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A (μ -hydrido)diborane(4) anion and its coordination chemistry with coinage metals†

Xiaofeng Mao, Jie Zhang, Zhenpin Lu ‡* and Zuwei Xie ID*

A tetra(*o*-tolyl) (μ -hydrido)diborane(4) anion **1**, an analogue of $[\text{B}_2\text{H}_5]^-$ species, was facilely prepared through the reaction of tetra(*o*-tolyl)diborane(4) with sodium hydride. Unlike common sp^2 - sp^3 diborane species, **1** exhibited a σ -B-B bond nucleophilicity towards NHC-coordinated transition-metal (Cu, Ag, and Au) halides, resulting in the formation of η^2 -B-B bonded complexes **2** as confirmed by single-crystal X-ray analyses. Compared with **1**, the structural data of **2** imply significant elongations of B-B bonds, following the order Au > Cu > Ag. DFT studies show that the diboron ligand interacts with the coinage metal through a three-center-two-electron B-M-B bonding mode. The fact that the B-B bond of the gold complex is much prolonged than the related Cu and Ag compounds might be ascribed to the superior electrophilicity of the gold atom.

Introduction

Diboron compounds are fascinating molecules,¹ and have demonstrated their potential as useful diboration reagents in organic synthesis² and unique ligands for the construction of σ/π -B-B bonded metal complexes.³ Most of these studies focused on the development of neutral diboron species.^{2b,3a} Until recently, anionic diboron compounds also received considerable research interest.⁴ On the one hand, anionic diboron compounds can be used as a type of nucleophilic boron reagents. Because of the high value in the preparation of new boron-element bonds in organic synthesis, since the first synthesis of nucleophilic boryllithium reagent by Yamashita, Nozaki, and co-workers in 2006,⁵ the studies on nucleophilic boron compounds have been an ongoing research interest of many groups.⁶ Anionic diboron compounds, such as $[(\text{RO})_2\text{B}-\text{B}(\text{OR})_2(\text{OR}')^-]$, can react as an equivalent of $[:\text{B}(\text{OR})_2]^-$ with electrophiles for further transformations, providing an alternative approach to nucleophilic boron compounds.⁷ However, for non-heteroatom-substituted diboron compounds, the example is scarce.⁸

On the other hand, diboron compounds are considered as B-B bonded ligands for transition metal complexes.⁹ $[\text{B}_2\text{H}_5]^-$, probably the simplest anionic diboron species, is not stable as

a free molecule. A computational study of $[\text{B}_2\text{H}_5]^-$ reveals that the non-classical bonding structure, where the two boron atoms are bridged by a hydrogen atom, is more stable in energy than

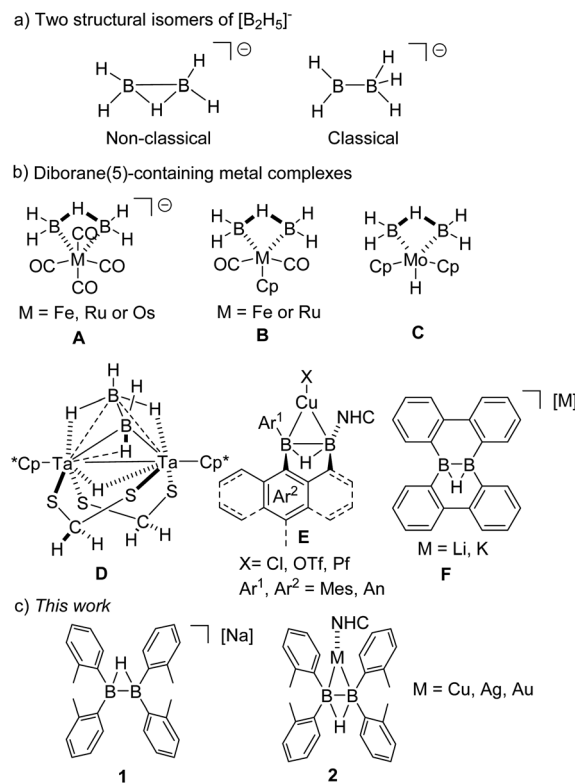


Fig. 1 (a) Structure of non-classical and classical $[\text{B}_2\text{H}_5]^-$; (b) reported diborane(5)-containing metal complexes; (c) new anionic diboron compound reported in this study.

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the classical structure featured with a B–B σ bond (Fig. 1a).^{10,11} Most of the reported $[\text{B}_2\text{H}_5]^-$ complexes with transition metals endowed the structures with a non-classical $[\text{B}_2\text{H}_5]^-$ core (A, B, and C; Fig. 1b).¹² The example of diboron compounds with the classical $[\text{B}_2\text{H}_5]^-$ core is extremely rare. Until 2019, Ghosh *et al.* reported a tantalum complex with the coordination of a classical $[\text{B}_2\text{H}_5]^-$, which is stabilized as a result of the electron donation from the tantalum template to the sp^2 -boron atom (D; Fig. 1b).¹¹ For the study on organic derivatives $[\text{B}_2\text{R}_4\text{H}]^-$ of $[\text{B}_2\text{H}_5]^-$, Braunschweig *et al.* demonstrated that neutral, base-stabilized diborane(5) compounds can be utilized as neutral analogues of $[\text{B}_2\text{H}_5]^-$ ligands to form related transition metal complexes with a characteristic σ B–B bond (E; Fig. 1b).¹³ Wagner *et al.* synthesized a derivative of $[\text{B}_2\text{R}_4\text{H}]^-$, F, from dimeric 9-H-9-borafluorene, which is stabilized through the π conjugated rings (F; Fig. 1b).⁸ Despite these endeavours, the reported examples of anionic non-heteroatom-stabilized diboron(5) compounds remain rare species probably due to the challenges in preparation. We envision that the reaction of diborane(4) species with metal hydride might provide a facile synthesis to new $[\text{B}_2\text{R}_4\text{H}]^-$ derivatives for further investigation. Herein, we report the synthesis of a novel diboron(5) anion **1**, which shows nucleophilic reactivity towards transition metal halides to generate σ -B–B bonded metal complexes **2** (Fig. 1c), and the results are presented in this article.

Results and discussion

Synthesis of tetra(*o*-tolyl)(μ -hydrido)diborane(4) anion **1**

The reaction of tetra(*o*-tolyl)diborane(4)¹⁴ **3** with NaH in THF afforded the desired anionic diboron product **1** in 84% isolated yield. The ¹¹B NMR of compound **1** in THF-*d*₈ displayed only a broad singlet at 30.2 ppm, indicating a symmetrical structure of this diboron compound in solution. This measured value is significantly upfield shifted concerning the 88.6 ppm observed in the ¹¹B NMR spectrum of **3**,¹⁴ but is close to those (31–38 ppm) found in $\text{B}_2(\text{o-tolyl})_4^{2-}$ dianion.¹⁵ Colorless crystals of **1** were obtained from recrystallization in a THF solution at –30 °C. Single-crystal X-ray analyses reveal that **1** is an ionic salt, consisting of a discrete cation $[\text{Na}(\text{THF})_6]^+$ and a hydrogen-bridged anion $[(\text{o-tolyl})_2\text{B}(\mu\text{-H})\text{B}(\text{tolyl})_2]^-$. The molecular structure of the anion in **1** is shown in Fig. 2. The C(8)–B(1')–B(1)–C(8')/C(1')–B(1')–B(1)–C(1) torsion angles in **1** are almost zero, which is similar to that observed in the $\text{B}_2(\text{o-tolyl})_4^{2-}$ dianion¹⁵ but in sharp contrast to those in **3** (75.7(7)–93.2(7)°).¹⁴ The B–B bond distance (1.628(5) Å) in **1** is very close to that of $\text{B}_2(\text{o-tolyl})_4^{2-}$ dianion (1.633(3), 1.639(6) Å), slightly shorter than that observed in compound **F** (1.651(6) Å) (Fig. 1b),⁸ but is considerably shorter than the one in **3** (1.686(9), 1.694(9) Å) and other neutral diborane species (1.67–1.68 Å).¹³ The aforementioned data suggest that the B–B bond in **1** has a double bond character (Scheme 1).

Synthesis of η^2 -B–B bonded complexes **2**

In our attempt to explore the nucleophilic reactivity of this new anionic diboron species, compound **1** was treated with different

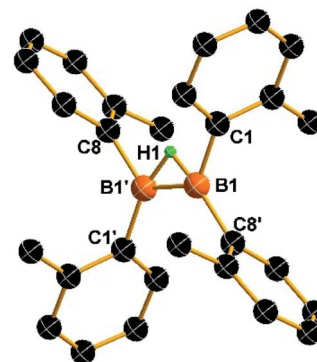
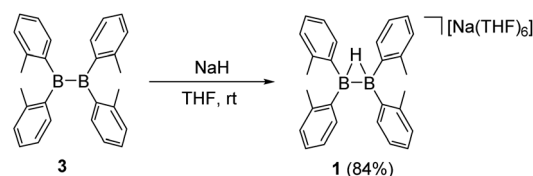


Fig. 2 Molecular structure of the anion in **1** (thermal ellipsoids are set at the 50% probability level; all hydrogen atoms are omitted for clarity except for the bridging H atom). Selected bond distances (Å) and angles (°): B1–B1' 1.628(5); C1–B1–B1' 121.4(3), C8–B1–B1' 122.6(3), C(1)–B(1)–C(8) 116.0(2).

NHC-supported transition-metal halides (Scheme 2). Although compound **1** did not work as an equivalent of BR_2^- to afford metal boryl species,¹⁶ the nucleophilic B–B σ bond of **1** can interact with the transition metals to generate new η^2 -bonded complexes **2**. They were fully characterized by NMR spectra, HRMS, and single-crystal X-ray analyses. The ¹¹B NMR spectra of **2** exhibited a broad singlet at 24–27 ppm, which was upfield-shifted compared with **1** (30 ppm), suggesting a back-donation from the metal to the boron atoms.

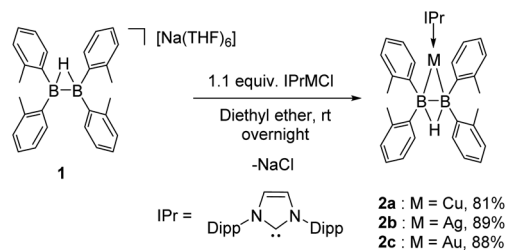
The electrochemical properties of compounds **1** and **2** were investigated by cyclic voltammetry (CV). Both compounds **2a** and **2b** exhibited a quasi-reversible reduction potential at around –1.6 V (*vs.* $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$), whereas compound **2c** showed a similar one at –1.9 V (Fig. S10, S15, and S20†). In comparison, compound **1** was not stable under electrochemical conditions, and no clear reduction potential was observed from the CV spectra (Fig. S5†), which indicated that the formation of B–B bonded transition metal complexes renders this anionic diboron species more robust upon the electrical reduction process.

The molecular structures of compounds **2** confirm the formation of two new metal–boron bonds that the B–B bond is bonded to the metal in an η^2 fashion (Fig. 3). Similar to that of **1**, the BHB unit is observed in compound **2**. Compounds **2a** and **2b** have C_2 symmetries, whereas **2c** is packing in an orthorhombic crystal system. For compound **2a**, the Cu–B bond distance (2.177(3) Å) is close to that of reported copper-based dianionic diboron complexes (2.178–2.186 Å)⁹ and copper(i) diborane complexes (2.146(3) Å and 2.149(3) Å).¹⁷ For the silver



Scheme 1 Synthesis of anionic diboron compound **1**.





Scheme 2 Synthesis of B–B bonded metal complexes 2.

complex, the Ag–B length in **2b** (2.328(5) Å) is similar to the reported symmetric diborane Ag(I) species (2.318(4) Å and 2.3664 Å).¹⁸ The Au–B bond length in **2c** (2.235(5) Å and 2.238(5) Å) are considerably longer than those of reported sp^2 boryl gold complexes (2.07–2.09 Å)¹⁹ and boride gold (2.11–2.19 Å),²⁰ but comparable to those of sp^3 boryl gold complexes (2.21–2.30 Å)²¹ and borylene gold species (2.17–2.22 Å).²²

Notably, the B–B bond lengths of compounds **2** (**2a**: 1.763(7) Å, **2b**: 1.761(10) Å, and **2c**: 1.822(8) Å) were significantly elongated compared with that of compound **1** (1.628(5) Å). These values are slightly longer than those of reported copper(I) diboron dianionic species (1.68–1.72 Å),⁹ but comparable to the reported base-stabilized diborane(5) metal complexes (1.76–1.79 Å)¹³ as well as those of metal-stabilized non-classical $[B_2H_5]^-$ complexes (**A**, **B** and **C**; Fig. 1b) (1.77–1.79 Å).¹² Particularly for **2c**, the B–B bond distance (1.822(8) Å) is considerably longer than common $B(sp^3)$ – $B(sp^3)$ single bond (1.76 Å).²³

DFT computational studies were conducted to elucidate the electronic structures of compounds **1** and **2** (Fig. 4). The HOMO of **1** consists of both σ - and π -orbitals, suggesting the presence of B=B double bond characteristics as evidenced by the Wiberg bond index (WBI) of 1.13 in **1**. In contrast, only σ -orbitals of B–B bond can be clearly seen from the HOMOs of compounds **2**, indicating the presence of metal to B–B bond back donation. Accordingly, the WBIs of the B–B bond in compounds **2** are all reduced (**2a**: 1.02, **2b**: 0.99, and **2c**: 0.83). These results are in good agreement with the measured B–B bond distances. In addition, the HOMO–12 of **2a**, HOMO–15 of **2b**, and HOMO–12 of **2c** are partially polarized towards the metal atoms, resulting in the generation of metallacycle-like structures.²⁴ It is also noted that gold atom exhibits a superior electrophilicity than Cu and Ag, which might explain that the B–B bond distance of **2c** is the longest one among these three derivatives.²⁵ The LUMOs of compounds **2** remain mainly on the NHC group, although for **2a** and **2c** the existence of π^* -orbitals of B–B bond could also be observed.

Natural bond orbital (NBO) analyses were carried out to investigate the bonding situation between the anionic B–B bond and the metal atom in compounds **2**. The second-order perturbation analyses indicate that donor–acceptor interaction from the σ -orbitals of the B–B bond to the metal atom is dominant (**2a**: 54.28 kcal mol⁻¹, **2b**: 60.24 kcal mol⁻¹ and **2c**: 174.24 kcal mol⁻¹), in which the stabilization energy of gold complex **2c** is much higher than the other two compounds. Moreover, localized molecular orbital (LMO) analyses suggested

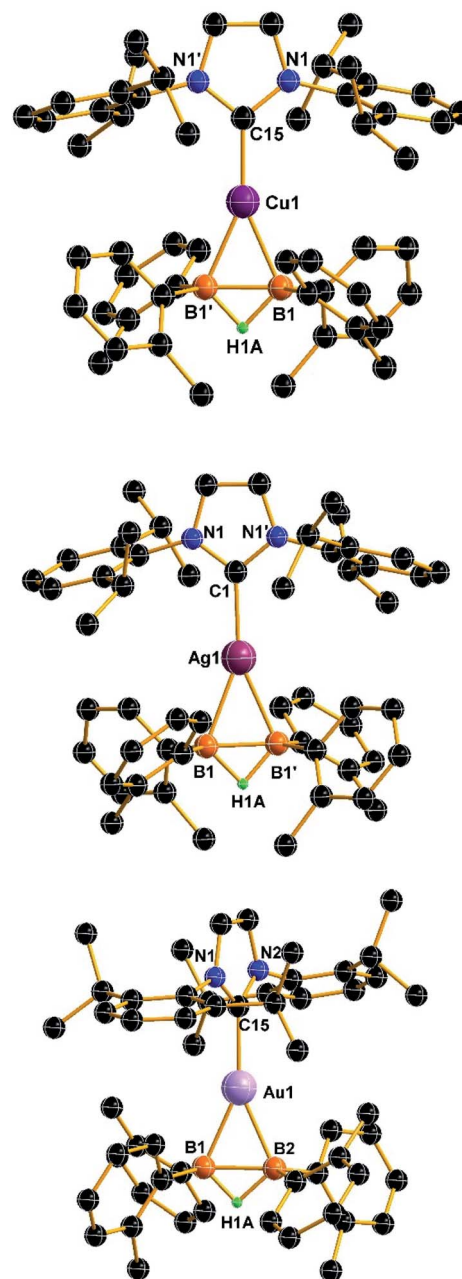


Fig. 3 Molecular structures of compounds **2** (thermal ellipsoids are set at the 50% probability level, and all hydrogen atoms are omitted for clarity except for the bridging H atom). Selected bond distances (Å): **2a** (top): Cu1–B1 2.177(4), Cu1–C15 1.948(4), B1–B1' 1.763(7); **2b** (middle): Ag1–B1 2.328(5), Ag1–C1 2.127(5), B1–B1' 1.761(10); **2c** (bottom): Au1–B1 2.235(5), Au1–C15 2.068(4), B1–B2 1.822(8).

the presence of three-center-two-electron B–M–B bonding interaction between the two boron atoms and metal in compounds **2**, in addition to B–H–B 3c–2e bonding interaction (Fig. S21 in ESI†). These data imply that the σ -B–B bond is highly polarized to the metal center, particularly in **2c**, leading to a significant activation of the B–B bond. In addition, a back donation from the occupied p/d-orbital of the metal atom to the B–B bond can also be observed: however, such interactions are far less significant (1.18 to 9.62 kcal mol⁻¹, see the ESI†).



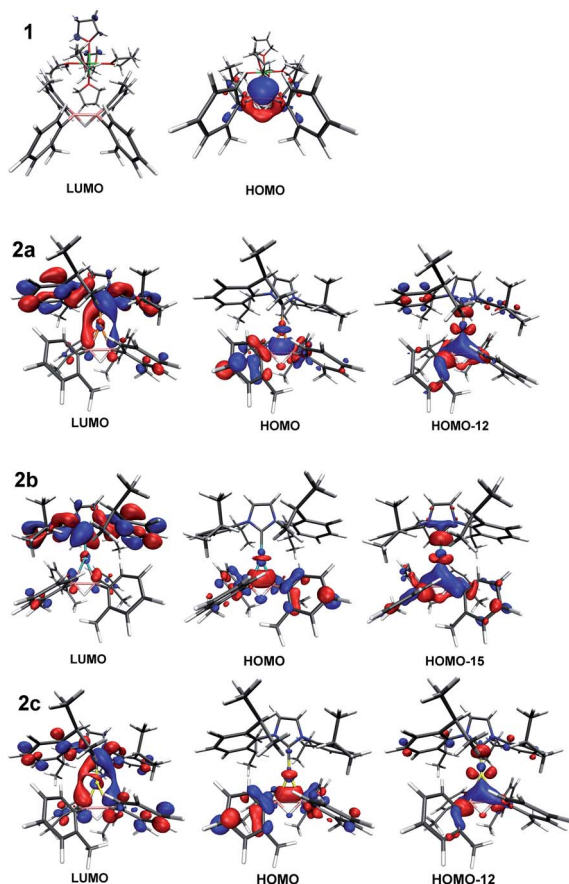


Fig. 4 Selected frontier molecular orbitals for 1, 2a, 2b, and 2c.

Conclusions

A new anionic diboron **1**, which can be viewed as an analogue of $[\text{B}_2\text{H}_5]^-$, was conveniently synthesized in 84% isolated yield by the treatment of tetra(*o*-tolyl)diborane(4) with sodium hydride. Compound **1** demonstrated the nucleophilicity towards NHC-supported transition-metal halides to afford corresponding η^2 -bonded complexes. Both structural data and DFT computational results showed that the B–B bonds were dramatically activated with the introduction of transition metals. The reactivity of **1** with other electrophiles is currently under investigation in our laboratory.

Data availability

Experimental procedure, NMR spectra, computational details are available in the ESI.† Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC 2133420–2133423 for **1**, **2a**, **2b**, and **2c**, respectively.

Author contributions

Z. X. and Z. L. conceived and directed the project. X. M. did the experiments. J. Z. performed the computational studies. All authors discussed the results and wrote the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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