**Supporting information**

**Chelate-Enforced Phosphine Coordination Enables $\alpha$-Abstraction to Give Zirconium Alkylidenes**

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$^{31}$P NMR analysis of the reaction of 3 with (Me)$_2$Mg in ether. 22 mg (0.035 mmol) of 3 and 3.8 mg (0.070 mmol) of (Me)$_2$Mg, 18 $\mu$L dioxane, 0.6 mL of ether were sealed in a J. Young NMR tube under argon. The reaction progress was monitored by $^{31}$P NMR. After 15 min, compound 4a was formed in 75% yield. After 4 h, compound 4a was formed in >86% yield.

$^{31}$P NMR analysis of the reaction of 3 with various amounts of (PhCH$_2$)$_2$Mg·2THF in toluene. Compound 3 (18 mg, 0.029 mmol), various amounts of (PhCH$_2$)$_2$Mg·2THF (5 mg, 0.014 mmol; 10 mg, 0.029 mmol; 15 mg, 0.043 mmol; 20 mg, 0.057 mmol; 25 mg, 0.071 mmol), 15 $\mu$L dioxane, and 0.6 mL of toluene were sealed under argon in 5 J. Young NMR tubes respectively. The reaction progress was monitored by $^{31}$P NMR. The results are the following:

1) If only 0.5 eq (PhCH$_2$)$_2$Mg·2THF was used, production of 5b was not observed even after 36 h. 2) If 1 eq (PhCH$_2$)$_2$Mg·2THF was used, NMR analysis indicates the
presence of 5b (30%) in addition to (PNP)MgCl and other unidentified compounds in the final mixture. 3) If ≥ 1.5eq of (PhCH₂)₂Mg·2THF was used, the reaction shows little or no dependence on the amount of (PhCH₂)₂Mg·2THF used. The ³¹P NMR analysis showed that 4b formed in 10 minutes (> 85%). 4b completely converted into 5b after 16 h. (PNP)MgCl (ca. 10%) was also observed.

**Control experiments in different solvents.** Three J. Young tubes were each charged with 3 (19.3 mg, 0.031 mmol), Mg(CH₂Ph)₂·2THF (15.5 mg, 0.046 mol) and 16 µL of dioxane and marked as A, B and C respectively. 1 mL of toluene was added to tube A, 1 mL of ether was added to tube B, and 1 mL of C₆D₆ was added to tube C. The ³¹P NMR analysis showed that the reaction proceeded with approximately the same rate in A, B, and C. After 24 h, all volatiles in the tube C were vacuum transferred. The transferred volatile material contained only toluene, dioxane and THF in C₆D₆ as identified by ¹H NMR.

**Reaction of 5c with d₆-acetone.** A reaction flask was charged with 5c (20 mg, 0.027 mmol) and d₆-acetone (0.70 mL, 8.6 mmol). The mixture was stirred for 2 minutes. The volatiles were vacuum transferred. The volatiles contain RCH₂D and RCH=C(CD₃)₂ (R = p-MePh) (by ¹H NMR). ¹H NMR for RCH₂D (d₆-acetone): δ 7.05 (s, 4H, Ar-H), 2.26 (s, 3H, Me), 2.24 (t, 2H, 2Jᴴᴰ = 2 Hz, CH₂D). ¹H NMR for RCH=C(CD₃)₂ (d₆-acetone): δ 7.12 (s, 4H, Ar-H), 6.23 (s, 1H, RCH=C(CD₃)₂), 2.29(s, 3H, Me).

**Reaction of 5c with acetone.** A reaction flask was charged with 5c (20 mg, 0.027 mmol) and acetone (0.70 mL, 8.6 mmol). The mixture was stirred for 2 minutes. The volatiles were vacuum transferred and then the lower boiling components were removed in vacuo with care. The residue mainly contains RCH=CMe₂ and CH₃COCH₂C(OH)Me₂.
$^1$H NMR for RCH=C(CMe$_3$)$_2$ (CDCl$_3$): δ 7.10 (s, 4H, Ar-H), 6.21 (s, 1H, RCH
RCH=C(CMe$_3$)$_2$), 2.31 (s, 3H, p-MePh ), 1.87 (s, 3H, Me), 1.83 (s, 3H, Me) . $^1$H NMR for CH$_3$COCH$_2$C(OH)Me$_2$ (CDCl$_3$): 3.74 (s, 1H, OH), 2.61 (s, 2H, CH$_2$), 2.16 (s, 3H, CH$_3$CO), 1.23 (s, 6H, C(OH)Me$_2$).

**GC/MS experiments.** General procedure: (CX$_3$)$_2$C=O (X = H, or D) (4 µL, 0.046 mmol) was added to 6.8 mg 5b or 5c (ca. 0.009 mmol) dissolved in 2 mL of ether. The red-brown color of 5b or 5c changed to light yellow instantly. The solution was passed through a pad of silica gel and then 1 µL 4-chlorotoluene was added as an internal standard. The amount of olefin formed was calculated from ratio percent from the GC/MS data (0.0076 mmol, 81% yield for 5b; 0.0073 mmol, 80% yield for 5c). Trace of acetone condensation products CX$_3$COCX$_2$(OX)(CX$_3$)$_2$ and CX$_3$COCX=C(CX$_3$)$_2$ were observed in both the cases. Complete products derived from 5b-c are listed below (ratio of (CX$_3$)$_2$C=CHR, X = H, D; R = Ph, C$_6$H$_4$CH$_3$ was taken to be 100%).

**5b with (CD$_3$)$_2$C=O:** compound (%): (CD$_3$)$_2$C(OH)CH$_2$Ph (7%), (CD$_3$)$_2$C=CHPh (100%), PhCH$_2$D (84%). (CD$_3$)$_2$C=CHPh GC-MS (EI) m/z (%) 138 (M$^+$, 80), 120 (M$^+$ - CD$_3$, 100). PhCH$_2$D GC-MS (EI) m/z (%) 93 (M$^+$, 48), 92 (M$^+$ -1, 100), 91 (M$^+$ -2, 67). (CD$_3$)$_2$C(OD)CH$_2$Ph GC-MS (EI) m/z (%) 138 (M$^+$-CD$_3$, 20), 92 (100), 65 (M$^+$-CH$_2$Ph, 50). **5b with (CH$_3$)$_2$C=O:** compound (%): (CH$_3$)$_2$C(OH)CH$_2$Ph (7%), (CH$_3$)$_2$C=CHPh (100%), PhCH$_2$H (90%).(CH$_3$)$_2$C=CHPh GC-MS (EI) m/z (%) 132 (M$^+$, 80), 117 (M$^+$ - 15, 100), 115 (42), 91 (1). PhCH$_3$ GC-MS (EI) m/z (%) 92 (M$^+$, 65), 91 (M$^+$ -H, 100). (CH$_3$)$_2$C(OH)CH$_2$Ph GC-MS (EI) m/z (%) 135 (M$^+$-CH$_3$, 10), 132 (M$^+$-18, 4), 92 (100), 91 (60), 59 (M$^+$-CH$_2$Ph, 64). **5c with (CD$_3$)$_2$C=O:** compound (%): (CD$_3$)$_2$C(OD)CH$_2$C$_6$H$_4$CH$_3$ (9%), (CD$_3$)$_2$C=C(H)C$_6$H$_4$CH$_3$ (100%), CH$_3$C$_6$H$_4$CH$_2$D
(74%). \((\text{CD}_3)_2\text{C}=\text{C(H)C}_6\text{H}_4\text{CH}_3\) GC-MS (EI) \(m/z\) (%): 152 (M\(^+\), 100), 137 (M\(^+\) - CH\(_3\), 50), 134 (M\(^+\) - CD\(_3\), 79). \(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{D}\) GC-MS (EI) \(m/z\) (%): 107 (M\(^+\), 40), 106 (M\(^+\) - 1, 52), 105 (M\(^+\) - 2, 23), 92 (M\(^+\) -CH\(_3\), 41), 91 (M\(^+\) -CH\(_2\)D, 100). \((\text{CD}_3)_2\text{C(OD)CH}_2\text{C}_6\text{H}_4\text{CH}_3\) GC-MS (EI) \(m/z\) (%): 152 (M\(^+\)-18, 11), 106 (100), 91 (50), 65 (M\(^+\)-105, 50).

**5c with (CH\(_3\))\(_2\)C=O:** compound (%): \((\text{CH}_3)_2\text{C(OH)CH}_2\text{C}_6\text{H}_4\text{CH}_3\) (8%), \((\text{CH}_3)_2\text{C}=\text{C(H)C}_6\text{H}_4\text{CH}_3\) (100%), \(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3\) (87%). \((\text{CH}_3)_2\text{C}=\text{C(H)C}_6\text{H}_4\text{CH}_3\) GC-MS (EI) \(m/z\) (%): 146 (M\(^+\), 73), 131 (M\(^+\) - 15, 100), 115 (23), 91 (25).\(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3\) GC-MS (EI) \(m/z\) (%): 106 (M\(^+\), 52), 91 (M\(^+\) -15, 100). \((\text{CH}_3)_2\text{C(OH)CH}_2\text{C}_6\text{H}_4\text{CH}_3\) GC-MS (EI) \(m/z\) (%): 149 (M\(^+\)-CH\(_3\), 11), 146 (M\(^+\)-18, 5), 106 (100), 91 (50), 59 (M\(^+\)-CH\(_2\)C\(_6\)H\(_4\)CH\(_3\), 50).

*(PNP)MgCl\(_\cdot\)1.5THF* (PNP)H (1) (20 mg, 0.046 mmol) was dissolved in 10 mL of THF. MeMgCl (15 \(\mu\)L, 0.046 mmol, 3.10 M in THF) was slowly added via syringe. The reaction mixture was stirred for 1 h and then all volatiles were removed under vacuum to afford the crude product (ca. 92% purity). \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 7.42 (dd, 2H, \(J = 6 \text{ Hz,} \ 3J_{HH} = 8 \text{ Hz, Ar-}H\)), 6.95 (d, 2H, \(J = 4 \text{ Hz, Ar-}H\)), 6.92 (d, 2H, \(3J_{HH} = 8 \text{ Hz, Ar-}H\)), 3.63 (br, s, 6H, OCH\(_2\)CH\(_2\)), 2.21 (s, 6H, Ar-Me), 2.00 (m, 4H, CHMe\(_2\)), 1.30-1.15 (m, 18H, O-CH\(_2\)CH\(_2\) and CHMe\(_2\) overlapped), 1.07 (dd, 12H, \(3J_{PH} = 13 \text{ Hz,} \ 3J_{HH} = 6 \text{ Hz, CHMe}_2\)). \(^{31}\)P\(^{1}\)H NMR (C\(_6\)D\(_6\)): \(\delta -18.6 \text{ (s).}\)

**NMR reaction of 3 with 4-methylbenzyl magnesium chloride.** One J. Young tube was charged with 4-methylbenzyl magnesium chloride (191 \(\mu\)L, 0.096 mmol, 0.5 M in THF). This tube was put under vacuum for 5 min then charged with 3 (20 mg, 0.032 mmol), 16 \(\mu\)L of dioxane, 1 mL C\(_6\)D\(_6\). After 1 h, \(^{31}\)P NMR analysis showed that ca. 60% of 4c was converted into 5c. After 12 h, \(^{31}\)P NMR indicated the presence of 5c (75%).
Then all volatiles in the NMR tube were vacuum transferred. The transferred volatile material contained $p$-xylene, dioxane and THF in C$_6$D$_6$ as identified by $^1$H NMR.

**Figure S-1.** ORTEP drawing (50% probability ellipsoids) of 4a showing only the immediate coordination environment of Zr.
Kinetic studies of conversion of 4b to 5b. General method for preparing NMR samples of 4b is as follows: To a flask charged with compound 3 (60 mg, 0.094 mmol) and Mg(CH$_2$Ph)$_2$·2THF (48 mg, 0.14 mmol) 5 ml ether was added. The mixture was stirred for 3 min and then all volatiles were removed under vacuum. The residue was extracted with 5 mL pentane twice, filtered, and then the pentane solution was pumped to dryness to afford yellow solid. The solid was dissolved in ~1.4 mL of C$_6$D$_6$ and then PCy$_3$ (12 mg, 0.042 mmol) was added as an internal integration standard. 0.4 mL of the final solution was added to each of 3 J-Young NMR tubes. These solutions were stored frozen in Dry Ice/acetone until retrieved to perform VT NMR kinetic studies. Each solution was monitored by $^{31}$P NMR during a period of time (two half-times for higher temperature runs or three hours for lower temperature runs) at each temperature. The decrease of the concentration of 4b over time was measured relative to the PCy$_3$ standard. Standard deviations for the determination of rate constants were obtained from the linear regression analysis by Microsoft Excel. The activation parameters were calculated using the Eyring equation. The graphs of ln([4b]/[PCy$_3$]) vs time for each temperature, and the Eyring plot are given below. Standard deviations for the activation parameters were calculated according to Girolami et al (Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. Organometallics, 1994, 13, 1646.). $\sigma k/k = 0.05$ was derived as double the average relative standard deviation in the determination of the individual rate constants. Temperature was measured before and after each run using the ethylene glycol chemical shift thermometer. The difference between the “before” and “after” temperatures was 0 to 1 K. The temperature value taken into calculations was $T = 2/3 \times T_{after} + 1/3 \times T_{before}$. The error in temperature determination was taken to be 1 K.
The rate constants at at 315.5 and 320.7 K were also measured by using H₃PO₄ as internal standard. The method is as the following: To a flask charged with compound 3 (95 mg, 0.151 mmol) and Mg(CH₂Ph)₂ · 2THF (82 mg, 0.242 mmol) 5 ml ether was added. The mixture was stirred for 3 min and then all volatiles were removed under vacuum. The residue was extracted with 10 mL pentane twice, filtered, and then the pentane solution was pumped to dryness to afford yellow solid. The solid was dissolved in ~1.0 mL of C₆D₆ and then ~0.4 mL solution was transferred to each of 2 J-Young NMR tubes. Instead of using PCy₃, a sealed capillary containing 85% H₃PO₄ was immersed into the NMR solvent and used as an internal integration standard. The differences between rates obtained with H₃PO₄ and PCy₃ standards were not statistically significant. This indicates that PCy₃ does not affect the rate.

The following values of rate constant for the rate law \( \text{d([4b])} = -k \times [4b] \times \text{dt} \) were found:

**Table S-1.** Rate constants at different temperatures.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>T, K</th>
<th>K*10⁵, s⁻¹</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.95</td>
<td>326.1</td>
<td>167(8)</td>
<td>PCy₃</td>
</tr>
<tr>
<td>47.15</td>
<td>320.3</td>
<td>81(4)</td>
<td>PCy₃</td>
</tr>
<tr>
<td>43.15</td>
<td>316.3</td>
<td>54(3)</td>
<td>PCy₃</td>
</tr>
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<td>39.35</td>
<td>312.5</td>
<td>34(2)</td>
<td>PCy₃</td>
</tr>
<tr>
<td>31.85</td>
<td>305</td>
<td>16.1(8)</td>
<td>PCy₃</td>
</tr>
<tr>
<td>24.55</td>
<td>297.7</td>
<td>7.6(4)</td>
<td>PCy₃</td>
</tr>
<tr>
<td>20.65</td>
<td>293.8</td>
<td>6.2(3)</td>
<td>PCy₃</td>
</tr>
<tr>
<td>47.55</td>
<td>320.7</td>
<td>92(5)</td>
<td>H₃PO₄</td>
</tr>
<tr>
<td>42.35</td>
<td>315.5</td>
<td>54(3)</td>
<td>H₃PO₄</td>
</tr>
</tbody>
</table>
T = 293.8 K

Eyring plot

\[ \ln \left( \frac{[4b]}{[PCy3]} \right) \text{ vs. Time (sec)} \]

\[ \ln(k/T) \text{ vs. } \frac{1}{T} (K^{-1}) \]