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

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Low temperature reaction of N-heterocyclic carbene : BEt3 with nBuLi (in THF) initially gives the C4-lithiated N-heterocyclic carbene : BEt3 complex (4), which isomerizes to the C2-lithiated abnormal N-heterocyclic carbene : BEt3 complex (2) in refluxing THF. While reaction of 2 with GaCl3 gives a 4-functionalized N-heterocyclic carbene : GaCl3 adduct (6), reaction of 4 with GaCl3 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 coordinating 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 carbene 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. Bertrand11 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 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 trimethylaluminum17 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 \( [\text{C}][\text{N}(2,6-	ext{Pr}^1\text{C}_6\text{H}_{13})]_{\text{III}}\text{CHClLi}]_{\text{III}} \).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 BEt3 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 and molecular structure of the first abnormal carbene–gallium chloride complex, 5.

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Footnote:
†Electronic supplementary information (ESI) available: Synthetic details and structural and spectral characterization, CCDC 990084, 990085 and 1003828. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00933a
Although the reaction of 1 with BEt₃ gives 2 via selective cleavage of Li-C₄ bonds,²⁴ the C₄-lithiated N-heterocyclic carbene : BEt₃ isomer (4) indeed can be obtained (in 98% yield) by reaction of N-heterocyclic carbene : BEt₃ with nBuLi in THF at -78 °C (Scheme 2). The BH₃ analogue of this complex has been reported.²⁵ In refluxing THF the thermal isomerization of 4 into THF-solvated 2 is confirmed by ¹H NMR, ¹¹B 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 substituents. Both 2-{THF}₂ and 4 have very similar ¹¹B NMR chemical shifts (-15.6 ppm for 2-{THF}₂; -13.9 ppm for 4). However, the imidazole ¹H NMR resonance of 4 shifts upward 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 GaCl₃ 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 BEt₃ 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 ¹H NMR spectrum. In contrast to 4, when combined with GaCl₃ under the same reaction conditions, isomer 2 is converted into 6, a diethylborane-substituted (at C₄) N-heterocyclic : GaCl₃ complex via eliminating an ethyllithium. Notably, functionalization of the C₄ carbon atoms of the N-heterocyclic carbenes has attracted much attention of chemists 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–C₄N₃C 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 : GaCl₃ 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) ⋅⋅⋅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.³³ 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 : GaCl₃ 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 ¹¹B 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 [2.033(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 GaCl₃ 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.
Conclusions

We have prepared the C4-lithiated N-heterocyclic carbene : BEt₃ complex, 4, by low-temperature lithiation of N-heterocyclic carbene : BEt₃, which behaves as an effective nucleophile reacting with gallium(II) chloride, affording the first abnormal N-heterocyclic carbene : GaCl₃ 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 : GaCl₃ adduct.

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Notes and references

34 See the ESI† for synthetic and crystallographic details.