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## Dehydrogenation of iron amido-borane and resaturation of the imino-borane complex†

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We report on the first isolation and structural characterization of an iron phosphinoimino-borane complex  $\text{Cp}^*\text{Fe}(\eta^2\text{-H}_2\text{B}=\text{NC}_6\text{H}_4\text{PPh}_2)$  by dehydrogenation of iron amido-borane precursor  $\text{Cp}^*\text{Fe}(\eta^1\text{-H}_3\text{B-NHC}_6\text{H}_4\text{PPh}_2)$ . Significantly, regeneration of the amido-borane complex has been realized by protonation of the iron(II) imino-borane to the amino-borane intermediate  $[\text{Cp}^*\text{Fe}(\eta^2\text{-H}_2\text{B-NHC}_6\text{H}_4\text{PPh}_2)]^+$  followed by hydride transfer. These new iron species are efficient catalysts for 1,2-selective transfer hydrogenation of quinolines with ammonia borane.

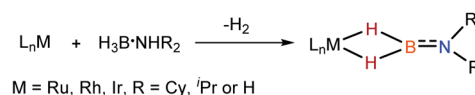
Because of relevance to  $\text{H}_2$  storage<sup>1–10</sup> and hydrogenation catalysis,<sup>11–15</sup> metal amine-borane complexes<sup>16–18</sup> and their dehydrogenated forms, such as amino-boranes<sup>20–22</sup> and imino-boranes<sup>4</sup> are arising as a significant family in organometallic chemistry. In transition metal-catalyzed hydrocoupling of amine-boranes and related transfer hydrogenations, the interactions between the metal and the borane fragment are essential to dehydrogenation and the consequent transformations.<sup>16–20</sup> Specifically, amino-borane complexes containing a  $\text{M-H}_2\text{B}=\text{NR}_2$  moiety are the primary dehydrogenated species and are often identified as a resting point in the catalysis (Scheme 1a).<sup>20–22</sup> Management of reversible dehydrogenation–regeneration reactions on a  $\text{M-BH}_2=\text{NR}_2$  platform could provide a strategy with which to design efficient catalysts capable of operating sustainable syntheses.

Wider exploration of metal amino-borane chemistry is challenging since  $\text{M-H}_2\text{B}=\text{NH}_2$  species are very reactive toward  $\text{H}_2$  release. In 2010, Aldridge *et al.* reported the isolation of  $[(\text{IMes})_2\text{Rh}(\text{H})_2(\eta^2\text{-H}_2\text{B}=\text{NR}_2)]$  and  $[(\text{IMes})_2\text{Ir}(\text{H})_2(\eta^2\text{-H}_2\text{B}=\text{NR}_2)]$  from the metal-catalyzed dehydrogenation of  $\text{R}_2\text{-HN}\cdot\text{BH}_3$ .<sup>21a</sup> At the same time, Alcaraz and Sabo-Etienne reported the preparation of  $(\text{PCy}_3)_2\text{Ru}(\text{H})_2(\eta^2\text{-H}_2\text{B}=\text{NH}_n\text{Me}_{2-n})$  ( $n = 0\text{--}2$ ) complexes<sup>22a</sup> by the dehydrogenation of amine-boranes with the corresponding ruthenium precursors. Subsequently, a straightforward synthesis of Ru, Rh, and Ir amino-borane complexes by reaction of  $\text{H}_2\text{B}=\text{NR}_2$  ( $\text{R} = \text{iPr}$  or  $\text{Cy}$ ) with the bis(hydrogen) complexes of  $\text{M}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2$  or

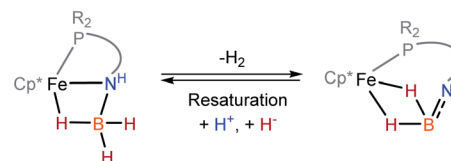
$[\text{CpRu}(\text{PR}_3)_2]^+$  fragments was developed.<sup>21b,22b</sup> Turculet *et al.* have shown that the ruthenium-alkoxide complex is able to activate  $\text{H}_3\text{B}\cdot\text{NHR}_2$  producing hydrido ruthenium complex.<sup>23</sup> Notably, Weller and Macgregor found that dehydrocoupling of ammonia-borane by  $[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\text{Rh}(\eta^6\text{-C}_6\text{H}_5\text{F})]$  affords a  $\mu$ -amino-borane bimetallic Rh complex, in which the simplest  $\text{H}_2\text{B}=\text{NH}_2$  moiety is trapped on a rhodium dimer.<sup>20a</sup>

Although iron-catalyzed hydrocoupling of amine-boranes has attracted great interest,<sup>24–29</sup> iron amine-borane complexes, their dehydrogenated derivatives, and especially the catalysis relevant to organic synthesis are largely unexplored. Recently, Kirchner *et al.* reported a pincer-type iron complex generated by protonation of the borohydride iron complex  $(\text{PNP})\text{Fe}(\text{H})(\eta^2\text{-BH}_4)$  with ammonium salts.<sup>30</sup> Inspired by earlier research on  $\text{M-H}_2\text{B}=\text{NR}_2$  chemistry, we intended to establish the reversible conversions of amino-borane complexes and their dehydrogenated forms in a synthetic piano-stool iron system. Herein, we report dehydrogenation of iron amido-borane complex  $\text{Cp}^*\text{Fe}(\eta^1\text{-H}_3\text{B-NHC}_6\text{H}_4\text{PPh}_2)$  (2) ( $\text{Cp}^* = \text{Me}_5\text{C}_5^-$ ) to the imino-borane complex  $\text{Cp}^*\text{Fe}(\eta^2\text{-H}_2\text{B}=\text{NC}_6\text{H}_4\text{PPh}_2)$  (3), and

a) Fundamental step involved in catalytic amine-borane dehydrogenation



b) Hypothetical dehydrogenation-regeneration of iron amido-borane



Scheme 1 Schematic representation of metal-based amine-borane dehydrogenation.

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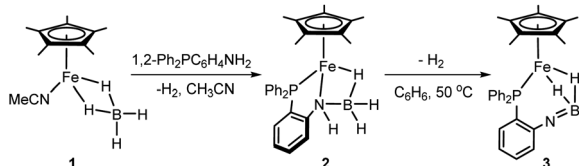


resaturation of the imino-borane by stepwise protonation and hydride transfer (Scheme 1b). This new class of iron species is capable of catalyzing 1,2-selective transfer hydrogenation of quinolines with  $\text{H}_3\text{N}\cdot\text{BH}_3$ .

To synthesize the iron amido-borane complex, a new monomer, the iron tetrahydridoborate precursor  $\text{Cp}^*\text{Fe}(\eta^2\text{-BH}_4)(\text{NCMe})$  (**1**), was prepared *in situ* by the reaction of  $[\text{Cp}^*\text{Fe}(\text{NCMe})_3]\text{PF}_6$  with  $\text{Bu}_4\text{NBH}_4$  in acetonitrile at room temperature for 5 min. Such ferrous borohydrides have been documented only rarely,<sup>31</sup> since they are prone to form polynuclear iron borate clusters.<sup>32,33</sup> The  $^{11}\text{B}$  NMR spectrum of the reaction solution shows a quintet at  $\delta$  15.4 ( $J_{\text{BH}} = 88$  Hz) for the  $\text{BH}_4^-$  ligand of **1**, and this stands in contrast to the signal at  $\delta$   $-32.0$  observed for  $\text{Bu}_4\text{NBH}_4$ . Upon storing the reaction mixture at  $-30$  °C overnight, single crystals suitable for X-ray diffraction were obtained. Crystallographic analysis confirmed the structure of **1** as a piano-stool iron tetrahydridoborate compound (ESI, Fig. S1†).

Addition of phosphinoamine ligand 1,2- $\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2$  to a solution of **1** in acetonitrile caused an instantaneous color change from deep blue to dark brown (Scheme 2). ESI-MS studies indicated the production of the iron amido-borane compound (**2**) with  $m/z = 481.1793$  (calcd  $m/z = 481.1770$ ), which was isolated in 87% yield. NMR spectra showed a boron resonance at  $\delta$   $-17.5$ , and a phosphorus resonance at  $\delta$  85.9. The  $^1\text{H}$  NMR spectrum exhibits a characteristic hydride signal at  $\delta$   $-13.98$ , which is assigned to the bridging hydride Fe–H–B. Owing to exchange between the hydrogen atoms at the boron,<sup>34</sup> the terminal B–H resonances in the  $^1\text{H}$  NMR spectrum are very broad and are obscured by the distinct  $\text{Cp}^*$  signals. To assign the B–H hydride signals, the deuterated compound  $\text{Cp}^*\text{Fe}(\text{D}_3\text{B-NHC}_6\text{H}_4\text{PPh}_2)$  (*d*-2) was synthesized from  $\text{Cp}^*\text{Fe}(\text{BD}_4)(\text{NCMe})$ . In addition to the Fe–D–B signal at  $\delta$   $-13.98$ , the  $^2\text{H}$  NMR spectrum of *d*-2 displayed discrete peaks at  $\delta$  2.23 and 0.19 for the terminal B–D hydrides (Fig. 1).

When a  $\text{C}_6\text{H}_6$  solution of **2** was held at 50 °C for 6 h the dehydrogenated imino-borane compound (**3**) was produced in 92% yield. The ESI-MS spectrum of **3** has a strong peak at  $m/z$  479.1626 (calcd  $m/z = 479.1637$ ) which can be compared to the peak at  $m/z = 481.1793$  for **2**. The isotopic distributions match well with the calculated values (see Fig. S3†). GC analysis shows that the reaction produced  $\text{H}_2$  nearly quantitatively (see Fig. S4†). In solution, the  $^{31}\text{P}$  NMR spectrum of **3** displays a sharp signal at  $\delta$  71.9, in contrast to the peak at  $\delta$  85.9 for **2**. The  $^{11}\text{B}$  resonance shifts significantly, from  $\delta$   $-17.5$  for **2** to  $\delta$  42.7 for **3** (Fig. S16†), and is particularly diagnostic of a three-coordinate boron atom.<sup>21,35</sup> This result indicates the B=N



Scheme 2 Synthetic route to imino-borane complex.

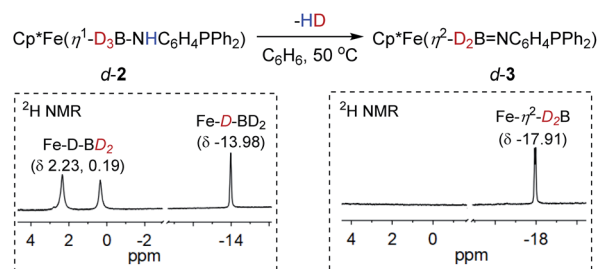


Fig. 1  $^2\text{H}$  NMR spectra for dehydrogenation of *d*-2 to *d*-3.

double bond character in the dehydrogenated form of the amido-borane complex. In the  $^1\text{H}$  NMR spectrum, the Fe–H–B signal was observed at  $\delta$   $-17.91$  with the integral of 2H, and no characteristic signal for a terminal B–H hydride was found. To confirm the formation of an imino-borane compound, the hydrogen decoupling was also carried out with compound *d*-2 and monitored by  $^2\text{H}$  NMR spectra. Only a deuterium signal was observed at  $\delta$   $-17.91$  for Fe–D–B, indicating the formation of *d*-3 (Fig. 1). When the dehydrogenation was conducted in a J-Young tube in  $\text{C}_6\text{D}_6$ , a characteristic triplet corresponding to HD appeared at  $\delta$  4.43 ( $J_{\text{HD}} = 45$  Hz) in the  $^1\text{H}$  NMR spectrum (Fig. S18†).<sup>36</sup>

The structures of **2** and **3** were verified by X-ray crystallographic analysis (Fig. 2). Consistent with NMR spectroscopic analysis, the  $\text{BH}_3$  moiety in **2** is stabilized by one of the B–H bonds binding at the Fe–NH unit to form an Fe–H–B–N four-membered metallacycle. This metal–ligand cooperative binding mode increased the B–H bond length in the bridging B–H(1) bond to 1.362 Å vs. 1.129 Å and 1.121 Å for the two terminal B–H bonds. The B–N bond length of 1.545(3) Å in **2** is slightly shorter than that in  $\text{H}_3\text{B}\cdot\text{NH}_3$  ( $d_{\text{B-N}} = 1.58(2)$  Å).<sup>37</sup> Crystallographic analysis of **3** confirmed an imino-borane complex with a  $\text{Cp}^*\text{Fe}(\eta^2\text{-H}_2\text{B}=\text{NC}_6\text{H}_4\text{PPh}_2)$  framework. After dehydrogenation of **2**, striking structural changes were observed. The N atom

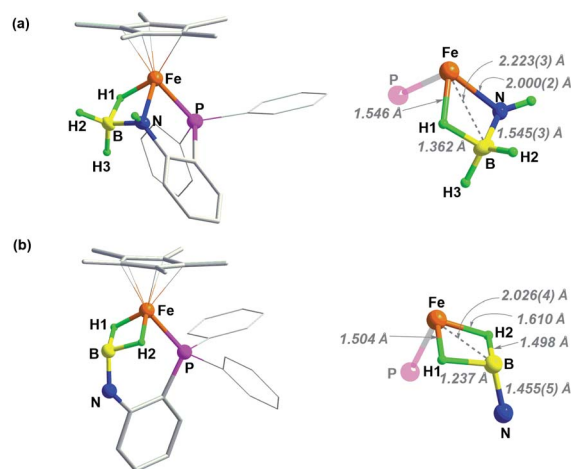
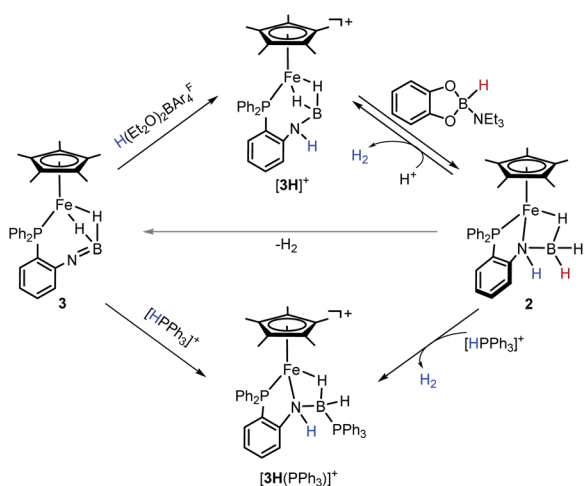


Fig. 2 Solid-state structure (50% probability thermal ellipsoids) of (a) complex **2** and (b) **3**. For clarity, hydrogen atoms of  $\text{Cp}^*$  and phenyl rings are omitted.

has been become detached from Fe, while the BH<sub>2</sub> fragment acts as a bis(σ-borane) ligand coordinated to the metal center.<sup>21–23</sup> The B–N bond distance of 1.455(5) Å in **3** is shorter by 0.09 Å than that in **2**, and is close to that reported for the cyclic trimer borazine (1.4355(21) Å).<sup>38</sup> Combined with the NMR results, the B–N bond length in **3** suggests some double bond character.<sup>21,22</sup> As the imino-borane fragment is tethered in the coordination sphere, the boron center adopts a quasi-tetrahedral geometry, and the B–N bond appears to be partially sp<sup>3</sup> hybridized. Dehydrogenation of the amido-borane complex also caused the decrease of the Fe...B distances from 2.223(3) Å to 2.026(4) Å which is shorter than the sum of the covalent radii of Fe and B atom (2.16 Å), indicating that the borane and the metal are bonded.

Notably, the amido-borane compound **2** can be regenerated by stepwise protonation of **3** and transfer of a hydride (Scheme 3). Complex **3** reacts readily with H(Et<sub>2</sub>O)<sub>2</sub>BAR<sub>4</sub><sup>F</sup> in C<sub>6</sub>H<sub>5</sub>F. The reaction solution was analyzed by ESI-MS spectroscopy, which showed an ionic peak at *m/z* = 480.1726 (calcd *m/z* = 480.1715), suggesting the formation of [3H]<sup>+</sup>. Alternatively, the reaction of complex **2** with H(Et<sub>2</sub>O)<sub>2</sub>BAR<sub>4</sub><sup>F</sup> unambiguously provides [3H]<sup>+</sup> and produces H<sub>2</sub>. X-ray crystallographic analysis reveals that the resulting cationic complex [3H]<sup>+</sup> exhibits a similar framework to its imino-borane precursor (**3**). The BH<sub>2</sub> moiety retains a binding mode of the bis(σ-BH<sub>2</sub>) fashion (Fig. 3). In contrast, the B–N distance in [3H]<sup>+</sup> (1.586(6) Å) is extended by 0.13 Å and the [3H]<sup>+</sup> framework becomes much less compact than that of **3**. Probably due to the fluxional structure of the seven-membered Fe–P–C–C–N–B(H) ring, the solution of [3H][BAR<sub>4</sub><sup>F</sup>] gives broad <sup>1</sup>H NMR resonances even at –60 °C. The phosphorus resonance arose at δ 72.0 as a singlet when the solution sample was cooled to –40 °C (Fig. S20 and S21†).

In [3H]<sup>+</sup>, the boron is coordinatively unsaturated, as manifested by its interaction with a σ-donor. For instance, treatment of **2** with [HPPH<sub>3</sub>][BAR<sub>4</sub><sup>F</sup>] (p*K*<sub>a</sub><sup>MeCN</sup> = 7.6)<sup>39</sup> provides a Ph<sub>3</sub>P-stabilized borane complex, [3H(PPh<sub>3</sub>)]<sup>+</sup> (*m/z* = 742.2620, calcd *m/z* = 742.2626). The <sup>1</sup>H NMR spectrum of [3H(PPh<sub>3</sub>)]<sup>+</sup> exhibits



Scheme 3 Conversions of iron imino-borane, amino-borane and amido-borane complexes.

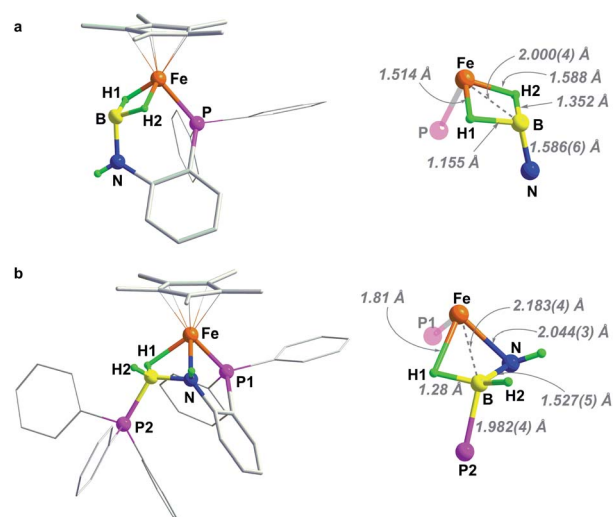
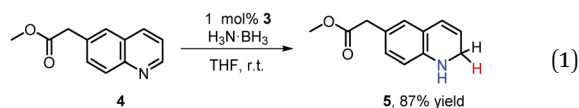


Fig. 3 Solid-state structures of (a) complex [3H]<sup>+</sup> and (b) [3H(PPh<sub>3</sub>)]<sup>+</sup>. For clarity, counterion [BAR<sub>4</sub><sup>F</sup>]<sup>–</sup>, hydrogen atoms of Cp\* and phenyl rings have been omitted.

an NH resonance at δ 4.68, suggesting that protonation occurred at the N site. The distinctive upfield hydride signal for Fe–H–B is observed at δ –15.58. In the <sup>31</sup>P NMR spectrum, two phosphorus signals at δ 78.90 and –1.26 correspond to the Fe–P and the B–P resonances, respectively. The <sup>11</sup>B signal at δ –13.72 indicates a tetracoordinated boron, which is further confirmed by crystallographic analysis of [3H(PPh<sub>3</sub>)]<sup>+</sup> (Fig. 3). In the solid-state structure, a Ph<sub>3</sub>P molecule is bound to the B center (*d*<sub>B–P</sub> = 1.982(4) Å), leading to the formation of a new Fe–H–B–N four-membered metallacycle. As an amido-borane complex, [3H(PPh<sub>3</sub>)]<sup>+</sup> has a B–N bond length of 1.527(5) Å, somewhat shorter than 1.545(3) Å in **2**.

After attaching a proton at the N atom, we subsequently explored restoration of the original borane moiety. Treatment of freshly prepared [3H][BAR<sub>4</sub><sup>F</sup>] in fluorobenzene with catecholborane-NEt<sub>3</sub> adduct (δ<sub>B</sub> = 10.56, *J*<sub>HB</sub> = 142.4 Hz)<sup>40</sup> results in the regeneration of **2**, as evidenced by the NMR spectra (Fig. S29 and S30†). The <sup>1</sup>H NMR spectrum of the reaction mixture displays a characteristic hydride signal at –13.97 ppm, indicating the recovery of the iron amido-borane complex. On the other side, concomitant formation of the borenium ion (δ<sub>B</sub> = 13.86) was also observed in the <sup>11</sup>B NMR spectrum, which agrees with the hydride transfer from the organohydride reagent to [3H]<sup>+</sup>. It was interesting that the ion [3H]<sup>+</sup> is stable towards 5,6-dihydrophenanthridine and Hantzsch ester. These results indicate that the hydride-donating ability (Δ*G*<sub>H<sup>–</sup></sub>) of **2** is in the range of 55–59 kcal mol<sup>–1</sup>.<sup>41</sup> The reactive nature of the hydride in **2** was demonstrated by the reaction with [HPPH<sub>3</sub>][BAR<sub>4</sub><sup>F</sup>], which produces [3H(PPh<sub>3</sub>)]<sup>+</sup> and releases H<sub>2</sub> (Scheme 3).



The metal amine-borane complexes and their dehydrogenated derivatives are implicated throughout the catalytic cycle of amine-borane dehydrogenation. We found both the iron complexes **2** and **3** are efficient catalysts for  $\text{H}_3\text{N}\cdot\text{BH}_3$  dehydrogenation at room temperature. In the presence of 1 mol% catalyst, a THF solution of  $\text{H}_3\text{N}\cdot\text{BH}_3$  (1.0 mmol) generates about 2.2 equivalent of  $\text{H}_2$  within 6 h based on GC quantification (Fig. S33†). More importantly, such catalytic dehydrocoupling systems allow for selective transfer hydrogenation of quinolines to dihydroquinolines, which are valuable synthons leading to many bio-active compounds.<sup>42</sup> For instance, addition of methyl-6-quinolineacetate (**4**) to the catalytic system containing one equiv. of  $\text{H}_3\text{N}\cdot\text{BH}_3$  and 1 mol% of **3** gave 1,2-dihydro-methyl-6-quinolineacetate (**5**) in excellent yield within 6 h (eqn (1)). The outcome of this reaction was unaffected by switching the catalyst from **3** to **2**, or by use of excess reducing agent or by an increase in the reaction temperature (Table S1†).

## Conclusions

By tethering the N–B unit within the coordination sphere, we have demonstrated an example of imino-borane iron(II) complex isolated from dehydrogenation of its phosphinoamido-borane precursor, and have realized the regeneration of an Fe– $\text{H}_3\text{B}$ –N(H)Ar fragment by submitting the dehydrogenated imino-borane to sequential protonation and hydride transfer reactions. Based on the dehydrogenation of ammonia-borane catalyzed by the two iron species, the catalytic reduction of quinoline to 1,2-dihydroquinoline was established. This work provides a new perspective for the studies of reversible conversions between amine-borane complexes and the dehydrogenated forms, and exploration of iron-based catalysis for important organic transformations.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## Notes and references

- Z. Huang, S. Wang, R. D. Dewhurst, N. V. Ignat'ev, M. Finze and H. Braunschweig, *Angew. Chem., Int. Ed.*, 2020, **59**, 8800.
- E. M. Leitao, T. Jurca and I. Manners, *Nat. Chem.*, 2013, **5**, 817.
- A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner, J. C. Gordon, T. Nakagawa, K. C. Ott, P. Robinson and M. Vasiliu, *Science*, 2011, **331**, 1426.
- L. Winner, W. C. Ewing, K. Geetharani, T. Dellermann, B. Jouppi, T. Kupfer, M. Schafer and H. Braunschweig, *Angew. Chem., Int. Ed.*, 2018, **57**, 12275.
- Z. Tang, X. Chen, H. Chen, L. Wu and X. Yu, *Angew. Chem., Int. Ed.*, 2013, **52**, 5832.
- (a) A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.*, 2010, **110**, 4079; (b) E. M. Leitao, N. E. Stubbs, A. P. M. Robertson, H. Helten, R. J. Cox, G. C. Lloyd-Jones and I. Manners, *J. Am. Chem. Soc.*, 2012, **134**, 16805.
- B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus, B. S. Scott and H. Frances, *Angew. Chem., Int. Ed.*, 2009, **48**, 6812.
- C. W. Yoon and L. G. Sneddon, *J. Am. Chem. Soc.*, 2006, **128**, 13992.
- W. Luo, P. G. Campbell, L. N. Zakharov and S.-Y. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 19326.
- H. Helten, A. P. M. Robertson, A. Staubitz, J. R. Vance, M. F. Haddow and I. Manners, *Chem.–Eur. J.*, 2012, **18**, 4665.
- S. Lau, D. Gasperini and R. Webster, *Angew. Chem., Int. Ed.*, 2020, DOI: 10.1002/anie.202010835.
- M. Pang, J.-Y. Chen, S. Zhang, R.-Z. Liao, C.-H. Tung and W. Wang, *Nat. Commun.*, 2020, **11**, 1249.
- S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.-P. Luo and Q. Liu, *J. Am. Chem. Soc.*, 2016, **138**, 8588.
- S. Bhunya, T. Malakar, G. Ganguly and A. Paul, *ACS Catal.*, 2016, **6**, 7907.
- (a) C. C. Chong and R. Kinjo, *ACS Catal.*, 2015, **5**, 3238; (b) C. C. Chong, H. Hirao and R. Kinjo, *Angew. Chem., Int. Ed.*, 2015, **54**, 190.
- (a) T. M. Douglas, A. B. Chaplin, A. S. Weller, X. Z. Yang and M. B. Hall, *J. Am. Chem. Soc.*, 2009, **42**, 15440; (b) T. M. Douglas, A. B. Chaplin and A. S. Weller, *J. Am. Chem. Soc.*, 2008, **130**, 14432.
- J. W. Nugent, M. García-Melchor and A. R. Fout, *Organometallics*, 2020, **39**, 2917.
- T.-P. Lin and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 15310.
- (a) C. Y. Tang, A. L. Thompson and S. Aldridge, *J. Am. Chem. Soc.*, 2010, **132**, 10578; (b) M. O'Neil, D. A. Addy, I. Riddlestone, M. Kelley, N. Phillips and S. Aldridge, *J. Am. Chem. Soc.*, 2011, **133**, 11500.
- (a) A. Kumar, N. A. Beattie, S. D. Pike, S. A. Macgregor and A. S. Weller, *Angew. Chem., Int. Ed.*, 2016, **55**, 6651; (b) V. Pons, R. T. Baker, N. K. Szymczak, D. J. Heldebrant, J. C. Linehan, M. H. Matus, D. J. Grant and D. A. Dixon, *Chem. Commun.*, 2008, 6597.
- (a) C. Y. Tang, A. L. Thompson and S. Aldridge, *Angew. Chem., Int. Ed.*, 2010, **49**, 921; (b) D. Vidovic, D. A. Addy, T. Kramer, J. McGrady and S. Aldridge, *J. Am. Chem. Soc.*, 2011, **133**, 8494.
- (a) G. Alcaraz and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2010, **49**, 918; (b) G. Alcaraz, A. B. Chaplin, C. J. Stevens, E. Clot, L. Vendier, A. S. Weller and S. Sabo-Etienne, *Organometallics*, 2010, **29**, 5591.
- M. C. MacInnis, R. McDonald, M. J. Ferguson, S. Tobisch and L. Turculet, *J. Am. Chem. Soc.*, 2011, **133**, 13622.
- (a) R. J. Keaton, J. M. Blacquièrre and R. T. Baker, *J. Am. Chem. Soc.*, 2007, **129**, 1844; (b) R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P.-H. Lin, S. Maguire, M. Murugesu, B. L. Scott and N. C. Smythe, *J. Am. Chem. Soc.*, 2012, **134**, 5598.

- 25 (a) J. R. Vance, A. Schäfer, A. P. M. Robertson, K. Lee, J. Turner, G. R. Whittell and I. Manners, *J. Am. Chem. Soc.*, 2014, **136**, 3048; (b) J. R. Vance, A. P. M. Robertson, K. Lee and I. Manners, *Chem.–Eur. J.*, 2011, **17**, 4099.
- 26 P. Bhattacharya, J. A. Krause and H. Guan, *J. Am. Chem. Soc.*, 2014, **136**, 11153.
- 27 C. Lichtenberg, L. Viciu, M. Adelhardt, J. Sutter, K. Meyer, B. de Bruin and H. Gretzmacher, *Angew. Chem., Int. Ed.*, 2015, **54**, 5766.
- 28 A. Glüer, M. Förster, V. R. Celinski, J. S. Auf der Günne, M. C. Holthausen and S. Schneider, *ACS Catal.*, 2015, **5**, 7214.
- 29 (a) F. Anke, D. Han, M. Klahn, A. Spannenberg and T. Beweries, *Dalton Trans.*, 2017, **46**, 6843; (b) F. Anke, S. Boye, A. Spannenberg, A. Lederer, D. Heller and T. Beweries, *Chem.–Eur. J.*, 2020, **26**, 7889.
- 30 N. Gorgas, B. Stöger, L. F. Veiros and K. Kirchner, *Angew. Chem., Int. Ed.*, 2019, **58**, 13874.
- 31 (a) D. V. Gutsulyak, G. K. Lyudmina, J. A. K. Howard, S. F. Vyboishchikov and G. I. Nikonov, *J. Am. Chem. Soc.*, 2008, **130**, 3732; (b) C. A. Ghilardi, P. Innocenti, S. Midollini and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1985, 605.
- 32 M. A. Peldo, A. M. Beatty and T. P. Fehlner, *Organometallics*, 2003, **22**, 3698.
- 33 J. C. Vites, C. Eigenbrot and T. P. Fehlner, *J. Am. Chem. Soc.*, 1984, **106**, 4633.
- 34 M. Besora and A. Lledós, Coordination Modes and Hydride Exchange Dynamics in Transition Metal Tetrahydroborate Complexes, in *Contemporary Metal Boron Chemistry I: Borylenes, Boryls, Borane  $\sigma$ -Complexes, and Borohydrides*, ed. T. B. Marder and Z. Lin, Springer, Berlin, Heidelberg, 2008, pp. 149–202.
- 35 (a) C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2003, **125**, 9424; (b) L. Euzenat, D. Horhant, Y. Ribourdouille, C. Duriez, G. Alcaraz and M. Vaultier, *Chem. Commun.*, 2003, 2280.
- 36 X. Zhao, I. P. Georgakaki, M. L. Miller, J. C. Yarbrough and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 2001, **123**, 9710.
- 37 W. Harshbarger, G. H. Lee, R. F. Porter and S. H. Bauer, *Inorg. Chem.*, 1969, **8**, 1683.
- 38 R. Boese, A. H. Maulitz and P. Stellberg, *Chem. Ber.*, 1994, **127**, 1887.
- 39 T. Li, A. J. Lough and R. H. Morris, *Chem.–Eur. J.*, 2007, **13**, 3796.
- 40 E. R. Clark, A. D. Grosso and M. J. Ingleson, *Chem.–Eur. J.*, 2013, **19**, 2462.
- 41 (a) Z. M. Heiden and A. P. Lathem, *Organometallics*, 2015, **34**, 1818; (b) X.-Q. Zhu, M.-T. Zhang, A. Yu, C. Wang and J.-P. Cheng, *J. Am. Chem. Soc.*, 2008, **130**, 2501.
- 42 (a) W. S. Johnson and B. G. Buell, *J. Am. Chem. Soc.*, 1952, **74**, 4517; (b) R. D. Dillard, D. E. Pavey and D. N. Benslay, *J. Med. Chem.*, 1973, **16**, 251; (c) H. Mizoguchi, H. Oikawa and H. Oguri, *Nat. Chem.*, 2014, **6**, 57.