


Cite this: *Chem. Sci.*, 2019, 10, 9084

All publication charges for this article have been paid for by the Royal Society of Chemistry

## CO<sub>2</sub> reduction with protons and electrons at a boron-based reaction center†

Jordan W. Taylor, Alex McSkimming, Laura A. Essex and W. Hill Harman \*

Borohydrides are widely used reducing agents in chemical synthesis and have emerging energy applications as hydrogen storage materials and reagents for the reduction of CO<sub>2</sub>. Unfortunately, the high energy cost associated with the multistep preparation of borohydrides starting from alkali metals precludes large scale implementation of these latter uses. One potential solution to this issue is the direct synthesis of borohydrides from the protonation of reduced boron compounds. We herein report reactions of the redox series [Au(B<sub>2</sub>P<sub>2</sub>)]<sup>n</sup> (*n* = +1, 0, −1) (B<sub>2</sub>P<sub>2</sub>, 9,10-bis(2-(diisopropylphosphino)phenyl)-9,10-dihydroboranthrene) and their conversion into corresponding mono- and diborohydride complexes. Crucially, the monoborohydride can be accessed *via* protonation of [Au(B<sub>2</sub>P<sub>2</sub>)]<sup>−</sup>, a masked borane dianion equivalent accessible at relatively mild potentials (−2.05 V vs. Fc/Fc<sup>+</sup>). This species reduces CO<sub>2</sub> to produce the corresponding formate complex. Cleavage of the formate complex can be achieved by reduction (*ca.* −1.7 V vs. Fc/Fc<sup>+</sup>) or by the addition of electrophiles including H<sup>+</sup>. Additionally, direct reaction of [Au(B<sub>2</sub>P<sub>2</sub>)]<sup>−</sup> with CO<sub>2</sub> results in reductive disproportionation to release CO and generate a carbonate complex. Together, these reactions constitute a synthetic cycle for CO<sub>2</sub> reduction at a boron-based reaction center that proceeds through a B–H unit generated *via* protonation of a reduced borane with weak organic acids.

Received 7th June 2019  
Accepted 30th July 2019

DOI: 10.1039/c9sc02792k

rsc.li/chemical-science

## Introduction

Since their discovery by Schlesinger and Brown in the 1940s,<sup>1</sup> borohydrides have become ubiquitous reducing agents in the synthesis of fine and commodity chemicals.<sup>2</sup> More recently, borohydrides have attracted interest in energy storage applications,<sup>3</sup> both as a dense and readily handled source of H<sub>2</sub> and in the reduction of CO<sub>2</sub> to fuels such as formic acid and methanol.<sup>4</sup> The first report of the reaction of NaBH<sub>4</sub> with CO<sub>2</sub> dates back to 1955 when Wartik and Pearson described the solution (dimethyl ether) and solid-state reactions with mass-balance and hydrolytic analysis of the products.<sup>5</sup> In 1967, the reaction of NaBH<sub>4</sub> with CO<sub>2</sub> in aqueous conditions was shown to produce sodium formate.<sup>6</sup> The intrinsic role of the borohydride ion in CO<sub>2</sub> reduction was later investigated by Mizuta in 2014 who showed that, in the presence of a catalytic amount of NaBH<sub>4</sub>, BH<sub>3</sub>·THF effectively reduces CO<sub>2</sub> to trimethylboroxine.<sup>7</sup> A year later, Cummins reported the direct reaction of NaBH<sub>4</sub> with CO<sub>2</sub> yields the triformatoborohydride that could be hydrolyzed to yield formic acid.<sup>8</sup> Additional studies over the last decade have found that in the presence of a suitable catalyst,

pinacol borane (HBpin) and catechol borane (HBcat) can reduce CO<sub>2</sub> to a range of products<sup>9</sup> including carbon monoxide<sup>10</sup> and formaldehyde,<sup>11</sup> formic acid,<sup>12</sup> and methanol equivalents.<sup>13</sup>

Despite their broad utility, one drawback to these reagents is the substantial energy required for their production. For example, millions of kg of NaBH<sub>4</sub> are produced each year by the NaH reduction of B(OMe)<sub>3</sub> in the Brown–Schlesinger process.<sup>14</sup>



NaH is prepared from the reaction of metallic Na with H<sub>2</sub> gas,<sup>14</sup> and the reduction of NaCl to metallic Na in the Downs process. The process requires high temperature (>600 °C) and operating potentials of 8 V or more for practical reaction rates.<sup>15</sup> As a result, the stoichiometric reduction of CO<sub>2</sub> with NaBH<sub>4</sub>, or similarly produced B–H species,<sup>16</sup> entails a significant energy cost.

One potential solution to this issue would involve the direct construction of B–H bonds from the protonation of reduced boron compounds accessed at potentials tolerable to common solvents. Such a process would be analogous to the generation of transition metal hydrides *via* the reduction and protonation of a transition metal complex (Fig. 1). Despite the difficulty in accessing doubly reduced boranes,<sup>17</sup> there has been recent progress in the protonation of low valent boron compounds to generate B–H bonds (Fig. 2). In 2006, Nozaki *et al.* reported the isolation of the boryllithium compound LiB(2,6-<sup>i</sup>PrC<sub>6</sub>H<sub>4</sub>)(NCH<sub>2</sub>)<sub>2</sub>,

Department of Chemistry, University of California, Riverside, California, 92521, USA.  
E-mail: hill.harman@ucr.edu

† Electronic supplementary information (ESI) available: Synthetic and experimental details and characterization data. CCDC 1921501–1921506. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc02792k





Fig. 1 Redox-coupled hydride formation at a transition metal complex (top) and borane (bottom) as a strategy for  $CO_2$  electro-reduction to formate.

which reacts as a boryl anion equivalent, and showed that it could be protonated with  $H_2O$  to give the corresponding hydroborane.<sup>18</sup> Bertrand *et al.* have prepared the carbene-stabilized borylene  $(CAAC)_2BH$  ( $CAAC = \text{cyclic (alkyl)(amino)carbene}$ ) that could be protonated with trifluoromethanesulfonic acid (TfOH) to yield the corresponding boronium salt.<sup>19</sup> A related bis(oxazol-2-ylidene)-phenylborylene system reported by Kinjo also produced a B–H moiety *via* protonation with TfOH.<sup>20</sup> Furthermore, Wagner synthesized a diborylmethane dianion and a doubly boron-doped dibenzo[*g,p*]chrysene dianion that could be protonated to yield the corresponding hydride bridged B–H–B species.<sup>21</sup> Additionally, Szymczak *et al.* reported a conceptually relevant series of Mn/Cr-borazine complexes that could be reduced and then protonated to yield a bridging metalborohydride.<sup>22</sup> The reactivities (in particular, towards hydride transfer) of these B–H bonds formed *via* protonation have not been reported.

We recently reported the synthesis of the diphosphine tethered diboraanthracene ligand  $B_2P_2$  (9,10-bis(2-

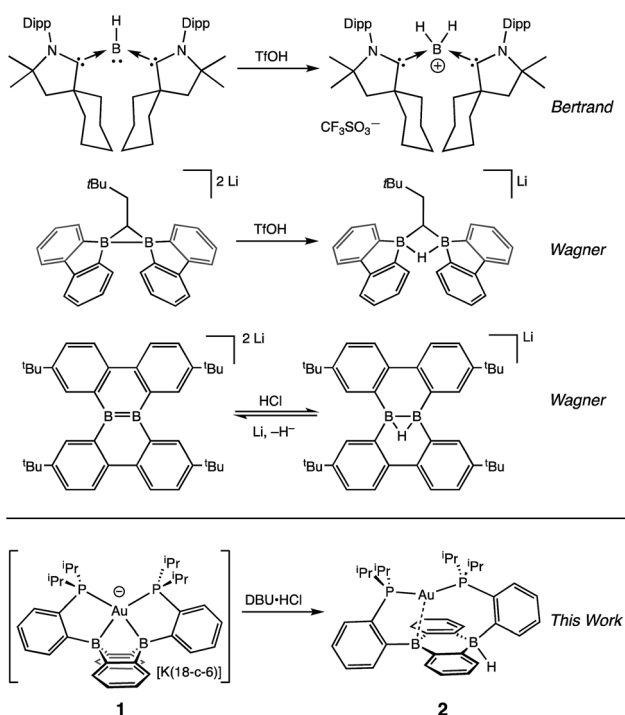


Fig. 2 Protonation of reduced boron compounds to give tetra-coordinate B–H moieties.

(diisopropylphosphino)phenyl)-9,10-dihydroboranthrene) and a series of its gold complexes in three states of charge. The anionic complex,  $[Au(B_2P_2)]^-[K(18-c-6)]$  (**1**), which features an unprecedented boraoauride moiety, could be accessed at remarkably mild potentials ( $-2.05$  V vs.  $Fc/Fc^+$ , MeCN)<sup>23</sup> owing to the formation of a strong 3-centered, 2-electron bond between Au and the two B atoms.<sup>24</sup> Considering that **1** can be thought of as a masked borane dianion, we wondered if protonation of this complex could provide direct access to a hydridic B–H unit (Fig. 2). We herein report the synthesis and characterization of this borohydride complex,  $Au(B_2P_2)H$  (**2**), which can be generated *via* direct hydride reduction of  $Au(B_2P_2)Cl$  (**3**), FLP-type dihydrogen activation, H-atom addition to the boron-centered radical complex  $Au(B_2P_2)$  (**4**) or, most notably, by protonation of **1** with mild organic acids. Borohydride **2** is sufficiently reactive to reduce  $CO_2$  to formate, and cleavage of the resulting B–OCHO bond can be achieved either by addition of an electrophile (including  $H^+$ ) or by one electron reduction. These results collectively represent a synthetic cycle for  $CO_2$  reduction to formate with protons and electrons, with the key finding being the generation of a hydridic borohydride unit *via* protonation of a reduced borane at modest potentials. This reaction sequence, along with Wagner's recent reports of  $CO_2$  hydrogenation<sup>25</sup> and the reductive disproportionation of  $CO_2$  (ref. 26) catalyzed by DBA derivatives, illustrates the promise of redox-active boranes in the reduction of  $CO_2$ , an area dominated by transition metal chemistry.<sup>27</sup> Furthermore, given the recent application of boron-doped graphene to  $CO_2$  electro-reduction,<sup>28</sup> these molecules offer well-defined molecular models<sup>29</sup> of fundamental chemical processes that may underlie small molecule reactivity at doped graphitic carbon surfaces.

## Results and discussion

Our initial synthetic approaches to a B–H containing derivative of  $Au(B_2P_2)$  began with direct hydride for halide substitution (Scheme 1). Addition of 1 equiv.  $K[sec-Bu_3BH]$  to **3** gave borohydride **2** in 89% yield. This complex could also be prepared in good yield by exposing **3** to an excess of  $Et_3SiH$ . Additionally, **2** could be synthesized *via* frustrated Lewis pair (FLP)  $H_2$  activation in the presence of DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene): exposure of a THF solution of equimolar **3** and DBU to 1 atm  $H_2$  resulted in the immediate formation of **2** as judged by  $^1H$ ,  $^{11}B$ , and  $^{31}P$  NMR spectroscopies. This reaction is presumably mediated by the pseudo-three-coordinate boron and is consistent with a relatively weak Au–B interaction in **3**. Single-crystal X-ray diffraction (XRD) studies of **2** show it to be a zwitterion in the solid state with an intact B–H bond on the DBA face opposite the Au center, analogous to the previously reported structure of zwitterion **3** (Fig. 3). The H atom was located in the electron difference map and is bound to a quasi-tetrahedral B atom ( $\sum \angle C-B-C = 340.5^\circ$ ). On the opposite side of the DBA linker, the Au ion is bound by both P donors in a roughly linear fashion ( $\angle P-Au-P = 156.8^\circ$ ) with a single Au–B interaction ( $d_{AuB} = 2.644(1)$  Å) to one nearly-planar B atom ( $\sum \angle C-B-C = 359.8^\circ$ ). The  $^1H$  NMR spectrum of **2** features a signal at 5.09 ppm for a B–H proton resonance with the



Scheme 1 Synthesis of Au(B<sub>2</sub>P<sub>2</sub>)H from H<sup>-</sup>, H<sup>+</sup>, and H<sup>+</sup>.

expected four-line pattern for coupling to a single <sup>11</sup>B atom ( $J_{\text{BH}} = 80$  Hz). The <sup>11</sup>B NMR shows a corresponding doublet at  $-10.01$  ppm ( $J_{\text{BH}} = 80$  Hz) while the <sup>31</sup>P NMR spectrum features two doublets at 58.4 and 55.9 ppm ( $J_{\text{PP}} = 255.0$  Hz), consistent with inequivalent phosphine ligands on the NMR timescale. Given the precedent for H-atom transfer reactivity at boron,<sup>30</sup> we also targeted the synthesis of **2** from the neutral radical species **4** via H-atom addition. Reaction of Au(B<sub>2</sub>P<sub>2</sub>) with one equivalent of Bu<sub>3</sub>SnH produces **2** and Bu<sub>6</sub>Sn<sub>2</sub> over 12 hours via apparent H-atom transfer as judged by NMR of reaction mixtures.

To probe the synthesis of **2** via protonation of **1**, we exposed **1** to a series of organic acids. Addition of one equivalent of solid [Ph<sub>2</sub>NH<sub>2</sub>][Cl] or [2,6-Me<sub>2</sub>pyH][Cl] to CD<sub>3</sub>CN solutions of **1** resulted in immediate effervescence and formation of dark purple reaction mixtures which were revealed by NMR analysis to contain a mixture of H<sub>2</sub>, **3**, and **4**. Fortunately, addition of one equivalent of DBU·HCl to a solution of **1** in CD<sub>3</sub>CN gave rise to a pale-yellow solution exhibiting <sup>1</sup>H, <sup>11</sup>B, and <sup>31</sup>P NMR resonances that matched authentic samples of **2** (Fig. S5–S7†) with no H<sub>2</sub> observed. Furthermore, **2** is stable to treatment with excess DBU·HCl.

With borohydride **2** in hand, we examined its reactivity with CO<sub>2</sub>. Exposure of a C<sub>6</sub>D<sub>6</sub> solution of **2** to 1 atm of CO<sub>2</sub> resulted in

quantitative formation of the corresponding formate complex Au(B<sub>2</sub>P<sub>2</sub>)(O<sub>2</sub>CH) (**5**) within seconds (Scheme 2). The solid-state structure of **5** confirms the insertion of CO<sub>2</sub> into the B–H bond, with the resulting formate ion bound through a single O to one boron atom (Fig. 3). The zwitterionic structure of **5** is analogous to **2** and **3**, with a tetrahedral boron center bound to the formate oxygen ( $\sum \angle \text{C–B–C} = 339.1^\circ$ ) and an intermediate length contact between Au and the non-formate bound B atom ( $d_{\text{AuB}} = 2.632$  Å). The <sup>1</sup>H NMR spectrum of **5** in CDCl<sub>3</sub> is consistent with C<sub>2v</sub> symmetry in solution, with a lone singlet in the <sup>31</sup>P NMR spectrum at 56.1 ppm and <sup>11</sup>B{<sup>1</sup>H} NMR displaying a broad singlet at 26.9 ppm. Similar to **3**, the observed C<sub>2v</sub> symmetry in solution along with a <sup>11</sup>B chemical shift between that of bona fide three- and four-coordinate B centers in DBA containing molecules<sup>17hf</sup> implies rapid exchange of the formate ion between each boron site of the DBA ring, a phenomenon also observed in **3**.<sup>22</sup> The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **5** contains a resonance at 168.2 ppm corresponding to the formate carbon atom, and FTIR spectroscopy revealed a strong band at 1672 cm<sup>-1</sup> for the formate C=O stretch.

Next, we assessed the ability of electrophiles such as TMSCl and HCl to effect B–O bond scission. Treatment of **5** with excess TMSCl resulted in the immediate formation of **3** as judged by <sup>1</sup>H and <sup>31</sup>P NMR along with new resonances for

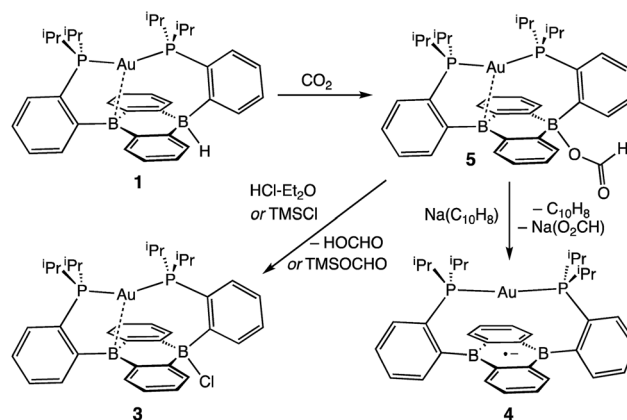
Scheme 2 CO<sub>2</sub> reduction to formate by Au(B<sub>2</sub>P<sub>2</sub>)H.

Fig. 3 Thermal ellipsoid plots (50%) of Au(B<sub>2</sub>P<sub>2</sub>)H (**2**, left) and Au(B<sub>2</sub>P<sub>2</sub>)(O<sub>2</sub>CH) (**5**, right). Unlabeled ellipsoids correspond to carbon. Solvent molecules and most hydrogen atoms have been omitted for clarity.



Fig. 4 Cyclic voltammogram of Au(B<sub>2</sub>P<sub>2</sub>)(O<sub>2</sub>CH) performed in 0.1 M [tBu<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>3</sub>CN at a scan rate of 100 mV s<sup>-1</sup>.



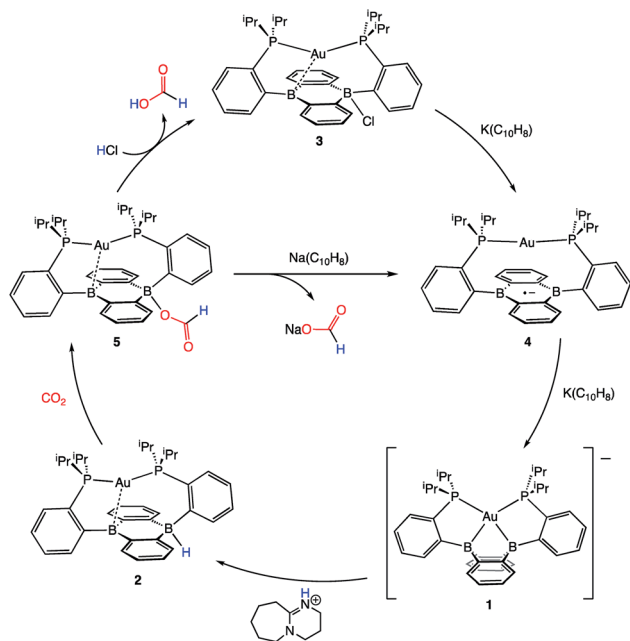


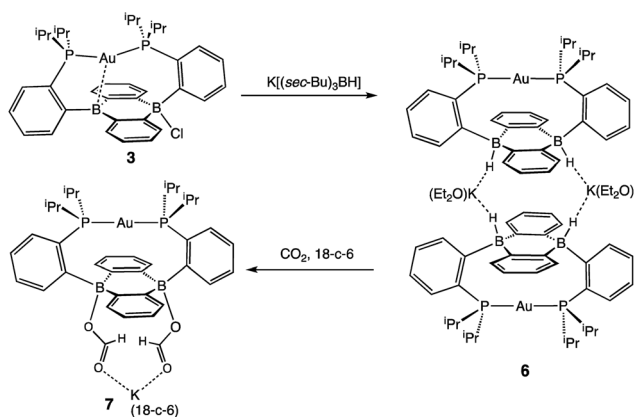
Fig. 5 A closed synthetic cycle for the reduction of  $\text{CO}_2$  to formic acid with protons and electrons mediated by a redox active, metal-stabilized diboraanthracene platform.

trimethylsilylformate (Fig. S13<sup>†</sup>), accomplishing the net hydrosilylation of  $\text{CO}_2$ .<sup>31</sup> While silyl electrophiles have strong precedent to mediate E–O bond cleavage in main group systems,<sup>32</sup> we wondered if a suitable acid would be able to protonate the B–OCHO bond to yield formic acid. To this end, addition of  $[\text{Ph}_2\text{NH}_2][\text{Cl}]$  or DBU·HCl to  $\text{CDCl}_3$  solutions of 5 saw no observable reaction over the course of days at room temperature. However, addition of one equivalent of HCl· $\text{Et}_2\text{O}$  to 5 resulted in the immediate formation of the chloride complex 3 by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy with resonances for  $\text{HCO}_2\text{H}$  observed in the  $^1\text{H}$  NMR spectrum.

Following successful electrophilic B–O bond cleavage in 5 to yield 3, the reductive cleavage of the B–OCHO unit was explored. Cyclic voltammetry (CV) performed on 5 revealed a quasireversible process at  $E_{1/2} = -1.74\text{ V vs. Fc/Fc}^+$  which gave rise to an

oxidative daughter wave at *ca.*  $-1.5\text{ V}$  (Fig. 4). This daughter wave occurs at roughly the same potential as the oxidation of  $[\text{Au}(\text{B}_2\text{P}_2)]^{0/+1}$ , consistent with the hypothesis that one electron reduction of 5 forms  $[\text{5}]^-$  which then undergoes formate dissociation on the CV timescale to afford neutral 4. To unambiguously confirm the liberation of formate ion, 5 was treated with 1 equivalent of  $\text{Na}(\text{C}_{10}\text{H}_8)$  in THF. A turbid, dark-purple solution immediately formed, indicating formation of 4. The precipitated solids were collected by filtration and dissolved in  $\text{D}_2\text{O}$  with  $^1\text{H}$  NMR analysis revealing formation of  $\text{NaCO}_2\text{H}$  (Fig. S12<sup>†</sup>). To our knowledge, this is the only example of reductive cleavage of a B–OCHO bond to yield formate. This process is presumably driven by the accessible one-electron reduction chemistry of 5 ( $-1.74\text{ V vs. Fc/Fc}^+$ ) enabled by the DBA core and speaks to the utility of frontier orbital modulation by incorporation of boron into polycyclic aromatic hydrocarbon frameworks.<sup>33</sup> Collectively, these results outline a synthetic cycle for  $\text{CO}_2$  reduction with protons and electrons mediated exclusively at boron (Fig. 5).

In addition to the monoborohydride chemistry described above, we were able to generate a diborohydride species *via* formal sequential hydride addition to 3. Two equivalents of  $\text{K}[\text{sec-Bu}_3\text{BH}]$  reacted with 3 in  $\text{Et}_2\text{O}$  to give the anionic diborohydride complex  $[\text{Au}(\text{B}_2\text{P}_2)\text{H}_2][\text{K}(\text{Et}_2\text{O})]$  (6) (Scheme 3). Single-crystal XRD reveals 6 to be a dimer in the solid state, (Fig. 6) with two  $[\text{Au}(\text{B}_2\text{P}_2)\text{H}_2]^-$  units bridged by two  $[\text{K}(\text{Et}_2\text{O})]^+$  cations *via* contacts between the B–H and K atoms. The  $[\text{Au}(\text{B}_2\text{P}_2)\text{H}_2]^-$  component features a linear P–Au–P moiety ( $\angle\text{P–Au–P} = 161.9^\circ$ ) that sits above the DBA core with no appreciable interaction between Au and B ( $d_{\text{AuB}} > 3.25\text{ \AA}$ ). The H atoms bound to both B atoms were located on the electron difference map and both B centers exhibit a pseudo-tetrahedral geometry ( $\sum\angle\text{C–B–C} = 337.5^\circ$ ).  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra feature a 4-line pattern and doublet, respectively, for the B–H moieties in 6, analogous to the monoborohydride 2 (Fig. S14<sup>†</sup>). Compound 6 is structurally related to the diborohydride species resulting from  $\text{H}_2$  activation by reduced DBA compounds reported by Wagner.<sup>34</sup>



Scheme 3 Synthesis of Diborohydride 6 and its reactivity with  $\text{CO}_2$ .

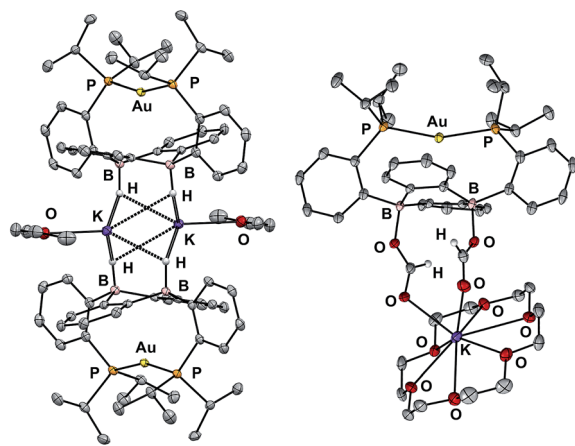


Fig. 6 Thermal ellipsoid plots (50%) of the dimer of  $[\text{Au}(\text{B}_2\text{P}_2)\text{H}_2][\text{K}(\text{Et}_2\text{O})]$  (6, left) and  $[\text{Au}(\text{B}_2\text{P}_2)(\text{O}_2\text{CH})_2][\text{K}(18\text{-c-}6)]$  (7, right). Unlabeled ellipsoids correspond to carbon. Solvent molecules, a disordered crown ether component in 6, and most hydrogen atoms have been omitted for clarity.





Fig. 7 Thermal ellipsoid plots (50%) of the anion  $[\text{Au}(\text{B}_2\text{P}_2)(\text{CO}_3)][\text{K}(18\text{-c-}6)]$  (**8**, left) and  $\text{Au}(\text{B}_2\text{P}_2)(\text{OSiPr}_3)$  (**9**, right). Unlabeled ellipsoids correspond to carbon. Solvent molecules, disordered components, and hydrogen atoms have been omitted for clarity.

Diborohydride **6** is also reactive towards  $\text{CO}_2$  (1 atm), cleanly generating the corresponding diformate complex, which was isolated as its 18-crown-6 adduct,  $[\text{Au}(\text{B}_2\text{P}_2)(\text{O}_2\text{CH}_2)_2][\text{K}(18\text{-c-}6)]$  (**7**). Single-crystal XRD confirmed the insertion of  $\text{CO}_2$  into both B–H bonds, with B atoms puckered out of planarity to accommodate each OCHO unit. Additionally, the formate moieties in **7** were identified by  $^1\text{H}$  NMR (8.34 ppm),  $^{13}\text{C}\{^1\text{H}\}$  NMR (168.2 ppm) and FTIR spectroscopy ( $\text{C}=\text{O}$ ,  $1672\text{ cm}^{-1}$ ).

Having probed the  $[\text{Au}(\text{B}_2\text{P}_2)]$  system for  $\text{CO}_2$  reduction chemistry from its mono- and dihydrides, we additionally explored the direct reaction of  $\text{CO}_2$  with **1**. Wagner *et al.* recently reported that 9,10-dithio-9,10-diborataanthracene reacts with  $\text{CO}_2$  to yield  $\text{CO}_3$  and  $\text{CO}$  *via* reductive disproportionation.<sup>25</sup> Reaction of **1** with 1 atm of  $\text{CO}_2$  in  $\text{C}_6\text{D}_6$  resulted in the immediate formation of a colorless solution with no detectable precipitate. A single crystal suitable for XRD studies was obtained from  $\text{CO}_2$  saturated reaction mixtures and revealed the product to be the carbonate adduct,  $[\text{Au}(\text{B}_2\text{P}_2)\text{CO}_3][\text{K}(18\text{-c-}6)]$  (**8**, Fig. 7) (Scheme 4). The asymmetric unit of **8** contains two crystallographically distinct molecules which are chemically equivalent in gross terms but exhibit minor differences in their geometries, most notably in their B–O distances, which range

from  $1.550(6)\text{ \AA}$  to  $1.578(8)\text{ \AA}$ . This spread of B–O distances is consistent with a soft  $[\text{CO}_3]^{2-}$  binding potential, in agreement with Wagner's results.<sup>25</sup> Solution NMR spectroscopy of **8** is consistent with  $C_{2v}$  symmetry and the  $[\text{CO}_3]^{2-}$  unit was identified by  $^{13}\text{C}\{^1\text{H}\}$  NMR (168.0 ppm) and FTIR ( $1592\text{ cm}^{-1}$ ) spectroscopies with  $^{13}\text{CO}_2$  experiments confirming these assignments (see ESI†).

In order to probe the mechanism of the formation of **8** from **1** and  $\text{CO}_2$ , we explored the reaction by NMR spectroscopy at low temperature. Recent reports on reduced boron-containing heterocycles,<sup>21</sup> offer extensive precedent for the cycloaddition of  $\text{CO}_2$  across the boron atoms, and we sought to probe whether a similar  $\text{CO}_2$  adduct,  $[\text{Au}(\text{B}_2\text{P}_2)\text{CO}_2]^-$  (**1-CO<sub>2</sub>**), might be an intermediate in the formation of **8**. Addition of a single equivalent of  $\text{CO}_2$  to a frozen solution of the anion **1** in  $d_8$ -toluene followed by insertion into a precooled ( $-50\text{ }^\circ\text{C}$ ) NMR spectrometer and subsequent variable temperature NMR monitoring resulted in a 1 : 1 mixture of starting material **1** and the carbonate adduct **8**. When the same experiment was carried out with  $^{13}\text{CO}_2$  enhanced intensity was observed corresponding to the  $\text{Au}(\text{B}_2\text{P}_2)^{13}\text{CO}_3$  resonance at 168.2 ppm along with free  $^{13}\text{CO}$  at 184.5 ppm. These results are consistent with endergonic binding of  $\text{CO}_2$  to the DBA core followed by rapid reaction with a second equivalent of  $\text{CO}_2$  to release  $\text{CO}$  and form **8**, analogous to the mechanism established by Wagner in a related system.<sup>25</sup> As we were unable to observe the putative  $\text{CO}_2$  adduct  $[\text{Au}(\text{B}_2\text{P}_2)\text{CO}_2]^-$ , we attempted to trap it by other chemical means during the reaction of **1** with  $\text{CO}_2$ . Solutions of **1** are stable in the presence of triisopropylsilylchloride (TIPSCl); however, addition of 1 atm  $\text{CO}_2$  to a thawing  $\text{C}_6\text{D}_6$  solution of **1** and TIPSCl resulted in the immediate formation of a pale-yellow solution. Single-crystal XRD studies revealed the product to be the zwitterion  $\text{Au}(\text{B}_2\text{P}_2)(\text{OSi}^i\text{Pr}_3)$  (**9**), which contains a triisopropylsilyloxy anion bound to one B atom (Fig. 7). The  $^{31}\text{P}$  NMR spectrum contains a set of doublets at 56.0 ( $J_{\text{P-P}} = 240\text{ Hz}$ ) and 52.5 ( $J_{\text{P-P}} = 240\text{ Hz}$ ) ppm while the  $^{11}\text{B}$  NMR spectrum featured a broad resonance at 51.5 and a sharper singlet at 2.99 ppm. Two crystallographically distinct molecules of **9** are present in the asymmetric unit although their geometries are essentially identical (Fig. S44†). The formation of **9** occurs with  $\text{CO}$  loss as judged by  $^{13}\text{CO}_2$  labeling experiments. Exposure of **9** to additional  $\text{CO}_2$  (1 atm) did not lead to any further reaction, ruling out additional reaction of the  $-\text{OTIPS}$  moiety with  $\text{CO}_2$  as has been previously observed for metal-siloxide units.<sup>35</sup>

## Conclusions

In conclusion, we have synthesized a reactive borohydride complex, **2**, *via* formal hydride addition, dihydrogen activation, radical H-atom addition, and, most crucially, reduction/protonation. The borohydride unit rapidly inserts  $\text{CO}_2$  to afford the formate complex **5**. Both CV and synthetic studies confirm that **5** can be reduced at  $E_{1/2} = -1.79\text{ V vs. Fe/Fe}^+$  and undergo formate loss to give the neutral radical **4** and formate *via* reductive B–O cleavage. The cleavage of the B–O bond in **5** can also be achieved *via* addition of electrophiles including  $\text{TMSCl}$  or  $\text{HCl}\cdot\text{Et}_2\text{O}$ , to give **3** and  $\text{TMSOCHO}$  or formic acid,



Scheme 4 Reduction of  $\text{CO}_2$  to  $\text{CO}$  by  $[\text{Au}(\text{B}_2\text{P}_2)]^-$ .



respectively. Additionally, direct reaction of the anion **1** with 1 atm of CO<sub>2</sub> results in the extrusion of CO and the formation of carbonate complex **8** *via* the reductive disproportionation of CO<sub>2</sub>. Collectively, these reactions outline a strategy for the reduction of CO<sub>2</sub> with protons and electrons *via* reactive borohydride species generated at redox-active, conjugated boranes, and efforts to extend this chemistry to electrocatalytic systems are underway.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This research was supported by the National Science Foundation (CHE-1752876) and the American Chemical Society Petroleum Research Fund (57314). NMR spectra were collected on instruments funded by an NSF MRI award (CHE-162673) and an Army Research Office instrumentation grant (W911NF-16-1-0523). W. H. H. is a member of the University of California, Riverside Center for Catalysis. Dr Fook Tham and Dr Charlene Tsay are acknowledged for X-ray crystallographic analysis.

## Notes and references

- H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, 1940, **62**, 3429.
- (a) H. C. Brown and S. Krishnamurthy, *Tetrahedron*, 1979, **35**, 567; (b) H. C. Brown, E. J. Mead and B. C. Subba Rao, *J. Am. Chem. Soc.*, 1955, **77**, 6209.
- (a) J. Ma, N. A. Choudhury and Y. Sahai, *Renewable Sustainable Energy Rev.*, 2010, **14**, 183; (b) M. Paskevicius, L. H. Jepsen, P. Schouwink, R. Cerny, D. Ravnsbaek, Y. Filinchuk, M. Dornheim, F. Besenbacher and T. R. Jensen, *Chem. Soc. Rev.*, 2017, **46**, 1565.
- S. Bontemps, *Coord. Chem. Rev.*, 2016, **308**, 117.
- (a) T. Wartik and R. K. Pearson, *J. Am. Chem. Soc.*, 1955, **77**, 1075; (b) T. Wartik and R. K. Pearson, *J. Inorg. Nucl. Chem.*, 1958, **7**, 404.
- F. Eisenberg Jr and A. H. Bolden, *Carbohydr. Res.*, 1967, **5**, 349–350.
- K. Fujiwara, S. Yasuda and T. Mizuta, *Organometallics*, 2014, **33**, 6692.
- I. Knopf and C. Cummins, *Organometallics*, 2015, **34**, 1601.
- S. Bontemps, *Coord. Chem. Rev.*, 2016, **308**, 117–130.
- (a) D. S. Laitar, P. Muller and J. P. Sadighi, *J. Am. Chem. Soc.*, 2005, **127**, 17196; (b) H. Zhao, Z. Lin and T. B. Marder, *J. Am. Chem. Soc.*, 2006, **128**, 15637.
- S. Bontemps, L. Vendler and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2012, **124**, 1703.
- (a) M.-A. Courtemanche, M.-A. Legare, L. Maron and F.-G. Fontaine, *J. Am. Chem. Soc.*, 2014, **136**, 10708; (b) R. Shintani and K. Nozaki, *Organometallics*, 2013, **32**, 2459; (c) H.-W. Suh, L. M. Guard and N. Hazari, *Chem. Sci.*, 2014, **5**, 3859.
- (a) S. Chakraborty, J. Zhang, J. Krause and H. Guan, *J. Am. Chem. Soc.*, 2010, **132**, 8872; (b) M. J. Sgro and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2012, **51**, 11343; (c) C. Das Neves Gomes, E. Biondiaux, P. Thuery and T. Cantat, *Chem.-Eur. J.*, 2014, **20**, 7098; (d) M. D. Anker, M. Arrowsmith, P. Bellham, M. S. Hill, G. Kociok-Kohn, D. J. Liptrot, M. F. Mahon and C. Weetman, *Chem. Sci.*, 2014, **5**, 2826–2830; (e) J. A. B. Abdalla, I. M. Riddlestone, R. Tirfoin and S. Aldridge, *Angew. Chem., Int. Ed.*, 2015, **54**, 5098–5102.
- U. Wietelmann, M. Felderhoff and P. Rittmeyer, Hydrides, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, 2016.
- A. Klemm, G. Hartmann and L. Lange, Sodium and Sodium Alloys, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, 2000.
- Virtually all B–H reagents are ultimately derived from alkali metal hydrides or NaBH<sub>4</sub>. See ref. 14.
- (a) H. Asakawa, K.-H. Lee, K. Furukawa, Z. Lin and M. Yamashita, *Chem.-Eur. J.*, 2015, **21**, 4267; (b) C.-W. Chiu and F. P. Gabbai, *Organometallics*, 2008, **27**, 1657; (c) C.-W. Chiu, Y. Kim and F. P. Gabbai, *J. Am. Chem. Soc.*, 2009, **131**, 60; (d) J. Edwin, M. Bochmann, M. C. Boehm, D. E. Brennan, W. E. Geiger, C. Krueger, J. Pebler, H. Pritzkow and W. Siebert, *J. Am. Chem. Soc.*, 1983, **105**, 2582; (e) G. E. Herberich, B. Buller, B. Hessner and W. Oschmann, *J. Organomet. Chem.*, 1980, **195**, 253; (f) E. Januszewski, M. Bolte, H.-W. Lerner, M. Holthausen and M. Wagner, *Dalton Trans.*, 2013, **42**(38), 13826; (g) R. J. Kwaan, J. C. Harlan and J. R. Norton, *Organometallics*, 2001, **20**, 3818; (h) A. Lorbach, A. Hubner and M. Wagner, *Dalton Trans.*, 2012, **41**, 6048; (i) P. Muller, B. Gangnus, H. Pritzkow, H. Schulz, M. Stephan and W. Siebert, *J. Organomet. Chem.*, 1995, **487**, 235.
- Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113.
- R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking and G. Bertrand, *Science*, 2011, **333**, 610.
- L. Kong, Y. Li, R. Ganguly, D. Vidovic and R. Kinjo, *Angew. Chem., Int. Ed.*, 2014, **53**, 9280.
- (a) A. Hübner, T. Kaese, M. Diefenbach, B. Endeward, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *J. Am. Chem. Soc.*, 2015, **137**, 3705; (b) T. Kaese, H. Budy, M. Bolte, H.-W. Lerner and M. Wagner, *Angew. Chem., Int. Ed.*, 2017, **56**, 7546.
- (a) T. J. Carter, J. W. Kampf and N. K. Szymczak, *Angew. Chem., Int. Ed.*, 2012, **51**, 13168; (b) T. J. Carter, J. Y. Wang and N. K. Szymczak, *Organometallics*, 2014, **33**, 1540; (c) T. J. Carter, Z. M. Heiden and N. K. Szymczak, *Chem. Sci.*, 2015, **6**, 7258.
- J. W. Taylor, A. McSkimming, M.-E. Moret and W. H. Harman, *Angew. Chem., Int. Ed.*, 2017, **56**, 10413.
- Wagner has recently shown that C-halogenation can render DBA derivatives significantly easier to reduce: S. Brend'amour, J. Gilmer, M. Bolte, H.-W. Lerner and M. Wagner, *Chem.-Eur. J.*, 2018, **24**, 16910–16918.



- 25 E. von Grotthuss, S. E. Prey, M. Bolte, H.-W. Lerner and M. Wagner, *J. Am. Chem. Soc.*, 2019, **141**, 6082.
- 26 E. von Grotthuss, S. E. Prey, M. Bolte, H.-W. Lerner and M. Wagner, *Angew. Chem., Int. Ed.*, 2018, **57**, 16491.
- 27 (a) E. Benson, C. Kubiak, A. Sathrum and J. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89; (b) A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer and G. L. Waldrop, *Chem. Rev.*, 2013, **113**, 6621; (c) J. Qiao, Y. Liu, F. Hong and J. A. Zhang, *Chem. Soc. Rev.*, 2014, **43**, 631; (d) C. Costentin, M. Robert and J.-M. Savéant, *Chem. Soc. Rev.*, 2013, **42**, 2423.
- 28 (a) N. Srekanth, M. A. Nazrulla, T. V. Vineesh, K. Sailaja and K. L. Phani, *Chem. Commun.*, 2015, **51**, 16061; (b) T. B. Tai and M. T. Nguyen, *Chemistry*, 2013, **19**, 2942.
- 29 (a) J. W. Taylor, A. McSkimming, C. F. Guzman and W. H. Harman, *J. Am. Chem. Soc.*, 2017, **139**, 11032; (b) D. Wu, L. Kong, Y. Li, R. Ganguly and R. Kinjo, *Nat. Commun.*, 2015, **6**, 7340.
- 30 (a) Y. Su and R. Kinjo, *Coord. Chem. Rev.*, 2017, **352**, 346; (b) P.-Y. Feng, Y.-H. Liu, T.-S. Lin, S.-M. Peng and C.-W. Chiu, *Angew. Chem., Int. Ed.*, 2014, **53**, 6237; (c) Y. Su, Y. Li, R. Ganguly and R. Kinjo, *Chem. Sci.*, 2017, **8**, 7419; (d) B. Wang, Y. Li, R. Ganguly, R. D. Webster and R. Kinjo, *Angew. Chem., Int. Ed.*, 2018, **57**, 7826.
- 31 F. J. Fernández-Alvarez, A. M. Aitani and L. A. Oro, *Catal. Sci. Technol.*, 2014, **4**, 611–624.
- 32 A. Schnurr, H. Vitze, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2010, **29**, 6012.
- 33 (a) C. A. Jaska, D. J. H. Emslie, M. J. D. Bosdet, W. E. Piers, T. S. Sorensen and M. Parvez, *J. Am. Chem. Soc.*, 2006, **128**, 10885; (b) Z. Zhang, E. S. Penev and B. I. Yakobson, *Chem. Soc. Rev.*, 2017, **46**, 6746; (c) V. M. Hertz, M. Bolte, H.-W. Lerner and M. Wagner, *Angew. Chem., Int. Ed.*, 2015, **54**, 8800; (d) B. Su and R. Kinjo, *Synthesis*, 2017, **49**, 2985.
- 34 E. von Grotthuss, M. Diefenbach, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *Angew. Chem., Int. Ed.*, 2016, **55**, 14067–14071.
- 35 (a) W. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2011, **133**, 9708; (b) A. N. Kornev, T. A. Chesnokova, E. V. Zhezlova, L. N. Zakharov, G. K. Fukin, Y. A. Kursky, G. A. Domrachev and P. D. Lickiss, *J. Organomet. Chem.*, 1999, **587**, 113.

