Zirconium–Nitrogen Intermolecular Frustrated Lewis Pairs

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* Supporting Information

ABSTRACT: A series of intermolecular transition metal frustrated Lewis pairs (FLPs) based on zirconocene alkoxide complexes ([CpZr(OMes)]+ 1 or ([Cp2Zr(OMes)])2 2) with nitrogen Lewis bases (NEt3, NEt4Pr2, pyridine, 2-methylpyridine, 2,6-lutidine) are reported. The interaction between Zr and N depends on the specific derivatives used, in general more sterically encumbered pairs leading to a more frustrated interaction; however, DOSY NMR spectroscopy reveals these interactions to be dynamic in nature. The pairs undergo typical FLP-type reactivity with D2, CO2, THF, and PhCCD. The catalytic dehydrocoupling of Me2NH-BH3 is also reported. Comparisons can be made with previous work employing phosphines as Lewis bases suggesting that hard–hard or hard–soft acid–base considerations are of little importance compared to the more prominent roles of steric bulk and basicity.

INTRODUCTION

Frustrated Lewis pairs (FLPs) first came to prominence over a decade ago,1 and the subject area is continuing to reveal powerful new chemistry for small molecule activation and catalysis. Main group FLPs have been the focus of much of this chemistry, having been used to perform a wide variety of transformations with both inter- and intramolecular systems.2,3 We have focused on the use of Zr(IV) cations as the Lewis acidic component in FLPs, which have predominantly taken the form of a zirconocene in combination with an intra-molecular phosphine moiety; other groups have taken a similar approach (Figure 1). The FLPs produced (A–H) have been used for the effective activation of a number of small molecules including H2, CO2, H2CO, PhCH2, C2H4, THF, Et2O, and Me2CO, in addition to performing the cleavage of C–Cl and C–F bonds, and catalytic amine-borane dehydrocoupling.4–11

Intermolecular main group FLPs have been explored in parallel with intramolecular examples;5 by contrast, intermolecular transition metal FLPs are far less explored with only the activation of N2O using a Zr(IV)/P3Bu3 FLP reported by Stephan et al. (Scheme 1),12 and a wider exploration of intermolecular Zr(IV)/phosphine systems reported by our group in 2016 (Scheme 2).13,14 The activation of CO2 and H2, along with the ring-opening of THF and activation of phenylacetylene (via both proton abstraction and 1,2-addition), by this latter system shows that these more easily modified (and less synthetically challenging) systems can achieve the same useful chemistry.

An outstanding question for Zr(IV)-based FLPs is the extent to which the hard–soft mismatch between the hard zirconocene center and the soft phosphine Lewis base influences the “frustration” of the FLP produced. Do Zr(IV)-

![Figure 1](https://example.com/figure1.png)

Figure 1. Intramolecular Zr/P FLPs developed by our group (A–C) and by Erker et al. (D–H). In all cases, the [B(C6F5)4]− or [MeB(C6F5)3]− counterion has been omitted for clarity.

† Supporting Information


Scheme 1. Intermolecular Zr/P FLP Used for N₂O Activation

\[ \text{Scheme 2. Intermolecular Zr/P FLPs Developed by Our Group}^a \]

\[ \text{Figure 2. Zr/N FLP M developed by Erker et al. [B(C₆F₅)₄]⁻ counterion omitted for clarity.} \]

\[ \text{Figure 3. Zr(IV) cations used in this work. The [B(C₆F₅)₄]⁻ counterions has been omitted for clarity.} \]

\[ \text{methylpyridine (d, pKₐ = 5.9) and 2,6-lutidine (2,6-dimethylpyridine) (e, pKₐ = 6.8).} \]

When 1 is mixed with a–e, a lightening of the yellow solution is seen in all cases upon addition of the Lewis base. The reaction of 2 with a, b, and e resulted in a color change from orange to deep red, whereas the addition of c and d gave green and lighter orange solutions, respectively. Examining these interactions by \[^{15}\text{N}\]NMR spectroscopy gave inconclusive results. However, by using \[^{15}\text{N}\]HMBC NMR spectroscopy reliable data were obtained; the results and comparison to the free Lewis base resonances are shown in Table 1. The

\[ \text{Table 1.} \]

<table>
<thead>
<tr>
<th>Lewis base</th>
<th>[^{15}\text{N}]-HMBC NMR, δ ppm</th>
<th>[^{15}\text{N}]-HMBC NMR, δ ppm</th>
<th>[^{15}\text{N}]-HMBC NMR, δ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEt₃ (a)</td>
<td>1a 163.5</td>
<td>2a 54.2</td>
<td></td>
</tr>
<tr>
<td>1Pr₂NEt (b)</td>
<td>1b 185.5</td>
<td>2b</td>
<td></td>
</tr>
<tr>
<td>C₅H₅N (c)</td>
<td>1c 260.5</td>
<td>2c</td>
<td></td>
</tr>
<tr>
<td>C₆H₄(CH₃)N (d)</td>
<td>1d 301.1</td>
<td>2d 261.1</td>
<td></td>
</tr>
<tr>
<td>C₆H₄(CH₃)₂N (e)</td>
<td>1e 294.8</td>
<td>2e 286.0</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

This paper demonstrates that pairs formed from zirconocenes with a wider variety of amine bases are effective and versatile FLPs.

#### RESULTS AND DISCUSSION

Previously, the Zr(IV) cations 1 and 2 (Figure 3) were combined with a series of phosphines in order to perform FLP-type reactions; the same Zr(IV) cations were explored in a similar way with a group of nitrogen-based Lewis bases. The selection of nitrogen compounds was chosen due to the varying basicities and steric bulk of the different species, with NEt₃ (a, pKₐ = 10.8) and 1Pr₂NEt (b, pKₐ = 11.4) being more basic than pyridine (c, pKₐ = 5.3) and its derivatives 2-.
Table 2. Diffusion Coefficients (D) of the Free and Combined Lewis Pair Species, with All Results Obtained Using PhBr-d₅ at a Concentration of 0.06 mol dm⁻³

<table>
<thead>
<tr>
<th>Lewis base</th>
<th>D of base (μm² s⁻¹)</th>
<th>D of base with 1 (μm² s⁻¹)</th>
<th>D of base with 2 (μm² s⁻¹)</th>
<th>D of 1 with base (μm² s⁻¹)</th>
<th>D of 2 with base (μm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEt₃ (a)</td>
<td>9.2</td>
<td>8.2</td>
<td>8.7</td>
<td>3.3</td>
<td>4.4</td>
</tr>
<tr>
<td>Pr₂NEt₃ (b)</td>
<td>8.6</td>
<td>9.0</td>
<td>9.0</td>
<td>3.3</td>
<td>3.6</td>
</tr>
<tr>
<td>C₂H₅N (c)</td>
<td>11.8</td>
<td>5.7</td>
<td>4.0</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>C₂H₅(CH₃)₂N (d)</td>
<td>11.0</td>
<td>5.2</td>
<td>5.2</td>
<td>2.5</td>
<td>2.3</td>
</tr>
<tr>
<td>C₅H₅(CH₃)₂N (e)</td>
<td>9.7</td>
<td>6.8</td>
<td>6.8</td>
<td>2.3</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*All values have units of x10⁻¹⁰ m² s⁻¹. D of 1 in absence of base is 6.0 x 10⁻¹⁰ m² s⁻¹. D of 2 in absence of base is 8.6 x 10⁻¹⁰ m² s⁻¹.

more persistent interaction. A possible explanation is the more planar geometry of c-e facilitating a minimization of steric clash in comparison to the more three-dimensional a and b. It is also noteworthy that 1 and 2, despite significant steric differences, show similar results. This is in contrast to similar experiments with phosphine bases where the less sterically encumbered 1 showed a marked tendency to form less dynamic pairs.

Single crystals of 2c and 2d suitable for X-ray diffraction study were obtained, and the solid-state structures of 2c and 2d are shown in Figure 4. 2c possesses a shorter Zr–N bond (2.326(3) Å) than 2d (2.386(4) Å), likely a result of the increased steric bulk of d. Complex 2c also has greater bending of the alkoxide fragment (bond angle Zr1 O1 C26 158.8(2)°) compared to 2d (Zr1 O1 C21 167.4(3)°); in 2, this angle is almost completely linear (176.7(2)°). While it is tempting to rationalize this effect in terms of the multiple bond character between the Zr and O atoms changing according to other donor ligands, alkoxide bond angles are known to be an unreliable indicator of such effects, and a steric rationale is also possible.¹³

Reactivity of Lewis Pairs with Dihydrogen (D₂). Initial investigations into the ability of these Zr/N systems to activate small molecules involved reactions with dihydrogen. D₂ was used in place of H₂ to allow for easier reaction monitoring via ¹H NMR spectroscopy.

For 1a–e, no reaction was observed upon addition of D₂ gas (1 bar) to a PhCl solution of the pair (Scheme 3). This is in line with previous work where at least one Cp⁺ ligand was necessary for the reaction to proceed and adds credence to the hypothesis that transient binding of H₂ to the Zr center is required for subsequent activation to occur, meaning that simply changing the Lewis base from a phosphine to a nitrogen compound does not seem to have any effect.

The reaction proceeded smoothly for Lewis pairs 2a, 2b, and 2e with the characteristic Zr-D singlet appearing in the ²H NMR spectra for each reaction (δ = 6.06 ppm) by the time spectra were recorded (less than 1 min). For 2a and 2b the ²H resonance for the ammonium salts was not seen, as these compounds are insoluble in PhCl. For 2e, a broad resonance is seen at 12.4 ppm in the ²H spectrum, corresponding to the [C₅H₅(CH₃)₂N-D]⁺ species.

Neither the 2c nor 2d pairs demonstrated reactivity toward D₂, likely a result of the lower basicity of the Lewis bases, in addition to the more persistent Zr–N interactions as evidenced by DOSY NMR studies.

Reactivity of Lewis Pairs with Carbon Dioxide. PhBr-d₅ solutions of the Lewis pairs 1a–e and 2a–e were exposed to 1 bar CO₂ (Scheme 4). The pairs 1a and 1b reacted almost instantly, with both turning much paler yellow. ¹⁵N-HMBD NMR spectra showed new peaks at 446.0 and 446.5 ppm respectively, which were assigned to the CO₂ activation product. No reaction was seen for 1c; however, both 1d and 1e reacted, albeit more slowly than 1a and 1b (<20 min), with the signals at 450.1 and 464.0 ppm respectively in the ¹⁵N-HMBD NMR spectra.

Upon addition of CO₂, 2a instantly changed color to yellow, with the new resonance in the ¹⁵N-HMBD NMR spectrum (δ = 343.3 ppm) assigned to the CO₂ activation product. In the case of 2b a signal in the ¹⁵N-HMBD NMR spectrum could not be obtained, and although a color change suggests reaction, further analysis proved inconclusive. Reactions were also seen for both 2d and 2e, with the CO₂ activation products assigned in the ¹⁵N-HMBD NMR (2d: δ = 438.1 ppm, 2e: δ = 466.1 ppm). Compound 2c was found to be inactive for CO₂ activation.

Reactivity of Lewis Pairs with Tetrahydrofuran (THF). The FLP systems were also tested for their ability to ring-open tetrahydrofuran (THF), with bromobenzene-d₅ solutions of 1a, 1b, 1d, and 1e undergoing a rapid color change to a bright yellow solution upon addition of THF indicating formation of the Zr-THF adduct (Scheme 5). Formation of the ring-opened products then followed, with the quickest reaction seen for 1a (24 h). No heating was required for this reaction to reach completion, although some unreacted Zr-THF adduct still remained. Heating at 80 °C for several days resulted in no further conversion. More sluggish reactivity was seen with 1d and 1e, with heating at 80 °C over 3 days required for the reactions to reach completion. 1b demonstrated much slower reactivity still, with very low conversion (20%) achieved after 3 days at 80 °C and no increase in conversion when left to heat.

![Figure 4. Molecular structures of 2c (top) and 2d (bottom), as determined by single crystal X-ray diffraction. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, the [B(C₆F₅)₄]⁻ counterion, and PhCl solvent of crystallization are omitted for clarity. Selected bond lengths (Å) and angles (deg): 2c: Zr1–O1 1.982(2), Zr1–N1 2.326(3), O1–C26 1.375(4), Zr1–O1–C26 158.8(2), C1–Zr–Cp* 135.5(7), 2d: Zr1–O1 1.375(3), Zr1–N1 2.386(4), O1–C21 1.369(5), Zr1–O1–C21 167.4(3), C1–Zr–Cp* 132.7(9).](image-url)
for a further 10 days. No product formed in the reaction of 1c, although the bound pyridine was eventually displaced by the THF after several days of heating at 80 °C.

Successful reactivity was also seen with 2a, 2d, and 2e, although all of these reactions required much longer timeframes than their Cp counterparts, with 5 days of heating at 80 °C required for the reactions to reach completion. Surprisingly, 2d was the most reactive of these three samples, achieving the highest yield of 40% (by NMR). 2a and 2e had very low yields of 17% and 7% respectively (by NMR), which may be a result of their higher steric bulk being more inhibitory for this reaction when Cp* ligands are present.
instead of Cp. The more electron-rich Cp* ligands may also result in comparatively reduced polarization/activation of the bound THF, thereby making subsequent attack from the Lewis base and consequent ring-opening less favorable.

Reactivity of Lewis Pairs with Phenylacetylene-d. Reactions of terminal alkynes with FLPs have been shown to proceed via 1,2-addition or deprotonation. In this present case, all of the pairs 1a, 1b, 1e and 2a, 2b, 2d, 2e react with phenylacetylene-d (PhCCD), via deprotonation of the alkyne (Scheme 6). For 1a, an instant color change is seen upon addition of PhCCD (to a lighter yellow), followed by the formation of [D-NEt][B(C6F5)4] crystals after several minutes and concurrent formation of the zirconium acetylide complex. Both 1b and 1e also demonstrate formation of the [D-3P2NEt][B(C6F5)4] and [2.6-Me-Py-D][B(C6F5)4] salts; however these reactions are more sluggish (5 and 30 min respectively). No reaction was seen for 1c and 1d. 2a, 2b, 2d, and 2e all reacted successfully with PhCCD, again yielding the deprotonation product.

Less basic, less sterically bulky phosphine Lewis bases have been shown to perform the 1,2-addition reaction previously. The results here suggest harder nitrogen bases are more likely to react via a deprotonation pathway.

Catalytic Dehydrocoupling of Me2NH-BH3. The ability of the Zr/N systems to perform catalysis was tested through the dehydrocoupling of Me2NH-BH3. The reactions were monitored by 11B{1H} NMR spectroscopy, employing a 10 mol % catalyst loading, with the results shown in Table 3. 1a, 1e, and 2e achieved complete conversion and >95% yields within 9.5, 10.5, and 7.5 h respectively, with 2,6-dimethylpyridine the only Lewis base producing high conversions and yields with both cations.

The ability of NEt3 to catalyze the reaction when combined with 1, but not with 2, is in line with previous work which employed phosphines as the Lewis base (P3Bu3, PCy3, PEt3, PPh3, PMes3, and P(C6F5)3). The poor performance of 2a and 2b is also likely to be a result of the degradation over time; when 2 and a or b are left together in solution, the precipitation of [H-NEt3][B(C6F5)4] or [H-3P2NEt][B(C6F5)4] crystals is observed within a few hours. We were unable to isolate and identify the Zr complex. Increasing reaction temperature to 60 °C improved reaction rates as expected; for 1a, 1e, and 2e, complete conversion was achieved within 30 min. The pairs 2c–e are surprisingly able catalysts for this reaction, outperforming previously reported Zr(IV)-phosphine FLP catalysts.

Using both basicity and sterical bulk as rational predictors of reactivity is still difficult. This is highlighted by the fact that P3Bu3 (pKs = 11.4) was the only phosphine (in combination with 1) shown to have reactivity similar to 1a, 1e, or 2e, whereas 1b showed very poor reactivity, despite b being more similar to P3Bu3 in terms of basicity and sterical bulk.

The mechanism of these reactions is proposed to follow the same cycle that has been previously reported, with the same distribution of intermediates seen in the 11B{1H} NMR spectra during the reactions (Figure 5). Indeed, examination of the catalytic cycle gives greater clues as to the reason for the varying results seen for each catalyst. The principle role of the Lewis base in the catalytic cycle is currently understood to be the deprotonation of Me2NH-BH3 (Scheme 7). Therefore, it may be that 1a, 1e, and 2e are more effective at both the deprotonation step and subsequent dihydrogen release. In the case of 1b, N,N-diisopropylethylamine may be too bulky to effectively deprotonate Me2NH-BH3, and the subsequent ammonium salt may be too stable for easy dihydrogen release.

If we compare the reaction profiles for the reactions of 1a (Figure 6) and 2e (Figure 7), it is clear that a larger concentration of Me2NH-BH2-Me2N-BH3 is present for 1a.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>temperature (°C)</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>conversion (%)</th>
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<tbody>
<tr>
<td>1a</td>
<td>25</td>
<td>9.5</td>
<td>97</td>
<td>100</td>
</tr>
<tr>
<td>1a</td>
<td>60</td>
<td>0.45</td>
<td>93</td>
<td>100</td>
</tr>
<tr>
<td>1b</td>
<td>25</td>
<td>14</td>
<td>7</td>
<td>26</td>
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<td>0</td>
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<td>1d</td>
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<td>1e</td>
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<td>14</td>
<td>98</td>
<td>100</td>
</tr>
<tr>
<td>1e</td>
<td>60</td>
<td>0.5</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>2a</td>
<td>25</td>
<td>14</td>
<td>9</td>
<td>10</td>
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<tr>
<td>2c</td>
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<tr>
<td>2d</td>
<td>25</td>
<td>14</td>
<td>36</td>
<td>42</td>
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<td>&gt;99</td>
<td>100</td>
</tr>
<tr>
<td>2e</td>
<td>60</td>
<td>0.5</td>
<td>98</td>
<td>100</td>
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</table>
This is one reason for slower product formation and is perhaps a result of the persistence of the ammonium salt in the reaction which, by preventing the release of H₂ through reaction with Cp₂Zr(H)OMes, means there is less [Cp₂ZrOMes]⁺ available for the conversion of Me₂NH·BH₂-Me₂N-BH₃, thus reducing the rate of product formation and overall catalytic turnover.

**CONCLUSION**

A range of intermolecular zirconium/nitrogen FLPs have been synthesized through combination of zirconocene cations with either an amine or a pyridine derivative. The nature of the Lewis acid/Lewis base interaction was elucidated through DOSY NMR spectroscopic studies, before the activation of a number of different small molecules was demonstrated. Steric effects once again play an important role, with pyridine (C) largely being shown to be an ineffective Lewis base for these reactions. The dehydrocoupling of Me₂NH·BH₃ was also achieved, with 2,6-dimethylpyridine and triethylamine shown to be the most effective Lewis bases. These results highlight that the hard-soft mismatch in previous intermolecular

**EXPERIMENTAL SECTION**

General Considerations. Unless otherwise stated, all manipulations were undertaken under an atmosphere of argon or nitrogen using standard glovebox (O₂ < 0.1 ppm, H₂O < 0.1 ppm) and Schlenk line techniques. All glassware was dried in an oven at 200 °C overnight and cooled under a vacuum prior to use. The complexes [Cp₂ZrOMes][B(C₆F₅)₄] and [Cp₂ZrOMes][B(C₆F₅)₄] were synthesized following a literature procedure. Triethylamine, N,N-diisopropylethylamine, pyridine, 2-methylpyridine, and 2,6-dimethylpyridine were purchased from Sigma-Aldrich and distilled from CaH₂ prior to use. Me₂NH·BH₃ was purchased from Sigma-Aldrich and purified by sublimation prior to use (25 °C, 2 × 10⁻² Torr).

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**Scheme 7. Proposed Reaction Mechanism for the Catalytic Dehydrocoupling of Me₂NH·BH₃ Using a Zr(IV)/FLP**

*The [B(C₆F₅)₄]⁻ counterion has been omitted for clarity.*

Figure 5. $^{11}$B $^1$H NMR spectrum (160 MHz, 25 °C, PhBr-d₅, 7.5 h) for the reaction between Me₂NH·BH₃ and 10 mol % 2.1b. a = Me₂N = BH₂ (36.6 ppm), b = HB(NMe₂)₂ (27.5 ppm), c = [Me₂N·BH₂]⁺ (4.03 ppm), d = Me₂NH·BH₂-Me₂N·BH₃ (0.82 ppm), e = Me₂NH·BH₃ and Me₂NH·BH₂·Me₂N·BH₃ (−14.5 ppm), f = [B(C₆F₅)₄]⁻ (~17.5 ppm), g = Me₂N(B₂H₅) (~18.7 ppm).

Figure 6. Reaction of 1a with Me₂NH·BH₃ (25 °C, PhBr-d₅, 14 h): (black □) Me₂NH·BH₃; (red ◼) [Me₂N·BH₂]⁺; (blue ■) Me₂NH·BH₂·Me₂N·BH₃; (purple ▼) Me₂N = BH₂; (green ▲) Me₂N(B₂H₅); (orange triangles) HB(NMe₂)₂.

Zr(IV)-phosphine FLPs is of little or secondary importance. Given the judicious choice of nitrogen base, very similar FLP reactivity is observed in these Zr(IV)-amine systems, with steric bulk and basicity remaining the key factors in determining reactivity.
Phenylacetylene-d was purchased from Sigma-Aldrich and purified by distillation before use. Reagent gases (D₂ and CO₂) were dried prior to use by passing through a ~78 °C trap. THF was purified using a Grubbs type purification system. Chlorobenzene was purchased from Sigma-Aldrich and dried over 4 Å molecular sieves prior to use. Spectra of 1a-d, 2a-e, 3a-e were recorded using Jeol ECS 300 (300 MHz), Bruker Avance III HD 500 Cryo (500 MHz) spectrometers.

1H NMR (500 MHz, PhBr-d₅) δ 8.19 (2H, m, o-Py-H), 7.46 (1H, m, m-Py-H), 7.10 (2H, m, n-Py-H), 6.73 (2H, s, Ar-H), 5.97 (10H, s, Cp), 2.18 (3H, s, p-Ar-CH₃), 1.79 (6H, s, o-Ar-CH₃) ppm. 13C N-HMBc NMR (500 MHz, 51 Mb, PhBr-d₅) signal not seen for FLP (see Results and Discussion). NB: pyridine δ = 318.9 ppm.

1H NMR (500 MHz, PhBr-d₅) δ 8.62 (1H, br, o-Py-H), 7.96 (1H, m, p-Py-H), 7.40 (2H, m, m-Py-H), 6.74 (2H, s, Ar-H), 5.99 (10H, s, Cp), 2.18 (3H, s, p-Ar-CH₃), 1.71 (3H, br, o-Py-CH₃), 1.83 (6H, s, o-Ar-CH₃) ppm. 13C N-HMBc NMR (500 MHz, 51 Mb, PhBr-d₅) δ 302.1 (Zr-NC₃(HCH)₃) ppm. NB: 2-methylpyridine δ = 317.7 ppm.

In a glovebox, 2 (34.1 mg, 0.029 mmol) was dissolved in bromobenzene-d₅ (0.5 mL) before the Lewis base (a = NEt₃ (4.1 µL, 0.029 mmol), b = Pr₂NEt (5.1 µL, 0.029 mmol), c = pyridine (2.4 µL, 0.029 mmol), d = 2-methylpyridine (2.9 µL, 0.029 mmol), e = 2,6-dimethylpyridine (3.4 µL, 0.029 mmol)) was added. A color change (dark orange to red) was observed for a, b, and e. The solution turned green upon addition of c, and slightly lightened in color upon addition of d.

The FLP was then used in situ for reactions with substrates, without isolation. However, crystals of 2c and 2d suitable for X-ray crystallography were obtained by layering a PhCl solution of 2c, and a PhBr-d₅ solution of 2d with pentane.

1H NMR (500 MHz, PhCl-d₅) δ 6.79 (2H, s, m-Ar-H), 3.37 (6H, s, NEt), 2.91 (2H, sept, JHH = 7.2 Hz, CH₂NEt₃), 2.20 (3H, s, Ar-CH₃), 1.73 (6H, s, o-Ar-CH₃), 1.64 (30H, s, Cp), 1.05–0.63 (15H, br, CH₂CH₂CH₂N(CHCH₃)₂) ppm. 13C N-HMBc NMR (500 MHz, 51 Mb, PhBr-d₅) signal not seen for FLP (see Results and Discussion).

1H NMR (500 MHz, PhBr-d₅) δ 8.55 (1H, br, o-Ar-H), 8.38 (1H, br, o-Ar-H), 7.32 (1H, br, p-Ar-H), 7.07–6.97 (2H, m, m-Ar-H) ppm. Mass spectrometry experiments were carried out by the University of Bristol Mass Spectrometry Service on a Bruker Daltonics MicroOTOF II with a TOF analyzer or a Waters Synapt G2S with an IMS-Q-TOF analyzer. All samples were run in predried PhCl or CH₃CN.

Generation of FLPs. [Cp₂ZrOMes][B(C₆F₅)₄] // LB (1a–e). In a glovebox, 1 (30 mg, 0.029 mmol) was dissolved in bromobenzene-d₅ (0.5 mL) before the Lewis base (a = NEt₃ (4.1 µL, 0.029 mmol), b = Pr₂NEt (5.1 µL, 0.029 mmol), c = pyridine (2.4 µL, 0.029 mmol), d = 2-methylpyridine (2.9 µL, 0.029 mmol), e = 2,6-dimethylpyridine (3.4 µL, 0.029 mmol)) was added. A color change (orange to yellow) was observed in each case.

The FLP was then used in situ for reactions with substrates, without isolation.

1a. 1H NMR (500 MHz, PhBr-d₅) δ 6.75 (2H, m, m-Ar-H), 6.10 (10H, s, Cp), 2.36 (6H, q, JHH = 7.2 Hz, N(CH₂CH₃)₃), 2.20 (3H, s, p-Ar-CH₃), 1.86 (6H, s, o-Ar-CH₃), 0.89 (9H, t, JHH = 7.2 Hz, N(CH₂CH₃)₃) ppm. 13C N-HMBc NMR (500 MHz, 51 Mb, PhBr-d₅) δ 163.5 (Zr-NEt₃) ppm. NB: NEt₃ δ = 47.6 ppm.

1b. 1H NMR (500 MHz, PhBr-d₅) δ 6.75 (2H, s, m-Ar-H), 6.10 (10H, s, Cp), 2.90 (2H, sept, JHH = 6.5 Hz, N(CH₂CH₃)₃), 2.37 (2H, q, JHH = 7.2 Hz, N(CH₂CH₃)₃), 2.19 (3H, s, p-Ar-CH₃), 1.86 (6H, s, o-Ar-CH₃), 1.04–0.58 (15H, br, CH₂CH₂N(CHCH₃)₂) ppm. 13C N-HMBc NMR (500 MHz, 51 Mb, PhBr-d₅) δ 185.5 (Zr-N(Pr₂Et)) ppm. NB: Pr₂NEt δ = 57.5 ppm.

Figure 7. Reaction of 2e with Me₂NH-BH₃ (25 °C, PhBr-d₅, 14 h): (black ■) Me₂NH-BH₃; (red ●) [Me₂N-BH₂]²⁺; (blue ▲) Me₂NH·BH₂-Me₂N-BH₃; (purple ▲) Me₂N = BH₂; (green ▼) Me₂N(Br₂H); (orange triangles) HB(NMe₂)²⁺.
diffusion delay of 100 ms. The results of the study can be found in the Supporting Information. All data were analyzed using MestReNova.

Reactions of Pairs with D2. Reactivity of [Cp2ZrOMes][B(C6F5)4] with D2 (1a–e). In a glovebox, 1 (30 mg, 0.029 mmol) was dissolved in PhCl (0.5 mL) in an NMR tube fitted with a J. Youngs valve, before CsD2 (one drop) was added for reference in 1H NMR spectra. An equimolar amount of the Lewis base (a = NEt3 (4.1 μL, 0.029 mmol), b = Pr2NEt (5.1 μL, 0.029 mmol), c = pyridine (2.4 μL, 0.029 mmol), d = 2-methylpyridine (2.9 μL, 0.029 mmol), e = 2,6-dimethylpyridine (3.4 μL, 0.029 mmol) was then added. Outside of the glovebox, the sample was degassed twice via freeze–pump–thaw, before being refilled with D2 gas (1 bar). In all cases, no change in the NMR spectra was seen.

Reactivity of [Cp2ZrOMes][B(C6F5)4] // LB (2a–e). In a glovebox, 2 (34.1 mg, 0.029 mmol) was dissolved in PhCl (0.5 mL) in an NMR tube fitted with a J. Youngs valve, before CsD2 (one drop) was added for reference in 1H NMR spectra. An equimolar amount of the Lewis base (a = NEt3 (4.1 μL, 0.029 mmol), b = Pr2NEt (5.1 μL, 0.029 mmol), c = pyridine (2.4 μL, 0.029 mmol), d = 2-methylpyridine (2.9 μL, 0.029 mmol), e = 2,6-dimethylpyridine (3.4 μL, 0.029 mmol) was then added. Outside of the glovebox, the sample was degassed twice via freeze–pump–thaw, before being refilled with D2 gas (1 bar). A color change from red to yellow was seen for 2a, 2b, and 2e. Isolation of any products was attempted but not possible, and no spectral data were obtained in situ. 2c did not react.

2a + CO2. 1H NMR (500 MHz, Phbr-ds) δ 6.71 (2H, s, m-ArH), 2.91 (2H, br, n(C2H5O)), 2.38 (2H, q, 3JHH = 7.2 Hz, n(CH2)], 2.16 (3H, s, o-Ar-CH3), 1.90 (6H, s, o-Ar-CH3), 1.83 (30H, s, C(Cp)), 1.00~1.07 (15H, br, CH(BH)2(N)) ppm. 13C NMR (125 MHz, PhBr-ds) δ 161.4 (s, C(O)), 155.9 (s, i-C), 124.7 (s, o-C), 121.3 (s, p-C), 56.1 (s, N(CH2CH2)2), 43.5 (s, N(CH2CH2)3), 21.1 (s, N(CH2CH2)2), 22.6 (s, p-CH3), 18.4 (s, o-CH3), 16.7 (s, N(CH2CH2)), 11.3 (s, C(Cp)) ppm. Remaining peaks obscured by solvent. 15N-HMBCC NMR (500 MHz, 51 MHz, PhBr-ds) δ 343.3 (Zr-CO2-NEt3) ppm.

2b + CO2. 1H NMR (500 MHz, Phbr-ds) δ 6.80 (2H, s, m-ArH), 2.91 (2H, br, n(C2H5O)), 2.38 (2H, q, 3JHH = 7.2 Hz, n(CH2)], 2.16 (3H, s, o-Ar-CH3), 1.88 (30H, s, C(Cp)), 1.75 (6H, s, o-Ar-CH3), ppm. 15N-HMBCC NMR (500 MHz, 51 MHz, PhBr-ds) δ 438.1 (Zr-CO2-N(CH2CH2)) ppm. 15N-HMBCC NMR (500 MHz, 51 MHz, PhBr-ds) δ 461.6 (Zr-CO2-N(CH2CH2)) ppm.

Reactions of Pairs with Tetrahydrofuran (THF). Reactivity of [Cp2ZrOMes][B(C6F5)4] // LB (1a–e). In a glovebox, 1 (30 mg, 0.029 mmol) was dissolved in PhBr-ds (0.5 mL) in an NMR tube fitted with a J. Youngs valve. An equimolar amount of the Lewis base (a = NEt3 (4.1 μL, 0.029 mmol), b = Pr2NEt (5.1 μL, 0.029 mmol), c = pyridine (2.4 μL, 0.029 mmol), d = 2-methylpyridine (2.9 μL, 0.029 mmol), e = 2,6-dimethylpyridine (3.4 μL, 0.029 mmol) was then added. Outside of the glovebox, the sample was degassed twice via freeze–pump–thaw, before being refilled with CO2 gas (1 bar) via a -78 °C trap. 1a, 1b, and 1d showed a lightening in color, whereas 1c showed no color change. Isolation of any products was attempted but not possible, and no spectral data were obtained in situ. 1c did not react.

1a + CO2. 1H NMR (500 MHz, Phbr-ds) δ 6.85 (2H, s, m-ArH), 6.17 (10H, s, Cp), 2.37 (6H, q, n(CH2)], 2.28 (2H, q, n(CH2)], 1.94 (6H, s, o-Ar-CH3), 1.85 (30H, s, C(Cp)), 1.00~1.07 (15H, br, CH(BH)2(N)) ppm. 13C NMR (125 MHz, PhBr-ds) δ 163.5 (s, C(O)), 135.8 (s, i-C), 124.9 (s, o-C), 121.9 (s, p-C), 47.0 (s, N(CH2CH2)2), 20.9 (s, p-CH3), 18.6 (s, o-CH3), 10.5 (s, N(CH2CH2)3) ppm. 15N-HMBCC NMR (500 MHz, 51 MHz, PhBr-ds) δ 446.0 (Zr-CO2-NEt3) ppm.

1b + CO2. 1H NMR (500 MHz, Phbr-ds) δ 6.85 (2H, s, m-ArH), 6.17 (10H, s, Cp), 2.29 (2H, sept., n(CH2)], 2.19 (6H, s, o-Ar-CH3), 1.94 (6H, s, o-Ar-CH3), 1.94 (6H, s, o-Ar-CH3), 1.85 (30H, s, C(Cp)), 1.00~1.07 (15H, br, CH(BH)2(N)) ppm. 13C NMR (125 MHz, PhBr-ds) δ 162.8 (s, C(O)), 161.8 (s, i-C), 128.6 (s, m-C), 124.9 (s, p-C), 112.9 (s, C(p)), 56.0 (s, N(CH2CH2)2), 43.4 (s, N(CH2CH2)3), 21.0 (s, p-CH3), 18.7 (s, o-CH3), 16.6 (s, N(CH2CH2)3) ppm. 15N-HMBCC NMR (500 MHz, 51 MHz, PhBr-ds) δ 446.5 (Zr-CO2-N(Pr2Et)) ppm. 1d + CO2. 1H NMR (500 MHz, Phbr-ds) δ 8.62 (1H, br, o-Py-H), 7.82 (1H, m-Py-H), 7.44 (2H, m-Ph-Py), 6.85 (2H, m-Ar-H), 6.17 (10H, s, Cp), 2.28 (3H, s, p-Ar-CH3), 2.17 (6H, s, Ar-CH3), 2.17 (6H, s, o-Ar-CH3), 2.17 (6H, s, o-Ar-CH3), 2.17 (6H, s, o-Ar-CH3), 2.17 (6H, s, o-Ar-CH3), 2.17 (6H, s, o-Ar-CH3). 15N-HMBCC NMR (500 MHz, 51 MHz, PhBr-ds) δ 450.1 (Zr-CO2-N(C6H5CH3)) ppm. 1e + CO2. 1H NMR (500 MHz, Phbr-ds) δ 7.33 (1H, t, 3JHH = 7.7 Hz, p-Py-H), 6.79 (2H, m-Py-H), 6.74 (2H, s-m-Ar-H), 6.14 (10H, s, Cp), 2.37 (3H, s, p-Ar-CH3), 2.15 (6H, s, o-Ar-H), ppm. C NMR (125 MHz, Phbr-ds) δ 160.9 (s, O(CO)), 160.5 (s, i-C), 155.5 (s, o-C(Py)), 140.0 (s, p-C(Py)), 128.6 (s, o-C(Mes)), 124.7 (s, p-C(Py)), 124.3 (s, o-C(Py)), 112.7 (s, C(p)), 25.4 (s, o-CH3), 20.6 (s, p-CH3), 18.4 (s, o-CH3) ppm. 15N-HMBCC NMR (500 MHz, 51 MHz, PhBr-ds) δ 464.0 (Zr-CO2-NC6H5(CH3)2) ppm. Remaining peaks obscured by PhBr-ds solvent.
Remaining peaks observed by PhBr-d5 solvent. 15N-HMBMC NMR (500 MHz, 51 Hz, PhBr-d5): δ 315.7 ppm, ESI-MS (+ve detection) 528.242 m/z [M]+, 174.1930 m/z [HO(C4H6)-NEt]+.

1b + THF. Yield = 17% (by NMR). Not enough product to isolate. 15N-HMBMC NMR (500 MHz, 51 Hz, PhBr-d5): δ 315.8 ppm, ESI-MS (+ve detection) 556.2742 m/z [M]+, 202.2217 m/z [HO(C4H6)-N(Pr)2Et]+.

1d + THF. Yield = 15.8 mg, 45%. 1H NMR (400 MHz, PhBr-d5): δ 7.56 (1H, m, o-ArH), 7.50–7.39 (1H, m, p-ArH), 6.99–6.86 (2H, m, m-ArH(Ph)), 6.80 (2H, s, Ar-H(Mes)), 6.05 (10H, s, Cp), 3.93–3.85 (4H, m, o-CH2 and β-CH2), 2.23 (3H, s, p-CH3), 2.17 (3H, s, o-CH3(Ph)), 2.09 (6H, s, o-CH3), 1.65 (2H, m, β-CH2), 1.35 (2H, m, γ-CH2) ppm.

1C NMR (125 MHz, PhBr-d5): δ 160.1 (s, i-C(Me3)), 154.6 (s, o-CH3(Ph)), 141.5 (s, p-CH3(Ph)), 127.4 (s, o-CH3(Mes)), 125.6 (s, m-CH3(Ph)), 124.6 (s, p-CH3(Ph)), 132.3 (s, m-CH(Ph)), 112.8 (s, Cp), 72.0 (s, o-CH2), 34.3 (s, β-CH2), 30.3 (s, γ-CH2), 27.3 (s, o-CH3(Ph)), 20.8 (s, p-CH3(Mes)), 19.4 (s, δ-CH2), 17.9 (s, o-CH3(Ph)) ppm. Remaining aromatic peaks observed by PhBr-d5 solvent. 15N-HMBMC NMR (500 MHz, 51 Hz, PhBr-d5): δ 411.6 ppm. ESI-MS (+ve detection) 520.1976 m/z [M]+, 166.1275 m/z [HO(C4H6)(CHO)(NMe4)]+.

1e + THF. Yield = 23 mg, 65%. 1H NMR (400 MHz, PhBr-d5): δ 7.37 (1H, t, JHH = 8 Hz, p-ArH), 6.82–6.72 (2H, m, m-ArH(Ph)), 6.80 (2H, s, Ar-H(Mes)), 6.05 (10H, s, Cp), 3.93 (2H, t, JHH = 6 Hz, o-CH2), 3.85 (2H, s, β-CH2), 2.26 (6H, s, o-CH3(Ph)), 2.23 (3H, s, p-CH3), 2.10 (6H, s, o-CH3), 1.58 (2H, m, β-CH2), 1.45 (2H, m, γ-CH2) ppm.

1C NMR (125 MHz, PhBr-d5): δ 161.0 (s, i-C(Me3)), 154.3 (s, o-CH3(Ph)), 143.8 (s, p-CH3(Ph)), 127.4 (s, o-CH3(Mes)), 124.6 (s, p-CH3(Ph)), 124.0 (s, m-CH3(Ph)), 112.8 (s, Cp), 71.8 (s, o-CH2), 34.3 (s, β-CH2), 30.7 (s, γ-CH2), 15.6 (s, o-CH3(Ph)), 20.8 (s, p-CH3(Mes)), 19.8 (s, δ-CH2), 17.9 (s, o-CH3(Ph)) ppm. Remaining aromatic peaks observed by PhBr-d5 solvent. 15N-HMBMC NMR (500 MHz, 51 Hz, PhBr-d5): δ 411.8 ppm. ESI-MS (+ve detection) 534.1938 m/z [M]+, 180.1436 m/z [HO(C4H6)(NMe4)(CHO)]+.

Reactivity of [Cp"2ZrOMes][B(C6F4)4] / LB (2a–e). In a glovebox, 2 (34 mg, 0.029 mmol) was dissolved in PhBr-d5 (0.5 mL) in an NMR tube fitted with a J. Youngs valve. An equimolar amount of the Lewis base (a = NEt3 (4.1 µL, 0.029 mmol), b = Pr2NEt5 (5.1 µL, 0.029 mmol), c = pyridine (2.4 µL, 0.029 mmol), d = 2-methylpyridine (2.9 µL, 0.029 mmol), e = 2,6-dimethylpyridine (3.4 µL, 0.029 mmol)) was then added. Tetrahydrofuran (THF, 2 mL, 0.029 mmol) was then added with 2a, 2d and 2e all forming yellow solutions. The reactions were heated at 80 °C for 5 days. Isolation of the products was not possible.

2a + THF. Yield = 17% (by NMR). 15N-HMBMC NMR (500 MHz, 51 Hz, PhBr-d5): δ 341.4 ppm. ESI-MS (+ve detection) 668.3975 m/z [M]+, 174.1888 m/z [HO(C4H6)-NEt]+.

2d + THF. Yield = 40% (by NMR). 15N-HMBMC NMR (500 MHz, 51 Hz, PhBr-d5): δ 411.3 ppm. ESI-MS (+ve detection) 660.3350 m/z [M]+, 166.1277 m/z [HO(C4H6)(NMe4)(CH3)CH]=.

Phenylacetylene-d (PhCD). Reactivity of [Cp"2ZrOMes][B(C6F4)4] / LB (1a–e). In a glovebox, 1 (30 mg, 0.029 mmol) was dissolved in PhBr-d5 (0.5 mL) in an NMR tube fitted with a J. Youngs valve. An equimolar amount of the Lewis base (a = NEt3 (4.1 µL, 0.029 mmol), b = Pr2NEt5 (5.1 µL, 0.029 mmol), c = pyridine (2.4 µL, 0.029 mmol), d = 2-methylpyridine (2.9 µL, 0.029 mmol), e = 2,6-dimethylpyridine (3.4 µL, 0.029 mmol)) was then added. Excess phenylacetylene-d (3 drops) was then added, resulting in a lightening of the yellow color for 1a and 1b, with no color change seen for the reactions of 1c–e. Neither 1c nor 1d demonstrated any reactivity. The Zr-acetylide complex could not be isolated in any reaction, so the spectral data was obtained in situ.

[Cp"2ZrOMes]CCPh. 1H NMR (500 MHz, PhBr-d5): δ 7.53 (2H, m, o-ArH), 7.18 (3H, m, p-CH2 and m-CH(Ph)), 6.76 (2H, s, m-
Catalytic Dehydrocoupling of Me2NH-BH3. Reactivity of [Cp2ZrOMes]2[B(C6F5)4] // LB (1a–e). In a glovebox, 1 (18.7 mg, 0.018 mmol) and Me2NH-BH3 (10.6 mg, 0.18 mmol) were weighed into separate vials and dissolved in PhBr-d5 (0.5 mL). The relevant Lewis bases (a = NEt3 (2.5 μL, 0.018 mmol), b = 1,3-BNNEt2 (3.2 μL, 0.018 mmol), c = pyridine (1.5 μL, 0.018 mmol), d = 1,2-dimethylpyridine (1.8 μL, 0.018 mmol), e = 2,6-dimethylpyridine (2.1 μL, 0.018 mmol)) were then added to 1. The two solutions were then combined, and the fully mixed solution was transferred to a quartz J. Youngs NMR tube before the relevant spectra were then collected. No reaction was seen for 1c; however, the relevant spectra for the reactions of 1a, 1b, 1d, and 1e can be found in the Supporting Information (Figures S16–S20).

Catalytic Dehydrocoupling of Me2NH-BH3 at 60 °C. The reactions were prepared for 1a, 1e, and 2e using the same method shown above, with the spectra then collected in an NMR spectrometer set to 60 °C. Please see the Supporting Information for the collected spectra (Figures S26–S31).

**ASSOCIATED CONTENT**

* Supporting Information

DOSY spectra for 1a–e and 2a–e, experimental procedures and analytical data (1H NMR spectra and reaction profiles) for all catalytic reactions, crystallographic data for 2c and 2d (PDF)

Accession Codes

CCDC 1898435–1898436 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

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