Electronic Supporting Information (ESI)

Synthesis of low oxidation state zinc(I) complexes and their catalytic studies in dehydroborylation of terminal alkynes†

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NMR spectra ($^1$H, $^{13}$C($^1$H), $^{11}$B NMR) of compound 2, precatalyst 3, and CBG zinc alkynyl complex 5 and stoichiometric experiments data.

Figure S1: $^1$H NMR spectrum of compound 2 (400 MHz, C$_6$D$_6$) {Reaction scale}.

Figure S2: $^{13}$C($^1$H) NMR spectrum of compound 2 (101 MHz, C$_6$D$_6$) {Reaction scale}.
Figure S3: $^1$H NMR spectrum of compound 2 and Cp*H (400 MHz, C$_6$D$_6$) {NMR scale}.

Figure S4: $^{13}$C{$^1$}H NMR spectrum of compound 2 and Cp*H (101 MHz, C$_6$D$_6$) {NMR scale}.
Figure S5: $^1$H NMR spectrum of compound 3 (400 MHz, C$_6$D$_6$) {Reaction scale}.

Figure S6: $^{13}$C($^1$H) NMR spectrum of compound 3 (101 MHz, C$_6$D$_6$) {Reaction scale}.
Figure S7: $^1$H NMR spectrum of Compound 3 and Cp*H (400 MHz, C$_6$D$_6$) {NMR scale}.

Figure S8: $^{13}$C($^1$H) NMR spectrum of Compound 3 and Cp*H (101 MHz, C$_6$D$_6$) {NMR scale}.
Figure S9. Annotated $^1$H NMR stack plot of the reaction between 2 equiv. of LH and Cp*$_2$Zn$_2$.

Figure S10: Zoom $^1$H NMR monitoring: Annotated $^1$H NMR stack plot of the reaction between 2 equiv. of LH and Cp*$_2$Zn$_2$. 
Figure S11: $^1$H NMR spectrum of compound 5 (400 MHz, C$_6$D$_6$).

Ar = 2,6-Et$_2$-C$_6$H$_3$

Figure S12: $^{13}$C{$^1$H} NMR spectrum of compound 5 (101 MHz, C$_6$D$_6$)

Ar = 2,6-Et$_2$-C$_6$H$_3$
Figure S13: $^1$H NMR spectrum of compound 5 and Cp*H (400 MHz, C$_6$D$_6$) [NMR scale].

Figure S14: $^{13}$C-$^1$H NMR spectrum of compound 5 and Cp*H (101 MHz, C$_6$D$_6$) [NMR scale].
Figure S15: $^1$H NMR (400 MHz, 25 °C, C$_6$D$_6$) spectrum of [LZnH]$_2$ & 7c.

Figure S16: $^{13}$C[$^1$H] NMR (101 MHz, 25 °C, C$_6$D$_6$) spectrum of [LZnH]$_2$ & 7c.
**Figure S17:** $^{11}$B NMR (128 MHz, 25 °C, C$_6$D$_6$) spectrum of [LZnH]$_2$ & 7c. A doublet peak at $\delta$ 29.17 – 27.81 ppm arises from free HBpin, and a peak at $\delta$ 21.85 ppm arises from B(OR)$_3$. A singlet peak was observed at $\delta$ 24.54 ppm due to compound 7c.

**Figure S18:** $^1$H NMR (400 MHz, 25 °C, C$_6$D$_6$) spectrum of compounds 5 & 7c.
**Figure S19**: $^{13}$C{$^{1}$H} NMR (101 MHz, 25 °C, C$_6$D$_6$) spectrum of compounds 5 & 7c.

**Figure S20**: $^{11}$B NMR (128 MHz, 25 °C, C$_6$D$_6$) spectrum of 5 & 7c. A doublet peak at δ 29.15 – 27.79 ppm arises from free HBpin, and a peak at δ 21.76 ppm arises from B(OR)$_3$. A singlet peak was observed at δ 24.77 ppm due to compound 7c.
$^1$H, $^{13}$C($^1$H) and $^{11}$B NMR Spectra of Dehydrogenative Borylation of Alkynes

Figure S21: $^1$H NMR spectrum of 7a without catalyst (400 MHz, CDCl$_3$).

Figure S22: $^{13}$C($^1$H) NMR spectrum of 7a without catalyst (101 MHz, CDCl$_3$).
**Figure S23:** $^{11}$B NMR spectrum of 7a without catalyst (128 MHz, CDCl$_3$).

**Figure S24:** $^1$H NMR spectrum of 7a catalyzed by Cp*H (400 MHz, CDCl$_3$).
**Figure S25**: $^{13}$C{$_1^1$H} NMR spectrum of 7a catalyzed by Cp*H (101 MHz, CDCl$_3$).

**Figure S26**: $^{11}$B NMR spectrum of 7a catalyzed by Cp*H (128 MHz, CDCl$_3$).
Figure S27: $^1$H NMR spectrum of 7a precatalyzed by Cp*ZnZnCp* (1) (400 MHz, CDCl$_3$).

Figure S28: $^{13}$C{$^1$H} NMR spectrum of 7a precatalyzed by Cp*ZnZnCp* (1) (101 MHz, CDCl$_3$).
Figure S29: $^{11}$B NMR spectrum of 7a precatalyzed by $\text{Cp}^*\text{ZnZnCp}^*$ (1) (128 MHz, CDCl$_3$).

Figure S30: $^1$H NMR spectrum of 7a precatalyzed by $\text{Cp}^*\text{ZnZnL}$ (2) (400 MHz, CDCl$_3$).
Figure S31: $^{13}$C($^1$H) NMR spectrum of 7a precatalyzed by Cp*ZnZnL (2) (101 MHz, CDCl$_3$).

Figure S32: $^{11}$B NMR spectrum of 7a precatalyzed by Cp*ZnZnL (2) (128 MHz, CDCl$_3$).
Figure S33: $^1$H NMR spectrum of 7a precatalyzed by LZnZnL (3) (400 MHz, CDCl$_3$).

Figure S34: $^{13}$C($^1$H) NMR spectrum of 7a precatalyzed by LZnZnL (3) (101 MHz, CDCl$_3$).
Figure S35: $^{11}$B NMR spectrum of 7a precatalyzed by $\text{LZnZnL}$ (3) (128 MHz, CDCl$_3$).

Figure S36: $^1$H NMR spectrum of 7b (400 MHz, CDCl$_3$).
Figure S37: $^{13}$C\{$^1$H\} NMR spectrum of 7b (101 MHz, CDCl$_3$).

Figure S38: $^1$H NMR spectrum of 7c (400 MHz, CDCl$_3$).
Figure S39: $^{13}$C{^1}H NMR spectrum of 7c (101 MHz, CDCl$_3$).

Figure S40: $^1$H NMR spectrum of 7d (400 MHz, CDCl$_3$).
Figure S41: $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 7d (101 MHz, CDCl$_3$).

Figure S42: \textsuperscript{1}H NMR spectrum of 7e (400 MHz, CDCl$_3$).
Figure S43: $^{13}$C{${}^1$H} NMR spectrum of 7e (101 MHz, CDCl$_3$).

Figure S44: $^1$H NMR spectrum of 7f (400 MHz, CDCl$_3$).
Figure S45: $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 7f (101 MHz, CDCl\textsubscript{3}).

Figure S46: \textsuperscript{1}H NMR spectrum of 7g (400 MHz, CDCl\textsubscript{3}).
**Figure S47:** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 7g (101 MHz, CDCl$_3$).

**Figure S48:** $^1\text{H}$ NMR spectrum of 7h (400 MHz, CDCl$_3$).
Figure S49: $^{13}$C{$^1$H} NMR spectrum of 7h (101 MHz, CDCl$_3$).

Figure S50: $^1$H NMR spectrum of 7i (400 MHz, CDCl$_3$). * = mesitylene is used as an internal standard.
Figure S51: $^1$H NMR spectrum of 7j (400 MHz, CDCl$_3$). * = mesitylene is used as an internal standard.

Figure S52: $^1$H NMR spectrum of 7k (400 MHz, CDCl$_3$).
Figure S53: $^{13}$C-$^1$H NMR spectrum of 7k (101 MHz, CDCl$_3$).

Figure S54: $^1$H NMR spectrum of 7l (400 MHz, CDCl$_3$).
**Figure S55:** $^{13}$C{H} NMR spectrum of $7l$ (101 MHz, CDCl$_3$).

**Figure S56:** $^1$H NMR spectrum of $7m$ (400 MHz, CDCl$_3$).
Figure S57: $^{13}$C{^1H} NMR spectrum of 7m (101 MHz, CDCl$_3$).

Figure S58: $^1$H NMR spectrum of 7n (400 MHz, CDCl$_3$).
**Figure S59:** $^{13}$C-$^1$H NMR spectrum of 7n (101 MHz, CDCl$_3$).

**Figure S60:** $^1$H NMR spectrum of 7o (400 MHz, CDCl$_3$).
Figure S61: $^{13}\text{C}(^{1}\text{H})$ NMR spectrum of 7o (101 MHz, CDCl$_3$).

Figure S62: $^1\text{H}$ NMR spectrum of 7p (400 MHz, CDCl$_3$).
**Figure S63**: $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 7p (101 MHz, CDCl\textsubscript{3}).

**Figure S64**: \textsuperscript{1}H NMR spectrum of 7q (400 MHz, CDCl\textsubscript{3}). * = mesitylene is used as an internal standard.
Figure S65: $^{13}$C{$^1$H} NMR spectrum of 7q (101 MHz, CDCl$_3$). * = mesitylene is used as an internal standard.

Figure S66: $^1$H NMR spectrum of 7r (400 MHz, CDCl$_3$).
Figure S67: $^{13}$C{$^1$H} NMR spectrum of 7r (101 MHz, CDCl$_3$).

X-ray Crystallographic Data of compounds 3 and 5

The single crystals of compounds 3 and 5 were crystallized from benzene and toluene as colorless blocks. The crystal data of compounds 3 and 5 were collected on a Rigaku Oxford diffractometer at 100 K. Selected data collection parameters and other crystallographic results are summarized in Table S2. The structure was determined using direct methods employed in ShelXT,$^1$ OleX,$^2$ and refinement was carried out using least-square minimization implemented in ShelXL.$^3$ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were fixed geometrically in idealized positions and were refined using a riding model.
Figure S68. Molecular structures of 3. The thermal ellipsoids are shown at 50% probability, and all the hydrogen atoms (except for H(4), H(5)) and ethyl groups have been removed for clarity. Selected bond lengths (Å) and angles (deg), For 3: Zn1-Zn1’ 2.4072(3), Zn1-N1 2.0021(12), Zn1-N2 2.0035(13); N1-Zn1-N2 91.08(5), N1-Zn1- Zn1’ 134.92(4), N2-Zn1- Zn1’ 134.00(4).
Figure S69. Molecular structures of 5. The thermal ellipsoids are shown at 50% probability, and all the hydrogen atoms (except for H(4), H(5)) and ethyl groups have been removed for clarity. Selected bond lengths (Å) and angles (deg), For 5: Zn1-Zn1’ 3.0400(4), Zn1-N1 1.9709(13), Zn1-N2 1.9663(13), Zn1-C1 2.0181(15), Zn1-C1’ 2.3360(16), C1-C2 1.187(2); N1-Zn1-N2 94.76(5), N1-Zn1-C1 119.73(6), N2-Zn1-C1 122.42(6), C1-Zn1-C1’ 91.75(6), Zn1-C1-Zn1’ 88.25(6).
**Table S1.** Crystallographic Data and Refinement Parameters for Compounds 3 and 5.

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<th>Compound</th>
<th>3</th>
<th>5</th>
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<td>Empirical Formula</td>
<td>C₈₄H₁ₐ₈N₁₀Zn₂</td>
<td>C₁₀₂H₁₂₂N₁₀Zn₂</td>
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<tr>
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<td>0.71073</td>
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<td>0.2×0.18×0.17</td>
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<td>γ (deg)°</td>
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<td>F(000)</td>
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<td>864.0</td>
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<td>-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18</td>
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<tr>
<td>Independent reflections</td>
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<td>8979 [R_int = 0.0343, R_sigma = 0.0246]</td>
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<td>Completeness to theta</td>
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<td>99 %</td>
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<tr>
<td>Data / restraints /parameters</td>
<td>7460 / 0 / 441</td>
<td>8979 / 0 / 517</td>
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<td>Goodness – of–fit on F²</td>
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<tr>
<td>Final R indices [I&gt;2 sigma(I)]</td>
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<td>R₁ = 0.0348, wR₂ = 0.0936</td>
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References:

