-bound yttrium(III)–anionic NHDC adduct (**III**) with Me₃SiCl, which resulted in the “normal” NHC–Y(III) complex **IV** (eq 2),²⁶ reaction of **II** with Me₃SiCl in THF affords the C2-silylated *a*NHC–BEt₃ adduct **V** in high yield (93.0%) (eq 3). In addition, reaction of **II** with highly electrophilic TfOMe (1:1) in toluene gives the C2-methylated *a*NHC–BEt₃ complex **VI** (89.8% yield) (eq 4). However, reaction of **II** with excess TfOMe (**II**:TfOMe = 1:5) yields a mixture of **VI** and the corresponding *a*NHC–boron monotriflate adduct (Figure S1, Supporting Information).²⁵

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The $\alpha\text{NHC-BEt}_3$ adduct (**VII**) was prepared by protonation of the C2 carbon of **II** using HCl-NEt_3 (81.6% yield) (Scheme 1)

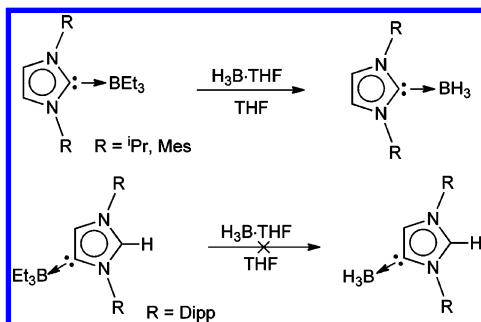
Scheme 1. Conversion between the Anionic NHDC-Borane **II and $\alpha\text{NHC-Borane Adduct VII}$**



or imidazolium chloride ($\text{NHC-H}^+\text{Cl}^-$, where $\text{NHC} = :\text{C}[\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)\text{CH}]_2$) as the protonation reagents.

Unlike the normal carbene-borane complexes NHC-BEt_3 ($\text{NHC} = :\text{C}[\text{N}(\text{Mes})\text{CH}]_2$, $:\text{C}[\text{N}(\text{tPr})\text{CH}]_2$), which undergo a BH_3 -substitution reaction to afford NHC-BH_3 adducts,²⁷ $\alpha\text{NHC-BEt}_3$ does not exhibit this reactivity (Scheme 2).

Scheme 2. Reactivity Comparison between NHC-Borane and $\alpha\text{NHC-Borane Adducts}$



This may be attributed to the donating ability of the C4 carbon being stronger than that of the C2 carbon of the imidazole ring,^{28,29} which is also consistent with the reported irreversible formation of a $\alpha\text{NHC-B}(\text{C}_6\text{F}_5)_3$ adduct.²¹ When it is combined with $n\text{BuLi}$ in hexane, **VII** is quantitatively converted back to **II** (Scheme 1). This **VII**-to-**II** synthetic strategy may be extended to prepare imidazole-based transition-metal binuclear complexes that may play an important role in the development of new catalysts and materials.³⁰

Single-crystal X-ray structural analyses²⁵ (Figure 1) show that in compounds **V-VII**, while C(1) is functionalized by trimethylsilyl, methyl, and proton, respectively, the abnormal carbene center (C(3)) binds to a triethylborane unit, achieving a tetrahedral geometry around the boron center. The B-C_{NHC} bond distances (1.657–1.661 Å) in **V-VII** are similar to that (1.656(3) Å)²³ in **II** and those (1.678(6)–1.683(5) Å) of NHC-BEt_3 adducts.²⁷ A ^{11}B NMR singlet resonance was observed at –14.4 ppm for **V**, –15.0 ppm for **VI**, and –15.2 ppm for **VII**, comparing well with the BEt_3 resonance (–15.6 ppm)²³ of **II** and those (–12.6 and –13.3 ppm) of C2-bound BEt_3 carbene complexes.²⁷

A logical preparative route to $\alpha\text{NHC-borane}$ complexes **V-VII** has been developed, which involves convenient functionalization of the “normal” carbene center (C2) of a C4-bound anionic NHDC-BEt_3 adduct (**II**). Moreover, $\alpha\text{NHC-BEt}_3$ adduct

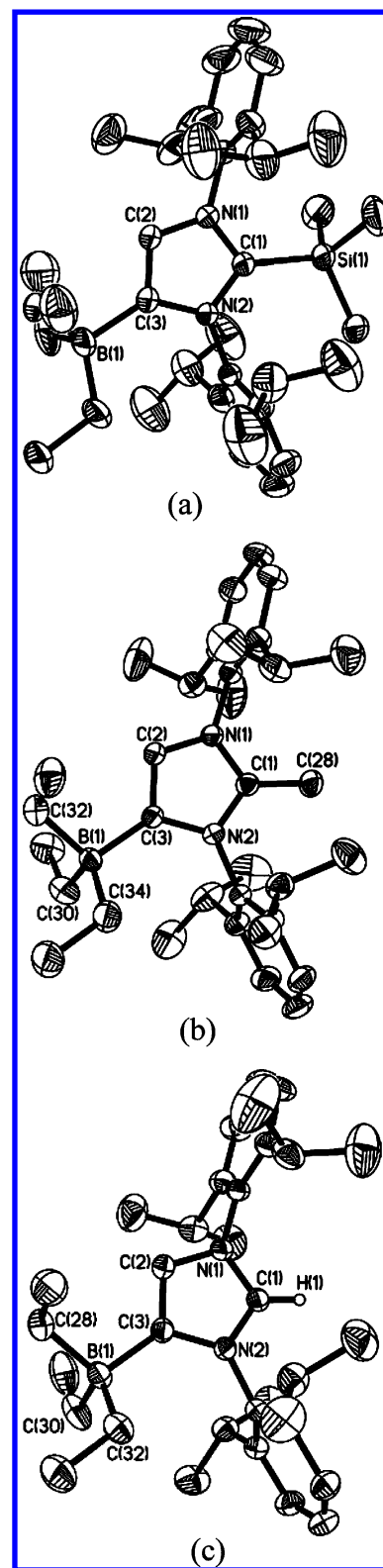


Figure 1. Molecular structures of (a) **V**, (b) **VI**, and (c) **VII**. Thermal ellipsoids represent 30% probability; hydrogen atoms on carbon are omitted for clarity, except for that at C(1) of **VII**. Selected bond distances (Å) and angles (deg): for **V**, $\text{B(1)-C(3)} = 1.661(5)$, $\text{C(1)-Si(1)} = 1.926(2)$, $\text{N(1)-C(1)-Si(1)} = 124.82(18)$, $\text{N(2)-C(1)-Si(1)} = 131.07(18)$, $\text{C(2)-C(3)-B(1)} = 125.3(2)$, $\text{N(2)-C(3)-B(1)} = 131.8(3)$; for **VI**, $\text{B(1)-C(3)} = 1.657(3)$, $\text{C(1)-C(28)} = 1.483(3)$, $\text{N(1)-C(1)-C(28)} = 125.09(19)$, $\text{N(2)-C(1)-C(28)} = 127.89(19)$, $\text{C(2)-C(3)-B(1)} = 126.51(19)$, $\text{N(2)-C(3)-B(1)} = 131.33(18)$; for **VII**, $\text{B(1)-C(3)} = 1.658(3)$, $\text{C(2)-C(3)-B(1)} = 128.1(2)$, $\text{N(2)-C(3)-B(1)} = 129.67(19)$.

(VII) may be quantitatively converted back to II through a simple lithiation.

■ ASSOCIATED CONTENT

■ Supporting Information

Text, figures, and CIF files giving full details of the syntheses and X-ray crystal determination. 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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