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School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS

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-phosphinoaryloxide ($-O(C_6H_4)PR_2$, R = ^tBu and 3,5-CF_3-(C_6H_3)) ligands are reported and their activity as catalysts for the dehydrocoupling of dimethylamine-borane ($Me_2NH•BH_3$) assessed. FLP system $[(C_9H_7)_2ZrO(C_6H_4)P^tBu_2][B(C_6F_5)_4]$ is shown to give unprecedented turnover frequencies (TOF) for a catalyst based on a group 4 metal (TOF = > 600 h^{-1}), whilst 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, 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*

1. Introduction

Catalytic dehydrogenation and dehydrocoupling of amine boranes is of broad current interest due to their potential applications as hydrogen storage materials,[1] 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 methodologies 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 ($H_3N•BH_3$).[6]
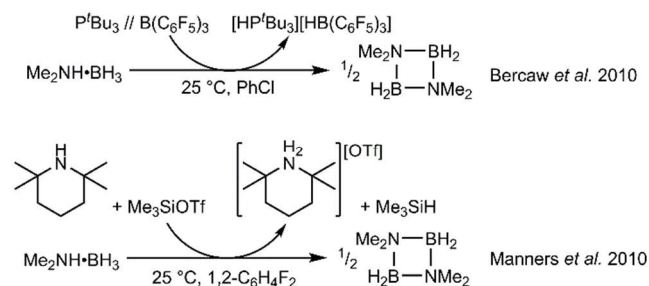
Scheme 1. Main-group FLPs capable of mediating the stoichiometric dehydrogenation of $Me_2NH•BH_3$

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 ($Me_2NH•BH_3$) 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, Slootweg et al. reported an intramolecular Al/P FLP capable of dehydrogenating $Me_2NH•BH_3$ under melt conditions (45 °C, 9.3 mol %), complete consumption of the monomer is achieved by heating to 90 °C for 45 mins, however, only a 71% yield of the desired 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 (RR'NH•BH$_3$, R = R' = H, R = Me and R' = H, R = R' = Me) however still requires elevated temperatures and long reaction times (1 mol%, CH_2Cl_2 or THF, 55 °C, 24-48 h) (Scheme 2).[10]
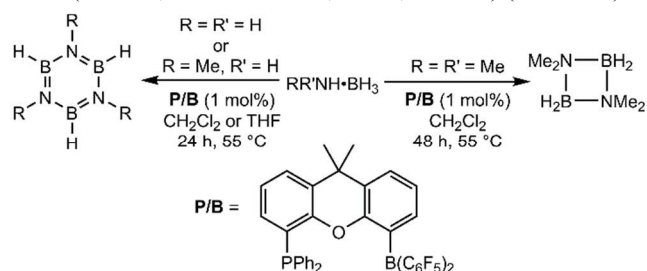
Scheme 2. P/B FLP developed by Aldridge et al. capable of mediating the catalytic dehydrocoupling of a range of amine-boranes

1

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 (**1**) have been shown to rapidly dehydrocouple several amine-borane substrates under ambient conditions to yield the expected products (Scheme 3).[11b]
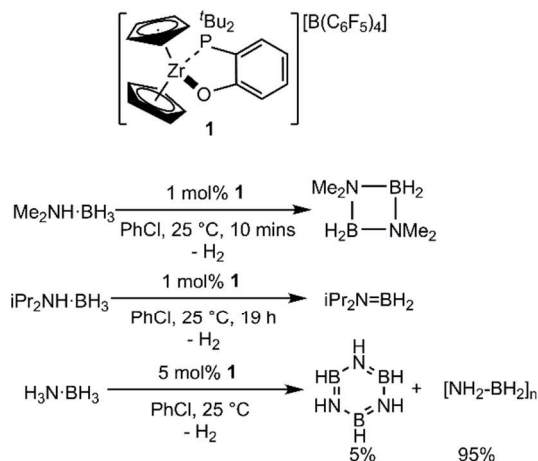
Scheme 3. Catalytic dehydrocoupling of amine-boranes using Zr/P FLP 1.

Herein we report a series of novel intramolecular Zr–P FLP systems featuring variations to the ancilliary ligands bound to Zr and also incorporating a weakly Lewis basic phosphine $(RP(3,5-CF_3(C_6H_3))_2)$. These were subsequently applied to the catalytic dehydrocoupling of $Me_2NH\cdot BH_3$. 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 $[Cp^R_2ZrOMes][B(C_6F_5)_4]$ // PR'_3 (R = Me/H, R' = ^tBu, Cy, Et, Ph, Mes, C_6F_5).[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 dimethylzirconocene precursor (R_2ZrMe_2) followed by protonolysis with the corresponding alcohol $(HO(C_6H_4)P^tBu_2)$. Subsequently the catalytically active cationic species was generated by reaction with $[H–DTBP][B(C_6F_5)_4]$ (DTBP = 2,6-di-tertbutylpyridine) with concomitant release of 1 equiv. methane (Scheme 4).

The generation of cationic species **2-4** can be monitored by ^{31}P NMR spectroscopy. Upon addition of $[H–DTBP][B(C_6F_5)_4]$ to the neutral precursors, protonation of the pendant phosphine moiety is observed. This is manifested as a new resonance in the ^{31}P NMR spectra (δ_P = 20-25 ppm in all cases) displaying a characteristic P-H splitting pattern (doublet, J_{PH} ca. 400 Hz). Effervescence (CH_4) and a concomitant color change (color-

less to yellow) is then observed, which is complete within 1 h, resulting in quantitative conversion to a new species as evidenced by the ^{31}P NMR spectra (**2** δ_P = 55.9 ppm, **3** δ_P = 58.1 ppm, **4** δ_P = 57.6 ppm). The chemical shift of these resonances, when compared 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 characterisation of **2-4** was therefore carried out *in situ* (^1H, ^{13}C and ^{31}P NMR spectroscopy and ESI-MS).
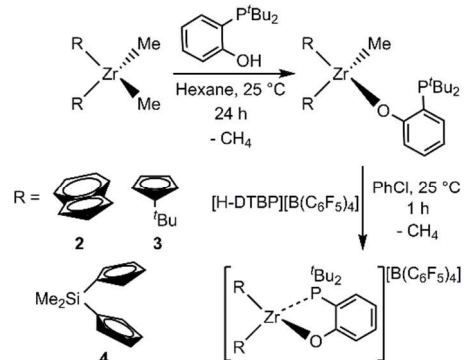
Scheme 4. Synthesis of Intramolecular Zr/P FLP systems 2-4 with a variety of ancillary ligands.

This methodology had to be adapted when using the more electron deficient phosphine moiety, as protonolysis by [H–DTBP][B(C_6F_5)_4] was found not to yield the desired product, which was attributed to the less basic nature of the phosphine. Upon addition of $[H–DTBP][B(C_6F_5)_4]$, 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 H_2O)[13] however the pKa of $[DTBP–H]^+$ under the same conditions is 4.95 (in H_2O).[14] As a consequence, $[CPh_3][B(C_6F_5)_4]$ was used to mediate the methyl abstraction reaction and generate the cationic species **5** (Scheme 5).
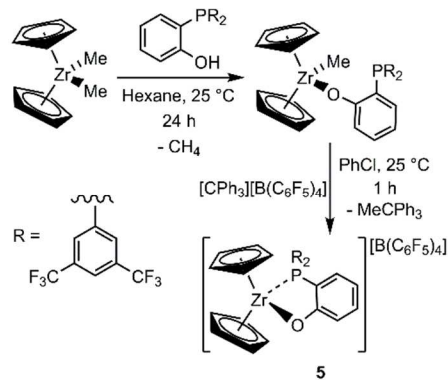
Scheme 5. Synthesis of Intramolecular Zr/P FLP system 5 with an electron deficient phosphine.

Interestingly, when this reaction was monitored by ^{31}P NMR spectroscopy, no change in the ^{31}P NMR spectrum was observed upon formation of **5**. This strongly suggests the 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 (δ_H = -0.07 in PhCl) and the ap-

pearance of a new resonance corresponding to triphenylethane (MeCPh$_3$, δ_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 Me$_2$NH•BH$_3$ Using 2-5

Catalyst systems **2-5** (Figure 1) were trialled in the catalytic dehydrocoupling of Me$_2$NH•BH$_3$. Initially a 5 mol% catalyst loading was employed and the reaction monitored by ^{11}B{^{1}H} NMR spectroscopy. The results are shown in Table 1, where the previously reported catalyst **1** is shown for comparison.

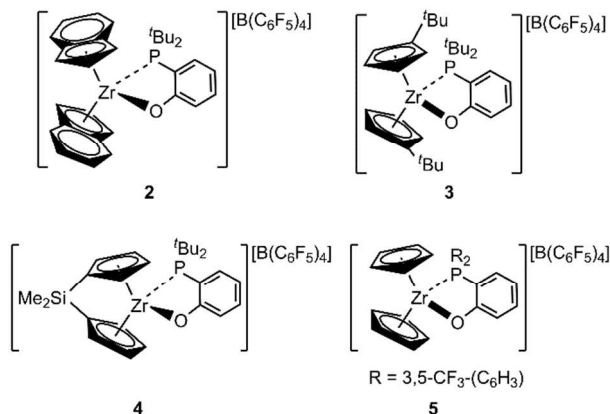Figure 1. FLP systems **2-5** trialled in the dehydrocoupling of Me$_2$NH•BH$_3$

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]

Table 1. Catalytic dehydrocoupling of Me$_2$NH•BH$_3$ using FLP systems 2-5 with the previously reported catalyst 1 included for comparison. All reactions were conducted in chlorobenzene in sealed NMR tubes

Catalyst	[Zr] (mol%)	Temperature (°C)	Time (mins)	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

Further to this it is observed that **2** is a highly efficient catalyst for the dehydrocoupling of Me$_2$NH•BH$_3$ and, in fact, possesses the highest TOF (Turnover Frequency) of any group 4 catalyst (> 600 h^{-1}), the previous highest being a Zr-amide species ([NSiN]^{Dipp}Zr(NMe$_2$)$_2$(μ-Cl)Li(THF)$_3$) reported by Rivard *et al.* (TOF = 420 h^{-1}).[15] Decreasing the steric bulk present in

compound **2** down to the single ^{t}Bu group, offered in compound **3,** leads to a decrease in TOF. This decrease continues with removal of the bulky ^{t}Bu 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 (Me$_2$Si)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}B{^{1}H} NMR spectroscopy revealed not only the expected dehydrocoupling product, cyclodiborazane [Me$_2$N-BH$_2$]$_2$, but also the linear diborazane Me$_2$NH-BH$_2$-Me$_2$N-BH$_3$ (**I**) and aminoborane Me$_2$N=BH$_2$ (**II**) intermediates (Figure 2). The amounts of each intermediate (**I** and **II**) varies 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.
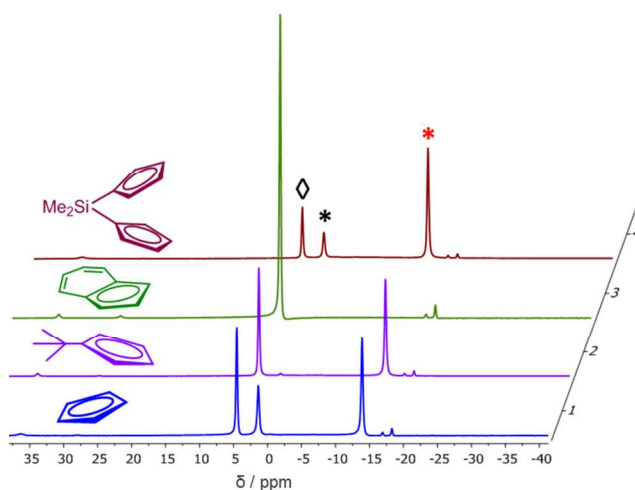

Figure 2. ^{11}B{^{1}H} NMR spectra after ca. 10 minutes (1 mol% [Zr], 25 °C, PhCl), for the catalytic dehydrocoupling of Me$_2$NH•BH$_3$ with (from back to front) **4**, **2**, **3** and **1**. * = Me$_2$NH•BH$_3$, ＊ = H$_3$B-NMe$_2$-BH$_2$-NHMe$_2$, ◊ = [Me$_2$N-BH$_2$]$_2$. Note that the terminal BH$_3$ peak for ＊ overlaps with *. Minor amounts of HB(NMe$_2$)$_2$ (~29 ppm), Me$_2$N=BH$_2$ (36.6 ppm) and Me$_2$N(B$_2$H$_5$) (~-17 ppm) are also observed.

The presence of both **I** and **II** in such dehydrocoupling reactions is unusual. There are thought to be three different mechanisms by which Me$_2$NH•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 Me$_2$NH•BH$_3$. In a further metal-mediated step, dehydrogenative cyclisation 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 Me$_2$NH•BH$_3$ is dehydrogenated to produce the aminoborane **II**.[18] The aminoborane then sponta-

3

neously dimerises to form the cyclic diborazane, $[Me_2N-BH_2]_2$. The third possible mechanism, and one which may be useful in this discussion, has been proposed by Schneider et al, calculations showing that rearrangement between $Me_2NH \cdot BH_3$, $[Me_2N-BH_2]_2$ and **II** is approximately thermoneutral (2.0 kcal mol^{-1}) and may take place if "kinetically feasible".[19]

In the previous literature it is the off-metal mechanism which is the favoured model for FLP catalysed dehydrocoupling of $Me_2NH \cdot BH_3$.[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 catalysed 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).
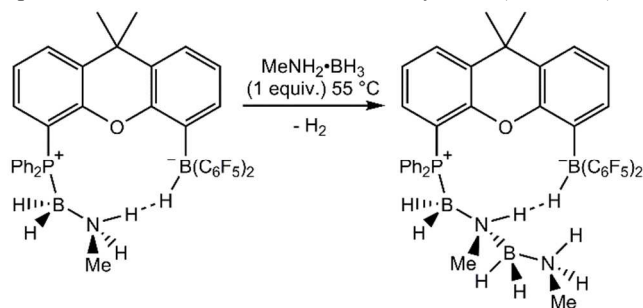
Scheme 6. Growth of a linear dimeric species on a P/B FLP synthesized by Aldridge *et al.*

In order to confirm the identity of **I** as a catalytically relevant intermediate, an authentic sample was treated with 5 mol% **1** in PhCl at 25 °C. Monitoring the reaction by ^{11}B NMR spectroscopy revealed a product distribution similar to that observed for the reaction of $Me_2NH \cdot BH_3$ with **1**. Species **I**, **II** and $Me_2NH \cdot BH_3$ were all identified in the ^{11}B{^{1}H} NMR spectrum shown in Figure 3. Full conversion to the cyclic diborazane was evident after 20 mins.
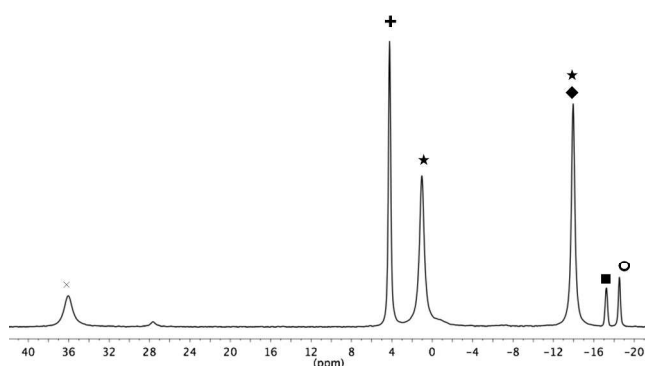

Figure 3. ^{11}B{^{1}H} NMR spectrum (300 MHz, PhCl, 25 °C, 2 mins) of (**I**) + 5 mol% **1**. ○ $MeNH(B_2H_5)$ (-18.8 ppm), ■ $[B(C_6F_5)_4]^-$ (-17.5 ppm), ◆ $Me_2NH \cdot BH_3$ (-14.4 ppm), ★ $Me_2NH-BH_2-Me_2N-BH_3$ (-14.4 and 0.84 ppm), ✚ $[Me_2N-BH_2]_2$ (4.02 ppm), ✕ $Me_2N=BH_2$ (36.6 ppm)

This leads us to propose that two different reaction mechanisms occurring simultaneously. The first cycle involves simple deprotonation of Zr-κ^2 amine-borane adduct by a sufficiently basic phosphine to form **II**, a phosphonium species $[R_3P-H]$ and a Zr-H. An intermediate zirconium amido-borane species is not observed in our experiments, suggesting a concerted pathway with simultaneous deprotonation 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 $Me_2NH \cdot BH_3$ to yield the linear diborazane (**I**) prior to a subsequent cyclisation 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 utilised a series of our recently reported analogous intermolecular Zr/P FLP systems to probe this reaction.[12]

2.3 Dehydrocoupling of $Me_2NH \cdot BH_3$ Using Intermolecular FLPs

Initially it was necessary to determine if the intermolecular analogues **7-19** (Scheme 7) retained their catalytic activity after removal of the aryl tether. It was found that treatment of $Me_2NH \cdot BH_3$ with 10 mol% $[Cp^*_2ZrOMes][B(C_6F_5)_4]$ // PR_3 (R = ^{t}Bu (**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 $[Me_2N-BH_2]_2$ over 24 h in all cases, as calculated by ^{11}B NMR spectroscopy, and when R = Ph, Mes and 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 consistent with previous observations, where intramolecular Zr/P FLPs, bearing Cp ancillary ligands, give significantly more rapid reactivity when compared to their Cp* cousins.[1] 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 orientate in such a way as to still not hinder substrate binding. Clearly the different electronic characteristics of these ligand 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 mat also play a role.
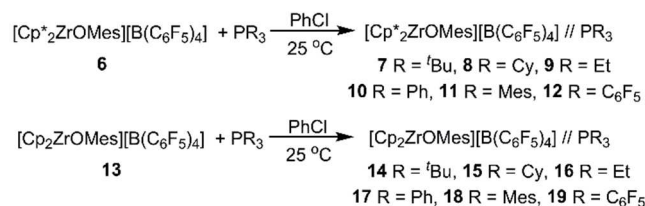
Scheme 7. Generation of previously reported intermolecular FLP systems.

FLP systems **15-19** (10 mol%, PhCl, 25 °C, 14 h) gave low conversion (< 5%) to [Me$_2$N-BH$_2$]$_2$ even after 14 h, with **17**, **18** and **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 [Me$_2$N-BH$_2$]$_2$ 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 [Me$_2$N-BH$_2$]$_2$. *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.
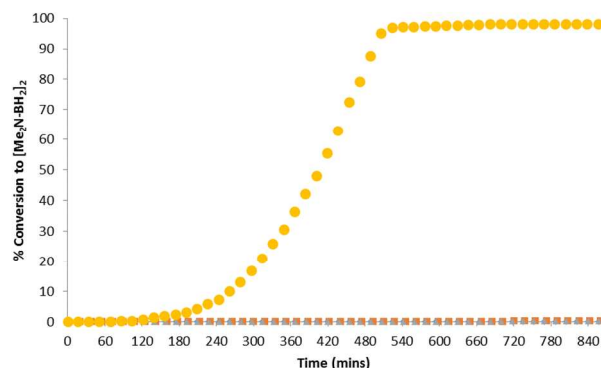

Figure 4. Reaction of Me$_2$NH•BH$_3$ with 10 mol% **14-19** (25 °C, PhCl, 14 h). ● = **14**, ■ = **15**, ▲ = **16**, **17**, **18** and **19** show no reaction with Me$_2$NH•BH$_3$

2.4 Mechanistic Investigation

Monitoring the reaction between Me$_2$NH•BH$_3$ and a catalytic amount of **14** (10 mol%, PhCl, 25 °C, 7.5 h) by ^{11}B{^{1}H} NMR spectroscopy led to a similar distribution of reaction intermediates as that observed for the reactions with catalysts **1-4** (Figure 1), with both Me$_2$NH-BH$_2$-Me$_2$N-BH$_3$ (**I**) and Me$_2$N=BH$_2$ (**II**) generated simultaneously (Figure 5 and Figure S1).
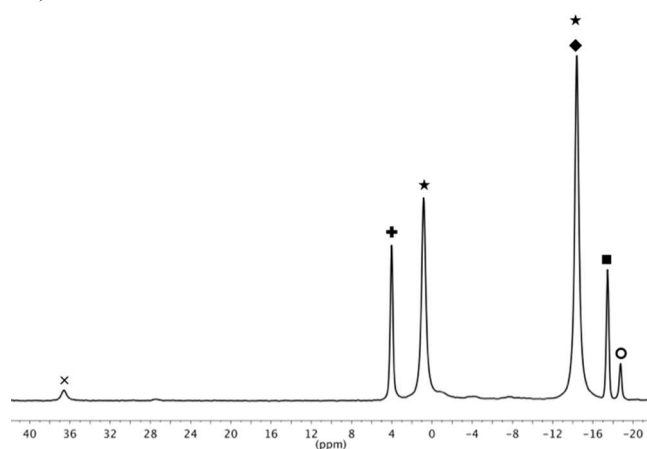
Figure 5. ^{11}B{H} NMR spectrum (300 MHz, PhCl, 25 °C, 280 mins) of Me$_2$NH•BH$_3$ + 10 mol% **14**. ○ MeNH(B$_2$H$_5$) (-18.8 ppm), ■ [B(C$_6$F$_5$)$_4$]$^-$ (-17.5 ppm), ◆ Me$_2$NH•BH$_3$ (-14.4 ppm), ★ Me$_2$NH-BH$_2$-Me$_2$N-BH$_3$ (**I**) (-14.4 and 0.84 ppm), ✚ [Me$_2$N-BH$_2$]$_2$ (4.02 ppm), ✕ Me$_2$N=BH$_2$ (**II**) (36.6 ppm)

In order to further probe the mechanism of the reaction, Me$_2$NH•BH$_3$ was treated with 10 mol% [Cp*$_2$ZrOMes][B(C$_6$F$_5$)$_4$] (**6**) and [Cp$_2$ZrOMes][B(C$_6$F$_5$)$_4$] (**13**) in the absence of a Lewis base. In neither case was dehydro-coupling was observed by ^{11}B NMR spectroscopy (24 h, 25 °C, PhCl), however a new Zr-amine borane complex was identified (^{11}B{^{1}H} δ = -11.5 (broad singlet, Me$_2$NH•BH$_3$), -16.9 (s, [B(C$_6$F$_5$)$_4$]$^-$)). In the case of **6**, this complex (**20**) was isolated through a stoichiometric reaction between **5** and Me$_2$NH•BH$_3$, the solid state structure of **20** is shown in Figure 6. From the solid state structure of **20** it is clear that Me$_2$NH•BH$_3$ is bound in a κ^2 fashion,[19] however, the ^{1}H NMR spectrum shows a broad resonance for three equivalent hydrides, suggesting a dynamic structure in solution, where the hydrides bound to Zr are exchanging on the NMR timescale. Structurally characterised 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.[19e,19g]

Subsequent reaction of **20** with phosphine Lewis bases (PhCl, 25 °C, < 10 mins) led to dehydrogenation, release of Me$_2$N=BH$_2$ (**II**) and formation of the corresponding phosphonium salt, [HPR$_3$][B(C$_6$F$_5$)$_4$] and a Zr-hydride. Aminoborane **II** subsequently dimerised to form the cyclic diborazane. Protonation of the Zr-hydride by the phosphonium species to release H$_2$ 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 (PR$_3$ R = ^{t}Bu, Cy, Et) show the deprotonation/dehydrogenation reactivity described above. Analogous treatment of **20** with PPh$_3$, PMes$_3$ or P(C$_6$F$_5$)$_3$ 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 Me$_2$NH•BH$_3$, 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 Me$_2$NH•BH$_3$, yielding either Me$_2$N=BH$_2$ (**II**) or Me$_2$NH-BH$_2$-Me$_2$N-BH$_3$ (**I**). Crucially, in support of this hypothesis, addition of further equivalents of Me$_2$NH•BH$_3$ to **20** leads to the formation of no new products on a catalytically relevant timescale (8 h, 25 °C)
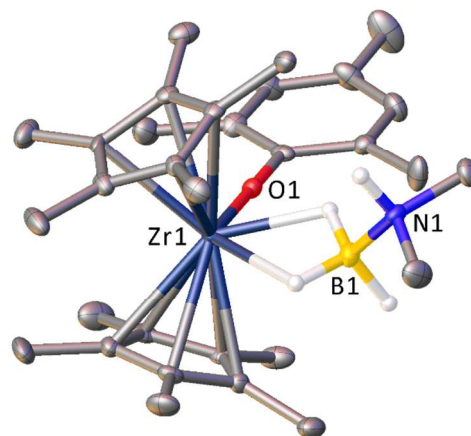
Figure 6. Solid state structure of the cation present in **20** as determined by X-ray crystallography. Second unique cation, nonessential hydrogens and two $[B(C_6F_5)_4]^-$ counterions are omitted for clarity. Selected bond lengths (Å) and angles (º): Zr1-O1 1.968(3), N1-B1 1.587(6), Cp*-Zr-Cp* 135.14(7). NB. Zr-B distance = 2.709(5) Å

To probe the intermediacy of linear diborazane (**I**) a chlorobenzene solution of **I** was treated with 20 mol% $[Cp_2ZrOMes][B(C_6F_5)_4]$ // P^tBu_3 (**14**) (PhCl, 25 °C, 6 h). In this case complete conversion to $[Me_2N-BH_2]_2$ 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, $Me_2NH\cdot BH_3$ are formed. Redistribution of such linear diborazanes to form amine-borane dehydrocoupling products has been previously reported by our group.[20]
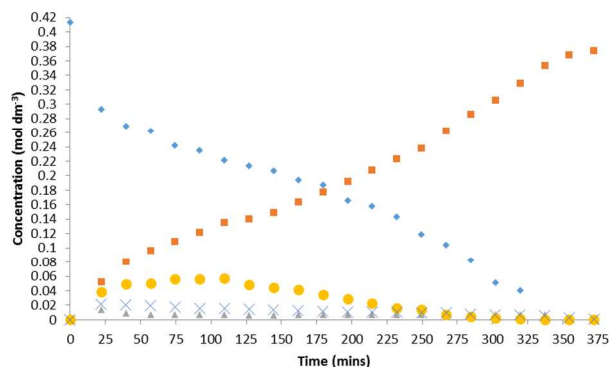

Figure 7. (**I**) with 20 mol% **14** (25 ºC, PhCl, 6h). ◆ = $Me_2NH-BH_2-Me_2N-BH_3$ (**I**), ■ = $[Me_2N-BH_2]_2$, ● = $Me_2NH\cdot BH_3$, ▲ = $Me_2N=BH_2$ (**II**), × = $Me_2N(B_2H_5)$

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 a redistribution of linear diborazane intermediate (**I**) to yield $Me_2NH\cdot BH_3$ and $Me_2N=BH_2$ (**II**), which subsequently cyclodimerized, as expected, to form the cyclic dimer, $[Me_2N-BH_2]_2$. We observe that $Me_2NH\cdot BH_3$ is not consumed in the absence of exogenous phosphine (no reaction is observed between complex **13** alone and $Me_2NH\cdot BH_3$)
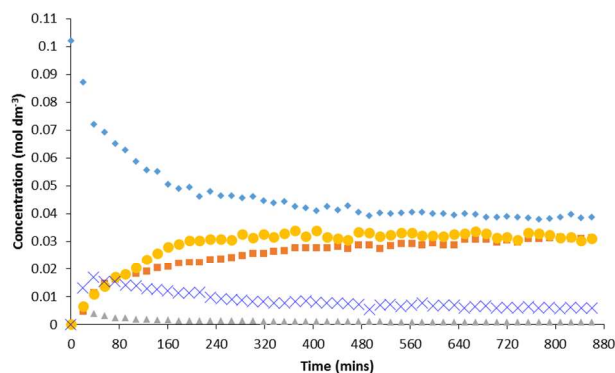

Figure 8. (**I**) with 20 mol% **13** (25 ºC, PhCl, 12 h). ◆ = $Me_2NH-BH_2-Me_2N-BH_3$ (**I**), ■ = $[Me_2N-BH_2]_2$, ● = $Me_2NH\cdot BH_3$, ▲ = $Me_2N=BH_2$ (**II**), × = $Me_2N(B_2H_5)$

The proposed mechanism for the Zr(IV)/P FLP catalysed dehydrocoupling of $Me_2NH\cdot BH_3$ 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 $Me_2NH\cdot BH_3$ forming the aminoborane **II**. The aminoborane spontaneously dimerises to form the cyclic diborazane product, $[Me_2N-BH_2]_2$. Alternatively, in the presence of a second equivalent of $Me_2NH\cdot BH_3$, 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 centre in an analogous fashion to that observed for **20**. Loss of the terminal Me_2NH group, as previously reported in other redistribution reactions,[20] then occurs, resulting in a μ-amido diborane species, $Me_2NH(B_2H_5)$. As shown in Figures 7 and 8, $Me_2NH(B_2H_5)$ is observed in solution throughout these reactions and is thus not thought to be bound to the Zr and, in fact, addition of $Me_2NH(B_2H_5)$ to **6** or **13** results in no reaction (*vide infra*). The fate of $Me_2NH(B_2H_5)$ remains uncertain. We believe it is likely that the formation of $Me_2NH\cdot BH_3$ and **II** could be via an alternative, concerted process from **I** as indicated in Scheme 8 (Cycle B). When formed, $Me_2N=BH_2$ would spontaneously dimerise to form $[Me_2N-BH_2]_2$. The formation of this dimer is thought to be the driving force for this step. In the presence of P^tBu_3, $Me_2NH\cdot BH_3$ could be dehydrocoupled to reform 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 TOF depending on 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 two equivalents of $Me_2NH\cdot BH_3$ are not able to organise 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.
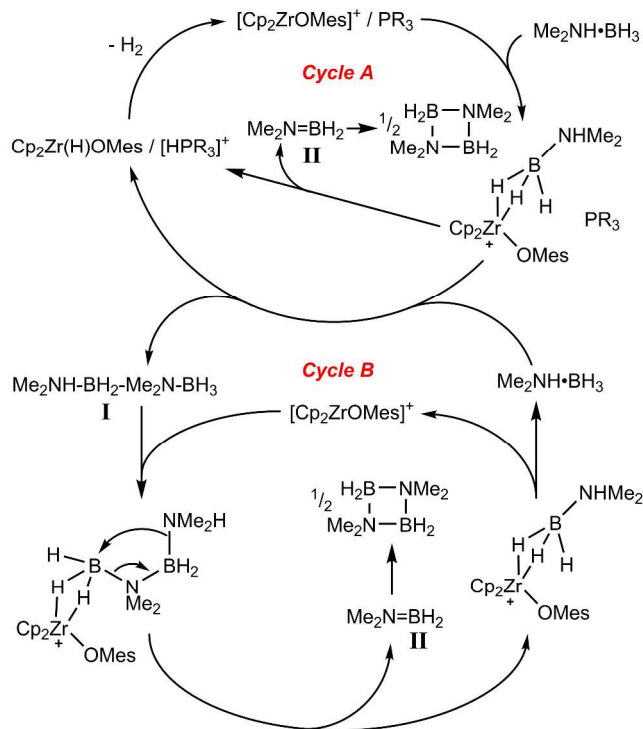
Scheme 8. Proposed reaction mechanism for the catalytic dehydrocoupling of Me₂NH•BH₃ using a Zr(IV)/P FLP

Figure 9. $^{i}Pr_2NH \cdot BH_3$ with 10 mol% **14** (25 ^{o}C, PhCl, 14h). ● = $^{i}Pr_2NH \cdot BH_3$, ● = $^{i}Pr_2N=BH_2$

As in the case of $Me_2NH \cdot BH_3$, reaction of **6** and **13** with $^{i}Pr_2NH \cdot BH_3$ resulted in no detectable conversion to dehydro-coupling 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 crystallo-graphically characterised (Figure 10).

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 $^{i}Pr_2NH \cdot BH_3$ by **14**. Due to the increased steric bulk around nitrogen, dehydrogenation of $^{i}Pr_2NH \cdot BH_3$ only yields one product, the corresponding aminoborane ($^{i}Pr_2N=BH_2$), 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 catalyti-cally viable pathway. Intramolecular FLP **1** has been shown to dehydrogenate $^{i}Pr_2NH \cdot BH_3$ (1 mol% [Zr], PhCl, 25 °C, 19 h) to yield $^{i}Pr_2N=BH_2$, however revisiting this reaction seemed pertinent in light of the current study.[11b] Upon treatment of a PhCl solution of $^{i}Pr_2NH \cdot BH_3$ with 10 mol% **14** (25 °C, 14 h) a 73% conversion to $^{i}Pr_2N=BH_2$ was observed with no other intermediates apparent (Figure 9).

Figure 10. Solid state structure of the cation present in **21** as de-termined by X-ray crystallography. Nonessential hydrogens, sol-vent of crystallisation (PhCl) and $[B(C_6F_5)_4]^-$ counterion are omit-ted for clarity. Selected bond lengths (Å) and angles (°): Zr1-O1 1.974(1), N1-B1 1.590(3), Cp*-Zr-Cp* 135.07(3). NB Zr-B dis-tance = 2.722(3) Å

The solid state structure of **21**, as was to be expected, proves to be nearly identical to that of **20**, with the amine-borane again bound in a κ^2 fashion.[19] In a similar manner to **20** treat-ment of **21** with a stoichiometric amount of $P^{t}Bu_3$ results in deprotonation of the bound amine-borane and formation of $^{i}Pr_2N=BH_2$. These results, when combined with the data in Figure 9, confirm the validity of a mechanistic pathway in-volving 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 synthesise 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 SI for further discussion) but this strategy also proved unsuccessful. In addition, attempts to isolate a Zr-μ-amidodiborane complex were made, but addition of $Me_2N(B_2H_5)$ 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. Firstly, that such complexes are transient in solution and therefore isolation is impossible, or secondly, that the conversion of $Me_2N(B_2H_5)$ 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, $Me_2N(B_2H_5)$ readily undergoes a ring-opening reaction to yield the corresponding linear diborazane **I**.[20]

Experiments using alternative linear diborazanes have provided insight into the decomposition pathway of **I**. Upon reaction of the linear diborazane $H_3B-NMeH-BH_2-NMe_2H$ with different substituents at nitrogen[20] with 10 mol% **13** (PhCl, 25 °C, 14 h) formation of $Me_2NH•BH_3$ was observed by ^{11}B NMR spectroscopy (Figure 11). This was accompanied by formation of trace amounts of *N*-methylborazine, $[HB-NMe]_3$, and μ-*N*-methylamidodiborane, $MeNH(B_2H_5)$.

Figure 11. Reaction of $Me_2NH-BH_2-MeNH-BH_3$ with 10 mol% **13** (25 °C, PhCl, 14h). ◆ = $Me_2NH-BH_2-MeNH-BH_3$, ● = $Me_2NH•BH_3$, ✕ = $MeNH(B_2H_5)$, ■ $[HB-NMe]_3$
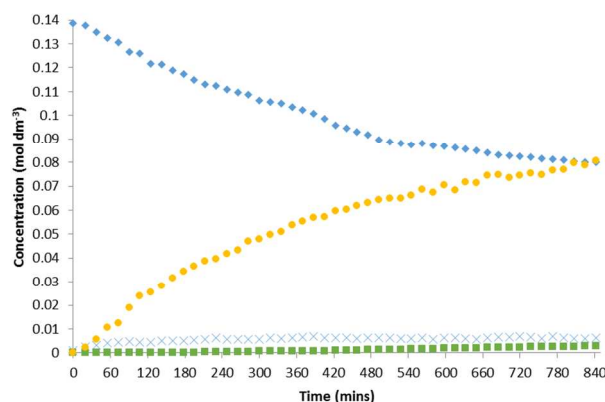
The origin of these intermediates provides useful information about Cycle B in Scheme 8. $MeNH(B_2H_5)$ appears to arise from elimination of the terminal Me_2NH moiety from $Me_2NH-BH_2-NMeH-BH_3$, with the formation of $Me_2NH•BH_3$ providing further evidence for the presence of both free amine and free BH_3 in solution. The lack of detectable amounts of $Me_2N=BH_2$ or $[Me_2N-BH_2]_2$ indicates that any aminoborane that is generated arises from the internal BN unit of the linear diborazane. In this case formation of $[HB-NMe]_3$ 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.[21] The borazine $[HB-NMe]_3$ is thought to arise through trimerisation of

$MeNH=BH_2$ to form $[MeNH-BH_2]_3$, which is further dehydrogenated through now well-established hydrogen transfer reactions.[2d,20]

3. Summary

A range of intramolecular Zr(IV)/P FLP catalysts have been prepared that are competent in the dehydrocoupling of $Me_2NH•BH_3$. 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-catalysed reactions. The first cycle involves a two-step process involving amine-borane coordination and subsequent phosphine-mediated H_2 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 catalysed reactions. Further studies are underway to widen the substrate scope for these reactions with, in the case of group 15-15 adducts, the formation of polymeric materials as a particular target.

4. Experimental

4.1 General Considerations

Unless otherwise stated, all manipulations were undertaken under an atmosphere of argon or nitrogen using standard glovebox (M-Braun $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) and Schlenk line techniques and all glassware was oven and vacuum dried prior to use. Cp_2ZrCl_2, $Cp*_2ZrCl_2$ MeLi (1.6M in Et_2O), P^tBu_3, PCy_3, PEt_3, PPh_3, $PMes_3$ and $P(C_6F_5)_3$ were purchased from Sigma-Aldrich and used as received. $[CPh_3][B(C_6F_5)_4]$ was purchased from Acros Organics and used as received. $Me_2NH•BH_3$ was purchased from sigma Aldrich and purified by sublimation prior to use (25°C, 2 x 10^{-2} Torr). $^iPr_2NH•BH_3$, $Me_2NH-BH_2-Me_2N-BH_3$, $[Cp*_2ZrOMes][B(C_6F_5)_4]$ (**5**), $[Cp_2ZrOMes][B(C_6F_5)_4]$ (**6**), $[Cp_2ZrO(C_6H_4)P^tBu_2][B(C_6F_5)_4]$ (**1**) and *ortho*-$tBu_2P(C_6H_4)OH$ were synthesized according to literature protocols.[11,20,21] All other reagents were used as obtained unless otherwise stated. Common laboratory solvents (Et_2O, DCM, Hexane, THF) were purified using a Grubbs type purification system.[22] Non-standard solvents (Chlorobenzene, Pentane) were purchased from Sigma-Aldrich and distilled from CaH_2 prior to use.

NMR spectra were recorded using JEOL ECP-300 (300 MHz), Varian-400 (400 MHz), Varian NMRS500 (500 MHz) spectrometers. Deuterated solvents were obtained from Sigma Aldrich (d_6-benzene, d_8-THF and d_2-DCM) or Apollo Scientific (d_5-PhBr) and distilled from CaH_2 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 Kα 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 Daltronics micrO TOF II with a TOF analyser. All samples were run in pre-dried PhCl.

4.2 Synthesis of Intramolecular Zr/P FLPs (2-4)

4.2.1 Synthesis of R$_2$ZrMe$_2$ precursors

Ind$_2$ZrMe$_2$ Following a modified literature procedure.[23] Methyl lithium (1.6 M in Et$_2$O, 32.3 mL, 51.6 mmol) was added dropwise to a solution of indene (3.00 mL, 25.8 mmol) in Et$_2$O (35 mL) at room temperature to give a yellow/orange solution. This solution was stirred for 30 minutes, before addition of ZrCl$_4$ (3.00 g, 12.9 mmol) slurried in hexane (40 mL). The resulting mixture was stirred for 2 hours, during which a white precipitate (LiCl) formed. The solvent was removed *in vacuo*, and the residue 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 is consistent with literature values.[24]

^{1}H NMR (400 MHz, C$_6$D$_6$): 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, H$_2$), -0.68 (s, 6H, Zr(CH$_3$)$_2$).

Me$_2$Si(C$_5$H$_4$)$_2$ZrMe$_2$ Adapted from a literature procedure.[25] Me$_2$Si(C$_5$H$_4$)$_2$ZrCl$_2$ (244 mg, 0.70 mmol) was suspended in hexane (20 mL) and cooled to -78 °C. Methyl lithium (1.6 M in Et$_2$O, 0.83 mL, 1.33 mmol) was added dropwise and the reaction warmed to room temperature and stirred for 2 hours. Solvent was removed *in vacuo* and the residue redissolved in hexane. The resulting solution was filtered through celite, the volume reduced to ~5 mL and cooled to -20 °C which resulted in the precipitation of white crystals of the title compound (172 mg, 80%). All recorded data consistent with literature values.[26]

^{1}H NMR (400 MHz, toluene-d$_8$): δ 6.88 (t, 4H, J = 2.2 Hz, Cp), 5.76 (t, 4H, J = 2.2 Hz, Cp), 0.52 (s, 6H, Si(CH$_3$)$_2$), -0.35 (s, 6H, Zr(CH$_3$)$_2$).

(^{t}Bu-C$_5$H$_4$)$_2$ZrMe$_2$ Methyl lithium (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 Et$_2$O (15 mL) at -78 °C. After addition, the reaction was warmed to room temperature and stirred overnight. Solvent was removed *in vacuo* and the resulting residue was extracted with hexanes and filtered through a celite plug. Solvent was removed *in vacuo* yielding a white solid (272 mg, 87%) of the title compound. All recorded data is consistent with literature values.[26]

^{1}H NMR (400 MHz, CDCl$_3$): δ 5.80-5.83 (m, 4H, Cp), 5.70-5.75 (m, 4H, Cp), 1.10 (s, 18H, CpC(CH$_3$)$_3$), 0.01 (s, 6H, Zr(CH$_3$)$_2$).

4.2.2 Synthesis of neutral complexes [R$_2$Zr(Me)(O^P(tBu)$_2$)]

General method: A solution of the dimethyl zirconocene (1 equiv.) and phosphinoalcohol (1 equiv.) were individually dissolved in the minimum amount of hexane prior to combining. The resulting solutions were stirred overnight and until no further gas evolution was observed. The solvent was removed *in vacuo* yielding the desired complexes.

(^{t}BuC$_5$H$_4$)$_2$Zr(Me)(OC$_6$H$_4$P(^{t}Bu)$_2$) Viscous oil (702 mg, 95%) **^{1}H NMR (400 MHz, C$_6$D$_6$):** 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, ^{3}J$_{HP}$ = 11.3 Hz, PC(CH$_3$)$_3$), 1.19 (s,18H, CpC(CH$_3$)$_3$), 0.75 (s, 3H, ZrCH$_3$); **^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$):** δ 169.8 (d, ^{2}J$_{CP}$ = 23.7 Hz, C1), 138.8 (s, *ipso*-Cp(*t*Bu)), 136.0 (d, ^{3}J$_{CP}$ = 3.2 Hz, C6), 130.1 (s, C3), 125.2 (d, ^{1}J$_{CP}$ = 25.3 Hz, C2), 120.1 (d, ^{4}J$_{CP}$ = 3.4 Hz, C5), 118.1 (s, C4), 110.8, 110.7, 109.8, 107.2 (Cp), 32.3 (d, ^{1}J$_{CP}$ = 24.7 Hz, PC(CH$_3$)$_3$), 30.9 (d, ^{2}J$_{CP}$ = 16.3 Hz, PC(CH$_3$)$_3$), 29.3 (s, CpC(CH$_3$)$_3$), 26.3 (d, J$_{CP}$ = 6.6 Hz, ZrCH$_3$), 22.9 (s, CpC(CH$_3$)$_3$) **^{31}P{^{1}H} NMR (161 MHz, C$_6$D$_6$):** δ 10.17 (s).

Ind$_2$Zr(Me)(OC$_6$H$_4$P(^{t}Bu)$_2$) White solid (567 mg, 95%)

^{1}H NMR (400 MHz, toluene-d$_8$): 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, H$_2$), 5.73 (ddd, 2H, J = 3.2, 2.1, 0.9 Hz, H$_{1,3}$), 1.20 (d, 18H, ^{3}J$_{H,P}$ = 11.4 Hz, C(CH$_3$)$_3$), -0.1 (s, 3H, ZrCH$_3$) **^{13}C{^{1}H} NMR (125 MHz, toluene-d$_8$):** 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, C$_2$), 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, ZrCH$_3$), 32.4 (d, ^{1}J$_{CP}$ = 24.9 Hz, C(CH$_3$)$_3$), 31.0 (d, ^{2}J$_{CP}$ = 15.7 Hz, C(CH$_3$)$_3$). **^{31}P{^{1}H} NMR (161 MHz, toluene-d$_8$):** δ 10.23 (s) **E. A.** – Calc (%): C 69.07, H 6.85. Found (%): C 68.92, H 6.93

Me$_2$Si(C$_5$H$_4$)$_2$Zr(Me)(OC$_6$H$_4$P(^{t}Bu)$_2$) Viscous colourless oil (227 mg, 98%) **^{1}H NMR (400 MHz, PhCl-d$_5$):** 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, ^{3}J$_{HP}$ = 10.2 Hz, C(CH$_3$)$_3$), 0.73 (s, 3H, SiCH$_3$), 0.60 (s, 3H, SiCH$_3$), 0.52 (s, 3H, ZrCH$_3$) **^{13}C{^{1}H} NMR (100 MHz, PhCl-d$_5$):** 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, ^{1}J$_{CP}$ = 24.0 Hz, C(CH$_3$)$_3$), 31.8 (s, ZrCH$_3$), 30.8 (d, ^{2}J$_{CP}$ = 15.9 Hz, C(CH$_3$)$_3$), -4.96, -5.67 (s, Si(CH$_3$)$_2$). **^{31}P{^{1}H} NMR (161 MHz, PhCl-d$_5$):** δ 9.96 (s). **ESI-MS:** 529.1621 [M-H]$^+$

4.2.3 Synthesis of cationic complexes [R$_2$Zr(O^P(^{t}Bu)$_2$)][B(C$_6$F$_5$)$_4$] **(2-5)**

Data for the [B(C$_6$F$_5$)$_4$] anion reported separately:

9

^{11}B{^{1}H} NMR (96 MHz, CD$_2$Cl$_2$): δ -17.60 (s).**^{19}F NMR (376 MHz, DCM-d$_2$):** δ -133.17 (s), -163.70 (s), -167.71 (s). **^{13}C{^{1}H} NMR (125 MHz, DCM-d$_2$):** δ 148.26 (d, J = 245.3 Hz, *o*-B(C$_6$F$_5$)$_4$), 136.68 (d, J = 242.4 Hz, *p*- B(C$_6$F$_5$)$_4$), 134.76 (d, J = 254.1 Hz, *m*- B(C$_6$F$_5$)$_4$), 124.30 (br, *ipso*-$\underline{C}$B)

Via protonolysis with [DTBP(H)][B(C$_6$F$_5$)$_4$]

In a glovebox, stoichiometric amounts of the relevant neutral complex **[R$_2$Zr(Me)(O∧P(^{t}Bu)$_2$)]** and [DTBP(H)][B(C$_6$F$_5$)$_4$] 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)][B(C$_6$F$_5$)$_4$] was added dropwise to the vial containing the zirconium complex. Gas evolution was evident and the resulting solution was stirred for 1 hour, yielding bright yellow solutions. Due to inherent instability, the complexes were used in situ to investigate the reactivity towards Me$_2$NH•BH$_3$.

Ind$_2$Zr(OC$_6$H$_4$P(^{t}Bu)$_2$)][B(C$_6$F$_5$)$_4$] (2) Near quantitative yield by ^{1}H NMR.**^{1}H NMR (400 MHz, PhCl-d$_5$):** δ 7.59-7.70 (m, 5H, $\underline{H}$6 and $\underline{H}_{4,7}$), 7.53 (pseudo t, 1H, J = 7.3 Hz, $\underline{H}$3), 7.30-7.40 (m, 5H, $\underline{H}_{6,5}$ and $\underline{H}$4), 6.57-6.61 (m, 1H, $\underline{H}$5), 6.27-6.31 (m, 2H, $\underline{H}_{1,3}$), 5.80-5.85 (m, 2H, $\underline{H}_2$), 5.74-5.80 (m, 2H, $\underline{H}_{1,3}$), 1.36 (18H, d, $^3J_{HP}$ = 14.6 Hz, PC(C$\underline{H}_3$)$_3$).**^{13}C{^{1}H} NMR (125 MHz, PhCl-d$_5$):** δ 166.2 (d, $^2J_{CP}$ = 15.6 Hz, $\underline{C}$1), 133.6 (d, $^4J_{CP}$ = 4.2 Hz, $\underline{C}$5), 132.4 (d, $^3J_{CP}$ = 1.2 Hz, $\underline{C}$4), 130.1 (s, $\underline{C}_{6,5}$), 129.1 (s, $\underline{C}_{3a,5a}$), 127.9 (s, $\underline{C}_{6,5}$), 125.5 (s, $\underline{C}_{3a,5a}$), 125.3 (s, $\underline{C}_{4,7}$), 124.4 s, (s, $\underline{C}_{4,7}$), 123.0 (d, $^1J_{CP}$ = 27.0 Hz, $\underline{C}$2), 122.8 (d, $^3J_{CP}$ = 3.4 Hz, $\underline{C}$6), 122.3 (s, $\underline{C}$2), 117.7 (d, $^2J_{CP}$ = 5.0 Hz, $\underline{C}$3), 103.6 (s, $\underline{C}_{1,3}$), 103.5 (s, $\underline{C}_{1,3}$), 37.0 (s, $^1J_{CP}$ = 7.4 Hz, P$\underline{C}$(CH$_3$)$_3$), 29.7 (d, $^2J_{CP}$ = 4.5 Hz, PC(C$\underline{H}_3$)$_3$)**^{31}P{^{1}H} NMR (161 MHz, PhCl-d$_5$):** δ 55.9 (s).**ESI-MS:** 589.1771 m/z [M + MeOH]

[(^{t}BuC$_5$H$_4$)$_2$Zr(OC$_6$H$_4$P(^{t}Bu)$_2$)][B(C$_6$F$_5$)$_4$] (3) Near quantitative yield by ^{1}H NMR. **^{1}H NMR (400 MHz, PhCl-d$_5$):** δ 7.13 (dt, 1H, J = 0.9, 7.7, $\underline{H}$6), 7.03 (ddd, 1H, J = 1.6, 6.0 Hz, $\underline{H}$4), 6.80-6.85 (m, 1H, $\underline{H}$5), 6.70-6.75 (m, 2H, Cp), 6.39 (dq, 1H, J = 1.0, 4.5 Hz, $\underline{H}$3), 6.25-6.30 (m, 2H, Cp), 6.00-6.08 (m, 4H, Cp), 1.11 (d, 18H, $^3J_{HP}$ = 14.8 Hz, PC(C$\underline{H}_3$)$_3$), 0.90 (s, 18H, CpC(C$\underline{H}_3$)$_3$).**^{13}C{^{1}H} NMR (125 MHz, PhCl-d$_5$):** δ 167.1 (d, $^2J_{CP}$ = 15.2 Hz, $\underline{C}$1), 149.9 (s, *ipso*-Cp(*t*Bu)), 133.8 (d, $^4J_{CP}$ = 2.8 Hz, $\underline{C}$5), 133.3 (d, $^3J_{CP}$ = 1.4 Hz, $\underline{C}$4), 122.1 (d, $^1J_{CP}$ = 21.3 Hz, $\underline{C}$2), 121.9 (s, $\underline{C}$6), 118.2 (d, $^2J_{CP}$ = 4.8 Hz, $\underline{C}$3), 115.7, 113.3, 113.2, 111.1 (Cp), 37.4 (d, J = 4.9 Hz, P$\underline{C}$(CH$_3$)$_3$), 31.7 (s, CpC(CH$_3$)$_3$), 30.3 (d, J = 4.7 Hz, PC(C$\underline{H}_3$)$_3$), 30.1 (s, CpC(C$\underline{H}_3$)$_3$) **^{31}P{^{1}H} NMR (161 MHz, PhCl-d$_5$):** δ 58.05 (s).

ESI-MS: 569.2483 m/z [M]$^+$

[Me$_2$Si(C$_5$H$_4$)$_2$Zr(OC$_6$H$_4$P(tBu)$_2$)][B(C$_6$F$_5$)$_4$] (4) Near quantitative yield by ^{1}H NMR. **^{1}H NMR (400 MHz, PhCl-d$_5$):** δ 7.41 (t, 1H, J = 7.8 Hz, $\underline{H}$5), 7.14-7.16 (m, 1H, $\underline{H}$4), 7.06-7.08 (m, 1H, $\underline{H}$6), 6.93 (br s, 2H, Cp), 6.63-6.65 (m, 1H, $\underline{H}$3), 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(C$\underline{H}_3$)$_3$), 0.82 (br s, 3H, SiC$\underline{H}_3$), 0.56 (br s, 3H, SiC$\underline{H}_3$). **^{13}C{^{1}H} (100 MHz, PhCl-d$_5$):** δ 165.3 (d, $^2J_{CP}$ = 15.4 Hz, $\underline{C}$1), 134.4 (d, $^4J_{CP}$ = 1.1 Hz, $\underline{C}$5), 132.8 (d, $^3J_{CP}$ = 1.5 Hz, $\underline{C}$4), 126.9 (br s, Cp), 122.7 (d, $^3J_{CP}$ = 4.4 Hz, $\underline{C}$6), 121.9 (d, $^1J_{CP}$ = 26.7 Hz, $\underline{C}$2), 119.0 (br s, Cp), 118.4 (br s,

Cp), 117.3 (d, $^2J_{CP}$ = 6.7 Hz, $\underline{C}$3), 116.0 (br s, Cp), 115.4 (s, *ipso*-CpSi), 37.6 (d, $^1J_{CP}$ = 6.0 Hz, P$\underline{C}$(CH$_3$)$_3$), 30.0 (d, $^2J_{CP}$ = 4.6 Hz, PC(C$\underline{H}_3$)$_3$), -5.2 (br s, Si$\underline{C}$H$_3$), -7.3 (br s, Si$\underline{C}$H$_3$). **^{31}P{^{1}H} NMR (161 MHz, PhCl-d$_5$):** 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 phosphinoalcohol

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 was stirred at room temperature for 1 hour, 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) 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 stirred for 2 hours, 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 consistent with literature.[27]

^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 70.4 (s).

Bis[3,5-bis(trifluoromethyl)phenyl]phosphine

A solution of (3,5-CF$_3$-C$_6$F$_3$)$_2$PCl (2.56 g, 5.21 mmol) in Et$_2$O (12 mL) was added dropwise to a suspension of LiAlH$_4$ (198 mg, 4.27 mmol) in Et$_2$O (40 mL) at room temperature. The solution was heated at reflux for 2 hours, then quenched with degassed H$_2$O (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 consistent with literature.[28]

^{1}H NMR (300 MHz, CDCl$_3$): 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, P$\underline{H}$).

^{31}P NMR (121 MHz, CDCl$_3$): δ -41.1 (d, $^1J_{PH}$ = 216.8 Hz).

(Bis(3,5-bis(trifluoromethyl)phenyl)phosphanyl)phenol

2-Iodophenol (371 mg, 1.69 mmol), (3,5-CF$_3$-C$_6$F$_3$)$_2$PH (773 mg, 1.69 mmol), Cs$_2$CO$_3$ (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 hours. The solution was filtered through a silica plug , eluted with DCM and the solvent removed *in vacuo* to give the desired product that was further purified by flash chromatography: silica, DCM:hexane (50:50). Brown solid (817 mg, 88%).

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.93 (s, 2H, P-Ar$\underline{H}$), 7.82-7.83 (pseudo d, 4H, J = 6.9 Hz, P-Ar$\underline{H}$), 7.44 (ddd, 1H, J = 1.7, 7.4, 8.1, $\underline{H}$6), 7.02 (dt, 1H, J = 0.9, 7.5, $\underline{H}$3), 6.91-6.97 (m, 2H, $\underline{H}$4 and $\underline{H}$5). **^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$):** δ -11.0 (s) **^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$):** δ 158.3 (d, J = 15.7 Hz, $\underline{C}$1), 138.7 (d, $^1J_{CP}$ = 15.7 Hz, *ipso*-P-Ar), 134.6 (d, J = 8.5 Hz, $\underline{C}$5), 133.4

10

(pseudo d, J = 21.3 Hz, P-Ar), 132.8 (s, $\underline{C}$6), 131.7 (dq, $^2J_{CF}$ = 6.3, 34.0 Hz, ipso-$\underline{C}$(CF$_3$)), 123.3 (q, $^1J_{CF}$ = 273.0 Hz, C($\underline{C}$F$_3$)), 123.2 (qu, $^3J_{CF}$ = 3.9 Hz, P-Ar), 121.9 (d, J = 3.7 Hz, $\underline{C}$3), 118.1 (d, J = 9.2 Hz, $\underline{C}$2), 115.9 (d, J = 1.6 Hz, $\underline{C}$4)

4.3.2 Synthesis of cationic complex [(C$_5$H$_5$)$_2$Zr(OC$_6$H$_4$P(m-CF$_3$C$_6$H$_3$)$_2$)][B(C$_6$F$_5$)$_4$] (5)

In a glovebox, a solution of the dimethyl zirconocene (1 equiv.) and phosphinoalcohol (1 equiv.) were individually dissolved in the minimum amount of PhF prior to combining. The resulting solutions were stirred for 30 minutes. [Ph$_3$C][B(C$_6$F$_5$)$_4$] (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 [Ph$_3$C][B(C$_6$F$_5$)$_4$] was added dropwise to the vial containing the zirconium complex. The resulting solution was stirred for 1 hour. Due to inherent instability, the complexes were used immediately to investigate the reaction towards Me$_2$NH•BH$_3$. Attempted isolation of both complexes resulted in decomposition.

^{1}H NMR (300 MHz, PhCl:toluene-d$_8$): δ Aromatic signals are obscured by PhF signals and could not be unambiguously identified. δ 6.68-6.72 (m, 2H, $\underline{H}$4 and $\underline{H}$5), 5.83 (s, 10H, C$_5$$\underline{H}$$_5$) **^{31}P{^{1}H} NMR (121 MHz, PhCl:toluene-d$_8$):** δ -13.9 (s).

4.4 Dehydrocoupling of Me$_2$NH•BH$_3$ 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. 0.5 mL of the solution (0.012 mmol) was added to a glass vial of preweighed Me$_2$NH•BH$_3$ (15 mg, 0.25 mmol). A colour change from yellow to colourless and evolution of gas was evident. The solution was transferred to a J-Youngs NMR tube, removed from the glovebox and the relevant spectra obtained.

TOF figures were calculated by integration of the ^{11}B NMR spectra.

4.5 Reaction of FLP system 1 (5 mol%) with Me$_2$NH-BH$_2$-Me$_2$N-BH$_3$

In a glovebox 1 (9 mg, 0.008 mmol) and Me$_2$NH-BH$_2$-Me$_2$N-BH$_3$ (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-Youngs NMR tube and then removed from the glovebox. The reaction was monitored by ^{11}B NMR spectroscopy and found to give complete conversion to [Me$_2$N-BH$_2$]$_2$ in 20 mins.

4.6 Dehydrocoupling of Me$_2$NH•BH$_3$ by complexes 7-12

In a glovebox [Cp*$_2$ZrOMes][B(C$_6$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 P(C$_6$F$_5$)$_3$ 10 mg) were weighed into glass vials. The phosphine was dissolved in PhCl (0.5 mL) and mixed with

[Cp*$_2$ZrOMes][B(C$_6$F$_5$)$_4$] (6). The resulting red solution was added to a glass vial containing Me$_2$NH•BH$_3$ (9.5 mg, 0.16 mmol), the solution was mixed to ensure full dissolution of the amine-borane before transferring to a quartz J-Youngs NMR tube. The tube was subsequently removed from the glovebox and the relevant spectra obtained. In all cases the reactions show <5% conversion to [Me$_2$N-BH$_2$]$_2$ after 24 h

4.7 Dehydrocoupling of Me$_2$NH•BH$_3$ by complexes 14-19

In a glovebox [Cp$_2$ZrOMes][B(C$_6$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 P(C$_6$F$_5$)$_3$ 10 mg) were weighed into glass vials. The phosphine was dissolved in PhCl (0.5 mL) and mixed with [Cp$_2$ZrOMes][B(C$_6$F$_5$)$_4$]. In the cases of 15-17 a colour change from orange to yellow was observed indicative of a persistent Zr-P bond. The resulting solutions were added to a glass vial containing Me$_2$NH•BH$_3$ (9.5 mg, 0.16 mmol), the solution was mixed to ensure full dissolution of the amine-borane before transferring to a quartz J-Youngs NMR tube. The tube was subsequently removed from the glovebox and the relevant spectra obtained. 15-17 showed < 5% conversion to [Me$_2$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.

4.8 Synthesis of compound 20

In a glovebox a chlorobenzene (1 mL) solution of Me$_2$NH•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 colour 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 x 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).

^{1}H NMR (500 MHz, d$_5$-PhBr): δ 0.54 (3H, br s, Me$_2$NH•B$\underline{H}$$_3$), 1.49 (30H, s, Cp*), 1.77 (6H, s, ortho-CH$_3$), 2.02 (3H, s, para-CH$_3$), 2.12 (6H, s, $\underline{Me}$$_2$NH•BH$_3$), 3.60 (1H, br s, Me$_2N\underline{H}$•BH$_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, $\underline{Me}$$_2$NH•BH$_3$), 128.5 (s, Cp*), 159.1 (s, ipso-C). Other aromatic peaks are obscured by the PhBr solvent. Signals corresponding to [B(C$_6$F$_5$)$_4$]$^-$ are also present as reported above. **^{11}B NMR (96 MHz, d$_5$-PhBr):** δ -16.9 (s, [B(C$_6$F$_5$)$_4$]$^-$), -11.5 (br s, Me$_2$NH•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, P(C$_6$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-Youngs NMR tube and removed from the glovebox. The reaction was monitored by ^{11}B and ^{31}P NMR spectroscopy.

11

4.10 Reaction between Me₂NH-BH₂-Me₂N-BH₃ and 20 mol% 14

In a glovebox [Cp₂ZrOMes][B(C₆F₅)₄] (37 mg, 0.036 mmol) and the PtBu₃ (8 mg, 0.036 mmol) were weighed into glass vials. The phosphine was dissolved in PhCl (0.5 mL) and mixed with [Cp₂ZrOMes][B(C₆F₅)₄]. The resulting solution was added to a glass vial containing Me₂NH-BH₂-Me₂N-BH₃ (18.6 mg, 0.16 mmol), the solution was mixed to ensure full dissolution of the amine-borane before transferring to a quartz J-Youngs NMR tube. The tube was subsequently removed from the glovebox and the relevant spectra obtained (Figure S2).

4.11 Reaction between Me₂NH-BH₂-Me₂N-BH₃ and 20 mol% 6

In a glovebox [Cp₂ZrOMes][B(C₆F₅)₄] (37 mg, 0.036 mmol) was weighed into a glass vial and dissolved in PhCl (0.5 mL). The resulting solution was added to a glass vial containing Me₂NH-BH₂-Me₂N-BH₃ (18.6 mg, 0.16 mmol), the solution was mixed to ensure full dissolution of the amine-borane before transferring to a quartz J-Youngs NMR tube. The tube was subsequently removed from the glovebox and the relevant spectra obtained (Figure S3).

4.12 Reaction between ᶦPr₂NH•BH₃ and 10 mol% 14

In a glovebox [Cp₂ZrOMes][B(C₆F₅)₄] (18 mg, 0.018 mmol) and the PtBu₃ (4 mg, 0.018 mmol) were weighed into glass vials. The phosphine was dissolved in PhCl (0.5 mL) and mixed with [Cp₂ZrOMes][B(C₆F₅)₄]. The resulting solution was added to a glass vial containing ᶦPr₂NH•BH₃ (20.5 mg, 0.18 mmol), the solution was mixed to ensure full dissolution of the amine-borane before transferring to a quartz J-Youngs NMR tube. The tube was subsequently removed from the glovebox and the relevant spectra obtained (Figure S4).

4.13 Synthesis of compound 21

An analogous methodology was used for the synthesis of **21** as was employed for the synthesis of **20**. In a glovebox a chlorobenzene (1 mL) solution of ᶦPr₂NH•BH₃ (4 mg, 0.03 mmol) was added dropwise to a chlorobenzene (1 mL) solution of **6** (40 mg, 0.03 mmol). An immediate colour 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 x 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, d₅-PhCl): δ 1.04 (12H, d, *ᶦPr₂*NH•BH₃), 1.69 (30H, s, Cp*), 1.97 (6H, s, *ortho*-CH₃), 2.18 (3H, s, *para*-CH₃), 3.09 (2H, m, *ᶦPr₂*NH•BH₃), 3.35 (1H, br s, Me₂N*H*•BH₃), 6.72 (2H, s, Ar-H) **¹³C NMR (125 MHz, d₅-PhCl):** δ 11.6 (s, Cp*), 19.4 (s, *ortho*-CH₃), 19.7 (s, ᶦPr), 26.2 (s, *para*-CH₃), 54.3 (s, ᶦPr), 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 [B(C₆F₅)₄]⁻ are also present as reported above. **¹¹B NMR (96 MHz, d₅-PhCl):** δ -16.9 (s, [B(C₆F₅)₄]⁻), -9.5 (br s, ᶦPr₂NH•*B*H₃)

ASSOCIATED CONTENT

Additional spectra, further synthetic details and crystallographic tables. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* duncan.wass@bristol.ac.uk
* *ian.manners@bristol.ac.uk*

Author Contributions

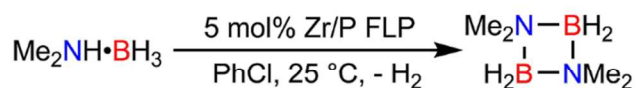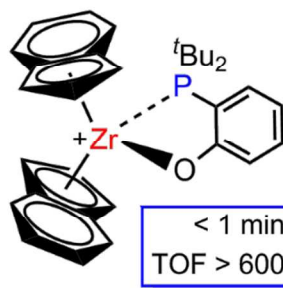All authors have given approval to the final version of the manuscript.
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7

FLP-Catalysed Dehydrocoupling

$Me_2NH \cdot BH_3 \xrightarrow[\text{PhCl, 25 °C, - H}_2]{\text{5 mol\% Zr/P FLP}}$ Me_2N-BH_2 / H_2B-NMe_2

< 1 min
TOF > 600 h^{-1}

- Highly efficient FLP dehydrocoupling catalyst

- Unique reaction mechanism

- Isolation of highly reactive intermediates