Supporting Information for:

**Early Transition Metal α-Diazoalkane Complexes: Synthesis and Reactivity**

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Typical procedure for the preparation of Complexes 13 and 14: To a solution of 4a (0.200 g, 0.299 mmol) [(0.170 g, 0.254 mmol) for 14] in tetrahydrofuran (5 mL) phenyl isocyanate 9 (0.032 mL, 0.299 mmol) [1-naphthyl isocyanate 10 (0.036 mL, 0.254 mmol) for 14] was added at room temperature. The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was washed with pentane (2 x 5 mL) and dried in vacuo to give 13 as an orange solid in 76% yield (0.179 g). IR (KBr): 1581 cm\(^{-1}\) \(\nu\) (C=N), 1705 cm\(^{-1}\) \(\nu\) (C=O), 3345 cm\(^{-1}\) \(\nu\) (N-H). \(^{31}\)P\(^{1}\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta = 57.0\) (s) ppm. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta = 1.11\) (d, 12H, \(J_{HH} = 5.6\) Hz, CH\(_3\)), 1.29 (d, 12H, \(J_{HH} = 6.6\) Hz, CH\(_3\)), 1.35 (t, 3H, \(J_{HH} = 6.9\) Hz, OCH\(_2\)CH\(_3\)), 3.66 (m, 4H, NCH), 4.28 (q, 2H, \(J_{HH} = 6.9\) Hz, CH\(_2\)), 5.63 (s, 10H, CH\(_{Cp}\)), 6.93-7.68 (m, 8H, CH\(_{arom}\)), 8.08 (m, 1H, CH\(_{arom}\)), 9.59 (d, 1H, \(J_{HP} = 4.3\) Hz, NH) ppm. \(^{13}\)C\(^{1}\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta = 14.7\) (s, OCH\(_2\)CH\(_3\)), 24.1 (br, CH\(_3\)), 49.1 (d, \(J_{CP} = 7.2\) Hz, NCH), 59.5 (s, CH\(_2\)), 111.1 (s, CH\(_{Cp}\)), 119.3 (s, =CCO\(_2\)Et), 122.3, 127.2, 128.9, 129.6, 129.7 and 140.5 (s, CH\(_{arom}\)), 129.5 (d, \(J_{CP} = 11.0\) Hz, CH\(_{arom}\)), 137.2 (s, Carom), 146.3 (d, \(J_{CP} = 26.3\) Hz, ZrCC), 161.7 and 162.6
(s, C=O and O-C=), 196.7 (d, J_{CP} = 6.2 Hz, ZrC), 201.3 (d, J_{CP} = 38.5 Hz, PC=N) ppm. Anal. calcd. for C_{40}H_{53}N_{6}O_{3}PZr (788.08): C, 60.96; H, 6.77; N, 10.66. Found: C, 60.92; H, 6.76; N, 10.70.

14, yellow solid, 74% yield (0.157 g). IR (KBr): 1566 cm\(^{-1}\) ν(C=N), 1720 cm\(^{-1}\) ν(C=O), 3335 cm\(^{-1}\) ν(N-H). \(^{31}\)P\{\(^{1}\)H\} NMR (C\(_6\)D\(_6\)): δ = 54.6 (s) ppm. \(^{1}\)H NMR (C\(_6\)D\(_6\)): δ = 1.12-1.27 (m, 27H, CH\(_3\) and OCH\(_2\)CH\(_3\)), 3.57 (m, 4H, NCH), 4.25 (q, 2H, J\(_{HH}\) = 7.1 Hz, CH\(_2\)), 5.37 (s, 10H, CH\(_{CP}\)), 7.00-7.74 (m, 10H, CH\(_{arom}\)), 8.31 (m, 1H, CH\(_{arom}\)), 9.73 (d, 1H, J\(_{HP}\) = 4.9 Hz, NH) ppm. \(^{13}\)C\{\(^{1}\)H\} NMR (C\(_6\)D\(_6\)): δ = 15.3 (s, OCH\(_2\)CH\(_3\)), 24.4 (d, J_{CP} = 5.8 Hz, CH\(_3\)), 24.7 (d, J_{CP} = 5.7 Hz, CH\(_3\)), 49.6 (d, J_{CP} = 10.9 Hz, NCH), 59.8 (s, CH\(_2\)), 111.4 (s, CH\(_{CP}\)), 119.9 (s, =CCO\(_2\)Et), 122.9, 124.4, 126.2, 126.7, 127.5, 127.7, 128.9, 129.4, 130.6 and 141.3 (s, CH\(_{arom}\)), 130.1 (d, J_{CP} = 17.1 Hz, CH\(_{arom}\)), 131.6, 134.9 and 135.1 (s, C\(_{arom}\)), 147.0 (d, J_{CP} = 27.7 Hz, ZrCC), 163.7 and 164.3 (s, C=O and O-C=), 197.9 (d, J_{CP} = 6.3 Hz, ZrC), 201.4 (d, J_{CP} = 39.1 Hz, PC=N) ppm. Anal. calcd. for C_{44}H_{55}N_{6}O_{3}PZr (838.15): C, 63.05; H, 6.61; N, 10.02. Found: C, 63.04; H, 6.65; N, 10.10.

**Typical procedure for the reactivity of Complexes 4a and 5a**

**with chlorophosphines R\(_2\)PCl, 19, 20:** To a solution of 5a (0.208 g, 0.311 mmol) in toluene (5 mL) chlorophosphine 20 (0.056 mL, 0.311 mmol) was added at room temperature. The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give 21 and 23 as the
unique products of the reaction according to $^{31}$P NMR. $^{23}$ was identified in the reaction mixture by comparison with an authentical sample.\textsuperscript{[22]} Independently, addition of HCl on 4a allowed to prepare and to isolate 21 as a yellow solid. IR (KBr): 1576 cm$^{-1} \nu$(C=N), 3305 cm$^{-1} \nu$(N-H). $^{31}$P{$^{1}$H} NMR (C$_6$D$_6$): $\delta$ = 58.2 (s) ppm. $^{1}$H NMR (C$_6$D$_6$): $\delta$ = 1.11 (d, 12H, $J_{HH}$ = 6.6 Hz, CH$_3$), 1.21 (d, 12H, $J_{HH}$ = 6.6 Hz, CH$_3$), 3.27 (d sept, 4H, $J_{HH}$ = 6.6 Hz, $J_{HP}$ = 12.1 Hz, NCH), 5.90 (s, 10H, CH$_{Cp}$), 7.20 (m, 2H, CH$_{arom}$), 7.88 (m, 4H, CH$_{arom}$), 8.25 (m, 1H, CH$_{arom}$), 10.12 (d, 1H, $J_{HP}$ = 5.0 Hz, NH) ppm. $^{13}$C{$^{1}$H} NMR (C$_6$D$_6$): $\delta$ = 24.4 (d, $J_{CP}$ = 6.8 Hz, CH$_3$), 25.1 (d, $J_{CP}$ = 5.0 Hz, CH$_3$), 49.6 (d, $J_{CP}$ = 11.2 Hz, NCH), 111.3 (s, CH$_{Cp}$), 122.8, 129.8 and 141.2 (s, CH$_{arom}$), 130.1 (d, $J_{CP}$ = 14.3 Hz, CH$_{arom}$), 146.1 (d, $J_{CP}$ = 24.1 Hz, ZrCC), 198.6 (d, $J_{CP}$ = 6.3 Hz, ZrC), 202.5 (d, $J_{CP}$ = 40.6 Hz, PC=N) ppm.