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Note

Synthesis and structure of a boron cation supported by a β-diketiminate ligand

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Abstract

The salt [HC(CMe)$_2$(NAr)$_2$BPh][Al$_2$Cl$_7$] (**3**); Ar = 2,6-i-Pr$_2$C$_6$H$_3$) has been synthesized via the in situ preparation of [HC(CMe)$_2$(NAr)$_2$BClPh], followed by treatment with AlCl$_3$. X-ray analysis of **3** reveals that the BN$_2$C$_3$ ring of the boron cation is planar and DFT calculations indicate π-type interactions in the HOMO-6 and HOMO-7 orbitals.
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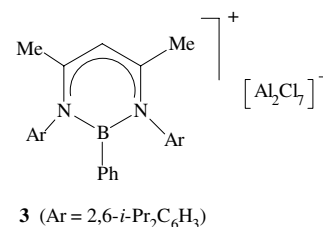*Keywords:* Boron; Cation; β-Diketiminate; X-ray; DFT calculation

1. Introduction

β-Diketiminate ligands are proving to be very effective for the support of a wide variety of elements in diverse coordination modes and oxidation states (for a review, see [1]). For example, in the context of group 13 chemistry, this type of ligand has been employed for the stabilization of novel aluminum(1) [2] and gallium(I) [3] derivatives. As an extension of our structural work on pentamethylcyclopentadienyl-substituted boron cations [4], we were prompted to investigate the molecular and electronic structure of a boron cation supported by a β-diketiminate ligand. A survey of the literature reveals that although β-diketiminate-substituted boron cations have been reported previously (**1** [5] and **2** [6]) no X-ray crystallographic data are available for cations of this type. In the case of **1**, NMR data suggested that the anion and cation are weakly associated in solution [5]. We report the first X-ray crystal structure for a β-diketiminate supported boron cation along with DFT calculations.

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1 (Ar = p-tolyl)

2 (X = F; Y = BF$_4^-$; X = Cl, C$_2$H$_5$, C$_6$H$_5$, Y = AlCl$_4^-$)

2. Results and discussion

Compound **3** was prepared by the metathetical reaction of [HC(CMe)$_2$(NAr)$_2$]K (Ar = 2,6,-i-Pr$_2$C$_6$H$_3$) with PhBCl$_2$, followed by treatment with AlCl$_3$.

3 (Ar = 2,6-i-Pr$_2$C$_6$H$_3$)

The X-ray crystal structure confirms that **3** is the $[Al_2Cl_7]^-$ salt of the target boron cation (**3**$^+$) and reveals that there are no close anion–cation contacts (Fig. 1). The B–N(1)–C(2)–C(3)–C(4)–N(2) ring is planar (sum of bond angles = 716.8°) and each atom of the six-membered ring adopts a trigonal planar geometry within experimental error. The C–C and C–N bond distances in **3**$^+$, which average 1.381(5) and 1.356(5) Å, respectively, are similar to those reported [5] for the neutral β-diketiminate complex, $[HC(CMe)_2(NAr)_2BF_2]$ (**4**, Ar = *p*-tolyl) which average 1.392(3) and 1.350(5) Å, respectively. As expected, the major structural differences between **3**$^+$ and **4** are evident at the boron center. Thus, the geometry at boron in **4** is tetrahedral, while that in **3**$^+$ is trigonal planar (sum of angles = 359.9(3)°). Moreover, the average B–N bond distance in **3**$^+$ (1.449(5) Å) is appreciably shorter than that in **4** (1.551(3) Å) but identical to that in the neutral BN_2C_3 ring compound $[\eta^2\text{-}CH_2=C(N\text{-}tolyl)CH=C(N\text{-}tolyl)Me]BCH_2SiMe_3$ (av. 1.441(3) Å) [5], thus highlighting further the effect of boron geometry change on B–N bond distances. In the two-coordinate boron cation $[(t\text{-}Bu_3PN)_2B]^+$, the B–N bond distance is 1.258(5) Å [7]. The relative shortness of this bond was attributed inter alia to multiple bond character.

Since all the ring atoms are trigonal planar and six π-electrons are available for the C_3N_2B ring, the question of the extent of π-delocalization is pertinent. To gain insight into this question, DFT calculations were carried out on **3**$^+$ at the B3LYP level of theory using the 3-21G* basis set [8]. The adequacy of the model was apparent from the fact that the maximum differences in bond lengths and bond angles between the optimized and experimental structures of **3**$^+$ are 0.03 Å and 1.27°,
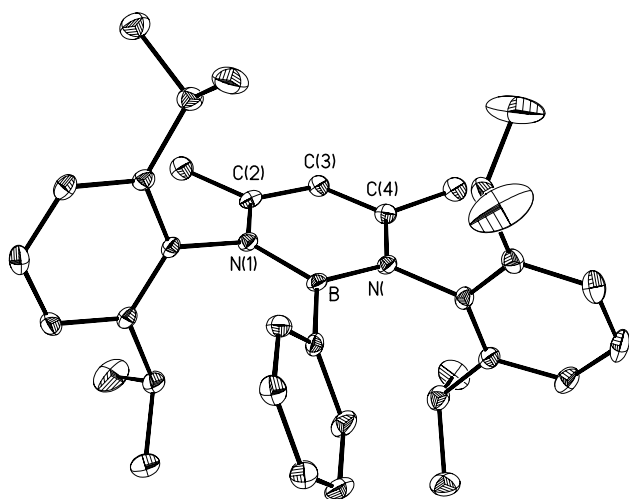

Fig. 2. (a) HOMO-6 and (b) HOMO-7 orbitals for boron cation **3**$^+$.

respectively. The HOMO is largely phenyl ring-π in nature, while the LUMO evidences considerable N–C π* character in the BN_2C_3 ring; the HOMO-LUMO gap is 92.40 kcal/mol. The BN_2C_3 ring π-bonding character is found in the HOMO-6 and HOMO-7 orbitals. As shown in Fig. 2(a), the HOMO-7 orbital comprises two π-allylic N–B–N and C–C–C fragments, while the HOMO-9 features two N–C π-bonds (Fig. 2(b)).

3. Experimental

All reactions were performed under a dry, oxygen-free atmosphere utilizing Schlenk manifold techniques or a drybox. All solvents were dried and distilled under nitrogen prior to use. NMR spectra were recorded on a General Electric QE 300 spectrometer at 295 K (^{1}H 300.16 MHz; ^{11}B 96.28 MHz) and chemical shifts are reported

Fig. 1. View of boron cation **3**$^+$ showing the atom numbering scheme. Important bond distances (Å) and bond angles (°): B–N(1) 1.449(5), N(1)–C(2) 1.354(4), C(2)–C(3) 1.383(5), C(3)–C(4) 1.380(5), N(2)–C(4) 1.358(5), B–N(2) 1.450(5), N(1)–B–N(2) 114.6(3), B–N(1)–C(2) 122.4(3), N(1)–C(2)–C(3) 118.7(3), C(2)–C(3)–C(4) 122.5(4), C(3)–C(4)–N(2) 119.1(3), C(4)–N(2)–B 121.8(3).
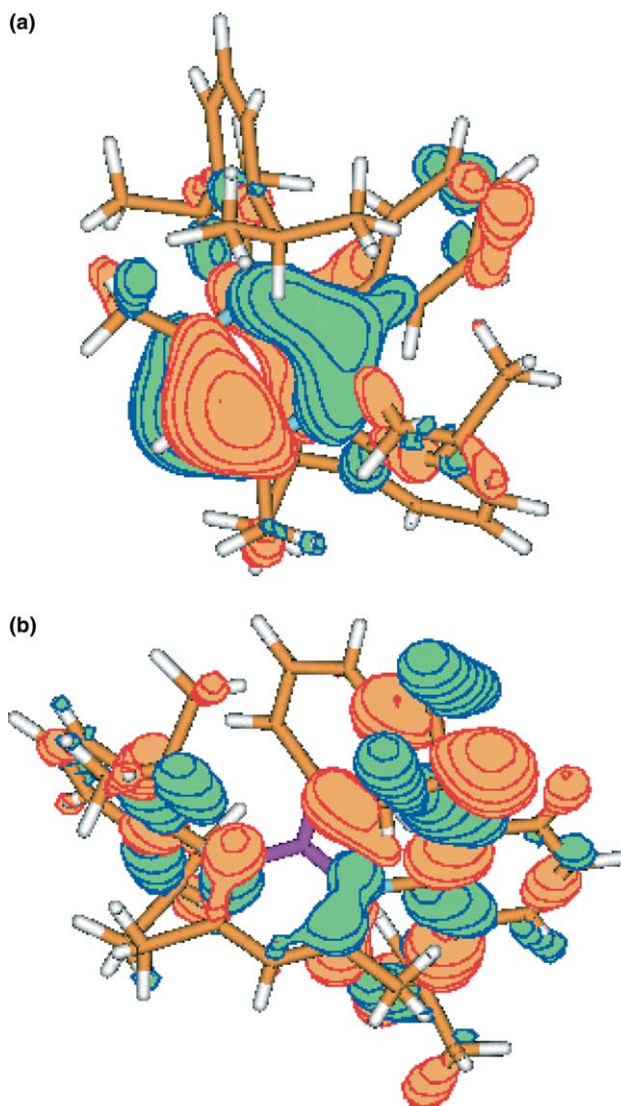
relative to SiMe$_4$ ($\delta = 0.00$). High resolution mass spectra were obtained using a VG Analytical ZABZ-E mass spectrometer operating in the chemical ionization mode with methane as the ionizing gas. Melting points were obtained in capillaries sealed under argon.

3.1. Preparation of [HC(CMe)$_2$(NAr)$_2$BPh][Al$_2$Cl$_7$] (3)

A solution of HC(CMe)$_2$(NAr)(NHAr) (1 g, 2.38 mmol) in 20 ml of Et$_2$O was added to a rapidly stirred suspension of KH (0.11 g, 2.62 mmol) in Et$_2$O at 25 °C. Neat PhBCl$_2$ (0.29 ml) was added to the [HC(CMe)$_2$(NAr)$_2$]K solution and the reaction mixture was stirred rapidly for 2 h at 25 °C. Following solvent removal under reduced pressure, the resulting residue was extracted with 30 ml of toluene. After filtration, the filtrate was transferred via cannula on to 0.30 g (2.24 mmol) of AlCl$_3$ and the reaction mixture was stirred for 3 h at 25 C. Filtration, concentration and cooling of the filtrate to -40 °C afforded a crop of pale yellow crystals of **3**, 0.41 g, 23.3% yield, m.p. 212 °C (decomp). HRMS (CI$^+$, CH$_4$) Anal. Calc. for C$_{35}$H$_{46}$BN$_2$, 505.3754; Found 505.3760. ^{1}H NMR (300.00 MHz, 295 K, CDCl$_3$): δ 0.78 (d, 12H, $J = 6.6$ Hz, CH(CH$_3$)$_2$), 1.06 (d, 12H, $J = 6.6$ Hz, CH(CH$_3$)$_2$), 2.16 (s, 6H, CH$_3$), 2.50 (septet, 4H, $J = 6.6$ Hz, C H(CH$_3$)$_2$), 6.33–7.42 (m, 12H, γ-CH + ArCH). ^{13}C NMR (75.48 MHz, 295 K, CD$_2$Cl$_2$): δ 172.5 (CN), 143.3, 135.7, 134.3, 131.3, 130.7, 127.4, 126.0 (Ph ring C), 115.1 (γ-C), 29.5 (CHMe), 24.9 (CHMe$_2$), 23.7 (CHMe$_2$), 23.4 (Me). ^{11}B NMR (96.28 MHz, 295 K, CDCl$_3$): $\delta + 72$ (s, br).

3.1.1. Crystal data

C$_{35}$H$_{46}$Al$_2$BCl$_7$N$_2$, $M = 807.66$, triclinic, space group $P\bar{1}$, $a = 10.371(5)$, $b = 12.220(5)$, $c = 17.297(5)$ Å, $\alpha = 97.258(5)$, $\beta = 102.094(5)$, $\gamma = 101.856(5)°$, $V = 2{,}064.6(14)$ Å^3, $D_{calc} = 1.299$ g cm^{-3}, $Z = 2$, λ(Mo K$\alpha = 0.71073$ Å, μ(Mo Kα) $= 0.550$ mm^{-1}. A total of 9325 independent reflections was collected on a Nonius Kappa diffractometer at 153(2) K with 2θ between 6.48 and 55.14°. The structure was solved by direct methods and refined by full-matrix least squares on F^2 to R_1 and wR_2 values of 0.1009 and 0.1618, respectively. There is slight disorder in the [Al$_2$Cl$_7$]$^-$ anion.

4. Supplementary material

X-ray crystallographic data for **3** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 232651. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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