

Cite this: *Chem. Sci.*, 2021, 12, 2885

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

Received 11th December 2020
Accepted 2nd January 2021

DOI: 10.1039/d0sc06787c

rsc.li/chemical-science

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

Xiaofang Zhai,^a Maofu Pang,^a Lei Feng,^a Jiong Jia,^a Chen-Ho Tung^{ID}^a and Wenguang Wang^{ID}^{*ab}

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.

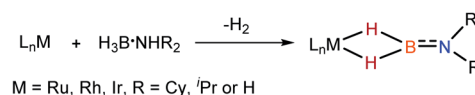
Because of relevance to H_2 storage¹⁻¹⁰ and hydrogenation catalysis,¹¹⁻¹⁵ metal amine-borane complexes¹⁶⁻¹⁸ and their dehydrogenated forms, such as amino-boranes²⁰⁻²² and imino-boranes⁴ are arising as a significant family in organometallic chemistry. In transition metal-catalyzed hydrocoupling of amine-boranes and related transfer hydrogenations, the interactions between the metal and the borane fragment are essential to dehydrogenation and the consequent transformations.¹⁶⁻²⁰ 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).²⁰⁻²² 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 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 $\text{R}_2\text{-HN}\cdot\text{BH}_3$.^{21a} At the same time, Alcaraz and Sabo-Etienne reported the preparation of $(\text{PCy}_3)_2\text{Ru}(\text{H})_2(\eta^2\text{-H}_2\text{B}=\text{NH}_n\text{Me}_{2-n})$ ($n = 0-2$) complexes^{22a} 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 $\text{H}_2\text{B}=\text{NR}_2$ ($\text{R} = i\text{Pr}$ or Cy) with the bis(hydrogen) complexes of $\text{M}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2$ or

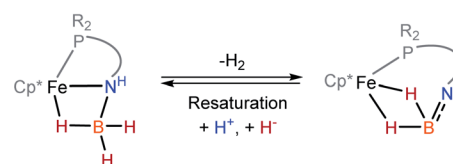
$[\text{CpRu}(\text{PR}_3)_2]^+$ fragments was developed.^{21b,22b} Turculet *et al.* have shown that the ruthenium-alkoxide complex is able to activate $\text{H}_3\text{B}\cdot\text{NHR}_2$ producing hydrido ruthenium complex.²³ Notably, Weller and Macgregor found that dehydrocoupling of ammonia-borane 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 μ -amino-borane bimetallic Rh complex, in which the simplest $\text{H}_2\text{B}=\text{NH}_2$ moiety is trapped on a rhodium dimer.^{20a}

Although iron-catalyzed hydrocoupling of amine-boranes has attracted great interest,²⁴⁻²⁹ 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.³⁰ 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.

^aSchool of Chemistry and Chemical Engineering, Shandong University, No. 27 South Shanda Road, Jinan 250100, China. E-mail: wwg@sdu.edu.cn^bCollege of Chemistry, Beijing Normal University, No. 19 Xinjiekouwai St, Beijing 100875, China

† Electronic supplementary information (ESI) available: For experimental details, spectroscopic data and crystallographic data. CCDC 2033258–2033262. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc06787c

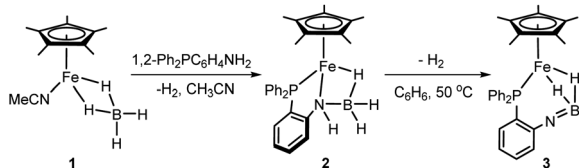


resaturation of the imino-borane by stepwise protonation and hydride transfer (Scheme 1b). This new class of iron species is capable of catalyzing 1,2-selective transfer hydrogenation of quinolines with $\text{H}_3\text{N}\cdot\text{BH}_3$.

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 Bu_4NBH_4 in acetonitrile at room temperature for 5 min. Such ferrous borohydrides have been documented only rarely,³¹ since they are prone to form polynuclear iron borate clusters.^{32,33} The ^{11}B NMR spectrum of the reaction solution shows a quintet at δ 15.4 ($J_{\text{BH}} = 88$ Hz) for the BH_4^- ligand of **1**, and this stands in contrast to the signal at δ -32.0 observed for Bu_4NBH_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 δ -17.5, and a phosphorus resonance at δ 85.9. The ^1H NMR spectrum exhibits a characteristic hydride signal at δ -13.98, which is assigned to the bridging hydride Fe-H-B. Owing to exchange between the hydrogen atoms at the boron,³⁴ the terminal B-H resonances in the ^1H NMR spectrum are very broad and are obscured by the distinct 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 δ -13.98, the ^2H NMR spectrum of *d*-2 displayed discrete peaks at δ 2.23 and 0.19 for the terminal B-D hydrides (Fig. 1).

When a C_6H_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 H_2 nearly quantitatively (see Fig. S4†). In solution, the ^{31}P NMR spectrum of **3** displays a sharp signal at δ 71.9, in contrast to the peak at δ 85.9 for **2**. The ^{11}B resonance shifts significantly, from δ -17.5 for **2** to δ 42.7 for **3** (Fig. S16†), and is particularly diagnostic of a three-coordinate boron atom.^{21,35} This result indicates the B=N



Scheme 2 Synthetic route to imino-borane complex.

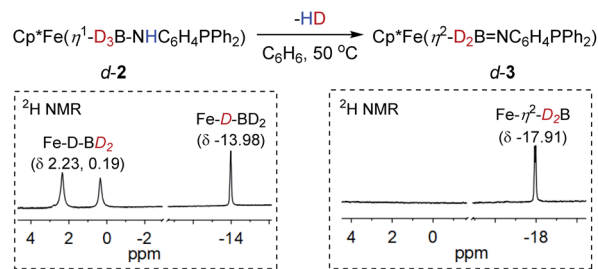


Fig. 1 ^2H NMR spectra for dehydrogenation of *d*-2 to *d*-3.

double bond character in the dehydrogenated form of the amido-borane complex. In the ^1H NMR spectrum, the Fe-H-B signal was observed at δ -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 ^2H NMR spectra. Only a deuterium signal was observed at δ -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 C_6D_6 , a characteristic triplet corresponding to HD appeared at δ 4.43 ($J_{\text{HD}} = 45$ Hz) in the ^1H NMR spectrum (Fig. S18†).³⁶

The structures of **2** and **3** were verified by X-ray crystallographic analysis (Fig. 2). Consistent with NMR spectroscopic analysis, the 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).³⁷ 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

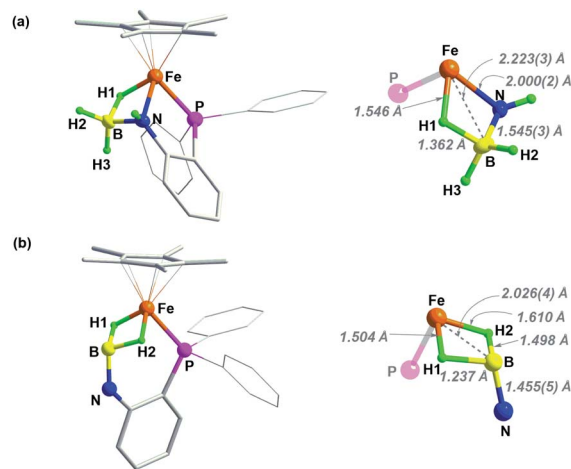


Fig. 2 Solid-state structure (50% probability thermal ellipsoids) of (a) complex **2** and (b) **3**. For clarity, hydrogen atoms of Cp^* and phenyl rings are omitted.



has been become detached from Fe, while the BH₂ fragment acts as a bis(σ-borane) ligand coordinated to the metal center.^{21–23} 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).³⁸ Combined with the NMR results, the B–N bond length in **3** suggests some double bond character.^{21,22} 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 sp³ 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(Et₂O)₂BAR₄^F in C₆H₅F. 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]⁺. Alternatively, the reaction of complex **2** with H(Et₂O)₂BAR₄^F unambiguously provides [3H]⁺ and produces H₂. X-ray crystallographic analysis reveals that the resulting cationic complex [3H]⁺ exhibits a similar framework to its imino-borane precursor (**3**). The BH₂ moiety retains a binding mode of the bis(σ-BH₂) fashion (Fig. 3). In contrast, the B–N distance in [3H]⁺ (1.586(6) Å) is extended by 0.13 Å and the [3H]⁺ 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][BAR₄^F] gives broad ¹H 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]⁺, the boron is coordinatively unsaturated, as manifested by its interaction with a σ-donor. For instance, treatment of **2** with [HPPH₃][BAR₄^F] (p*K*_a^{MeCN} = 7.6)³⁹ provides a Ph₃P-stabilized borane complex, [3H(PPh₃)]⁺ (*m/z* = 742.2620, calcd *m/z* = 742.2626). The ¹H NMR spectrum of [3H(PPh₃)]⁺ exhibits

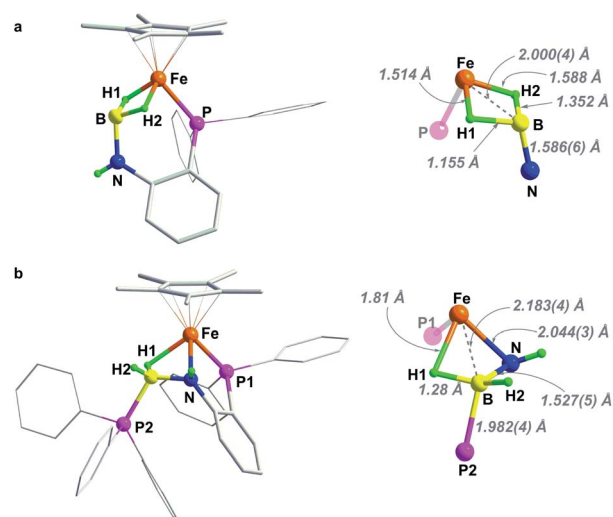
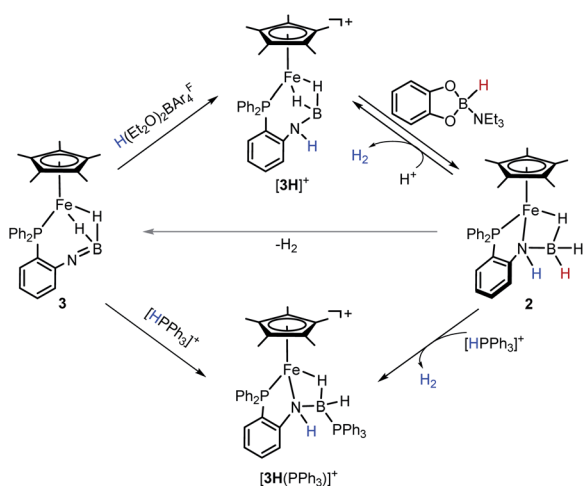
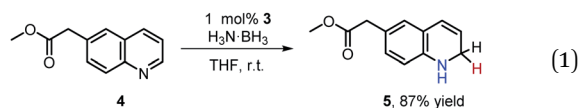


Fig. 3 Solid-state structures of (a) complex [3H]⁺ and (b) [3H(PPh₃)]⁺. For clarity, counterion [BAR₄^F][–], hydrogen atoms of Cp* and phenyl rings have been omitted.

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 ³¹P NMR spectrum, two phosphorus signals at δ 78.90 and –1.26 correspond to the Fe–P and the B–P resonances, respectively. The ¹¹B signal at δ –13.72 indicates a tetracoordinated boron, which is further confirmed by crystallographic analysis of [3H(PPh₃)]⁺ (Fig. 3). In the solid-state structure, a Ph₃P molecule is bound to the B center (*d*_{B–P} = 1.982(4) Å), leading to the formation of a new Fe–H–B–N four-membered metallacycle. As an amido-borane complex, [3H(PPh₃)]⁺ 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][BAR₄^F] in fluorobenzene with catecholborane-NEt₃ adduct (δ_B = 10.56, *J*_{HB} = 142.4 Hz)⁴⁰ results in the regeneration of **2**, as evidenced by the NMR spectra (Fig. S29 and S30†). The ¹H 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_B = 13.86) was also observed in the ¹¹B NMR spectrum, which agrees with the hydride transfer from the organohydride reagent to [3H]⁺. It was interesting that the ion [3H]⁺ is stable towards 5,6-dihydrophenanthridine and Hantzsch ester. These results indicate that the hydride-donating ability (Δ*G*_{H[–]}) of **2** is in the range of 55–59 kcal mol^{–1}.⁴¹ The reactive nature of the hydride in **2** was demonstrated by the reaction with [HPPH₃][BAR₄^F], which produces [3H(PPh₃)]⁺ and releases H₂ (Scheme 3).



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

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 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.⁴² 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– H_3B –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

We thank the National Natural Science Foundation of China (22022102, 22071010, and 21871166) and Natural Science Foundation of Shandong Province (ZR2019ZD45) for their financial support.

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 σ -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.

