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Catalytic Dehydrocoupling of Amine–Boranes using Cationic Zirconium(IV)–Phosphine Frustrated Lewis Pairs

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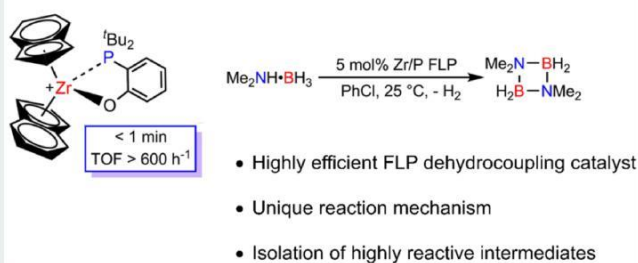
* Supporting Information

ABSTRACT: A series of novel, intramolecular Zr(IV)/P frustrated Lewis pairs (FLPs) based on cationic zirconocene fragments with a variety of ancillary cyclopentadienyl and 2-phosphinoaryloxy ($-\text{O}(\text{C}_6\text{H}_4)\text{PR}_2$, $\text{R} = \text{}^t\text{Bu}$ and 3,5- CF_3 - C_6H_3) ligands are reported and their activity as catalysts for the dehydrocoupling of dimethylamine–borane ($\text{Me}_2\text{NH}\cdot\text{BH}_3$) assessed. The FLP system $[(\text{C}_9\text{H}_7)_2\text{ZrO}(\text{C}_6\text{H}_4)\text{P}^t\text{Bu}_2]\text{B}(\text{C}_6\text{F}_5)_4$ is shown to give unprecedented turnover frequencies (TOF) for a catalyst based on a group 4 metal ($\text{TOF} \geq 600 \text{ h}^{-1}$), while also proving to be the most efficient FLP catalyst reported to date. The mechanism of this reaction has been probed using analogous intermolecular Zr(IV)/P

FLPs, permitting deconvolution of the reactions taking place at both the Lewis acidic and basic sites. Elucidation of this mechanism revealed an interesting cooperative two-cycle process where one cycle is FLP mediated and the other, a redistribution of a linear diborazane intermediate, relies solely on the presence of a Zr(IV) Lewis acid.

KEYWORDS: frustrated Lewis pairs, FLP, amine–borane, dehydrocoupling, zirconocenes

FLP-Catalysed Dehydrocoupling

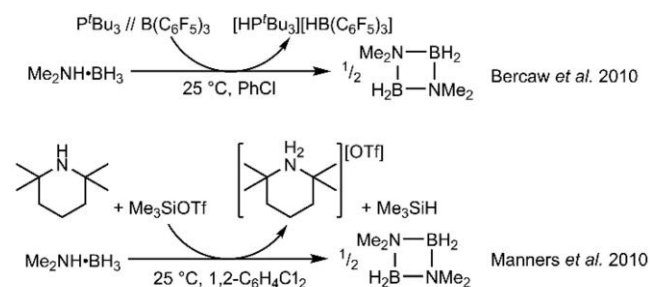


1. INTRODUCTION

Catalytic dehydrogenation and dehydrocoupling of amine–boranes is of broad current interest due to their potential applications as hydrogen storage materials,¹ as reagents for hydrogen transfer to organic or inorganic substrates,² and as precursors to BN-based ceramics and polymeric materials.³ There exists a wide range of transition-metal-based catalysts which facilitate these transformations;⁴ however, work has also been carried out exploring the use of catalysts based on main-group elements. As a consequence dehydrogenation method-ologies which employ catalysts based on elements from group 2 (Mg, Ca) and group 3 (Al, Ga, Sc, Y) are now known.⁵ Furthermore, simple Brønsted acid/base and Lewis acid catalysts can be used to promote hydrogen release from ammonia–borane ($\text{H}_3\text{N}\cdot\text{BH}_3$).⁶

In recent years solution-phase combinations of sterically encumbered Lewis acids and Lewis bases, frustrated Lewis pairs (FLPs),⁷ have also been shown to mediate these dehydrogenation reactions. Initially the focus was on metal-free FLP systems which were able to dehydrocouple dimethylamine–borane ($\text{Me}_2\text{NH}\cdot\text{BH}_3$) stoichiometrically (Scheme 1).⁸ More recently, however, there have been reports of FLPs based on main-group elements which are able to mediate this transformation in a catalytic fashion. In 2013 Uhl, Sloatweg, et al. reported an intramolecular Al/P FLP capable of dehydrogenating $\text{Me}_2\text{NH}\cdot\text{BH}_3$ under melt conditions (45 °C, 9.3 mol %), complete consumption of the monomer is achieved by heating to 90 °C for 45 min, however, only a 71% yield of the desired

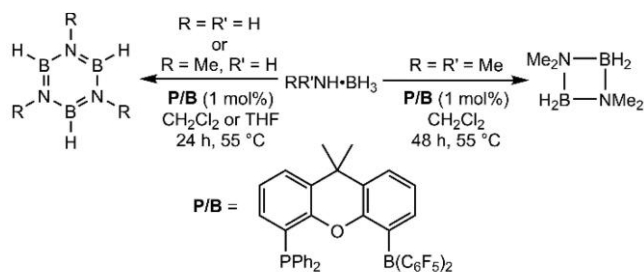
Scheme 1. Main-Group FLPs Capable of Mediating the Stoichiometric Dehydrogenation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$



product was obtained.⁹ Aldridge et al. have developed a P/B FLP, based on a dimethylxanthene backbone, which is able to dehydrogenate a wider range of amine–borane substrates ($\text{RR}'\text{NH}\cdot\text{BH}_3$, $\text{R} = \text{R}' = \text{H}$, $\text{R} = \text{Me}$ and $\text{R}' = \text{H}$, $\text{R} = \text{R}' = \text{Me}$); however, the reaction still requires elevated temperatures and long reaction times (1 mol %, CH_2Cl_2 or THF, 55 °C, 24–48 h) (Scheme 2).¹⁰

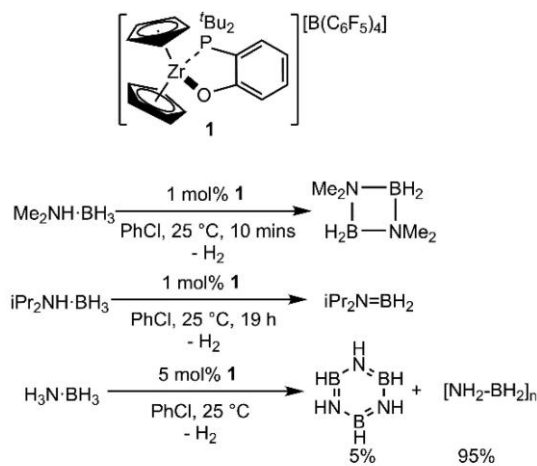
Alongside these breakthroughs, we have developed a range of zirconium(IV) based FLPs with the aim of combining the fascinating small-molecule activation chemistry of FLPs with the well-established catalytic chemistry of the transition metals.¹¹ These transition-metal-based FLP systems (e.g., 1)

Scheme 2. P/B FLP Developed by Aldridge et al. Capable of Mediating the Catalytic Dehydrocoupling of a Range of Amine-Boranes



have been shown to rapidly dehydrocouple several amine-borane substrates under ambient conditions to yield the expected products (Scheme 3).^{11b}

Scheme 3. Catalytic Dehydrocoupling of Amine-Boranes using Zr/P FLP 1



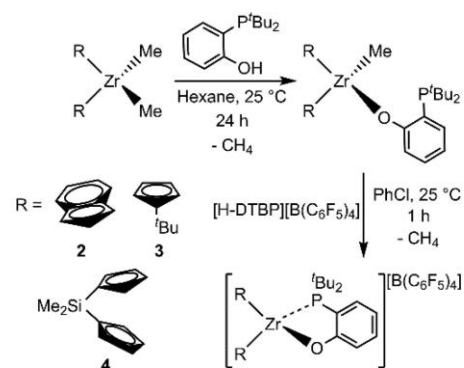
Herein we report a series of novel intramolecular Zr/P FLP systems featuring variations to the ancillary ligands bound to Zr and also incorporating a weakly Lewis basic phosphine (RP(3,5-CF₃(C₆H₃))₂). These were subsequently applied to the catalytic dehydrocoupling of Me₂NH·BH₃. Crucial insights into the mechanism of this reaction was gained by using a range of previously reported intermolecular Zr(IV)/P FLPs of the type [Cp^R₂ZrOMes][B(C₆F₅)₄]/PR'₃ (R = Me, H; R' = ^tBu, Cy, Et, Ph, Mes, C₆F₅).¹² Such systems permitted deconvolution of the mechanism owing to the ability to separate Lewis acid and Lewis base mediated reactions.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Novel Intramolecular Zr/P FLP Systems. The synthetic approach employed is analogous to that previously used by us to access intramolecular FLP system 1.¹¹ This involved synthesis of the relevant dimethylzircono-cene precursor (R₂ZrMe₂) followed by protonolysis with the corresponding alcohol (HO(C₆H₄)P^tBu₂). Subsequently the catalytically active cationic species was generated by reaction with [H-DTBP][B(C₆F₅)₄] (DTBP = 2,6-di-tert-butylpyridine) with concomitant release of 1 equiv of methane (Scheme 4).

The generation of cationic species 2–4 can be monitored by ³¹P NMR spectroscopy. Upon addition of [H-DTBP][B(C₆F₅)₄] to the neutral precursors, protonation of the pendant

Scheme 4. Synthesis of Intramolecular Zr/P FLP Systems 2–4 with a Variety of Ancillary Ligands

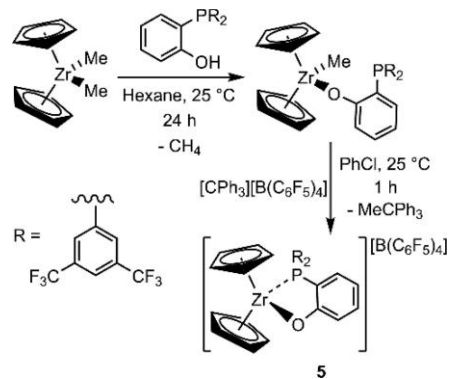


phosphine moiety is observed. This is manifested as a new resonance in the ³¹P NMR spectra (δ_P 20–25 ppm in all cases) displaying a characteristic P–H splitting pattern (doublet, J_{PH} ca. 400 Hz). Effervescence (CH₄) and a concomitant color change (colorless to yellow) is then observed, which is complete within 1 h, resulting in quantitative conversion to a new species, as evidenced by the ³¹P NMR spectra (2, δ_P 55.9 ppm; 3, δ_P 58.1 ppm; 4, δ_P 57.6 ppm). The chemical shifts of these resonances, in comparison to that of 1, suggest the presence of a Zr–P interaction in all cases (for comparison the free ligand δ_P –5.7 ppm). Attempts to isolate 2–4 by layering PhCl solutions of the species with hexane were unsuccessful and yielded intractable oils. The characterization of 2–4 was therefore carried out in situ (¹H, ¹³C, and ³¹P NMR spectroscopy and ESI-MS).

This methodology had to be adapted when using the more electron deficient phosphine moiety, as protonolysis by [H-DTBP][B(C₆F₅)₄] was found not to yield the desired product, which was attributed to the less basic nature of the phosphine. Upon addition of [H-DTBP][B(C₆F₅)₄], protonation of the pendant phosphine moiety did not occur. This is not unexpected, as the pK_a of the related compound [(p-FPh)₃P-H]⁺ is known to be 1.97 (in H₂O);¹³ however, the pK_a of [DTBP-H]⁺ under the same conditions is 4.95 (in H₂O).¹⁴ As a consequence, [CPh₃][B(C₆F₅)₄] was used to mediate the methyl abstraction reaction and generate the cationic species 5 (Scheme 5).

Interestingly, when this reaction was monitored by ³¹P NMR spectroscopy, no change in the ³¹P NMR spectrum was observed upon formation of 5. This strongly suggests the

Scheme 5. Synthesis of Intramolecular Zr/P FLP System 5 with an Electron-Deficient Phosphine



absence of a Zr–P interaction. Formation of 5 is, however, clearly evidenced by the ^1H NMR spectrum, where loss of the resonance corresponding to the Zr–Me ($\delta_{\text{H}} -0.07$ in PhCl) and the appearance of a new resonance corresponding to triphenylethane (MeCPh_3 , $\delta_{\text{H}} 2.09$). Again, isolation of the cationic species was attempted by precipitation into hexanes. However, this only resulted in the generation of intractable solutions and 5 was therefore used in situ.

2.2. Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ using 2–5. Catalyst systems 2–5 (Figure 1) were trialled in the catalytic

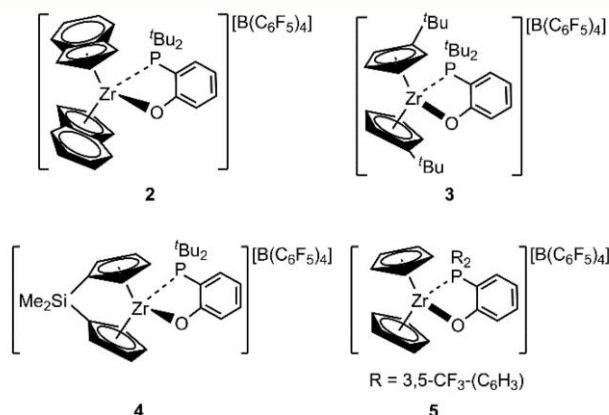


Figure 1. FLP systems 2–5 trialled in the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$.

dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$. Initially a 5 mol % catalyst loading was employed and the reaction monitored by $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy. The results are shown in Table 1, where the previously reported catalyst 1 is shown for comparison.

Table 1. Catalytic Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ using FLP Systems 2–5 with the Previously Reported Catalyst 1 Included for Comparison^a

| catalyst | [Zr] (mol %) | temp (°C) | time (min) | TOF (h^{-1}) |
|----------|--------------|-----------|------------|-------------------------|
| 1 | 2 | 25 | 14 | 210 |
| 2 | 5 | 25 | 1 | >600 |
| 3 | 5 | 25 | 4 | 282 |
| 4 | 5 | 25 | 9 | 138 |
| 5 | 5 | 25 | >60 | 0 |

^aAll reactions were conducted in chlorobenzene in sealed NMR tubes.

From these data it can be seen that catalyst 5, possessing the electron-withdrawing phosphine, shows no activity even after heating to 80 °C for 7 days. This suggests that the phosphine moiety is required to possess a certain degree of basicity in order to mediate the dehydrocoupling. This strongly implies that NH deprotonation is a key step in the catalytic cycle. This is in good agreement with the behavior noted for the main-group systems and also corroborates the mechanism previously proposed by our group.^{11b}

Further to this, it is observed that 2 is a highly efficient catalyst for the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and, in fact, possesses the highest TOF (turnover frequency) of any group 4 catalyst (>600 h^{-1}), the previous highest being the Zr-amide species $([\text{NSiN}]^{\text{Dipp}}\text{Zr}(\text{NMe}_2)_2(\mu\text{-Cl})\text{Li}(\text{THF})_3)$ reported by Rivard et al. (TOF = 420 h^{-1}).¹⁵ Decreasing the steric bulk present in compound 2 down to the single ^tBu group, offered in compound 3, leads to a decrease in TOF. This decrease

continues with removal of the bulky ^tBu moiety in 1, and finally the lowest TOF is observed with the least sterically hindered system 4 (TOF: 2 > 3 > 1 > 4). However, this is also mirrored by the electronic properties of these species. Indenyl ligands (present in 2) are known to be significantly more electron donating than Cp ligands in 1,¹⁶ with Cp (1) and $(\text{Me}_2\text{Si})\text{Cp}_2$ (4) thought to be similar. Due to this, it is difficult to discern whether this change in rate is electronic or steric in nature.

Further examination of the product distribution and intermediates present during the reactions by $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy revealed not only the expected dehydrocoupling product, cyclodiborazane $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$, but also the linear diborazane $\text{Me}_2\text{N}\cdot\text{BH}\cdot\text{Me}\cdot\text{N}\cdot\text{BH}$ (I) and aminoborane $\text{Me}_2\text{N}\cdot\text{BH}_2$ (II) intermediates (Figure 2). The amounts of

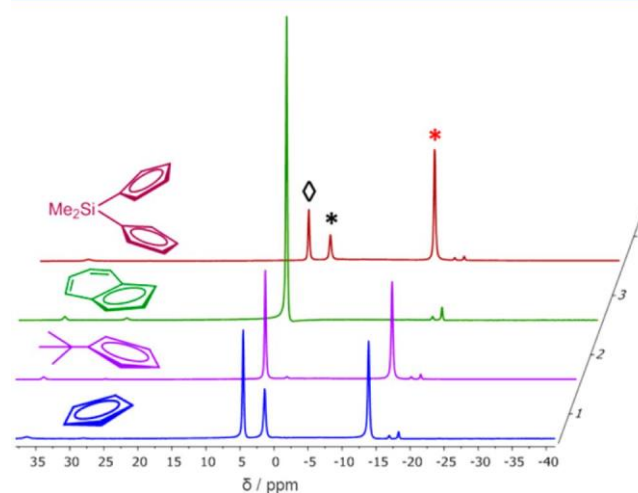


Figure 2. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra after ca. 10 min (1 mol % [Zr], 25 °C, PhCl), for the catalytic dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ with (from back to front) 4, 2, 3 and 1: (black *) $\text{Me}_2\text{NH}\cdot\text{BH}_3$; (red *) $\text{H}_3\text{B}\cdot\text{NMe}_2\cdot\text{BH}_2\cdot\text{NHMe}_2$; (black \diamond) $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$. Note that the terminal BH peak for * overlaps with *. Minor amounts of

$\text{HB}(\text{NMe}_2)_2$ (29 ppm), $\text{Me}_2\text{N}\cdot\text{BH}_2$ (36.6 ppm), and $\text{Me}_2\text{N}(\text{BH}_2)$ (-17 ppm) are also observed.

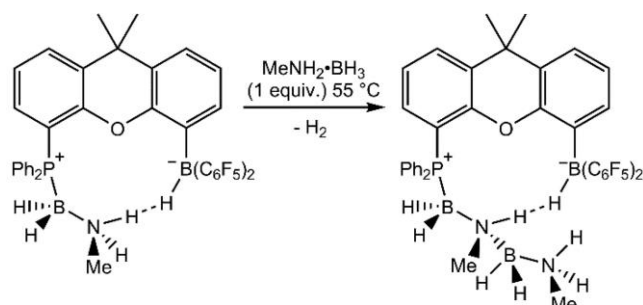
each intermediate (I and II) vary with the ancillary ligand employed. Increasing the steric bulk in the order 4 < 1 < 3 < 2 leads to less I being observed, indicating that the predominant mechanism in these cases involves preferential formation of II. Due to the rapid nature of these reactions, however, the exact ratios of these intermediates could not be calculated.

The presence of both I and II in such dehydrocoupling reactions is unusual. There are thought to be three different mechanisms by which $\text{Me}_2\text{NH}\cdot\text{BH}_3$ is converted to the cyclic diborazane product. One possible mechanism is an “on-metal” process where linear diborazane I, the sole intermediate,¹⁷ is generated from a metal-mediated intermolecular dehydrocoupling of two molecules of $\text{Me}_2\text{NH}\cdot\text{BH}_3$. In a further metal-mediated step, dehydrogenative cyclization could occur to yield the cyclic diborazane product. In an alternative “off-metal” mechanism only one of the steps is thought to be metal mediated. In this step one molecule of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ is dehydrogenated to produce the aminoborane II.¹⁸ The aminoborane then spontaneously dimerizes to form the cyclic diborazane $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$. The third possible mechanism, and one which may be useful in this discussion, has been proposed by Schneider et al.; their calculations show that rearrangement among $\text{Me}_2\text{NH}\cdot\text{BH}_3$, $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$ and II is approximately

thermoneutral ($2.0 \text{ kcal mol}^{-1}$) and may take place if “kinetically feasible”.¹⁹

In the previous literature it is the off-metal mechanism which is the favored model for FLP-catalyzed dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$.^{8,11b} However, with the recent report by Aldridge et al. strongly supporting the viability of a linear chain growth on an FLP catalyst, it appears that the previously proposed mechanisms may require some modification.¹⁰ In their work Aldridge et al. isolated several key intermediates in the P/B FLP catalyzed dehydrocoupling of amine-boranes, suggesting that insertion of 1 equiv of amine-borane into an FLP-bound amine-borane results in the formation of linear oligomeric species akin to those observed with our systems (Scheme 6).

Scheme 6. Growth of a Linear Dimeric Species on a P/B FLP Synthesized by Aldridge et al.



In order to confirm the identity of I as a catalytically relevant intermediate, an authentic sample was treated with 5 mol % of I in PhCl at 25 °C. Monitoring the reaction by ¹¹B NMR spectroscopy revealed a product distribution similar to that observed for the reaction of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ with 1. Species I, II, and $\text{Me}_2\text{NH}\cdot\text{BH}_3$ were all identified in the ¹¹B{¹H} NMR spectrum shown in Figure 3. Full conversion to the cyclic diborazane was evident after 20 min.

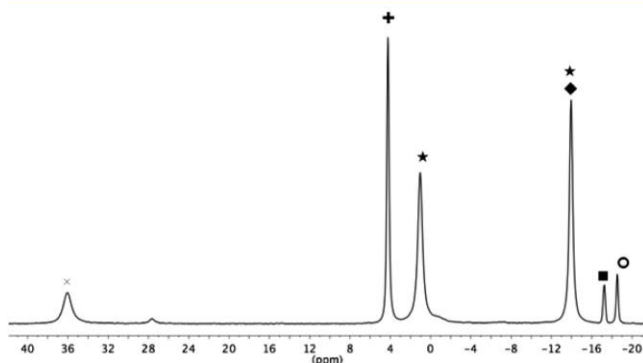


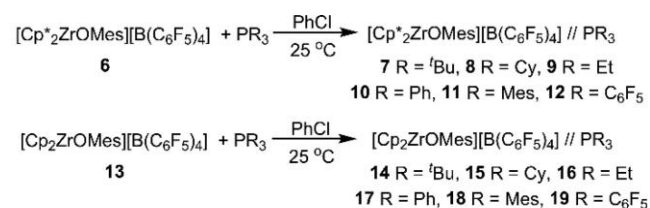
Figure 3. ¹¹B{¹H} NMR spectrum (300 MHz, PhCl, 25 °C, 2 min) of I + 5 mol % 1: (o) $\text{MeNH}(\text{B}_2\text{H}_5)$ (-18.8 ppm); (■) $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (-17.5 ppm); (♦) $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (-14.4 ppm); (★) $\text{Me}_2\text{NH}\cdot\text{BH}_2\text{-Me}_2\text{N}\cdot\text{BH}_3$ (-14.4 and 0.84 ppm); (+) $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$ (4.02 ppm); (x) $\text{Me}_2\text{N}\cdot\text{BH}_2$ (36.6 ppm).

This leads us to propose that two different reaction mechanisms occur simultaneously. The first cycle involves simple deprotonation of a Zr κ^2 -amine-borane adduct by a sufficiently basic phosphine to form II, the phosphonium species $[\text{R}_3\text{P}\cdot\text{H}]^+$, and Zr-H. An intermediate zirconium amido-borane species is not observed in our experiments, suggesting a concerted pathway with simultaneous deprotona-

tion and hydride abstraction in line with other FLP-type reactions. Subsequent release of H_2 from the phosphonium species and the Zr-H renders the process catalytic. This is similar to the mechanism proposed in our previous work.^{11b} The second proposed process involves insertion of a second equivalent of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ to yield the linear diborazane I prior to a subsequent cyclization step. The exact nature of this alternative “on-metal” pathway, however, remains unclear and the roles of the Lewis acid and Lewis base in each step was judged to require further investigation. As discussed above, the formation of I may also be reversible and this could prove to be the origin of II in the reaction. To this end we utilized a series of our recently reported analogous intermolecular Zr/P FLP systems to probe this reaction.¹²

2.3. Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ using Intermolecular FLPs. Initially it was necessary to determine if the intermolecular analogues 7–19 (Scheme 7) retained their

Scheme 7. Generation of Previously Reported Intermolecular FLP Systems



catalytic activity after removal of the aryl tether. It was found that treatment of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ with 10 mol % of $[\text{Cp}^*\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{PR}_3$ (R = ^tBu (7), Cy (8), Et (9), Ph (10), Mes (11), C_6F_5 (12)) in PhCl (25 °C) led to a sluggish reaction resulting in <5% conversion to $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$ over 24 h in all cases, as calculated by ¹¹B NMR spectroscopy, and when R = Ph, Mes, C_6F_5 no conversion was observed. Changing the ancillary ligands on Zr from Cp* (pentamethylcyclopentadienyl) to Cp (14–19) led to a marked improvement in the reactivity, as shown in Figure 4. This is

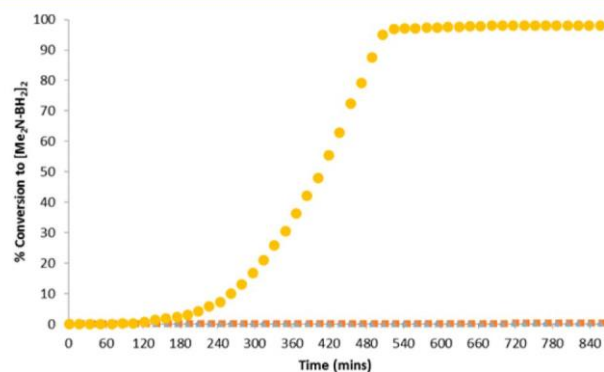


Figure 4. Reaction of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ with 10 mol % 14–19 (25 °C, PhCl, 14 h): (yellow ●) 14; (orange ■) 15; (gray ▲) 16. 17–19 show no reaction with $\text{Me}_2\text{NH}\cdot\text{BH}_3$.

consistent with previous observations, where intramolecular Zr/P FLPs, bearing Cp ancillary ligands, give significantly more rapid reactivity in comparison to their Cp* cousins.¹¹ Ligands with intermediate steric bulk, specifically in complexes 2 and 3, lead to more subtle effects, with complex 2 in particular giving a highly active catalyst despite having more bulky indenyl ligands.

In contrast to Cp*, the indenyl ligands (and indeed the ligand in complex 3) may orient themselves in such a way as to still not hinder substrate binding. Clearly the different electronic characteristics of these ligands may then come into play in yielding a more active catalyst. The possibility for more facile η^5 to η^3 ring slippage for indenyl during the catalytic cycle may also play a role.

FLP systems 15–19 (10 mol %, PhCl, 25 °C, 14 h) gave low conversion (<5%) to [Me₂N-BH₂]₂ even after 14 h, with 17–19 showing no conversion over the same period. The lack of conversion using 19 bearing an electron-withdrawing phosphine is consistent with the result observed with 5. Despite this,

14 shows 97% conversion to [Me₂N-BH₂]₂ in 7.5 h. Interestingly, Figure 4 shows an induction period; this is attributed to the formation of I prior to its consumption to generate [Me₂N-BH₂]₂. In operando NMR spectroscopy (see later) gives no evidence for any gross changes to the catalyst structure during this initiation period; there is also no evidence for the formation of heterogeneous or colloidal species.

2.4. Mechanistic Investigation. Monitoring the reaction between Me₂NH·BH₃ and a catalytic amount of 14 (10 mol %, PhCl, 25 °C, 7.5 h) by ¹¹B{¹H} NMR spectroscopy led to a distribution of reaction intermediates similar to that observed for the reactions with catalysts 1–4 (Figure 1), with both Me₂NH·BH₂-Me₂N-BH₃ (I) and Me₂N BH₂ (II) generated simultaneously (Figure 5 and Figure S1 in the Supporting Information).

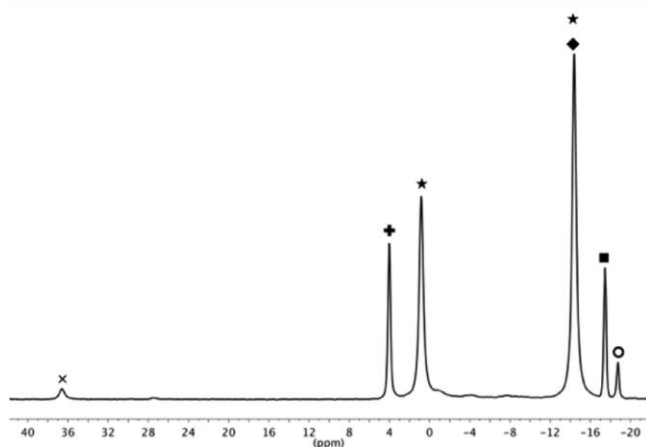


Figure 5. ¹¹B{¹H} NMR spectrum (300 MHz, PhCl, 25 °C, 280 min) of Me₂NH·BH₃ + 10 mol % 14: (◐) MeNH(B₂H₅) (-18.8 ppm); (◑) [B(C₆F₅)₄]⁻ (-17.5 ppm); (•) Me₂NH·BH₃ (-14.4 ppm); (★) [Me₂NH·BH₂-Me₂N-BH₃] (I) (-14.4 and 0.84 ppm); (+) [Me₂N-BH₂]₂ (II) (4.02 ppm); (x) Me₂N BH₂ (II) (36.6 ppm).

In order to further probe the mechanism of the reaction, Me₂NH·BH₃ was treated with 10 mol % of [Cp*₂ZrOMe]-[B(C₆F₅)₄] (6) and [Cp₂ZrOMe][B(C₆F₅)₄] (13) in the absence of a Lewis base. In neither case was dehydrocoupling observed by ¹¹B NMR spectroscopy (24 h, 25 °C, PhCl); however a new Zr amine-borane complex was identified (¹¹B{¹H} δ -11.5 (broad singlet, Me₂NH·BH₃), -16.9 (s, [B(C₆F₅)₄]⁻)). In the case of 6, this complex (20) was isolated through a stoichiometric reaction between 5 and Me₂NH·BH₃; the solid-state structure of 20 is shown in Figure 6. From the solid-state structure of 20 it is clear that Me₂NH·BH₃ is bound in a κ² fashion;¹⁹ however, the ¹H NMR spectrum shows a broad resonance for three equivalent hydrides, suggesting a

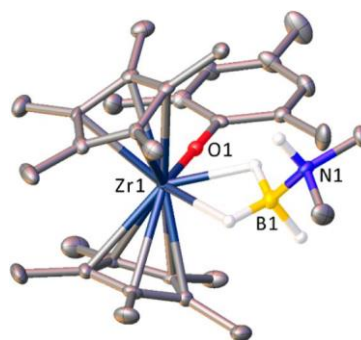


Figure 6. Solid-state structure of the cation present in 20 as determined by X-ray crystallography. Ellipsoids depicted at the 50% probability level. The second unique cation, nonessential hydrogens, and two [B(C₆F₅)₄]⁻ counterions are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1-O1 1.968(3), N1-B1 1.587(6); Cp*–Zr–Cp* 135.14(7). The Zr–B distance is 2.709(5) Å.

dynamic structure in solution, where the hydrides bound to Zr are exchanging on the NMR time scale. Structurally characterized transition-metal complexes of amine-boranes bearing N–H moieties are rare, as the isolation of such compounds is usually hindered by subsequent dehydrocoupling reactivity.^{20e,g}

Subsequent reaction of 20 with phosphine Lewis bases (PhCl, 25 °C, <10 min) led to dehydrogenation, release of Me₂N BH₂ (II), and formation of the corresponding phosphonium salt [HPR₃][B(C₆F₅)₄] and a Zr hydride. Aminoborane II subsequently dimerized to form the cyclic diborazane. Protonation of the Zr hydride by the phosphonium species to release H₂ is sluggish (PhCl, 25 °C, <6 h) in the case of the Zr species bearing the Cp* ligands. This is consistent with the slow catalytic turnover achieved with catalyst systems 7–12.

Varying the phosphine is seen to have a dramatic effect on this transformation. More basic phosphines (PR₃, R = ^tBu, Cy, Et) show the deprotonation/dehydrogenation reactivity described above. Analogous treatment of 20 with PPh₃, PMe₃, or P(C₆F₅)₃ showed no reaction after 6 h. This is consistent with the fact that 14–16 are catalysts for the dehydrocoupling reaction, whereas 17–19 show little to no conversion. This dehydrogenation of a Zr-bound amine-borane could be one mechanism for the dehydrocoupling of Me₂NH·BH₃; however, this process does not account for the observation of the linear diborazane I. Nevertheless, these findings do indicate the necessity for both the Lewis acidic and Lewis basic fragments in the initial dehydrogenation of Me₂NH·BH₃, yielding either Me₂N BH₂ (II) or Me₂NH·BH₂-Me₂N-BH₃ (I). Crucially, in support of this hypothesis, addition of further amounts of Me₂NH·BH₃ to 20 leads to the formation of no new products on a catalytically relevant time scale (8 h, 25 °C).

To probe the intermediacy of linear diborazane (I), a chlorobenzene solution of I was treated with 20 mol % of [Cp₂ZrOMe][B(C₆F₅)₄] // P^tBu₃ (14) (PhCl, 25 °C, 6 h). In this case complete conversion to [Me₂N-BH₂]₂ was observed in 6 h (Figure 7). It is evident from Figure 2 that, upon consumption of I, both II and the parent amine-borane, Me₂NH·BH₃ are formed. Redistribution of such linear diborazanes to form amine-borane dehydrocoupling products has been previously reported by our group.²¹

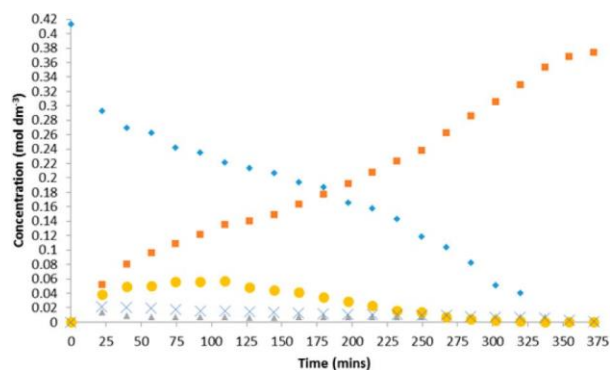
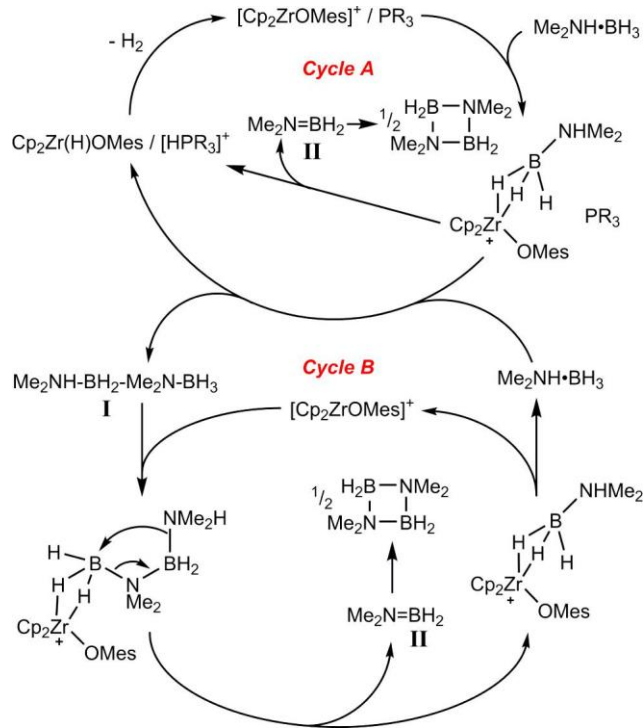


Figure 7. I with 20 mol % 14 (25 °C, PhCl, 6 h): (blue \blacklozenge) $\text{Me}_2\text{NH}\cdot\text{BH}_3$; (orange \blacksquare) $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$; (yellow \bullet) $\text{Me}_2\text{NH}\cdot\text{BH}_2$; (gray \blacktriangle) $\text{Me}_2\text{N}\cdot\text{BH}_2$ (II); (light blue \times) $\text{Me}_2\text{N}(\text{B}_2\text{H}_5)$.

In order to determine if this second step in the cycle also requires both Lewis acidic and Lewis basic fragments, the Lewis base (P^tBu_3) was removed. Reaction of I with 20 mol % 13 (PhCl, 25 °C, 14 h) resulted in the redistribution of linear diborazane intermediate I to yield $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and $\text{Me}_2\text{N}\cdot\text{BH}_2$ (II), which subsequently cyclodimerized, as expected, to form the cyclic diborazane dimer $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$. We observe that $\text{Me}_2\text{NH}\cdot\text{BH}_3$ is not consumed in the absence of exogenous phosphine (no reaction is observed between complex 13 alone and $\text{Me}_2\text{NH}\cdot\text{BH}_3$).

The proposed mechanism for the Zr(IV)/P FLP catalyzed dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ is shown in Scheme 8. Cycle A is analogous to the previously reported mechanism for this transformation,^{11b} wherein the FLP mediates an intramolecular loss of H_2 from $\text{Me}_2\text{NH}\cdot\text{BH}_3$, forming the aminoborane II. The aminoborane spontaneously dimerizes to form the cyclic diborazane product $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$. Alternatively, in the

Scheme 8. Proposed Reaction Mechanism for the Catalytic Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ using a Zr(IV)/P FLP



presence of another 1 equiv of $\text{Me}_2\text{NH}\cdot\text{BH}_3$, an intermolecular dehydrocoupling event could occur to yield the linear diborazane I. This then feeds into cycle B. Cycle B is the phosphine-independent redistribution of I and involves initial complexation of I to the Zr center in a fashion analogous to that observed for 20. Loss of the terminal Me_2NH group, as previously reported in other redistribution reactions,²¹ then occurs, resulting in a μ -amido diborane species, $\text{Me}_2\text{NH}(\text{B}_2\text{H}_5)$. As shown in Figures 7 and 8, $\text{Me}_2\text{NH}(\text{B}_2\text{H}_5)$ is observed in

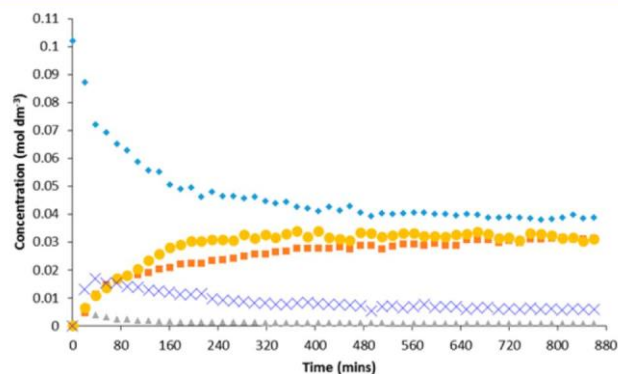


Figure 8. I with 20 mol % 13 (25 °C, PhCl, 12 h): (blue \blacklozenge) $\text{Me}_2\text{NH}\cdot\text{BH}_3$; (orange \blacksquare) $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$; (yellow \bullet) $\text{Me}_2\text{NH}\cdot\text{BH}_2$; (gray \blacktriangle) $\text{Me}_2\text{N}\cdot\text{BH}_2$ (II); (light blue \times) $\text{Me}_2\text{N}(\text{B}_2\text{H}_5)$.

solution throughout these reactions and is thus not thought to be bound to the Zr; in fact, addition of $\text{Me}_2\text{NH}(\text{B}_2\text{H}_5)$ to 6 or 13 results in no reaction (vide infra). The fate of $\text{Me}_2\text{NH}(\text{B}_2\text{H}_5)$ remains uncertain. We believe it is likely that the formation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and II could be via an alternative, concerted process from I, as indicated in Scheme 8 (cycle B). When formed, $\text{Me}_2\text{N}\cdot\text{BH}_2$ would spontaneously dimerize to form $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$. The formation of this dimer is thought to be the driving force for this step. In the presence of P^tBu_3 , $\text{Me}_2\text{NH}\cdot\text{BH}_3$ could be dehydrocoupled to re-form the linear diborazane I. However, as mentioned above, it is thought that such a transformation cannot occur in the absence of phosphine.

This mechanism also provides some insight into the cause of the differing TOFs depending on the steric bulk of the ancillary ligands in the intramolecular systems (1–4). The increase in steric bulk is thought to preclude the formation of linear diborazane (II), as 2 equiv of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ is not able to organize around the sterically congested catalytic site. It is therefore thought that in the case of the most sterically bulky system, 2, cycle A is far more dominant and decreasing steric bulk allows cycle B to become more viable.

2.5. Model System for Proposed Cycle A. The intermolecular nature of FLP 14 also allowed us to further probe both cycles A and B. Additional insight into the validity of cycle A can be gained through a systematic study of the dehydrogenation of $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ by 14. Due to the increased steric bulk around nitrogen, dehydrogenation of $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ only yields one product, the corresponding aminoborane ($^i\text{Pr}_2\text{N}\cdot\text{BH}_2$), through an intramolecular loss of H_2 .^{17f} This substrate therefore provides an ideal model for cycle A where we propose this intramolecular H_2 elimination to be a catalytically viable pathway. Intramolecular FLP 1 has been shown to dehydrogenate $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ (1 mol % [Zr], PhCl, 25

C, 19 h) to yield $^i\text{Pr}_2\text{N}\cdot\text{BH}_2$; however, revisiting this reaction seemed pertinent in light of the current study.^{11b} Upon

treatment of a PhCl solution of $^1\text{Pr NH}\cdot\text{BH}$ with 10 mol % of 14 (25 °C, 14 h) a 73% conversion to $^1\text{Pr}_2\text{N BH}_2$ was observed with no other intermediates apparent (Figure 9).²³

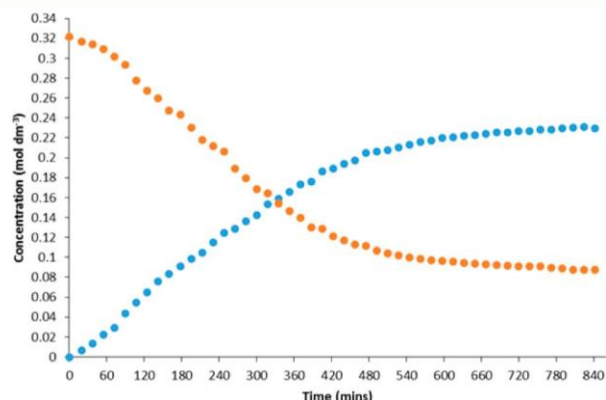


Figure 9. $^1\text{Pr NH}\cdot\text{BH}$ with 10 mol % 14 (25 °C, PhCl, 14h): (blue \bullet) $^1\text{Pr}_2\text{NH BH}_3$; (orange \bullet) $^1\text{Pr}_2\text{N BH}_2$.

As in the case of $\text{Me}_2\text{NH}\cdot\text{BH}_3$, reaction of 6 and 13 with $^1\text{Pr}_2\text{NH}\cdot\text{BH}_3$ resulted in no detectable conversion to dehydrocoupling products, but formation of an amine–borane complex was again observed. In the case of the system bearing the Cp^* ligand set, this complex (21) has been isolated and crystallographically characterized (Figure 10).

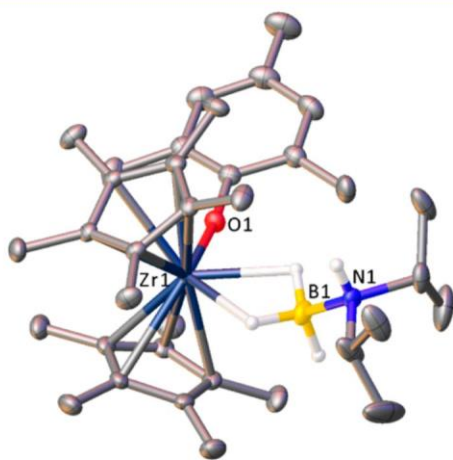


Figure 10. Solid-state structure of the cation present in 21 as determined by X-ray crystallography. Ellipsoids depicted at the 50% probability level. Nonessential hydrogens, solvent of crystallization (PhCl), and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ counterion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1–O1 1.974(1), N1–B1 1.590(3), $\text{Cp}^*\text{--Zr--Cp}^*$ 135.07(3). The Zr–B distance is 2.722(3) Å.

The solid-state structure of 21, as was to be expected, proves to be nearly identical with that of 20, with the amine–borane again bound in a κ^2 fashion.²⁰ In a manner similar to that for 20 treatment of 21 with a stoichiometric amount of P^tBu_3 results in deprotonation of the bound amine–borane and formation of $^1\text{Pr}_2\text{N BH}_2$. These results, when combined with the data in Figure 9, confirm the validity of a mechanistic pathway involving the intramolecular loss of H_2 from an amine–borane mediated by a Zr/P FLP.

2.6. Model System for Proposed Cycle B. Gaining more detailed insight into cycle B has proven to be more of a

challenge, as our initial attempts to isolate the proposed intermediates have been unsuccessful. Attempts to synthesize a Zr-bound linear diborazane have been precluded by the redistribution chemistry described above. Efforts to block this reactivity were also made by capping the linear diborazane with other Lewis bases (DMAP, PMe_3 ; see the Supporting Information for further discussion) but this strategy also proved unsuccessful. In addition, attempts to isolate a Zr μ -amidodiborane complex were made, but addition of $\text{Me}_2\text{N}(\text{B}_2\text{H}_5)$ to 6 or 13 resulted in the formation of no new products, as observed by ^{11}B NMR spectroscopy. Two possible conclusions may be drawn from this. First, that such complexes are transient in solution and therefore isolation is impossible, or second, that the conversion of $\text{Me}_2\text{N}(\text{B}_2\text{H}_5)$ to the observed products is in fact not metal-mediated. The latter, however, appears unlikely, as it is known that, in the absence of a catalyst but in the presence of Me_2NH , $\text{Me}_2\text{N}(\text{B}_2\text{H}_5)$ readily undergoes a ring-opening reaction to yield the corresponding linear diborazane I.²¹

Experiments using alternative linear diborazanes have provided insight into the decomposition pathway of I. Upon reaction of the linear diborazane $\text{H}_3\text{B-NMeH-BH}_2\text{-NMe}_2\text{H}$ with different substituents at nitrogen²⁰ with 10 mol % of 13 (PhCl, 25 °C, 14 h) formation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ was observed by ^{11}B NMR spectroscopy (Figure 11). This was accompanied by formation of trace amounts of N-methylborazine, $[\text{HB-NMe}]_3$, and μ -N-methylamidodiborane, $\text{MeNH}(\text{B}_2\text{H}_5)$.

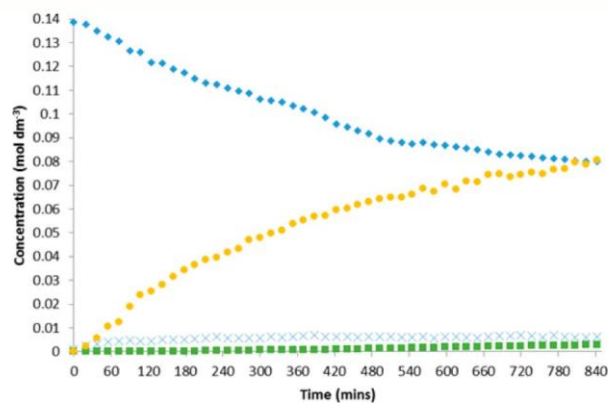


Figure 11. Reaction of $\text{Me}_2\text{NH}\cdot\text{BH}_2\text{-MeNH}\cdot\text{BH}_3$ with 10 mol % 13 (25 °C, PhCl, 14 h): (blue \blacklozenge) $\text{Me}_2\text{NH}\cdot\text{BH}_2\text{-MeNH}\cdot\text{BH}_3$; (orange \bullet) $\text{Me}_2\text{NH}\cdot\text{BH}_3$; (light blue \times) $\text{MeNH}(\text{B}_2\text{H}_5)$; (green \blacksquare) $[\text{HB-NMe}]_3$.

The origin of these intermediates provides useful information about cycle B in Scheme 8. $\text{MeNH}(\text{B}_2\text{H}_5)$ appears to arise from elimination of the terminal Me_2NH moiety from $\text{Me}_2\text{NH}\cdot\text{BH}_2\text{-NMeH}\cdot\text{BH}_3$, with the formation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ providing further evidence for the presence of both free amine and free BH_3 in solution. The lack of detectable amounts of $\text{Me}_2\text{N BH}_2$ or $[\text{Me}_2\text{N-BH}_2]_2$ indicates that any aminoborane that is generated arises from the internal BN unit of the linear diborazane. In this case formation of $[\text{HB-NMe}]_3$ provides further evidence for the presence of MeNH BH_2 , as direct observation of this aminoborane by ^{11}B NMR spectroscopy under ambient conditions would prove impossible.²² The borazine $[\text{HB-NMe}]_3$ is thought to arise through trimerization of MeNH BH_2 to form $[\text{MeNH-BH}_2]_3$, which is further dehydrogenated through now well-established hydrogen transfer reactions.^{2d,21}

3. SUMMARY

A range of intramolecular Zr(IV)/P FLP catalysts have been prepared that are competent in the dehydrocoupling of Me₂NH·BH₃. Moreover, FLP system 2 exhibited the highest TOF yet reported for a catalyst based on a group IV transition metal. Studies of intermolecular FLP analogues allowed elucidation of a novel reaction mechanism comprising two cooperative cycles which provides a new concept for FLP-catalyzed reactions. The first cycle involves a two-step process involving amine–borane coordination and subsequent phosphine-mediated H₂ loss. The second cycle is based on Lewis acid mediated redistribution of a linear diborazane intermediate. The concept that the Lewis acidic and Lewis basic fragments can mediate transformations independently, in addition to acting as an FLP, may have wide-reaching consequences for other FLP-catalyzed reactions. Further studies are underway to widen the substrate scope for these reactions with, in the case of group 13–15 adducts, the formation of polymeric materials as a particular target.

4. EXPERIMENTAL SECTION

4.1. General Considerations. Unless otherwise stated, all manipulations were undertaken under an atmosphere of argon or nitrogen using standard glovebox (MBraun O₂ <0.1 ppm, H₂O <0.1 ppm) and Schlenk line techniques and all glassware was oven and vacuum-dried prior to use. Cp₂ZrCl₂, Cp*₂ZrCl₂, MeLi (1.6 M in Et₂O), P^tBu₃, PCy₃, PEt₃, PPh₃, PMes₃, and P(C₆F₅)₃ were purchased from Sigma-Aldrich and used as received. [CPh₃][B(C₆F₅)₄] was purchased from Acros Organics and used as received. Me₂NH·BH₃ was purchased from Sigma Aldrich and purified by sublimation prior to use (25 °C, 2 × 10⁻² Torr). ¹Pr₂NH·BH₃, Me₂NH·BH₂·Me₂N·BH₃, [Cp*₂ZrOMes][B(C₆F₅)₄] (5), [Cp₂ZrOMes][B(C₆F₅)₄] (6), [Cp₂ZrO(C₆H₄)P^tBu₂][B(C₆F₅)₄] (1), and o-tBu₂P(C₆H₄)OH were synthesized according to literature protocols.^{11,21,22} All other reagents were used as obtained unless otherwise stated. Common laboratory solvents (Et₂O, DCM, hexane, THF) were purified using a Grubbs type purification system.²³ Nonstandard solvents (chlorobenzene, pentane) were purchased from Sigma-Aldrich and distilled from CaH₂ prior to use.

NMR spectra were recorded using JEOL ECP-300 (300 MHz), Varian-400 (400 MHz), and Varian NMR500 (500 MHz) spectrometers. Deuterated solvents were obtained from Sigma-Aldrich (d₆-benzene, d₈-THF, and d₂-DCM) or Apollo Scientific (d₅-PhBr) and distilled from CaH₂ prior to use. Spectra of air-sensitive compounds were recorded using NMR tubes fitted with J. Young valves. NMR spectra of boron-containing compounds were obtained in quartz NMR tubes fitted with J. Young valves.

X-ray diffraction experiments were carried out on a Bruker APEX II diffractometer using Mo K α radiation (λ = 0.71073 Å). For further details see the [Supporting Information](#).

Mass spectrometry experiments were carried out by the University of Bristol Mass Spectroscopy Service on a Bruker Daltonics micrO TOF II with a TOF analyzer. All samples were run in predried PhCl.

4.2. Synthesis of Intramolecular Zr/P FLPs (2–4). **4.2.1. Synthesis of R₂ZrMe₂ Precursors.** **4.2.1.1. Ind₂ZrMe₂.** This compound was obtained by following a modified literature procedure.²⁴ Methylithium (1.6 M in Et₂O, 32.3 mL, 51.6 mmol) was added dropwise to a solution of indene (3.00 mL, 25.8 mmol) in Et₂O (35 mL) at room temperature to give a yellow-orange solution. This solution was stirred for 30 min, before addition of ZrCl₄ (3.00 g, 12.9 mmol) slurried in hexane (40 mL). The resulting mixture was stirred for 2 h, during which a white precipitate (LiCl) formed. The solvent was removed in vacuo, and the residue was dissolved in hot hexane (50 mL) and filtered through Celite. Removal of the solvent in vacuo gave the desired product as a white powder (3.54 g, 78%) that was recrystallized from hexane at -40 °C. All recorded data are consistent with literature values.²⁴ ¹H NMR (400 MHz, C₆D₆): δ 7.36 (dd, 4H, J

= 2.9, 6.7 Hz, H_{4,7}), 7.06 (dd, 4H, J = 3.1, 6.7 Hz, H_{6,5}), 5.95 (d, 4H, J = 2.9 Hz, H_{1,3}), 5.79 (t, 2H, J = 3.1 Hz, H₂), -0.68 (s, 6H, Zr(CH₃)₂).

4.2.1.2. Me₂Si(C₅H₄)₂ZrMe₂. The preparation of this compound was adapted from a literature procedure.²⁵ Me₂Si(C₅H₄)₂ZrCl₂ (244 mg, 0.70 mmol) was suspended in hexane (20 mL) and cooled to -78 °C. Methylithium (1.6 M in Et₂O, 0.83 mL, 1.33 mmol) was added dropwise, and the reaction mixture was warmed to room temperature and stirred for 2 h. Solvent was removed in vacuo, and the residue was redissolved in hexane. The resulting solution was filtered through Celite, the volume was reduced to ~5 mL, and the temperature was lowered to -20 °C, which resulted in the precipitation of white crystals of the title compound (172 mg, 80%). All recorded data are consistent with literature values.²⁶ ¹H NMR (400 MHz, toluene-d₈): δ 6.88 (t, 4H, J = 2.2 Hz, Cp), 5.76 (t, 4H, J = 2.2 Hz, Cp), 0.52 (s, 6H, Si(CH₃)₂), -0.35 (s, 6H, Zr(CH₃)₂).

4.2.1.3. (tBu-C₅H₄)₂ZrMe₂. Methylithium (1.6 M in hexanes, 0.54 mL, 0.86 mmol) was added dropwise to a stirred solution of the zirconocene dichloride (165 mg, 0.41 mmol) in Et₂O (15 mL) at -78 °C. After addition, the reaction mixture was warmed to room temperature and stirred overnight. Solvent was removed in vacuo, and the resulting residue was extracted with hexanes and the extract filtered through a Celite plug. Solvent was removed in vacuo, yielding a white solid (272 mg, 87%) of the title compound. All recorded data are consistent with literature values.²⁶ ¹H NMR (400 MHz, CDCl₃): δ 5.80–5.83 (m, 4H, Cp), 5.70–5.75 (m, 4H, Cp), 1.10 (s, 18H, CpC(CH₃)₃), 0.01 (s, 6H, Zr(CH₃)₂).

4.2.2. Synthesis of Neutral Complexes [R₂Zr(Me)(O[^]P(tBu)₂].

4.2.2.1. General Method. A solution of the dimethylzirconocene (1 equiv) and phosphino alcohol (1 equiv) were individually dissolved in the minimum amount of hexane prior to combination. The resulting solutions were stirred overnight and until no further gas evolution was observed. The solvent was removed in vacuo, yielding the desired complexes.

4.2.2.2. (tBuC₅H₄)₂Zr(Me)(OC₆H₄P^tBu₂). Viscous oil (702 mg, 95%). ¹H NMR (400 MHz, C₆D₆): δ 7.61 (dt, 1H, J = 7.6, 1.8 Hz, H₆), 7.12–7.16 (m, 1H, H₃), 6.77 (t, 1H, J = 7.6 Hz, H₄), 6.55 (dd, 1H, J = 5.1, 2.6 Hz, H₅), 6.11–6.15 (m, 2H, Cp), 5.90–5.94 (m, 2H, Cp), 5.87–5.89 (m, 4H, Cp), 1.25 (d, 18H, ³J_{HP} = 11.3 Hz, PC(CH₃)₃), 1.19 (s, 18H, CpC(CH₃)₃), 0.75 (s, 3H, ZrCH₃); ¹³C{¹H} NMR (125 MHz, C₆D₆): δ 169.8 (d, ²J_{CP} = 23.7 Hz, C₁), 138.8 (s, ipso-Cp(tBu)), 136.0 (d, ³J_{CP} = 3.2 Hz, C₆), 130.1 (s, C₃), 125.2 (d, ¹J_{CP} = 25.3 Hz, C₂), 120.1 (d, ⁴J_{CP} = 3.4 Hz, C₅), 118.1 (s, C₄), 110.8, 110.7, 109.8, 107.2 (Cp), 32.3 (d, ¹J_{CP} = 24.7 Hz, PC(CH₃)₃), 30.9 (d, ²J_{CP} = 16.3 Hz, PC(CH₃)₃), 29.3 (s, CpC(CH₃)₃), 26.3 (d, J_{CP} = 6.6 Hz, ZrCH₃), 22.9 (s, CpC(CH₃)₃).

³¹P{¹H} NMR (161 MHz, C₆D₆): δ 10.17 (s).

4.2.2.3. Ind₂Zr(Me)(OC₆H₄P^tBu₂). White solid (567 mg, 95%). ¹H NMR (400 MHz, toluene-d₈): δ 7.57 (dt, 1H, J = 7.7, 1.8 Hz, H₆), 7.28 (dq, 2H, J = 8.4, 1.0 Hz, H_{4,7}), 7.21 (dq, 2H, J = 8.4, 1.0 Hz, H_{4,7}), 7.10 (ddd, 1H, J = 8.1, 7.1, 1.7 Hz, H₃), 6.87 (ddd, 2H, J = 8.4, 6.6, 1.2 Hz, H_{6,5}), 6.80 (ddd, 2H, J = 8.4, 6.6, 1.2 Hz, H_{6,5}), 6.76 (dt, 1H, J = 7.4, 1.3 Hz, H₄), 6.33 (ddd, 1H, J = 8.1, 5.0, 1.3 Hz, H₅), 6.06 (ddd, 2H, J = 3.2, 2.1, 0.9 Hz, H_{1,3}), 5.96 (t, 2H, J = 3.3 Hz, H₂), 5.73 (ddd, 2H, J = 3.2, 2.1, 0.9 Hz, H_{1,3}), 1.20 (d, 18H, ³J_{HP} = 11.4 Hz, C(CH₃)₃), -0.1 (s, 3H, ZrCH₃). ¹³C{¹H} NMR (125 MHz, toluene-d₈): δ 168.6 (d, J = 23.9 Hz, C₁), 135.6 (d, J = 7.1, C₆), 129.8 (s, C₃),

125.4 (d, J = 22.7 Hz, C₂), 125.2 (s, C_{3a,7a}), 125.0 (s, C_{3a,7a}), 124.4 (s, C_{5,6}), 124.3 (m, C_{4,7}), 124.0 (s, C_{5,6}), 120.29 (d, J = 3.3 Hz, C₅), 118.6 (s, C₄), 117.6 (d, J = 1.9 Hz, C₂), 101.5 (d, J = 1.2 Hz, C_{1,3}), 98.9 (d, J = 1.3 Hz, C_{1,3}), 32.8 (d, J_{CP} = 7.5 Hz, ZrCH₃), 32.4 (d, ¹J_{CP} = 24.9 Hz, C(CH₃)₃), 31.0 (d, ²J_{CP} = 15.7 Hz, C(CH₃)₃). ³¹P{¹H} NMR (161 MHz, toluene-d₈): δ 10.23 (s). Anal. Calcd: C, 69.07; H, 6.85. Found: C, 68.92; H, 6.93.

4.2.2.4. Me₂Si(C₅H₄)₂Zr(Me)(OC₆H₄P^tBu₂). Viscous colorless oil (227 mg, 98%). ¹H NMR (400 MHz, PhCl-d₅): δ 7.76 (dt, 1H, J = 7.5, 1.5 Hz, H₆), 7.32 (dt, 1H, J = 7.1, 1.2 Hz, H₃), 6.96 (dt, 1H, J = 7.7, 1.6 Hz, H₄), 6.80–6.82 (m, 2H, Cp), 6.77–6.80 (m, 1H, H₅), 6.44–6.46 (m, 4H, Cp), 5.70–5.73 (m, 2H, Cp), 1.36 (d, 18H, ³J_{HP} = 10.2 Hz, C(CH₃)₃), 0.73 (s, 3H, SiCH₃), 0.60 (s, 3H, SiCH₃), 0.52 (s, 3H, ZrCH₃). ¹³C{¹H} NMR (100 MHz, PhCl-d₅): δ 169.9 (d, J = 22.1 Hz,

C1), 135.5 (d, $J = 3.5$ Hz, C6), 130.3 (d, $J = 0.5$ Hz, C3), 124.2 (d, $J = 22.7$ Hz, C2), 122.0 (s, ipso-CpSi), 119.7 (d, $J = 2.2$ Hz, C5), 119.5 (d, $J = 2.7$ Hz, C4), 118.4 (s, Cp), 113.6 (s, Cp), 110.6 (s, Cp), 110.5 (s, Cp), 107.5 (s, Cp), 32.2 (d, $^1J_{CP} = 24.0$ Hz, C(CH₃)₃), 31.8 (s, ZrCH₃), 30.8 (d, $^2J_{CP} = 15.9$ Hz, C(CH₃)₃), -4.96, -5.67 (s, Si(CH₃)₂). $^{31}P\{^1H\}$ NMR (161 MHz, PhCl-d₅): δ 9.96 (s). ESI-MS: 529.1621 [M - H]⁺.

4.2.3. Synthesis of Cationic Complexes [R₂Zr(OⁱP(^tBu)₂)][(C₆F₅)₄] (2–5). Data for the [B(C₆F₅)₄] anion are reported separately. $^{11}B\{^1H\}$ NMR (96 MHz, CD₂Cl₂): δ -17.60 (s). ^{19}F NMR (376 MHz, DCM-d₂): δ -133.17 (s), -163.70 (s), -167.71 (s). $^{13}C\{^1H\}$ NMR (125 MHz, DCM-d₂): δ 148.26 (d, $J = 245.3$ Hz, o-B(C₆F₅)₄), 136.68 (d, $J = 242.4$ Hz, p-B(C₆F₅)₄), 134.76 (d, $J = 254.1$ Hz, m-B(C₆F₅)₄), 124.30 (br, ipso-CB).

4.2.3.1. Via Protonolysis with [DTBP(H)][(C₆F₅)₄]. In a glovebox, stoichiometric amounts of the relevant neutral complex [R₂Zr(Me)-(OⁱP(^tBu)₂)] and [DTBP(H)][(C₆F₅)₄] were weighed into separate vials and dissolved in the minimum amount of PhF (note that PhCl and PhBr can be used interchangeably). The solution of [DTBP(H)][(C₆F₅)₄] was added dropwise to the vial containing the zirconium complex. Gas evolution was evident, and the resulting solution was stirred for 1 h, yielding bright yellow solutions. Due to inherent instability, the complexes were used in situ to investigate the reactivity toward Me₂NH·BH₃.

4.2.3.2. [(Ind₂Zr(OC₆H₄P(^tBu)₂)][(C₆F₅)₄] (2). Near-quantitative yield by 1H NMR. 1H NMR (400 MHz, PhCl-d₅): δ 7.59–7.70 (m, 5H, H6 and H4,7), 7.53 (pseudo t, 1H, $J = 7.3$ Hz, H3), 7.30–7.40 (m, 5H, H6,5 and H4), 6.57–6.61 (m, 1H, H5), 6.27–6.31 (m, 2H, H1,3), 5.80–5.85 (m, 2H, H2), 5.74–5.80 (m, 2H, H1,3), 1.36 (18H, d, $^3J_{HP} = 14.6$ Hz, PC(CH₃)₃). $^{13}C\{^1H\}$ NMR (125 MHz, PhCl-d₅): δ 166.2 (d, $^2J_{CP} = 15.6$ Hz, C1), 133.6 (d, $^4J_{CP} = 4.2$ Hz, C5), 132.4 (d, $^3J_{CP} = 1.2$ Hz, C4), 130.1 (s, C6,5), 129.1 (s, C3a,5a), 127.9 (s, C6,5), 125.5 (s, C3a,5a), 125.3 (s, C4,7), 124.4 (s, C4,7), 123.0 (d, $^1J_{CP} = 27.0$ Hz, C2), 122.8 (d, $^3J_{CP} = 3.4$ Hz, C6), 122.3 (s, C2), 117.7 (d, $^2J_{CP} = 5.0$ Hz, C3), 103.6 (s, C1,3), 103.5 (s, C1,3), 37.0 (s, $^1J_{CP} = 7.4$ Hz, PC(CH₃)₃), 29.7 (d, $^2J_{CP} = 4.5$ Hz, PC(CH₃)₃). $^{31}P\{^1H\}$ NMR (161 MHz, PhCl-d₅): δ 55.9 (s). ESI-MS: 589.1771 m/z [M + MeOH].

4.2.3.3. [(^tBuC₅H₄)₂Zr(OC₆H₄P(^tBu)₂)][(C₆F₅)₄] (3). Near-quantitative yield by 1H NMR. 1H NMR (400 MHz, PhCl-d₅): δ 7.13 (dt, 1H, $J = 0.9, 7.7$ Hz, H6), 7.03 (ddd, 1H, $J = 1.6, 6.0$ Hz, H4), 6.80–6.85 (m, 1H, H5), 6.70–6.75 (m, 2H, Cp), 6.39 (dq, 1H, $J = 1.0, 4.5$ Hz, H3), 6.25–6.30 (m, 2H, Cp), 6.00–6.08 (m, 4H, Cp), 1.11 (d, 18H, $^3J_{HP} = 14.8$ Hz, PC(CH₃)₃), 0.90 (s, 18H, CpC(CH₃)₃). $^{13}C\{^1H\}$ NMR (125 MHz, PhCl-d₅): δ 167.1 (d, $^2J_{CP} = 15.2$ Hz, C1), 149.9 (s, ipso-Cp(^tBu)), 133.8 (d, $^4J_{CP} = 2.8$ Hz, C5), 133.3 (d, $^3J_{CP} = 1.4$ Hz, C4), 122.1 (d, $^1J_{CP} = 21.3$ Hz, C2), 121.9 (s, C6), 118.2 (d, $^2J_{CP} = 4.8$ Hz, C3), 115.7, 113.3, 113.2, 111.1 (Cp), 37.4 (d, $J = 4.9$ Hz, PC(CH₃)₃), 31.7 (s, CpC(CH₃)₃), 30.3 (d, $J = 4.7$ Hz, PC(CH₃)₃), 30.1 (s, CpC(CH₃)₃). $^{31}P\{^1H\}$ NMR (161 MHz, PhCl-d₅): δ 58.05 (s). ESI-MS: 569.2483 m/z [M]⁺.

4.2.3.4. [Me₂Si(C₅H₄)₂Zr(OC₆H₄P(^tBu)₂)][(C₆F₅)₄] (4). Near-quantitative yield by 1H NMR. 1H NMR (400 MHz, PhCl-d₅): δ 7.41 (t, 1H, $J = 7.8$ Hz, H5), 7.14–7.16 (m, 1H, H4), 7.06–7.08 (m, 1H, H6), 6.93 (br s, 2H, Cp), 6.63–6.65 (m, 1H, H3), 6.28 (br s, 2H, Cp), 6.20 (br s, 2H, Cp), 5.37 (br s, 2H, Cp), 1.12 (d, 18H, $^3J_{HP} = 13.3$ Hz, C(CH₃)₃), 0.82 (br s, 3H, SiCH₃), 0.56 (br s, 3H, SiCH₃). $^{13}C\{^1H\}$ (100 MHz, PhCl-d₅): δ 165.3 (d, $^2J_{CP} = 15.4$ Hz, C1), 134.4 (d, $^4J_{CP} = 1.1$ Hz, C5), 132.8 (d, $^3J_{CP} = 1.5$ Hz, C4), 126.9 (br s, Cp), 122.7 (d, $^3J_{CP} = 4.4$ Hz, C6), 121.9 (d, $^1J_{CP} = 26.7$ Hz, C2), 119.0 (br s, Cp), 118.4 (br s, Cp), 117.3 (d, $^2J_{CP} = 6.7$ Hz, C3), 116.0 (br s, Cp), 115.4 (s, ipso-CpSi), 37.6 (d, $^1J_{CP} = 6.0$ Hz, PC(CH₃)₃), 30.0 (d, $^2J_{CP} = 4.6$ Hz, PC(CH₃)₃), -5.2 (br s, SiCH₃), -7.3 (br s, SiCH₃). $^{31}P\{^1H\}$ NMR (161 MHz, PhCl-d₅): δ 57.57 (s). ESI-MS: 513.1313 m/z [M]⁺.

4.3. Synthesis of Intramolecular FLP System 5. 4.3.1. Synthesis of Electron Deficient Phosphino Alcohol. 4.3.1.1. Bis[3,5-bis-(trifluoromethyl)phenyl]chlorophosphine. Magnesium turnings (700 mg) were covered with THF and a solution of 1,3-bis-(trifluoromethyl)-5-bromobenzene (4.91 mL, 28.5 mmol) in THF (20 mL) added dropwise with cooling (0 °C). The reaction mixture was stirred at room temperature for 1 h, leading to formation of a

brown solution. The reaction mixture was cooled to 0 °C, and a solution of diethylphosphoramidous dichloride (2.00 mL, 13.7 mmol) in THF (10 mL) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the resulting residue dissolved in hexane, filtered through Celite, and concentrated to ~20 mL. Hydrogen chloride solution (2.0 M in Et₂O, 13.7 mL, 27.4 mmol) was added dropwise at room temperature and the reaction mixture stirred for 2 h, yielding a white precipitate of the amine hydrochloride. Subsequent filtration and removal of solvent in vacuo yielded the desired chlorophosphine as a white solid (4.45 g, 66%). All recorded data are consistent with those in the literature.²⁷ $^{31}P\{^1H\}$ NMR (121 MHz, CDCl₃): δ 70.4 (s).

4.3.1.2. Bis[3,5-bis-(trifluoromethyl)phenyl]phosphine. A solution of (3,5-CF₃-C₆F₃)₂PCl (2.56 g, 5.21 mmol) in Et₂O (12 mL) was added dropwise to a suspension of LiAlH₄ (198 mg, 4.27 mmol) in Et₂O (40 mL) at room temperature. The solution was heated at reflux for 2 h and then quenched with degassed H₂O (0.15 mL). Filtration through Celite and removal of solvent in vacuo yielded the desired phosphine as a white solid (2.10 g, 88%). All recorded data are consistent with those in the literature.^{28,29} 1H NMR (300 MHz, CDCl₃): δ 7.55 (s, 1H, ArH), 7.44 (ps d, 2H, $J = 5.7$ Hz, ArH), 4.56 (d, 1H, $^1J_{PH} = 223.9$ Hz, PH). ^{31}P NMR (121 MHz, CDCl₃): δ -41.1 (d, $^1J_{PH} = 216.8$ Hz).

4.3.1.3. [Bis(3,5-bis-(trifluoromethyl)phenyl)phosphanyl]phenol. 2-Iodophenol (371 mg, 1.69 mmol), (3,5-CF₃-C₆F₃)₂PH (773 mg, 1.69 mmol), Cs₂CO₃ (1.10 g, 3.37 mmol), and palladium(II) acetate (37 mg, 0.17 mmol) were combined in a Schlenk tube and dissolved in toluene (15 mL). The reaction mixture was heated at 100 °C for 16 h. The solution was filtered through a silica plug and eluted with DCM and the solvent removed in vacuo to give the desired product, which was further purified by flash chromatography: silica, DCM/hexane (50/50). Brown solid (817 mg, 88%). 1H NMR (300 MHz, C₆D₆): δ 7.93 (s, 2H, P-ArH), 7.82–7.83 (pseudo d, 4H, $J = 6.9$ Hz, P-ArH), 7.44 (ddd, 1H, $J = 1.7, 7.4, 8.1$ Hz, H6), 7.02 (dt, 1H, $J = 0.9, 7.5$ Hz, H3), 6.91–6.97 (m, 2H, H4 and H5). $^{31}P\{^1H\}$ NMR (121 MHz, C₆D₆): δ -11.0 (s). $^{13}C\{^1H\}$ NMR (125 MHz, C₆D₆): δ 158.3 (d, $J = 15.7$ Hz, C1), 138.7 (d, $^1J_{CP} = 15.7$ Hz, ipso-P-Ar), 134.6 (d, $J = 8.5$ Hz, C5), 133.4 (pseudo d, $J = 21.3$ Hz, P-Ar), 132.8 (s, C6), 131.7 (dq, $^1J_{CF} = 6.3, 34.0$ Hz, ipso-C(CF₃)), 123.3 (q, $^1J_{CF} = 273.0$ Hz, C(CF₃)), 123.2 (qu, $^3J_{CF} = 3.9$ Hz, P-Ar), 121.9 (d, $J = 3.7$ Hz, C3), 118.1 (d, $J = 9.2$ Hz, C2), 115.9 (d, $J = 1.6$ Hz, C4).

4.3.2. Synthesis of Cationic Complex [(C₅H₅)₂Zr(OC₆H₄P(m-CF₃C₆H₃)₂)][(C₆F₅)₄] (5). In a glovebox, a solution of the dimethyl zirconocene (1 equiv) and phosphino alcohol (1 equiv) were individually dissolved in the minimum amount of PhF prior to combination. The resulting solutions were stirred for 30 min. [Ph₃C] [(C₆F₅)₄] (1 equiv) was weighed into a separate vial and dissolved in the minimum amount of PhF (note that PhCl and PhBr can be used interchangeably). The solution of [Ph₃C] [(C₆F₅)₄] was added dropwise to the vial containing the zirconium complex. The resulting solution was stirred for 1 h. Due to inherent instability, the complexes were used immediately to investigate the reaction toward Me₂NH·BH₃. Attempted isolation of both complexes resulted in decomposition. 1H NMR (300 MHz, PhCl/toluene-d₈; aromatic signals are obscured by PhF signals and could not be unambiguously identified): δ 6.68–6.72 (m, 2H, H4 and H5), 5.83 (s, 10H, C₅H₅). $^{31}P\{^1H\}$ NMR (121 MHz, PhCl/toluene-d₈): δ -13.9 (s).

4.4. Dehydrocoupling of Me₂NH·BH₃ by Complexes 2–5. General Method. In a glovebox, a PhCl stock solution of the cationic zirconocene complex (0.025 M) was made as detailed above. A 0.5 mL portion of the solution (0.012 mmol) was added to a glass vial of preweighed Me₂NH·BH₃ (15 mg, 0.25 mmol). A color change from yellow to colorless and evolution of gas was evident. The solution was transferred to a J. Young NMR tube and removed from the glovebox, and the relevant spectra were obtained.

4.5. Reaction of FLP System 1 (5 mol %) with Me₂NH·BH₂·Me₂N·BH₃. In a glovebox 1 (9 mg, 0.008 mmol) and Me₂NH·BH₂·Me₂N·BH₃ (18.6 mg, 0.16 mmol) were weighed out into glass vials and combined in PhCl (0.5 mL). The solution was transferred to a

quartz J. Young NMR tube and then removed from the glovebox. The reaction was monitored by ^{11}B NMR spectroscopy and found to give complete conversion to $[\text{Me}_2\text{N-BH}_2]_2$ in 20 min.

4.6. Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ by Complexes 7–12. In a glovebox $[\text{Cp}^*_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$ (6; 21 mg, 0.018 mmol) and the relevant phosphine (0.018 mmol; 7, PtBu_3 4 mg; 8, PCy_3 5 mg; 9, PEt_3 2 mg; 10, PPh_3 5 mg; 11, PMes_3 7 mg; 12, $\text{P}(\text{C}_6\text{F}_5)_3$ 10 mg) were weighed into glass vials. The phosphine was dissolved in PhCl (0.5 mL) and mixed with $[\text{Cp}^*_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$ (6). The resulting red solution was added to a glass vial containing $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (9.5 mg, 0.16 mmol), and the solution was mixed to ensure full dissolution of the amine–borane before it was transferred to a quartz J. Young NMR tube. The tube was subsequently removed from the glovebox, and the relevant spectra were obtained. In all cases the reactions show <5% conversion to $[\text{Me}_2\text{N-BH}_2]_2$ after 24 h.

4.7. Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ by Complexes 14–19.

In a glovebox $[\text{Cp}_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$ (19 mg, 0.018 mmol) and the relevant phosphine (0.018 mmol; 14, PtBu_3 4 mg; 15, PCy_3 5 mg; 16, PEt_3 2 mg; 17, PPh_3 5 mg; 18, PMes_3 7 mg; 19, $\text{P}(\text{C}_6\text{F}_5)_3$ 10 mg) were weighed into glass vials. The phosphine was dissolved in PhCl (0.5 mL) and mixed with $[\text{Cp}_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$. In the cases of 15–17 a color change from orange to yellow was observed indicative of a persistent Zr–P bond. The resulting solutions were added to a glass vial containing $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (9.5 mg, 0.16 mmol), and the solution was mixed to ensure full dissolution of the amine–borane before it was transferred to a quartz J. Young NMR tube. The tube was subsequently removed from the glovebox, and the relevant spectra were obtained. 15–17 showed <5% conversion to $[\text{Me}_2\text{N-BH}_2]_2$ after 14 h. The reaction using 14 was followed by ^{11}B NMR spectroscopy, and the stacked spectra are shown in Figure S1 in the Supporting Information.

4.8. Synthesis of Compound 20. In a glovebox a chlorobenzene (1 mL) solution of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (4 mg, 0.07 mmol) was added dropwise to a chlorobenzene (1 mL) solution of 6 (78 mg, 0.07 mmol). An immediate color change from orange to yellow was observed. The resulting solution was precipitated into a large volume (20 mL) of rapidly stirred pentane. The solvent was decanted off before washing with pentane (3×5 mL). The resulting yellow solid was dried in vacuo (65 mg, 79%). Crystals of 20 suitable for analysis by X-ray crystallography were obtained by layering a PhCl solution of 20 with pentane (5 days). ^1H NMR (500 MHz, d_5 - PhBr): δ 0.54 (3H, br s, $\text{Me}_2\text{NH}\cdot\text{BH}_3$), 1.49 (30H, s, Cp^*), 1.77 (6H, s, ortho- CH_3), 2.02 (3H, s, para- CH_3), 2.12 (6H, s, $\text{Me}_2\text{NH}\cdot\text{BH}_3$), 3.60 (1H, br s, $\text{Me}_2\text{NH}\cdot\text{BH}_3$), 6.56 (2H, s, Ar-H). ^{13}C NMR (125 MHz, d_5 - PhBr): δ 15.3 (s, Cp^*), 24.0 (s, ortho- CH_3), 26.2 (s, para- CH_3), 47.7 (s, $\text{Me}_2\text{NH}\cdot\text{BH}_3$), 128.5 (s, Cp^*), 159.1 (s, ipso-C). Other aromatic peaks are obscured by the PhBr solvent. Signals corresponding to $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ are also present as reported above. ^{11}B NMR (96 MHz, d_5 - PhBr): δ -16.9 (s, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$), -11.5 (br s, $\text{Me}_2\text{NH}\cdot\text{BH}_3$).

4.9. Deprotonation of 20 with PR_3 . In a glovebox 20 (20 mg, 0.016 mmol) and the corresponding phosphine (0.016 mmol; PtBu_3 3 mg; PCy_3 5 mg; PEt_3 2 mg; PPh_3 5 mg; PMes_3 6 mg; $\text{P}(\text{C}_6\text{F}_5)_3$ 9 mg) were weighed into a glass vial and dissolved in chlorobenzene (0.5 mL). The resulting solution was transferred to a quartz J. Young NMR tube and removed from the glovebox. The reaction was monitored by ^{11}B and ^{31}P NMR spectroscopy.

4.10. Reaction between $\text{Me}_2\text{NH}\cdot\text{BH}_2\text{-Me}_2\text{N}\cdot\text{BH}_3$ and 20 mol % of 14. In a glovebox $[\text{Cp}_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$ (37 mg, 0.036 mmol) and the PtBu_3 (8 mg, 0.036 mmol) were weighed into glass vials. The phosphine was dissolved in PhCl (0.5 mL) and mixed with $[\text{Cp}_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$. The resulting solution was placed in a glass vial containing $\text{Me}_2\text{NH}\cdot\text{BH}_2\text{-Me}_2\text{N}\cdot\text{BH}_3$ (18.6 mg, 0.16 mmol), and the solution was mixed to ensure full dissolution of the amine–borane before it was transferred to a quartz J. Young NMR tube. The tube was subsequently removed from the glovebox, and the relevant spectra were obtained (Figure S2 in the Supporting Information).

4.11. Reaction between $\text{Me}_2\text{NH}\cdot\text{BH}_2\text{-Me}_2\text{N}\cdot\text{BH}_3$ and 20 mol % of 6. In a glovebox $[\text{Cp}_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$ (37 mg, 0.036 mmol) was weighed into a glass vial and dissolved in PhCl (0.5 mL). The resulting solution was placed in a glass vial containing $\text{Me}_2\text{NH}\cdot\text{BH}_2\text{-}$

$\text{Me}_2\text{N}\cdot\text{BH}_3$ (18.6 mg, 0.16 mmol), and the solution was mixed to ensure full dissolution of the amine–borane before it was transferred to a quartz J. Young NMR tube. The tube was subsequently removed from the glovebox, and the relevant spectra were obtained (Figure S3 in the Supporting Information).

4.12. Reaction between $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ and 10 mol % of 14. In a glovebox $[\text{Cp}_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$ (18 mg, 0.018 mmol) and the PtBu_3 (4 mg, 0.018 mmol) were weighed into glass vials. The phosphine was dissolved in PhCl (0.5 mL) and mixed with $[\text{Cp}_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$. The resulting solution was placed in a glass vial containing $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ (20.5 mg, 0.18 mmol), and the solution was mixed to ensure full dissolution of the amine–borane before it was transferred to a quartz J. Young NMR tube. The tube was subsequently removed from the glovebox, and the relevant spectra were obtained (Figure S4 in the Supporting Information).

4.13. Synthesis of Compound 21. The methodology used for the synthesis of 21 was analogous to that employed for the synthesis of 20. In a glovebox a chlorobenzene (1 mL) solution of $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ (4 mg, 0.03 mmol) was added dropwise to a chlorobenzene (1 mL) solution of 6 (40 mg, 0.03 mmol). An immediate color change from orange to yellow was observed. The resulting solution was precipitated into a large volume (20 mL) of rapidly stirred pentane. The solvent was decanted off before washing with pentane (3×5 mL). The resulting yellow solid was dried in vacuo (35 mg, 79%). Crystals of 21 suitable for analysis by X-ray crystallography were obtained by layering a PhCl solution of 21 with pentane (2 days). ^1H NMR (500 MHz, d_5 - PhCl): δ 1.04 (12H, d, $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$), 1.69 (30H, s, Cp^*), 1.97 (6H, s, ortho- CH_3), 2.18 (3H, s, para- CH_3), 3.09 (2H, m, $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$), 3.35 (1H, br s, $\text{Me}_2\text{NH}\cdot\text{BH}_3$), 6.72 (2H, s, Ar-H). ^{13}C NMR (125 MHz, d_5 - PhCl): δ 11.6 (s, Cp^*), 19.4 (s, ortho- CH_3), 19.7 (s, ^iPr), 26.2 (s, para- CH_3), 54.3 (s, ^iPr), 123.3 (s, meta-C), 128.5 (s, Cp^*), 155.7 (s, ipso-C). Other aromatic peaks are obscured by the PhCl solvent. Signals corresponding to $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ are also present as reported above. ^{11}B NMR (96 MHz, d_5 - PhCl): δ -16.9 (s, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$), -9.5 (br s, $^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$).

ASSOCIATED CONTENT

* Supporting Information

Additional spectra, further synthetic details, and crystallo-graphic data (PDF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* 2007, 2613–2626. (b) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. *Chem. Rev.* 2010, 110, 4023. (c) Smythe, N. C.; Gordon, J. C. *Eur. J. Inorg. Chem.* 2010, 2010, 509–521. (d) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* 2009, 38, 279.
- (2) (a) Jiang, Y.; Berke, H. *Chem. Commun.* 2007, 3571–3573. (b) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. *Organometallics* 2009, 28, 5493–5504. (c) Sloan, M. E.; Staubitz, A.; Lee, K.; Manners, I. *Eur. J. Org. Chem.* 2011, 672. (d) Leitao, E. L.;

- Stubbs, N. E.; Robertson, A. P. M.; Helten, H.; Cox, R. J.; Lloyd-Jones, G. C.; Manners, I. *J. Am. Chem. Soc.* 2012, 134, 16805.
- (3) (a) Staubitz, A.; Robertson, A. P. M.; Manners, I. *Chem. Rev.* 2010, 110, 4079. (b) Staubitz, A.; Presa Soto, A.; Manners, I. *Angew. Chem., Int. Ed.* 2008, 47, 6212. (c) Ledoux, A.; Larini, P.; Boisson, C.; Monteil, V.; Raynaud, J.; Lacôte, E. *Angew. Chem., Int. Ed.* 2015, 54, 15744. (d) Lorenz, T.; Lik, A.; Plamper, F. A.; Helten, H. *Angew. Chem., Int. Ed.* 2016, 55, 7236. (e) Dallanegra, R.; Robertson, A. P. M.; Chaplin, A. B.; Manners, I.; Weller, A. S. *Chem. Commun.* 2011, 47, 3763.
- (4) (a) Leitao, E. M.; Jurca, T. J.; Manners, I. *Nat. Chem.* 2013, 5, 817. (b) Johnson, H. C.; Hooper, T. N.; Weller, A. S. *Top. Organomet. Chem.* 2015, 49, 153. (c) Staubitz, A.; Sloan, M. E.; Robertson, A. P. M.; Friedrich, A.; Schneider, S.; Gates, P. J.; auf der Günne, J. S.; Manners, I. *J. Am. Chem. Soc.* 2010, 132, 13332. (d) Baker, R. T.; Gordon, J. C.; Hamilton, C. W.; Henson, N. J.; Lin, P. H.; Maguire, S.; Murugesu, M.; Scott, B. L.; Smythe, N. C. *J. Am. Chem. Soc.* 2012, 134, 5598. (e) Marziale, A. N.; Friedrich, A.; Klopsch, I.; Drees, M.; Celinski, V. R.; auf der Günne, J. S.; Schneider, S. *J. Am. Chem. Soc.* 2013, 135, 13342. (f) Sewell, L. J.; Lloyd-Jones, G. C.; Weller, A. S. *J. Am. Chem. Soc.* 2012, 134, 3598. (g) Sonnenberg, J. F.; Morris, R. H. *ACS Catal.* 2013, 3, 1092. (h) Ledger, A. E. W.; Ellul, C. E.; Mahon, M. F.; Williams, J. M. J.; Whittlesey, M. *Chem. - Eur. J.* 2011, 17, 8704.
- (i) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. *Organometallics* 2009, 28, 5493. (j) Yang, X.; Zhao, L.; Fox, T.; Wang, Z. - X.; Berke, H. *Angew. Chem., Int. Ed.* 2010, 49, 2058. (k) Pun, D.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* 2007, 3297.
- (5) (a) Bellham, P.; Hill, M. S.; Kociok-Köhn, G. *Organometallics* 2014, 33, 5716–5721. (b) Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; MacDougall, D. J. *Chem. - Eur. J.* 2010, 16, 8508–8515. (c) Cowley, H. J.; Holt, M. S.; Melen, R. L.; Rawson, J. M.; Wright, D. S. *Chem. Commun.* 2011, 47, 2682–2684. (d) Hansmann, M. M.; Melen, R. L.; Wright, D. S. *Chem. Sci.* 2011, 2, 1554–1559. (e) Less, R. J.; Simmonds, H. R.; Dane, S. B. J.; Wright, D. S. *Dalton Trans.* 2013, 42, 6337–6343. (f) Hill, M. S.; Kociok-Köhn, G.; Robinson, T. P. *Chem. Commun.* 2010, 46, 7587–7589.
- (6) (a) Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem., Int. Ed.* 2007, 46, 746–749. (b) Himmelberger, D. W.; Yoon, C. W.; Bluhm, M. E.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* 2009, 131, 14101–14110.
- (7) (a) Stephan, D. W. *J. Am. Chem. Soc.* 2015, 137, 10018–10032. (b) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* 2015, 54, 6400–6441.
- (8) (a) Miller, J. M.; Bercaw, J. E. *Chem. Commun.* 2010, 46, 1709. (b) Whittell, G. R.; Balmond, E. I.; Robertson, A. P. M.; Patra, S. K.; Haddow, M. F.; Manners, I. *Eur. J. Inorg. Chem.* 2010, 3967.
- (9) Appelt, C.; Slootweg, J. C.; Lammerstma, K.; Uhl, W. *Angew. Chem., Int. Ed.* 2013, 52, 4256.
- (10) Mo, Z.; Rit, A.; Campos, J.; Kolychev, E. L.; Aldridge, S. J. *Am. Chem. Soc.* 2016, 138, 3306–3309.
- (11) (a) Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* 2011, 133, 18463. (b) Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* 2011, 133, 8826.
- (12) Metters, O. J.; Forrest, S. J. K.; Sparkes, H. A.; Manners, I.; Wass, D. F. *J. Am. Chem. Soc.* 2016, 138, 1994.
- (13) Allman, T.; Goel, R. G. *Can. J. Chem.* 1982, 60, 716–722.
- (14) Benoit, R. L.; Frechette, M.; Lefebvre, D. *Can. J. Chem.* 1988, 66, 1159–1162 and references therein.
- (15) Lummis, P. A.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Dalton Trans.* 2015, 44, 7009–7020.
- (16) Treichel, P. M.; Johnson, J. W.; Wagner, K. P. *J. Organomet. Chem.* 1975, 88, 227.
- (17) (a) Helten, H.; Dutta, B.; Vance, J. R.; Sloan, M. E.; Haddow, M. F.; Sproules, S.; Collison, D.; Whittell, G. R.; Lloyd-Jones, G. C.; Manners, I. *Angew. Chem., Int. Ed.* 2013, 52, 437. (b) Sloan, M. E.; Staubitz, A.; Clark, T. J.; Russell, C. A.; Lloyd-Jones, G. C.; Manners, I. *J. Am. Chem. Soc.* 2010, 132, 3831. (c) Johnson, H. C.; Robertson, A. P. M.; Chaplin, A. B.; Sewell, L. C.; Thompson, A. L.; Haddow, M. F.; Manners, I.; Weller, A. S. *J. Am. Chem. Soc.* 2011, 133, 11076.
- (d) Friedrich, A.; Drees, M.; Schneider, S. *Chem. - Eur. J.* 2009, 15, 10339. (e) Douglas, T. M.; Chaplin, A. B.; Weller, A. S.; Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* 2009, 131, 15440. (f) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* 2003, 125, 9424. (g) Pons, V.; Baker, R. T.; Szymczak, N. K.; Heldebrant, D. J.; Linehan, J. C.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Chem. Commun.* 2008, 6597.
- (h) Chen, X.; Zhao, J.-C.; Shore, S. G. *J. Am. Chem. Soc.* 2010, 132, 10658. (i) Chen, X.; Bao, X.; Zhao, J.-C.; Shore, S. G. *J. Am. Chem. Soc.* 2011, 133, 14172. (j) Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; MacDougall, D. J. *Chem. - Eur. J.* 2010, 16, 8508. (k) Spielmann, J.; Jansen, G.; Bandmann, H.; Harder, S. *Angew. Chem., Int. Ed.* 2008, 47, 6290.
- (18) (a) Wallis, C. J.; Alcaraz, G.; Petit, A. S.; Poblador-Bahamonde, A. I.; Clot, E.; Bijani, C.; Vendier, L.; Sabo-Etienne, S. *Chem. - Eur. J.* 2015, 21, 13080. (b) Wallis, C. J.; Dyer, H.; Vendier, L.; Alcaraz, G.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* 2012, 51, 3646. (c) Alcaraz, G.; Chaplin, A. B.; Stevens, C. J.; Clot, E.; Vendier, L.; Weller, A. S.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* 2010, 49, 918. (d) Vance, J. R.; Schafer, A.; Robertson, A. P. M.; Lee, K.; Turner, J.; Whittell, G. R.; Manners, I. *J. Am. Chem. Soc.* 2014, 136, 3048. (e) Vance, J. R.; Robertson, A. P. M.; Lee, K.; Manners, I. *Chem. - Eur. J.* 2011, 17, 4099. (f) Stevens, C. J.; Dallanegra, R.; Chaplin, A. B.; Weller, A. S.; MacGregor, S. A.; Ward, B.; McKay, D.; Alcaraz, G.; Sabo-Etienne, S. *Chem. - Eur. J.* 2011, 17, 3011. (g) Alcaraz, G.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* 2010, 49, 7170. (h) Vidovic, D.; Addy, D. A.; Kramer, T.; McGrady, J.; Aldridge, S. *J. Am. Chem. Soc.* 2011, 133, 8494.
- (i) Shimoi, M.; Nagai, S.; Ichikawa, M.; Kawano, Y.; Kato, K.; Uruichi, M.; Ogino, H. *J. Am. Chem. Soc.* 1999, 121, 11704. (j) Pons, V.; Baker, R. T.; Szymczak, N. K.; Heldebrant, D. J.; Linehan, J. C.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Chem. Commun.* 2008, 6597.
- (19) Friedrich, A.; Drees, M.; Schneider, S. *Chem. - Eur. J.* 2009, 15, 10339–10342.
- (20) For examples of κ^2 coordination of amine-boranes and aminoboranes see: (a) Johnson, H. C.; Weller, A. S. *J. Organomet. Chem.* 2012, 721–722, 17. (b) Tang, C. Y.; Thompson, A. L.; Aldridge, S. *Angew. Chem., Int. Ed.* 2010, 49, 921. (c) Algarra, A. G.; Sewell, L. J.; Johnson, H. C.; Macgregor, S. A.; Weller, A. S. *Dalton Trans.* 2014, 43, 11118. (d) Tang, C. Y.; Phillips, N.; Bates, J. I.; Thompson, A. L.; Gutmann, M. J.; Aldridge, S. *Chem. Commun.* 2012, 48, 8096–8098. (e) Tang, C. Y.; Thompson, A. L.; Aldridge, S. *J. Am. Chem. Soc.* 2010, 132, 10578–10591. (f) Chaplin, A. B.; Weller, A. S. *Inorg. Chem.* 2010, 49, 1111. (g) Johnson, H. C.; Robertson, A. P. M.; Chaplin, A. B.; Sewell, L. J.; Thompson, A. L.; Haddow, M. F.; Manners, I.; Weller, A. S. *J. Am. Chem. Soc.* 2011, 133, 11076.
- (h) Dallanegra, R.; Robertson, A. P. M.; Chaplin, A. B.; Manners, I.; Weller, A. S. *Chem. Commun.* 2011, 47, 3763–3765.
- (21) (a) Robertson, A. P. M.; Leitao, E. M.; Jurca, T.; Haddow, M. F.; Helten, H.; Lloyd-Jones, G. C.; Manners, I. *J. Am. Chem. Soc.* 2013, 135, 12670. (b) Robertson, A. P. M.; Leitao, E. M.; Manners, I. *J. Am. Chem. Soc.* 2011, 133, 19322.
- (22) Metters, O. J.; Chapman, A. M.; Robertson, A. P. M.; Woodall, C. H.; Gates, P. J.; Wass, D. F.; Manners, I. *Chem. Commun.* 2014, 50, 12146.
- (23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* 1996, 15, 1518.
- (24) Balboni, D.; Camurati, I.; Ingurgio, A. C.; Guidotti, S.; Focante, F.; Resconi, L. J. *J. Organomet. Chem.* 2003, 683, 2–10.
- (25) Couturier, S.; Gautheron, B. *J. Organomet. Chem.* 1978, 157, C61.
- (26) Rocchigiani, L.; Bellachioma, G.; Zuccaccia, C.; Macchioni, A. J. *J. Organomet. Chem.* 2012, 714, 32–40.
- (27) Jutzi, P.; Muller, C.; Stammer, A.; Stammer, H.-G. *Organo-metallics* 2000, 19, 1442.
- (28) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. J. Am. Chem. Soc.* 1994, 116, 9869.
- (29) Casey, C. P.; Paulsen, E. L.; Beuttenmueller, E. W.; Proft, B. R.; Petrovich, L. M.; Matter, B. A.; Powell, D. R. *J. Am. Chem. Soc.* 1997, 119, 11817–11825.