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

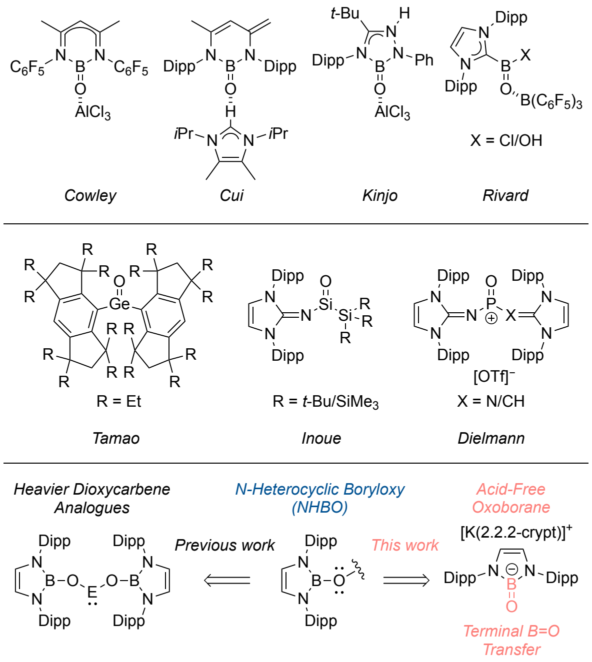
Supporting Information Placeholder

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

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-$^iPr_2C_6H_3$).

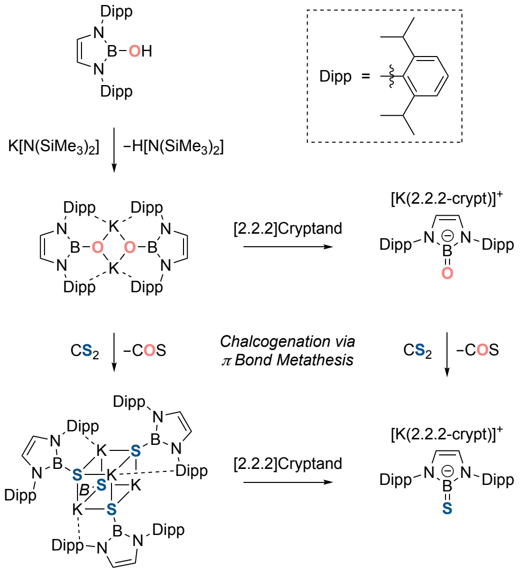


Oxoboranes (R−B=O) represent one such class of organoboron species (albeit transiently stable) that contain a B=O double bond.[4] The quest for isolable oxoboranes is hampered by the high polarity of the BO fragment and the Lewis acidic nature of the boron atom, making such species prone to head-to-tail 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/Brønsted 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 trapping 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 coworkers 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.

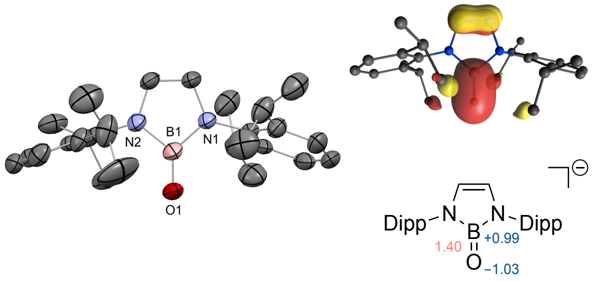


Figure 1. Solid-state structure of **1**, Kohn-Sham HOMO−2, WBI bond order (red) and NPA charges (blue). For clarity, $[K(2.2.2\text{-crypt})]^+$ and hydrogen atoms are omitted. Thermal ellipsoids set at 50% probability. Key bond lengths (Å) and angles (°): B1−O1 1.273(8), B1−N1 1.484(7), B1−N2 1.489(7), 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 $[K(2.2.2\text{-crypt})]^+$ 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 methylene units of the cryptand (*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)$_2$BOH (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 compounds) 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 $[K(2.2.2\text{-crypt})][(HCDippN)_2BS]$ (**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 intermediate $\{K[(HCDippN)_2BS]\}_4$ (**3**; Scheme 2 and Figure 3); subsequent treatment with [2.2.2]cryptand leads to sequestration of the K^+ cations to give monomeric **2**.

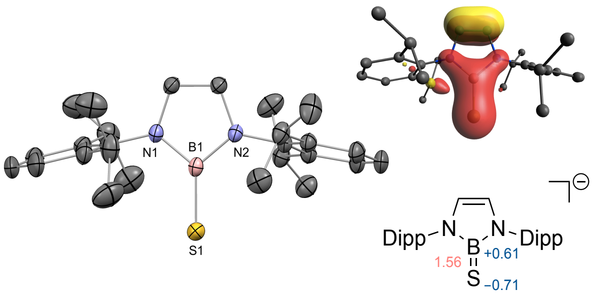


Figure 2. Solid-state structure of **2**, Kohn-Sham HOMO−2, WBI bond order (red) and NPA charges (blue). For clarity, $[K(2.2.2\text{-crypt})]^+$ and hydrogen atoms are omitted. Thermal ellipsoids set at 50% probability. Key bond lengths (Å) and angles (°): B1−S1 1.774(1), B1−N1 1.457(2), B1−N2 1.461(2),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

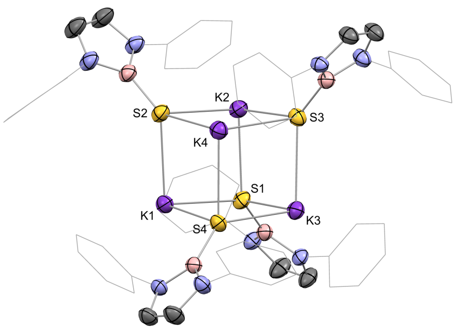
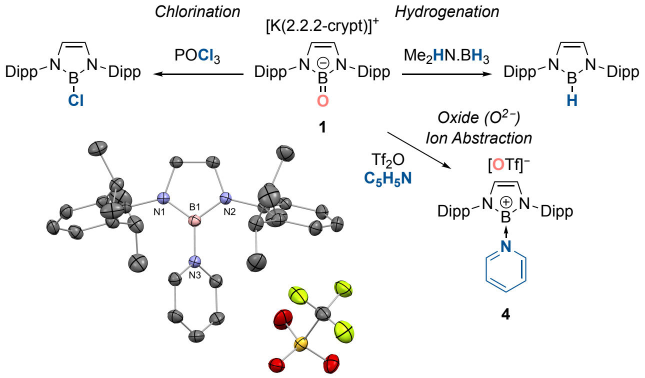


Figure 3. Solid-state structure of **3**. For clarity, hydrogen atoms and *i*-Pr groups are omitted, Dipp groups are simplified as wireframes. Thermal ellipsoids set at 50% probability. Key bond lengths (Å) and angles (°): B1−S1 1.789(4), S1−K1 3.112(1), S1−K2 3.084(1), S1−K3 3.185(1).

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 to the B=O bond. A key fundamental reaction of the carbonyl function is hydrogenation, typically accomplished by highly reactive metal hydride reagents. In the case of **1**, hydrogenation can be achieved with dimethylamineborane, $Me_2HN{\cdot}BH_3$ as the hydrogen transfer source 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 the B=O double bond in **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). ^1H NMR monitoring reveals clean

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

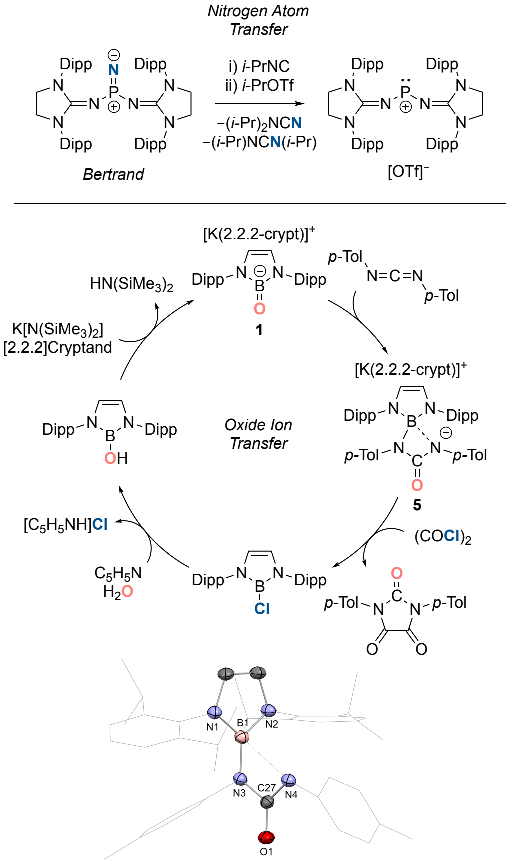


conversion to a new species, which can be shown to be the chloroborane $(HCDippN)_2BCl$.[10] Due to its labile nature, B−Cl containing compounds are versatile building blocks for key organoboron species, such as boronic acids for Suzuki coupling, or even boryl nucleophiles boron for umpolung B−C bond 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 in 2012 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 relationship 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]

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).



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 ^1H NMR of **5** shows a single *p*-Tol group environment in solution, hinting at the facile fluxional exchange. Formally, this transformation can be considered as 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.

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REFERENCES

(1) For bond dissociation energies: Haynes, W. M. *CRC Handbook of Chemistry and Physics, Vol. 96*; CRC Press: Boca Raton, 2015.

(2) For minerals: Klein, C.; Hurlbut, C. S. *Manual of Mineralogy*; Wiley: New York, 1985.

(3) (a) Miyaura, N.; Suzuki, A. Palladium-catalyzed cross-coupling reactions of organoboron compounds. *Chem. Rev.* **1995**, *95*, 2457-2483. (b) Brown, H. C. Hydroboration – a powerful synthetic tool. *Tetrahedron* **1961**, *12*, 117-138.

(4) See for example: (a) Franz, D.; Inoue, S. Advances in the development of complexes that contain a group 13 element chalcogen multiple bond. *Dalton Trans.* **2016**, *45*, 9385-9397. (b) Fischer, R. C.; Power, P. P. π-Bonding and the lone pair effect in multiple bonds involving heavier main group elements: developments in the new millennium. *Chem. Rev.* **2010**, *110*, 3877-3923.

(5) For gas phase studies: (a) Hildenbrand, D. L.; Theard, L. P.; Saul, A. M. Transpiration and mass spectrometric studies of equilibria involving BOF(g) and $(\mathrm{BOF})_{3-}$(g). *J. Chem. Phys.* **1963**, *39*, 1973-1978. (b) Bock, H.; Cederbaum, L.; Niessen, W. v.; Paetzold, P; Rosmus, R.; Solouki, B. Methylboron oxide, H_3CBO. *Angew. Chem., Int. Ed.* **1989**, *28*, 88-90. For matrix isolation: (c) Burkholder, T. R.; Andrews, L. Reactions of boron atoms with molecular oxygen. Infrared spectra of BO, BO_2, B_2O_2, B_2O_3, and BO^{-}_{2} in solid argon. *J. Chem. Phys.* **1991**, *95*, 8697-8709. (d) Lanzisera, D. V.; Andrews, L. Reactions of laser-ablated boron atoms with methanol. Infrared spectra and *ab initio* calculations of CH_3BO, CH_2BOH, and CH_2BO in solid argon. *J. Phys. Chem. A.* **1997**, *101*, 1482-1487. (e) Bettinger, H. F. Reversible formation of organyl(oxo)boranes (RBO) (R = C_6H_5 or CH_3) from boroxins ($(RBO)_3$): a matrix isolation study. *Organometallics* **2007**, *26*, 6263-6267. For chemical trapping: (f) Ito, M.; Tokitoh, N.; Okazaki, R. A novel approach to an oxoborane and its Lewis base complex *Tetrahedron Lett.* **1997**, *38*, 4451-4454. (g) Ito, M.; Tokitoh, N.; Okazaki, R. Formation of oxoborane and thioxoborane from a dithiastannaboretane derivative. *Phosphorus, Sulfur Silicon Relat. Elem.* **1997**, *124*, 533-536. (h) Paetzold, P.; Neyses. S.; Geret. L. Oxo(trisyl)boran $(Me_3Si)_3CBO$ als zwischenstufe. *Z. Anorg. Allg. Chem.* **1995**, *621*, 732-736. (i) Groteklaes, M.; Paetzold, P. Oxo(tri-*tert*-butylphenyl)boran ArBO als zwischenstufe. *Chem. Ber.* **1988**, *121*, 809-810. (j) Pachchaly, B.; West, R. Synthesis of a 1,3-dioxa-2,4-diboretane, an oxoborane precursor. *J. Am. Chem. Soc.* **1985**, *107*, 2987-2988. (k) Hanecker, R.; Noth, H.; Wietelmann, U. Beiträge zur chemie des bors, 171. Kristall- und molekülstruktur von 2,4-bis(2,2,6,6-tetramethylpiperidino)-1,3,2,4-dichalcogendiboretanen. *Chem. Ber.* **1986**, *119*, 1904-1910.

(6) For acid-stabilized monomeric oxoboranes: (a) Vidovic, D.; Moore, J. A.; Jones, J. N.; Cowley, A. H. Synthesis and characterization of a coordinated oxoborane: Lewis acid stabilization of a boron−oxygen double bond. *J. Am. Chem. Soc.* **2005**, *127*, 4566-4567. (b) Wang, Y.; Hu, H.; Zhang, J.; Cui, C. Comparison of anionic and Lewis acid stabilized N-heterocyclic oxoboranes: their facile synthesis from a borinic acid. *Angew. Chem., Int. Ed.* **2011**, *50*, 2816-2819. (c) Loh, Y. K.; Chong, C. C.; Ganguly, R.; Li, Y.; Vidovic, D.; Kinjo, R. 1,2,4,3-Triazaborole-based neutral oxoborane stabilized by a Lewis acid. *Chem. Commun.* **2014**, *50*, 8561-8564. (d) Swarnarkar, A. K.; Hering-Junghans, C.; Ferguson, M. J.; Mcdonald, R.; Rivard, E. Oxoborane (RBO) complexation and concomitant electrophilic bond activation processes. *Chem. Eur. J.* **2017**, *23*, 8628-8631.

(7) For transition metal oxoboranes: (a) Braunschweig, H.; Radacki, K.; Schneider, A. Oxoboryl complexes: boron-oxygen triple bonds stabilized in the coordination sphere of platinum. *Science* **2010**, *328*, 345-347. (b) Westcott S. A. BO chemistry comes full circle. *Angew. Chem., Int. Ed.* **2010**, *49*, 9045-9046. (c) Braunschweig, H.; Radacki, K.; Schneider, A. Reactivity of an oxoboryl complex toward fluorinated aryl boron reagents. *Chem. Commun.* **2010**, *46*, 6473-6475. (d) Bertsch, S.; Brand, J.; Braunschweig, H.; Hupp, F.; Radacki, K. Platinum oxoboryl complexes as substrates for the formation of 1:1, 1:2, and 2:1 Lewis acid–base adducts and 1,2-dipolar additions. *Chem. Eur. J.* **2015**, *21*, 6278-6285. (e) Miyada, T.; Yamashita, M. Oxygenation of a ruthenium complex bearing a PBP-pincer ligand inducing the formation of a boronato ligand with a weak Ru–O bond. *Organometallics* **2013**, *32*, 5281-5284.

(8) For acid/base free main group E=O bonds: (a) Li, L.; Fukawa, T.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. A stable germanone as the first isolated heavy ketone with a terminal oxygen atom. *Nat. Chem.* **2012**, *4*, 361-365. (b) Alvarado-Beltran, I.; Rosas-Sanchez, A.; Baceiredo, A.; Saffon-Merceron, N.; Branchadell, V.; Kato, T. A fairly stable crystalline silanone. *Angew. Chem., Int. Ed.* **2017**, *56*, 10481-10485. (c) Wendel, D.; Reiter, D.; Porzelt, A.; Altmann, J.; Inoue, S.; Rieger, B. Silicon and oxygen's bond of affection: an acyclic three-coordinate silanone and its transformation to an iminosiloxysilylene. *J. Am. Chem. Soc.* **2017**, *139*, 17193-17198. (d) Rosas-Sanchez, A.; Alvarado-Beltran, I.; Baceiredo, A.; Saffon-Merceron, N.; Massou, S.; Hashizume, D.; Branchadell, V.; Kato, T. Cyclic (amino)(phosphonium bora-ylide)silanone: a remarkable room-temperature-persistent silanone. *Angew. Chem., Int. Ed.* **2017**, *56*, 15916-15920. (e) Wünsche, M. A.; Witteler, T.; Dielmann, F. Lewis base free oxophosphonium ions: tunable, trigonal-planar Lewis acids. *Angew. Chem., Int. Ed.* **2018**, *57*, 7234-7239.

(9) Loh, Y. K.; Ying, L.; Fuentes, M. A.; Do, D. C. H.; Aldridge, S. An N-heterocyclic boryloxy ligand isoelectronic with N-heterocyclic imines: access to an acyclic dioxysilylene and its heavier congeners. *Angew. Chem., Int. Ed.* **2019**, *58*, 4847-4851.

(10) Segawa, Y.; Suzuki, Y.; Yamashita, M.; Nozaki, N. Chemistry of boryllithium: synthesis, structure and reactivity. *J. Am. Chem. Soc.* **2008**, *130*, 16069-16079.

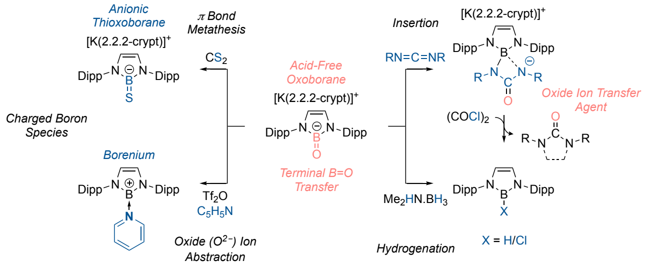
(11) For monomeric thioxoboranes: (a) Wang. H.; Zhang, J.; Hu, H.; Cui, C. Access to B═S and B═Se double bonds via sulfur and selenium insertion into a B−H bond and hydrogen migration. *J. Am. Chem. Soc.* **2010**, *132*, 10998-10999. (b) Jaiswal, K.; Prashanth, B.; Ravi, S.; Shasundar, K. R.; Singh, S. Reactivity of a dihydroboron species: synthesis of a hydroborenium complex and an expedient entry into stable thioxo- and selenoxo-boranes. *Dalton Trans.* **2015**, *44*, 15779-15785. (c) Liu, S.; Legare, M.; Hofmann, A.; Braunschweig, H. A boradiselenirane and a boraditellurirane: isolable heavy analogs of dioxiranes and dithiiranes. *J. Am. Chem. Soc.* **2018**, *140*, 11223-11226. (d) Franz, D.; Irran, E.; Inoue, S. Isolation of a three-coordinate boron cation with a boron–sulfur double bond. *Angew. Chem., Int. Ed.* **2014**, *53*, 14264-14268.

(12) Baraznenok, I. L.; Nenajdenko, V. G.; Balenkova, E. S. Chemical transformations induced by triflic anhydride. *Tetrahedron* **2000**, *56*, 3077-3119.

(13) See for example: Franz, D.; Inoue, S. Cationic complexes of boron and aluminum: an early 21st century viewpoint. *Chem. Eur. J.* **2019**, *25*, 2898-2926.

(14) (a) Dielmann, F.; Back, O.; Henry-Ellinger, M.; Jerabek, P.; Frenking, G.; Bertrand, G. A crystalline singlet phosphinonitrene: a nitrogen atom–transfer agent. *Science* **2012**, *337*, 1526-1528. (b) Schulz, A.; Villinger, A. Stabilized transient R_2PN species. *Angew. Chem., Int. Ed.* **2013**, *52*, 3068-3070. (c) Dielmann, F.; Moore, C. E.; Rheingold, A. L.; Bertrand, G. Crystalline, Lewis base-free, cationic phosphoranimines (iminophosphonium salts). *J. Am. Chem. Soc.* **2013**, *135*, 14071-14073. (d) Dielmann, F.; Andrada, D. M.; Frenking, G.; Bertrand, G. Isolation of bridging and terminal coinage metal-nitrene complexes. *J. Am. Chem. Soc.* **2014**, *136*, 3800-3802. (e) Dielmann, F.; Bertrand, G. Reactivity of a stable phosphinonitrene towards small molecules. *Chem. Eur. J.* **2015**, *21*, 191-198.

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