JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.9b03600 • Publication Date (Web): 02 May 2019

An Acid-Free Anionic Oxoborane Isoelectronic with Carbonyl: Facile Access and Transfer of a Terminal B=O Double Bond

Ying Kai Loh, Kieran Porteous, M. Ángeles Fuentes, Dinh Cao Huan Do, Jamie Hicks, Simon Aldridge*

Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR UK

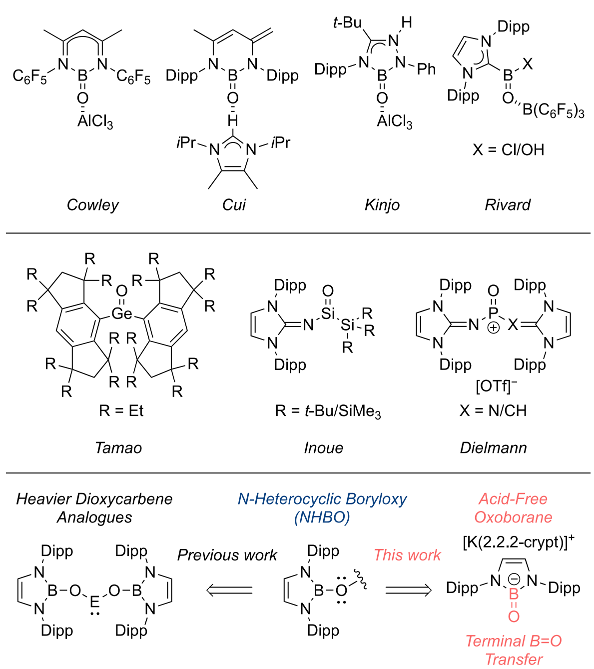
Supporting Information Placeholder

ABSTRACT: We disclose the synthesis and structural characterization of the first acid-free anionic oxoborane, [K(2.2.2-crypt)][$(HCDippN)_2BO$] (**1**), which is isoelectronic with classical carbonyl compounds. **1** can readily be accessed from its borinic acid by a simple deprotonation/sequestration sequence. Crystallographic and DFT analyses support the presence of a polarized terminal B=O double bond. Subsequent π bond metathesis converts the B=O bond to a heavier B=S containing system, affording the first anionic thioxoborane [K(2.2.2-crypt)] [$(HCDippN)_2BS$] (**2**), isoelectronic with thiocarbonyls. Facile B=O bond cleavage can also be achieved to access B–H and B–Cl bonds, and via a remarkable oxide (O^{2-}) ion abstraction to generate a borenium cation [$(HCDippN)_2B(NC_5H_5)$][OTf] (**4**). By extension, **1** can act as an oxide transfer agent to organic substrates, a synthetic role traditionally associated with transition metal compounds. Hence we show that B–O linkages, which are often considered to be thermodynamic sinks, can be activated under mild conditions towards bond cleavage and transfer, by exploiting the higher reactivity inherent in the B=O double bond.

Boron has great affinity for oxygen, forming thermodynamically strong B–O bonds (809 kJ mol^{-1});[1] naturally occurring boron is therefore typically found in the form of borate minerals.[2] In synthetic chemistry, the highly oxophilic nature of boron is exploited to drive important transformations such as Suzuki coupling and carbonyl hydroboration.[3] While these processes are increasingly being adopted in pharmaceutical production, the chemical recycling of B–O bonds requires harsh conditions and/or reagents – as in the commercial production of BCl_3 from B_2O_3, carbon and Cl_2 at 500 °C.

Given the higher reactivity typically found for E=O multiple bonds (*e.g.* relatively inert C–O single bonds in ethers versus more reactive C=O double bonds in carbonyls), we sought to explore new modes of reactivity

Scheme 1. Examples of acid-stabilized oxoboranes (top), acid- and base-free main group E=O doubly bonded species (middle); Previous work with the NHBO ligand and present work (bottom). (Dipp = 2,6-$^iPr_2C_6H_3$).

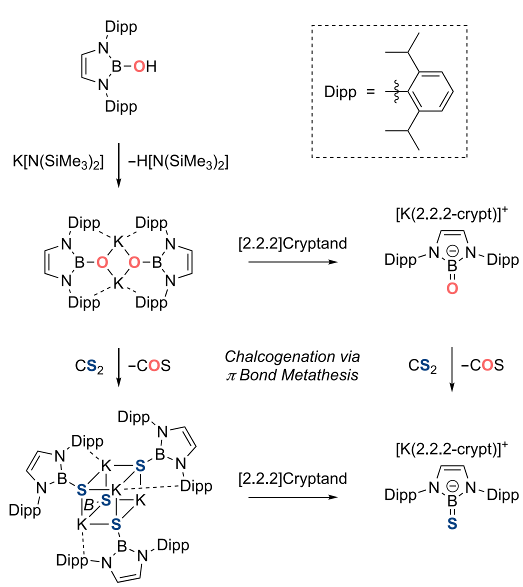


for the BO fragment by developing the chemistry of simple isolable B=O double bonds.

Oxoboranes (R–B=O) represent one such class of organoboron species (albeit transiently stable) that contain a B=O double bond.[4] The quest for isolable oxoboranes is hampered by the high polarity of the BO fragment and the Lewis acidic nature of the boron atom, making such species prone to head-to-tail oligomerization. Thus, monomeric species are highly elusive and observable only in the gas phase, in a low-temperature matrix, or by means of chemical trapping.[5] In 2005, Cowley *et al.* exploited an additional neutral donor at boron and Lewis acid coordination at oxygen, to generate a monomeric oxoborane featuring a short B=O distance (1.304(2) Å; Scheme 1).[6a] Subsequently, the concept of Lewis/Brøn-sted acid stabilization has at O been successfully employed to generate other protected oxoboranes featuring similar B=O distances.[6] Another strategy for the isolation of systems containing BO multiple bonds is by trap-ping within the coordination sphere of a transition metal, as exemplified by Braunschweig[7a-d] and by Yamashita.[7e]

Aside from boron, significant progress has been made recently in the isolation of compounds featuring acid- and base-free main group element E=O double bonds, which are isoelectronic with the C=O double bonds of classical carbonyl compounds. In 2012, Tamao and co-workers documented a stable monomeric germanone [R_2Ge=O], a heavier ketone analogue possessing a Ge=O double bond (Scheme 1).[8a] Another landmark achievement was the fulfillment of "Kipping's dream" by the groups of Kato and Inoue, through the isolation of silanones, R_2Si=O, featuring Si=O double bonds.[8b-d] In addition, Dielmann and co-workers have described a Lewis base free oxophosphonium cation, [R_2P=O]$^+$, containing a P=O double bond.[8e] Inspired by these reports, we wondered whether an isoelectronic acid-free anionic oxoborane of the type [R_2B=O]$^-$ could be accessed.

Scheme 2. Synthesis of [K(2.2.2-crypt)][(HCDippN)$_2$BO] (1), and its subsequent chalcogenation to give [K(2.2.2-crypt)][(HCDippN)$_2$BS] (2) and {K[(HCDippN)$_2$BS]}$_4$ (3).



Very recently, we introduced a new class of N-heterocyclic boryloxy (NHBO) ligand, (HCDippN)$_2$BO-, and demonstrated its ability to stabilize heavier group 14 dioxycarbene analogues (Scheme 1).[9] We speculated whether the NHBO framework, possessing a 6π electron diazaborolyl scaffold flanked by sterically demanding Dipp groups, would possess the necessary attributes for the isolation of a monomeric, acid-free oxoborane. With this in mind, we exploited the potassiated ligand {K[(HCDippN)$_2$BO]}$_2$ (which is dimeric in the solid state) as the starting point of our investigation. To sequester the potassium ion, [2.2.2]cryptand was employed (Scheme 2), resulting in an immediate colour change from yellow to red. The resulting ^{11}B{^{1}H} NMR spectrum displays a broad singlet at 20.7 ppm, which is upfield shifted by *ca.* 2 ppm, suggesting slightly increased electron density at boron. Single crystals obtained by slow evaporation from a benzene solution were subjected to X-ray diffraction analysis.

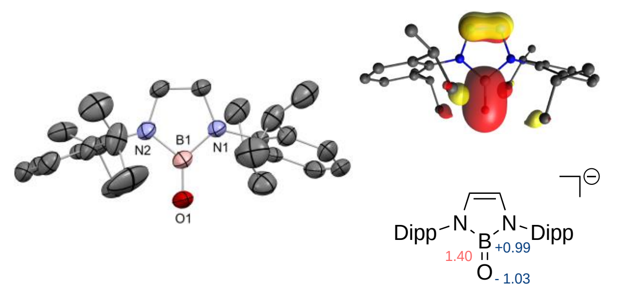


Figure 1. Solid-state structure of **1**, Kohn-Sham HOMO–2, WBI bond order (red) and NPA charges (blue). For clarity, [K(2.2.2-crypt)]$^+$ and hydrogen atoms are omitted. Thermal ellipsoids set at 50% probability. Key bond lengths (Å) and angles (°): B1–O1 1.273(8), B1–N1 1.484(7), B1–N2 1.489(7), N1–B1–N2 100.6(4).

The solid-state structure reveals successful sequestration of the potassium ion and the generation of a monomeric anionic oxoborane (**1**, as the [K(2.2.2-crypt)]$^+$ salt) (Figure 1). The oxygen atom assumes a terminal position, with the closest contacts being an O1–K1 distance of 5.919(6) Å, and O–H interactions involving the C–H bonds of the flanking ^{i}Pr groups or the cryptand methylene units (*ca.* 2.5 Å). As such, **1** represents the first example of a simple (*i.e.* non-acid stabilized) oxoborane. The central boron atom adopts a trigonal planar geometry, and the most striking feature is the very short B–O bond distance of 1.273(8) Å, which is towards the shorter end of the range of reported distances for Lewis/Brønsted acid stabilized B=O double bonds (1.287(4)–1.329(6) Å).[6] In comparison with the parent borinic acid (HCDippN)$_2$BOH (1.373(3) Å),[10] shortening of the B–O distance by 0.1 Å (*ca.* 8%) suggests delocalization of additional electron density by O-to-B π donation, leading to significant B=O double bond character.

Consistently, the adjacent B–N bonds are lengthened markedly from $(HCDippN)_2BOH$ (mean 1.429(3) Å) to **1** (mean 1.487(7) Å).

To probe the electronic structure of **1**, we exploited Density Functional Theory (DFT) using a PBE1PBE hybrid exchange-correlation functional and TZVP basis set. B=O π bond character can be located in the HOMO–2 (Figure 1); the Wiberg bond index (WBI) of 1.40, and NPA charges on B (+0.99) and O (–1.03) support a description as a B=O double bond that is polarized towards oxygen. For comparison, analogous calculations on the isoelectronic carbonyl compound (the cyclic urea $(HCDippN)_2CO$) reveal a WBI of 1.61 for the C=O fragment and NPA charges of +0.72(C)/–0.64(O).

In contrast to its lighter congener, monomeric thioxoboranes (R–B=S) have been isolated in the absence of acid protection, as demonstrated by reports from the groups of Cui,[11a] Singh[11b] and Braunschweig.[11c] While a cationic thioxoborane has subsequently been reported by Inoue and co-workers,[11d] the anionic counterpart $[R_2B{=}S]^-$ (which is isoelectronic with thiocarbonyl com-pounds) remains unknown. With this in mind, the unquenched B=O motif in **1** was thought to be an ideal candidate to explore carbonyl-like metathesis of the terminal oxygen.

Treatment of **1** with carbon disulfide, CS_2 at room temperature leads to an upfield shift of the $^{11}B\{^1H\}$ NMR signal by *ca.* 12 ppm to 33.1 ppm, which is close to that of Inoue's cationic thioxoborane (33.9 ppm) (Scheme 2).[11d] In addition, a signal at 153.4 ppm was detected in the $^{13}C\{^1H\}$ NMR spectrum due to carbonyl sulfide, COS, hinting at successful B=O / B=S metathesis. X-ray crystallography unambiguously revealed the identity of the product as [K(2.2.2-crypt)][$(HCDipp\text{-}N)_2BS$] (**2**). **2** is isostructural with **1**, with sulfur in a terminal position (Figure 2), and therefore represents the first example of a monomeric thioxoborane anion. Closer inspection reveals the B–S distance to be 1.774(1) Å, which is marginally longer than those found in previously reported neutral (1.739(2)-1.752(5) Å)[11a-c] and cationic (1.710(5) Å)[11d] systems, indicating a stepwise decrease in bond order with accumulation of negative charge on the BS fragment. As with **1**, we turned to DFT calculations for further insight. The B=S π bond can be located in the HOMO–2 (Figure 2); the WBI of 1.56 and NPA charges on B (+0.61) and S (–0.71) support a description as a B=S double bond that is polarized towards the chalcogen, although to a lesser extent than in **1**.

2 can also be synthesized from dimeric $\{K[(HCDippN)_2BO]\}_2$ via an analogous reaction with CS_2. This reaction initially generates the tetrameric inter

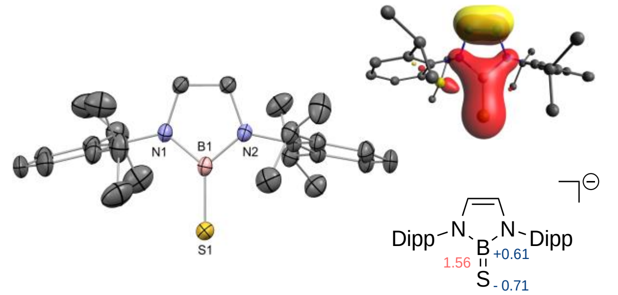


Figure 2. Solid-state structure of **2**, Kohn-Sham HOMO–2, WBI bond order (red) and NPA charges (blue). For clarity, $[K(2.2.2\text{-crypt})]^+$ and hydrogen atoms are omitted. Thermal ellipsoids set at 50% probability. Key bond lengths (Å) and angles (°): B1–S1 1.774(1), B1–N1 1.457(2), B1–N2 1.461(2), N1–B1–N2 101.4(9).

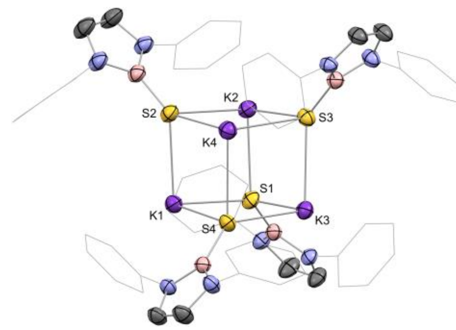


Figure 3. Solid-state structure of **3**. For clarity, hydrogen atoms and ^{i}Pr groups are omitted, Dipp groups are simplified as wireframes. Thermal ellipsoids set at 50% probability. Key bond lengths (Å) and angles (°): B1–S1 1.789(4), S1–K1 3.112(1), S1–K2 3.084(1), S1–K3 3.185(1).

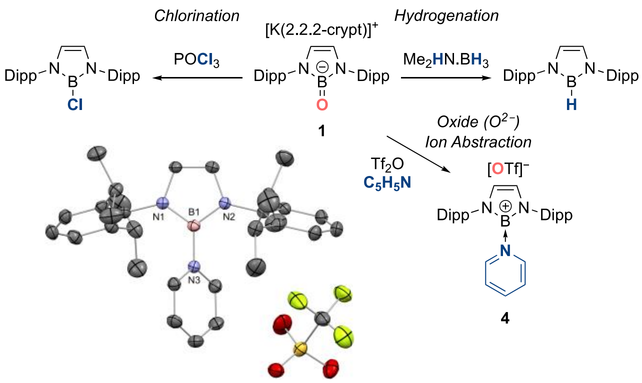
-mediate $\{K[(HCDippN)_2BS]\}_4$ (**3**; Scheme 2 and Figure 3); subsequent treatment with [2.2.2]cryptand leads to sequestration of the K^+ cations to give monomeric **2**.

The facile access of a B=S bond via π bond metathesis from its lighter congener resembles the chalcogenation of carbonyl compounds. With this in mind, we wanted to explore the applicability of other classical carbonyl transformations (such as hydrogenation) to the B=O bond. In the case of **1**, hydrogenation can be achieved with dimethylamineborane, $Me_2HN{\cdot}BH_3$ to afford $(HCDippN)_2BH$ (Scheme 3),[10] by analogy with hydrogen transfer from $H_3N{\cdot}BH_3$ to a cationic thioxoborane reported by Inoue and co-workers.[11d]

While B–H containing compounds are valuable reagents in their own right, we wondered whether broader scope could be demonstrated for the conversion of **1** to species of the type R_2BX. A conventional protocol to activate carbonyl groups towards nucleophilic attack is by chlorination. To probe this analogy, we exposed **1** to $POCl_3$ at room temperature, leading to an immediate colour change from red to yellow

(Scheme 3). [1]H NMR monitoring reveals clean conversion to the chloroborane $(HCDippN)_2BCl$.[10] Due to its labile nature, B–Cl containing compounds are versatile building g blocks for

Scheme 3. Carbonyl-like reactions of 1 to give $(HCDippN)_2BH$, $(HCDippN)_2BCl$, $[(HCDippN)_2B(NC_5H_5)][OTf]$ (4).

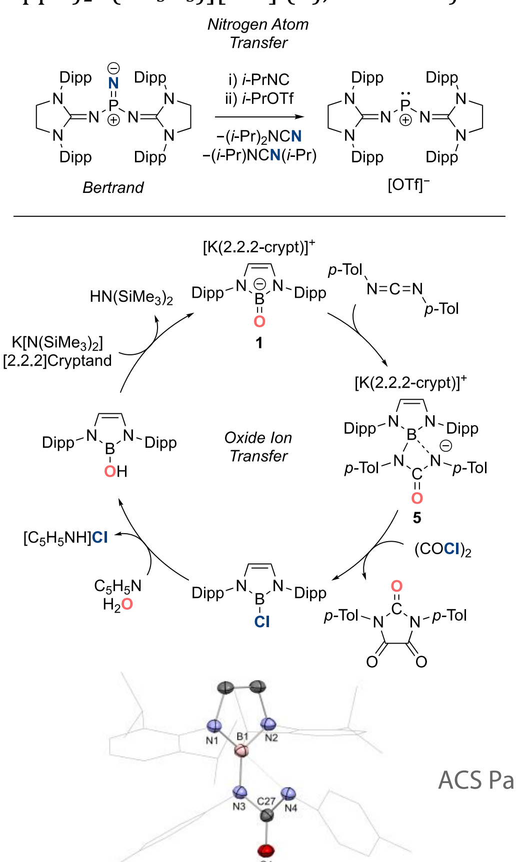


key organoboron species, such as boronic acids for Suzuki coupling, or even boryl nucleophiles boron for umpolung B–C bond formation.[10]

Carbonyl compounds are also known to undergo rearrangements in the presence of trifluoromethanesulfonic anhydride, Tf_2O, and transient cations are often proposed as reactive intermediates.[12] With this in mind we wondered whether we could generate a boron cation in analogous fashion, in effect by removal of oxide ion (O^{2-}) from **1**. Accordingly, the reaction of **1** with Tf_2O in the presence of pyridine generates the triflate anion, and a cationic species which can be shown by X-ray crystallography to feature a pyridine-ligated borenium cation (*i.e.* $[(HCDippN)_2B(NC_5H_5)][OTf]$ (**4**), Scheme 3).[13]

In a landmark report, Bertrand and co-workers demonstrated that a main group compound could mimic a transition metal complex in acting as a nitrogen atom transfer agent (Scheme 4). Reaction of an isolable phosphinonitrene with isonitrile initially forms an adduct, which can subsequently be cleaved with an alkyltriflate to afford a mixture of cyanamide and carbodiimide products.[14] The isoelectronic BO^- /PN relation

Scheme 4. Bertrand's phosphinonitrene as a nitrogen atom transfer agent (top); an analogous synthetic cycle with 1 as an oxide ion transfer agent (middle); solid-state structure of 5 (bottom).



-ship between **1** and this phosphinonitrene prompted us to investigate the possibility of using **1** as an oxide ion transfer agent, a task typically accomplished by transition metal systems.[15]

As a proof of concept, we treated **1** with 1,3-di-*p*-tolylcarbodiimide. X-ray diffraction analysis of the product reveals not simple adduct formation, but 1,2-addition of the B=O bond across the C=N double bond to afford iso-ureate **5**. Although unsymmetrical binding of the NC(O)N fragment at boron is implied by crystallography, the [1]H NMR of **5** shows a single *p*-Tol group environment in solution, hinting at the facile fluxional exchange. Formally, this transformation involves insertion of a carbodiimide into the B=O double bond. To release the functionalized substrate, oxalyl chloride was employed to generate the cyclic urea derivative $(OC(p\text{-Tol})N)_2CO$ and $(HCDippN)_2BCl$.[10] While this stepwise procedure closely resembles the N-transfer reported by Bertrand, we could also achieve the same transformation in a one-pot sequence without isolation of intermediate **5**. Moreover, to close the oxide ion transfer cycle, $(HCDippN)_2BCl$ can be converted to borinic acid $(HCDippN)_2BOH$ using water in the presence of pyridine and subsequently back to **1** via simple deprotonation and cation sequestration.[9]

In conclusion, we disclose the first acid-free anionic oxoborane **1**, which exhibits classical carbonyl-like reactivity, and also mimics the activity of transition metal systems by acting as an oxide ion transfer agent. Hence, boron-oxygen linkages which are often considered to be thermodynamic sinks, can be shown to be activated towards facile bond cleavage and transfer, by exploiting the higher reactivity intrinsic in the B=O double bond.

ASSOCIATED CONTENT

Supporting Information. Full synthetic and characterizing data for new compounds, representative NMR spectra, details of crystallographic and computational studies (PDF). CIFs for X-ray crystal structures (CCDC:

1906845-1906849). The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

Prof Simon Aldridge, simon.aldridge@chem.ox.ac.uk.

Funding Sources

A*STAR (scholarship for YKL), the Jardine-Oxford Scholarship (DDCH) and EPSRC (MAF, EP/K014714/1).

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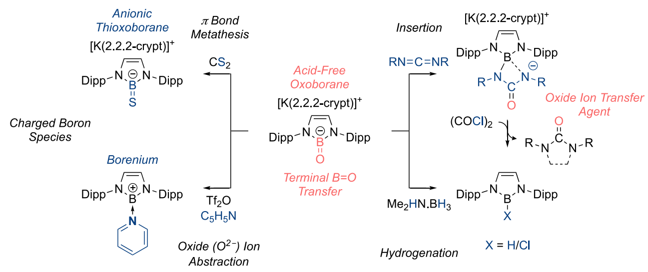
(15) For oxide ion transfer by transition metals, see for example: Lee, G. R.; Cooper, N. J. Transfer of an oxide ion from an anionic carbon dioxide complex to a cationic carbonyl complex. *Organometallics* **1985**, *4*, 1467-1468.


Anionic Thioxoborane
[K(2.2.2-crypt)]+
π Bond Metathesis
CS2
Charged Boron Species
Borenium
Tf2O
C5H5N
Oxide (O2−) Ion Abstraction
Acid-Free Oxoborane
[K(2.2.2-crypt)]+
Terminal B=O Transfer
Insertion
RN=C=NR
[K(2.2.2-crypt)]+
Oxide Ion Transfer Agent
(COCl)2
Me2HN.BH3
Hydrogenation
X = H/Cl