The Elusive Three-Coordinate Dicationic Hydrido Boron Complex

Wen-Ching Chen,† Ching-Yu Lee,‡ Bo-Chao Lin,† Yu-Chen Hsu,† Jiun-Shian Shen,‡ Chao-Ping Hsu,*† Glenn P. A. Yap,† and Tiow-Gan Ong*†,‡

†Institute of Chemistry, Academia Sinica, Nangang, Taipei, Taiwan, Republic of China
‡Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, Republic of China
§The Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, Republic of China
*Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States

Supporting Information

ABSTRACT: The formation of a hitherto unknown three-coordinate dicationic hydrido boron complex is described. Interestingly, supporting ligand carbodicarbene gave unprecedented reaction with BH₃ without using more highly electrophilic Lewis acid precursors. Spectroscopic, crystallographic, and computational analysis was performed to understand the electronic features of these species.

The search for unique bonding environments of boron species featuring elusive electronic configurations has been a central theme in molecular main group chemistry.¹ To date, three classes of monocationic boron(II) adducts have been isolated and identified as boronium [R₂BL₂]⁺, borenium [R₂BL]⁺, and borinium [R₂B]⁺ ions.² Such fundamental investigations on cationic boron species have led to an accumulation of knowledge for a broad range of potential applications including polymerization,³ hydroboration of alkenes,⁴ and dehydrogenation of ammonia-borane.⁵ In stark contrast to monocationic boron, persistent dicationic boron is less common and poorly defined. The groups of Cowley (I), Himmel (II), and Braunschweig (III) have contributed pioneering work for boron dication chemistry (Scheme 1, top row).⁶⁻⁷ However, since then relatively few dicationic hydrido boron complexes (IV–VI) have been reported.⁸⁻¹² The majority of these dicationic derivatives are isolated and characterized as either four-coordinate or bridging adducts at boron.

Stable singlet carbenes featuring strong electron-pair donation such as N-heterocyclic carbenes (NHCs)⁷³ and cyclic(alkyl)- (amino)carbenes (CAACs)⁸ have been successfully utilized to stabilize highly reactive boron species like boryl radicals⁹ and borenium cations,¹⁰ boryl anions,¹¹ boronanes,¹² diborene,¹³ and diboryne.¹⁴ Yet, to date a dicationic species of three-coordinate hydrido boron, [L₂B–H]⁺⁺ still remains elusive. Recent work by Alcarazo utilized a more unconventional strong σ-donating ligand framework (carbodiphosphoranes) containing two electron lone pairs to support highly reactive dihydrido-borenium cation species.¹⁰b Similarly, another subgroup of potential ligand candidates, so-called carbodicarbenes,¹⁵ or bent allenes are rarely explored in supporting main group elements.¹⁶ Owing to its two dative electron pairs residing on the carbon atom and unique structural morphology, and with the hopes of challenging conceptual limitations and uncovering novel reactivity, we sought to extend the utilities of this ligand scaffold to the realm of boron compounds. Herein, we report a serendipitous discovery of the parent three-coordinate dicationic boron hydride via carbodicarbone routes. The synthesis, isolation, characterization, and computational analysis of these species are discussed.

Previously, we have successfully prepared carbodicarbone 1 with sterically encumbered isopropyl side arms as illustrated in Scheme 2.¹⁷ With the carbodicarbone in hand, we attempted to investigate the coordination chemistry of 1 toward group 13 elements. Addition of carbodicarbone 1 to a slightly excess of BH₃-THF (2 equiv) in THF solution afforded compound 3a as a yellow solid in moderate yield (Scheme 2). In marked contrast to most borane–NHC complexes,¹⁸ 3a is found to be sparingly soluble in most organic solvents with the exception of dichloromethane, indicating a possible formation of ionic species but negating the existence of product borane 2. The ¹H NMR spectrum of 3a is notably different from its starting material 1 with two distinct septet environments at 5.48 and 4.25 ppm assigned as isopropyl methine protons. In addition, two high-field peaks at 0.06/−0.55 ppm of equal intensity which integrate for 8 protons and display characteristic coupling of ¹¹B and ¹⁰B are assigned as BH₄⁻ anion.

Scheme 1. Various Boron Dications I–VI

Received: December 4, 2013
Published: January 2, 2014
Crystals of 3a suitable for single-crystal X-ray diffraction analysis were obtained by cooling a saturated solution in dichloromethane and ether at −15 °C (Figure 1). To our astonishment, the solid-state structure revealed the parent molecule of 3a to contain a dicaticonic boron complex and BH₄⁻ anions cocry stallized with two dichloromethane molecules; this is markedly different than the coordination environment observed for NHC-BH₄⁻. Compound 3a features a trigonal planar boron environment with C35−B1−C12 bond angle of 127.5(3)° coordinated via two carbodicarbene 1 and a hydride ligand. The carbodicarbene carbons C12 and C35, boron, and hydrogen H1 are in a perfectly planar arrangement around the B atom (sum of angles = 359.8°). Boron−carbodicarbene bond distances in 3a are 1.534 (7) and 1.523 (7) Å, which are shorter than C−B single bonds known for other borenium cations supported by NHC (1.58 Å).¹⁰ The C−B bond distances of borenium cation ligated by carbodiphosphoranes (1.5030 Å)¹⁰b and borylene (H−B) (1.517 Å)¹²c stabilized by cyclic (alkyl)(amino)carbene are shorter than 3a.

In addition to single crystal X-ray analysis, ¹¹B NMR and IR spectroscopic analysis was also conducted. The decoupled ¹¹B NMR of dicaticionic 3 displayed two signals at δ ~38.6 and ~25.4 ppm. The former boron resonance is identified as BH₄⁻, while the latter slightly downfield shifted signal is assigned to a cationic borane species. Examination of the solid-state IR spectra of 3a shows four strong IR absorptions bands at 2395.6, 2282.9, 2217.3, and 2148.3 cm⁻¹ in the spectral region ascribed to B−H stretching. However, the B−H stretching mode of a cationic B−H cannot be discerned clearly from that of BH₄⁻ in order to resolve this ambiguity, replacement of BH₄⁻ with other anionic components was attempted. To our delight, dicaticionic boron 3b bearing iodide anions could be obtained through the reaction of 3a with methyl iodide in quantitative yield, which is verified by single crystal X-ray diffraction (see Figure S2). The structural features of 3b are no different from 3a, thus it warrants no further discussion. The IR of 3b was performed, and a weak absorption at 2452 cm⁻¹ assigned to the B−H stretching mode confirmed the presence of the hydrogen atom at boron. To the best of our knowledge, compound 3 represents the first isolated three-coordinate dicaticionic hydrido boron species. More intriguingly, the formation of 3 based on the carbodicarbene scaffold gave unprecedented reaction with BH₄⁻ without using a more highly electrophilic Lewis acid. This reaction behavior has not been observed for other common NHC ligands supporting borane, where typical reactivity would lead to the formation of a bridging hydride species in order to compensate for the inherent electron deficiency in the boron atom.⁶e

Motivated by the unique structural features manifested in 3, we wanted to explore another neutral electropositive group 13 element like Al for comparative purposes.⁶ Carbodicarbene 1 was allowed to react with AlCl₃ in THF at ambient temperature to furnish 4 in high yield (79%). Crystals of 4 suitable for single crystal X-ray diffraction analysis were obtained by slow cooling of saturated solution of 4 in toluene at −15 °C, the resulting solid-state structure is presented in Figure 2. Complex 4 is the first isolated Al complex supported by the carbodicarbene ligand framework. The structure consists of a distorted tetrahedral Al center with an Al-carbodicarbene bond length of 1.976(3) Å, which is slightly shorter than those typically reported for Al-NHC’s.³⁰ Careful examination of the structural parameters of 4, reveals an increase in bond length within the C−C−C allenic moiety (1.453(3) and 1.374(4) Å) with respect to the free carbodicarbene 1 (1.335 Å).¹⁰d,e This is attributed to donation of electron density from the carbodicarbene to the electron poor AlCl₃ moiety. This would in turn significantly shorten the bond lengths of N(3)−C(13)−N(4) (1.359(3) and 1.344(3) Å) in only one of the benzimidazolium groups within the ligand framework (Scheme 3 (left)). Compared to 4, the bond lengthening and electron depletion within allenic moieties of 3a (~1.43 Å) is even more pronounced than its aluminum
anallogues, indicating the highly positive nature of boron species 3a.

In an effort to further understand the electronic nature of 3 and 4, computational calculations at the B3LYP/6-31G* level were undertaken. Based on natural population analysis (Figure 3, top left)\(^2\)\(^1\)\(^2\)\(^1\)\(^2\)\(^3\) the boron of compound 3 has a small positive charge (+0.36), since each C(12/35) on benzimidazolyl fragment carries a value of –0.65. Additionally, natural bond orbital (NBO) analysis\(^2\)\(^2\) of 3 also indicates the existence of both \(\sigma\) and \(\pi\)-bonds between B and the two C atoms (Figure 3, bottom). Both bonding modes feature significant contribution from the C atom (68 and 83%, respectively), indicating an electron-donating effect from C to B involving two electron pairs of carbodicarbene ligand.

Likewise, calculations showed that the stability of the dicaticonic boron is further enhanced via electronic conjugation within the allenic NHC motif by dispersing away positive charge accumulated on the boron atom, as seen by the positive 0.72–0.78 charges accumulated in each of the four benzimidazolyl groups (Figure 3, top left). On the contrary, for compound 4, the positive charge is more concentrated on the Al atom, +1.46 (Figure 3, top right). The two benzimidazolyl groups bear +0.70 and +0.41 charges, respectively. The asymmetric C=–C bond lengths in the allenic moiety are consistent with those in the X-ray structure. The higher resonance conjugation observed in 4 also contributes to the stability of the dication with the highly electron-deficient B center.

In conclusion, we have described the formation of a hitherto unknown three-coordinate dicaticonic borane bearing a hydride ligand. Interestingly, supporting ligand carbodicarbene gave unprecedented reaction with BH\(_3\) without using more highly electrophilic Lewis acid precursors; a reaction behavior not observed for other common NHC ligands. The subtle variation in bonding parameters of carbodicarbene ligands vs NHC ligand reveals the potential for this strategy to the isolation of other highly electrophilic boron species for the discovery of unprecedented bonding arrangements and novel concomitant reactivity.

---

**ASSOCIATED CONTENT**

* Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

* Corresponding Author

tgong@gate.sinica.edu.tw

*Notes*

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is financially supported by National Science Council of Taiwan (NSC-101-2628-M-001-002-MY3 grant) and Academia Sinica Funding. We also thank Dr. Mei-Chin Tseng for generous technical support for using the Mass Analysis facility. Finally, we are grateful for Professor Ching-Wen Chiu (National Taiwan University, Taipei) and Dr. Titel Jurca (University of Bristol) for their valuable suggestions and discussions.
REFERENCES


(23) Bottom panel of Figure 3 was produced with VMD software. Humphrey, W.; Dalke, A.; Schulten, K. J. Mol. Graphics 1995, 14, 33.