COMMUNICATION

Synthesis and molecular structure of an abnormal carbene–gallium chloride complex†

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Low temperature reaction of N-heterocyclic carbene : BEt$_3$ with *n*BuLi (in THF) initially gives the C4-lithiated N-heterocyclic carbene : BEt$_3$ complex (4), which isomerizes to the C2-lithiated abnormal N-heterocyclic carbene : BEt$_3$ complex (2) in refluxing THF. While reaction of 2 with GaCl$_3$ gives a 4-functionalized N-heterocyclic carbene : GaCl$_3$ adduct (6), reaction of 4 with GaCl$_3$ affords the first abnormal carbene–gallium chloride complexes (5).

The chemistry of N-heterocyclic carbenes has developed at a remarkable pace considering that the first such complex was reported little more than two decades ago.[1] As strong neutral σ-donor ligands, N-heterocyclic carbenes possess potent co-ordinating capabilities, particularly to transition metals, and have thus been extensively utilized in associated catalytic systems.[2] Indeed, N-heterocyclic carbenes are quite versatile and have also shown potential as excellent organic catalysts.[2] A particularly interesting aspect of these molecules is their recently realized capabilities in low-oxidation-state main group chemistry.[3–10]

"Normal" N-heterocyclic carbenes ligands contain the iconic C2–carbene centre (Fig. 1, **I**). As the C4 bound carbene isomers of **I**, "abnormal" N-heterocyclic carbenes (Fig. 1, **II**) are both kinetically and energetically less stable than **I**. Bertrand[11] recently reported the first metal-free abnormal N-heterocyclic carbene while Crabtree reported an abnormal N-heterocyclic carbene-transition metal complex some years earlier.[12]

A number of abnormal N-heterocyclic carbene complexes have subsequently been reported with some finding important roles in synthetic and catalytic applications.[13–15] In contrast, the literature reveals a paucity of studies concerning the chemistry of abnormal N-heterocyclic carbene-main group element complexes. The first abnormal N-heterocyclic carbene-main
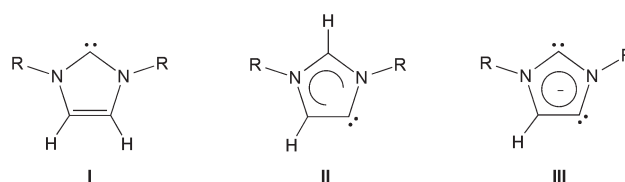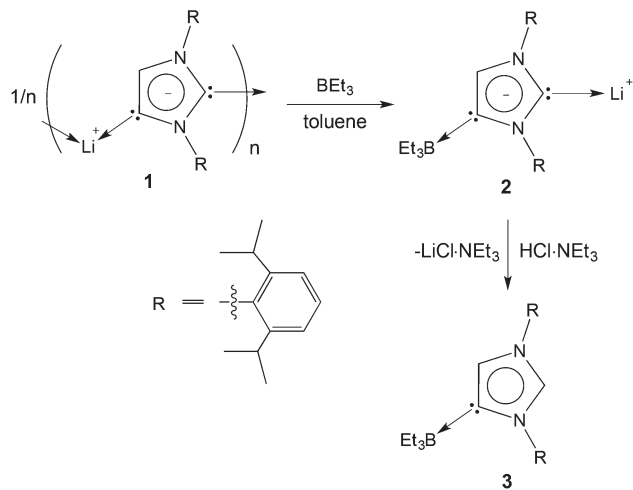
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Fig. 1 Various N-heterocyclic carbenes.

group element adduct—a stabilized μ-phosphinidene complex —was reported in 2006.[16] Steric congestion was proposed as a driving force for the formation of this complex, which is consistent with the (thermal) rearrangement of C2-bound N-heterocyclic carbene complexes into C4-bound isomers observed in subsequently reported trimethylaluminum[17] and borane complexes.[18–20] Abnormal N-heterocyclic carbene-based Zn(II), Al(III), Sn(II), Ge(II), and Si(IV) complexes have also been reported.[21–23] Indeed, the Zn(II) and Al(III) complexes have shown the ability to catalyse the ring-opening polymerization of cyclic esters.[23]
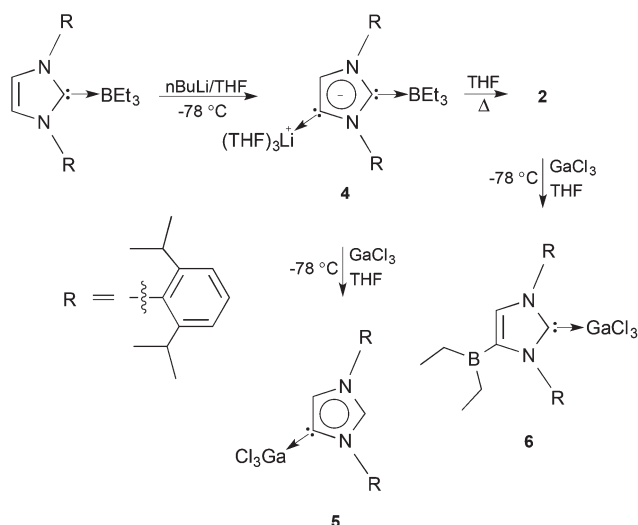
In contrast to **I** and **II**, the anionic N-heterocyclic dicarbene (NHDC) (Fig. 1, **III**) bears carbene centres at both the C2 and C4 positions. The first such N-heterocyclic dicarbene ligand (1) was prepared *via* lithiation of a N-heterocyclic carbene resulting in a polymeric chain structure [:C{[N(2,6-Pr$^i_2$C$_6$H$_3$)]$_2$-CHCLi}]$_n$.[24,25] Although each lithium cation in **1** is associated with both C2 and C4 carbene sites from two N-heterocyclic dicarbene fragments, only the C2-lithiated **2** was isolated when **1** was allowed to react with BEt$_3$ in toluene (Scheme 1).[24] The subsequent protonation of the C2 carbon of **2** resulted in the abnormal N-heterocyclic carbene complex **3**.[26] Additional abnormal N-heterocyclic carbene–boron and zinc complexes have been isolated using the synthetic route illustrated in Scheme 1.[26,27] Among a small group of N-heterocyclic carbene–gallium(III) chlorides,[28–33] normal carbene-complexed gallium(III) dichloride cations have been utilized as π-acid catalysts.[32,33] Herein, we report the synthesis[34] and molecular structure[34] of the first abnormal carbene : gallium chloride complex, **5**.

Scheme 1 NHDC-based synthesis of **3**.

Scheme 2 NHDC-based synthesis of **5** and **6**.

Although the reaction of **1** with BEt_3 gives **2** via selective cleavage of Li–C4 bonds,[24] the C4-lithiated N-heterocyclic carbene : BEt_3 isomer (**4**) indeed can be obtained (in 98% yield) by reaction of N-heterocyclic carbene : BEt_3 with nBuLi in THF at −78 °C (Scheme 2). The BH_3 analogue of this complex has been reported.[35] In refluxing THF the thermal isomerization of **4** into THF-solvated **2** is confirmed by ^{1}H NMR, ^{11}B NMR, and single crystal X-ray diffraction analysis. The fact that **2** is thermodynamically more stable than **4** may be attributed to the stronger steric contact between triethylborane and the two flanking 2,6-diisopropylphenyl substitutes. Both **2**·(THF)$_2$ and **4** have very similar ^{11}B NMR chemical shifts (−15.6 ppm for **2**·(THF)$_2$; −13.9 ppm for **4**). However, the imidazole ^{1}H NMR resonance of **4** shifts upfield to 6.08 ppm with compared to that (6.42 ppm) for **2**·(THF)$_2$. Compound **5** is prepared in 67% yield by combining **4** with $GaCl_3$ in a ratio

of 1 : 1. While the mechanism remains obscure, the formation of **5** may initiate from the nucleophilic attack of the C4 carbene center on gallium trichloride. The binding of gallium trichloride at C4 carbon could push the neighboring 2,6-diisopropylphenyl substitute towards C2 carbon. Such increased steric repulsion would subsequently have BEt_3 prone to leave, providing an open anionic carbene site (C2). Neutral **5** is finally achieved through solvent-mediated protonation of the C2 carbon. Indeed, the proton at the C2 carbon of **5** is observed as a singlet at 9.51 ppm in the ^{1}H NMR spectrum. In contrast to **4**, when combined with $GaCl_3$ under the same reaction conditions, isomer **2** is converted into **6**, a diethylborane-substituted (at C4) N-heterocyclic : $GaCl_3$ complex via eliminating an ethyllithium. Notably, functionalization of the C4 carbon atoms of the N-heterocyclic carbenes has attracted much attention of chemists[36–38] since the electronic properties of the carbene center are significantly affected by the substitute at the C4 carbon.

The molecular structure of **4** (Fig. 2a) reveals that the anionic N-heterocyclic dicarbene ligand bonds to the boron atom of a triethylboron fragment via the C2 carbene atom and to the THF-solvated lithium cation using the C4 carbene centre.[34] Both lithium and boron atoms are four-coordinate adopting distorted tetrahedral geometries. While the C–B bond distance in **4** (1.676(7) Å) compares well with that of **2**·(THF)$_2$ (1.656(3) Å), the Li–C bond (2.151(9) Å) in **4** is about 0.06 Å longer than that (2.096(4) Å) in **2**·(THF)$_2$.[24] These values compare well with documented Li–C_{NHC} bond distances (2.093 to 2.339 Å).[39–42]

Compound **5** (Fig. 2b) crystallizes in the orthorhombic space group $Pbca$.[34] The asymmetric unit cell contains one aNHC : $GaCl_3$ molecule, in which the four-coordinate gallium atom adopts a distorted tetrahedral geometry, and one THF solvent molecule. A moderate C–H⋯O hydrogen bond [distance (C⋯O) = 3.031 Å; C–H⋯O bond angle = 167°] may be proposed between the C(1)–H(1A) unit of **5** and the O atom of THF solvent molecule.[43] The Ga–C bond distance in **5** (1.978(3) Å) is only marginally shorter than that (2.016(2) Å) in its C2-bound N-heterocyclic carbene : $GaCl_3$ isomer.[29] The Ga–Cl bond distances [2.1480(11) to 2.1864(12) Å] is consistent with the typical Ga–Cl single bond distances.[29]

The X-ray structure of compound **6** (Fig. 2c) confirms that the boron atom at the C4 carbon is three-coordinate and adopts a trigonal planar geometry. The ^{11}B NMR resonance of the boron core in **6** is −14.8 ppm, which compares well to that in **2**·(THF)$_2$ (−15.6 ppm) and in **4** (−13.9 ppm). The B–C bond in **6** [1.576(5) Å] is somewhat shorter than those of **2**·(THF)$_2$ [1.656(3) Å] and **4** [1.676(7) Å]. The four-coordinate gallium atom binds to the C2 carbene center of **6**, possessing a similar distorted tetrahedral geometry. However, the Ga–C bond distance [2.035(4) Å] in **6** is about 0.06 Å longer than that in **5** [1.978(3) Å], which may be ascribed to the relatively stronger steric repulsion between the carbene ligand and the chlorine groups of $GaCl_3$ in **6**, and the stronger donating ability of the C4 carbene site in **5** with respect to that of the normal carbene ligand in **6**.
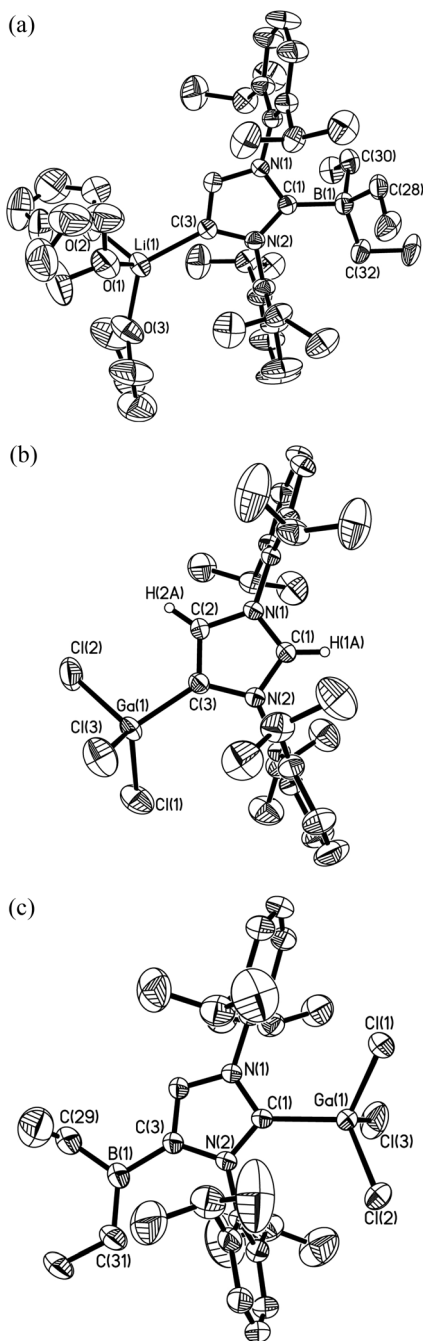
(a)

(b)

(c)

Fig. 2 Molecular structures of (a) **4**, (b) **5** and (c) **6**. Thermal ellipsoids represent 30% probability: hydrogen atoms on carbon are omitted for clarity, except for those at C(1) and C(2) of **5**. Selected bond distances (Å) and angles (°) are as follows. For **4**, B(1)−C(1) 1.676(7), Li(1)−C(3) 2.151(9), N(1)−C(1)−B(1) 127.1(4), N(2)−C(1)−B(1) 131.2(4), N(2)−C(3)−Li(1) 137.3(4), C(2)−C(3)−Li(1) 122.8(5). For **5**, C(3)−Ga(1) 1.978(3), Ga(1)−Cl(1) 2.1636(12)(9), Ga(1)−C(3)−N(2) 131.4(2), Ga(1)−C(3)−C(2) 124.3(2). For **6**, C(1)−Ga(1) 2.035(4), Ga(1)−Cl(1) 2.126(3), B(1)−C(3) 1.576(5), Ga(1)−C(1)−N(1) 125.0(2), B(1)−C(3)−N(2) 130.9(3).

Conclusions

We have prepared the C4-lithiated N-heterocyclic carbene : BEt$_3$ complex, **4**, by low-temperature lithiation of N-heterocyclic

carbene : BEt$_3$, which behaves as an effective nucleophile reacting with gallium(III) chloride, affording the first abnormal N-heterocyclic carbene : GaCl$_3$ complex, **5**. In contrast, under the same reaction conditions, **2**, the isomer of **4**, may be converted into a diethylborane-substituted (at C4) N-heterocyclic carbene : GaCl$_3$ adduct.

Acknowledgements

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