Supporting Information

Reaction of Pentafulvene Titanium and Zirconium Complexes with Phosphorus Ylides: Stoichiometric Reactions and Catalytic Intramolecular Proton Shuttles

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General Considerations

All reactions were carried out under an inert atmosphere of argon or nitrogen with rigorous exclusion of oxygen and moisture using standard gloveboxes or Schlenk techniques. The glass equipment was stored in an oven at 120 °C and evacuated prior to use. Solvents were dried according to standard procedures over Na/K alloy with benzophenone as indicator and distilled under a nitrogen atmosphere. NMR spectra were recorded on Bruker Avance 300, Bruker Avance 500, and Bruker Avance III 500 spectrometers. 1H-NMR spectra were referenced to the residual solvent resonance as internal standard (benzene-d6 (C6D6), δ(1H) C6D6H 7.16 ppm) and 13C-NMR spectra by using the central line of the solvent signal (benzene-d6 (C6D6), δ(13C{1H}) C6D6 128.06 ppm). 31P{1H} NMR spectra were referenced against an external standard (δ(31P{1H} H3PO4 0.0 ppm). Given chemical shifts of 15N resulted from 1H,15N-HMBC or -HMQC NMR experiments with nitromethane as external standard (δ = 378.9 vs NH3). Infrared spectra were performed on a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system. Elemental analyses were carried out on a EuroEA 3000 Elemental Analyzer. The carbon value in the elemental analysis is often lowered by carbide formation. The hydrogen value is found in some cases to be higher due to residual traces of solvents. Although in some cases satisfactory elemental analysis could not be obtained, the data is included to demonstrate the best results to date. The combustion analysis of group 4 organometallics is known to be difficult.[1,2] Melting points were determined using a “Mel-Temp” apparatus by Laboratory Devices, Cambridge, U.K.

Synthesis and characterization of compounds:

The bis(η5:η1-pentafulvene)titanium complexes Ti1a/b as well as the mono(η5:η1-pentafulvene)metal complexes Ti3, Zr1a/b-benzo and Zr1b/b-benzo were synthesized according to literature procedures.[3-6] The ylides Y1-Y5 were prepared using the corresponding phosphonium salts according to standard procedures.[7-9] The phosphonium salts are either commercially available or can be prepared by a Grignard reaction of an aryl- or alkyl halide and subsequent methylation using methyl iodide.[8]
Synthesis of Ti2a:

Ti1a (0.500 g, 1.13 mmol) and Y1 (0.311 g, 1.13 mmol) were placed in a Schlenk tube and 10 ml of n-hexane was added. The former blue suspensions turns red and was stirred at room temperature overnight. The mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo afforded 0.711 g (0.99 mmol, 88%) of Ti2a as red-brown solid, m.p. 140 °C.

$^{1}$H-NMR (500 MHz, C$_6$D$_6$, 305 K): $\delta$ = 1.49–2.89 (Ad), 3.11 (s, 1 H, CH$_{exo}$), 4.27 (m, 1 H, C$_5$H$_4$), 5.10 (m, 1 H, C$_5$H$_4$), 5.14 (m, 1 H, C$_5$H$_4$), 5.23 (m, 1 H, C$_5$H$_4$), 5.31 (m, 1 H, C$_5$H$_4$), 5.98 (m, 1 H, C$_5$H$_4$), 6.03 (m, 1 H, C$_5$H$_4$), 6.43 (d, $^2J_{PH} = 12.4$ Hz, 1 H, CH$_{ylide}$), 6.44 (m, 1 H, C$_5$H$_4$), 7.07–7.09 (m, 9 H, PPh$_3$), 7.60–7.64 (m, 6 H, PPh$_3$) ppm.

$^{13}$C-NMR (125 MHz, C$_6$D$_6$, 305 K): $\delta$ = 28.5 (Ad CH), 28.6 (Ad CH), 29.4 (Ad CH), 29.9 (Ad CH), 32.4 (Ad CH), 32.5 (2 x Ad CH$_2$), 33.4 (Ad CH), 36.1 (Ad CH), 37.5 (Ad CH$_2$), 38.5 (Ad CH$_2$), 39.1 (Ad CH$_2$), 39.2 (Ad CH$_2$), 39.3 (Ad CH), 39.4 (Ad CH$_2$), 39.4 (Ad CH$_2$), 44.1 (Ad CH$_2$), 45.1 (Ad CH$_2$), 45.2 (CH$_{exo}$), 100.4 (C$_5$H$_4$), 103.6 (C$_5$H$_4$), 107.5 (C$_5$H$_4$), 107.8 (C$_5$H$_4$), 107.9 (C$_5$H$_4$), 108.4 (C$_5$H$_4$), 110.4 (C$_5$H$_4$), 110.6 (C$_5$H$_4$), 114.0 (C$_{exo}$ Fv), 119.9 (d, $^1J_{PC} = 15.4$ Hz, CH$_{ylide}$), 122.9 (C$_{ipso}$ Fv), 123.9 (C$_{ipso}$ Cp), 128.2 (d, J = 10.7 Hz, PPh$_3$), 130.7 (d, J = 2.8 Hz, PPh$_3$), 133.4 (d, J = 8.9 Hz, PPh$_3$), 135.6 (d, $^1J_{PC} = 78$ Hz, PPh$_3$) ppm.

$^{31}$P-NMR (202 MHz, C$_6$D$_6$, 305 K): $\delta$ = 13.0 ($^1J_{PC} = 78$ Hz) ppm.

IR (ATR, 16 scans): $\tilde{\nu}$ = 3055, 2899, 2847, 2668, 1634, 1589, 1482, 1467, 1448, 1437, 1353, 1261, 1196, 1117, 1099, 1060, 1027, 998, 930, 874, 705, 775, 742, 720, 692, 627, 597, 580 cm$^{-1}$. 

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Synthesis of Ti2b:

Ti1a (0.250 g, 0.56 mmol) and Y2 (0.166 g, 0.56 mmol) were placed in a Schlenk tube and a small amount of n-hexane was added. The former blue suspensions turns red and was stirred at room temperature overnight. The mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo afforded 0.301 g (0.41 mmol, 72%) of Ti2a as red solid, m.p. 115 °C.

Single crystals suitable for x-ray diffraction were obtained from a saturated solution of Ti2b in n-hexane at 5 °C.

1H-NMR (500 MHz, C6D6, 305 K): δ = 1.07–2.61 (Ad + Cy), 3.12 (s, 1 H, CHexo), 4.36 (m, 1 H, C5H4), 5.21 (m, 1 H, C5H4), 5.32 (m, 1 H, C5H4), 5.43 (m, 1 H, C5H4), 5.66 (m, 1 H, CHylene), 6.08 (m, 1 H, C5H4), 6.38 (m, 1 H, C5H4), 6.45 (m, 1 H, C5H4) ppm.

13C-NMR (125 MHz, C6D6, 305 K): δ = 26.8 (CH2), 27.7 (CH2), 27.8 (CH2), 27.9 (CH2), 28.1 (CH2), 28.3 (CH2), 28.5 (CH), 28.7 (CH), 29.5 (CH), 30.0 (CH), 32.4 (CH2), 32.6 (CH), 33.9 (CH), 35.7 (CH), 36.1 (CH), 36.3 (CH), 37.6 (CH2), 38.6 (CH2), 39.2 (CH2), 39.4 (CH), 39.4 (CH2), 40.1 (CH2), 44.0 (CH2), 45.1 (CHexo), 45.1 (CH2), 98.7 (C5H4), 103.0 (C5H4), 106.7 (C5H4), 107.2 (C5H4), 107.8 (C5H4), 107.8 (C5H4), 108.2 (C5H4), 108.4 (C5H4), 111.4 (Cexo Fv), 121.6 (Cipso Fv or Cipso Cp), 121.7 (Cipso Fv or Cipso Cp), 127.0 (d, 10.0 Hz, CHylene) ppm.

31P-NMR (202 MHz, C6D6, 305 K): δ = 25.5 (1JPC = 46 Hz) ppm.

IR (ATR, 16 scans): ν = 2924, 2899, 2849, 1632, 1445, 1353, 1259 8w), 1174, 1128, 1098, 1060, 1045, 1000, 942, 886, 847, 829, 801, 785, 772, 745, 725, 687, 581, 562 cm⁻¹.
Synthesis of Ti2c:

Ti1a (0.250 g, 0.56 mmol) and Y3 (0.206 g, 0.56 mmol) were placed in a Schlenk tube and a small amount of n-hexane was added. The former blue suspensions turns ochre and was stirred at room temperature overnight. The mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo afforded 0.312 g (0.39 mmol, 68%) of Ti2c as ochre solid, m.p. 74 °C (dec.).

$^1$H-NMR (500 MHz, C$_6$D$_6$, 305 K): $\delta = 1.52$–2.45 (Ad), 3.17 (s, 1 H, CH$_{exo}$), 3.23 (s, 9 H, OC$_3$H$_3$), 4.33 (m, 1 H, C$_5$H$_4$), 5.18 (m, 1 H, C$_5$H$_4$), 5.20 (m, 1 H, C$_5$H$_4$), 5.36 (m, 1 H, C$_5$H$_4$), 5.38 (m, 1 H, C$_5$H$_4$), 6.07 (m, 1 H, C$_5$H$_4$), 6.18 (m, 1 H, C$_5$H$_4$), 6.50 (m, 1 H, C$_5$H$_4$), 6.77 (m, 1 H, C$_5$H$_4$), 6.77 (m, 6 H, Anisol$_3$P), 7.64 (m, 6 H, Anisol$_3$P) ppm.

$^{13}$C-NMR (125 MHz, C$_6$D$_6$, 305 K): $\delta = 28.5$ (Ad CH), 28.6 (Ad CH), 29.5 (Ad CH), 30.0 (Ad CH), 32.3 (Ad CH), 32.5 (2 x Ad CH$_2$), 33.4 (Ad CH), 36.1 (Ad CH), 37.5 (Ad CH$_2$), 38.5 (Ad CH$_2$), 39.1 (Ad CH$_2$), 39.2 (Ad CH$_2$), 39.4 (Ad CH$_2$), 39.5 (Ad CH$_2$), 39.6 (Ad CH), 44.2 (Ad CH$_2$), 45.1 (Ad CH$_2$), 45.1 (CH$_{exo}$), 54.8 (OCH$_3$), 100.1 (C$_5$H$_4$), 103.3 (C$_5$H$_4$), 107.1 (C$_5$H$_4$), 107.3 (C$_5$H$_4$), 107.4 (C$_5$H$_4$), 108.2 (C$_5$H$_4$), 110.0 (C$_5$H$_4$), 110.4 (C$_5$H$_4$), 113.1 (C$_{exo}$ Fv), 113.8 (d, $J = 11.6$ Hz, Anisol$_3$P), 122.9 (C$_{ipso}$ Fv), 123.4 (C$_{ipso}$ Cp), 126.6 (d, $^1J_{PC} = 18.2$ Hz, CH$_{ylide}$), 126.7 (d, $^1J_{PC} = 84$ Hz, Anisol$_3$P), 135.1 (d, $J = 10.3$ Hz, Anisol$_3$P), 161.9 (d, $J = 2.4$ Hz, Anisol$_3$P) ppm.

$^{31}$P-NMR (202 MHz, C$_6$D$_6$, 305 K): $\delta = 10.9$ ppm.

IR (ATR, 16 scans): $\tilde{\nu} = 2961, 2899, 2847, 1634, 1594, 1568, 1504, 1448, 1411, 1353, 1295, 1260, 1181, 1114, 1097, 1059, 1023, 932, 984, 875, 797, 721, 690, 675, 627, 579$ cm$^{-1}$. 
Synthesis of Ti2d:

Ti1a (0.250 g, 0.56 mmol) and Y4 (0.358 g, 1.12 mmol) were placed in a Schlenk tube and a small amount of n-hexane was added. The former blue suspensions turns ochre and was stirred at room temperature overnight. The reaction mixture was filtrated to remove excessive ylide, subsequent drying in vacuo afforded 0.366 g (0.48 mmol, 85%) of Ti2d as ochre solid, m.p. 96 °C.

\(^1\)H-NMR (500 MHz, C\(_6\)D\(_6\), 305 K): \(\delta = 1.53–2.46\) (28 H, Ad), 2.02 (s, 9 H, CH\(_3\)), 3.19 (s, 1 H, CH\(_{\text{exo}}\)), 4.30 (m, 1 H, C\(_5\)H\(_4\)), 5.14 (m, 1 H, C\(_5\)H\(_4\)), 5.18 (m, 1 H, C\(_5\)H\(_4\)), 5.35 (m, 1 H, C\(_5\)H\(_4\)), 5.37 (m, 1 H, C\(_5\)H\(_4\)), 6.05 (m, 1 H, C\(_5\)H\(_4\)), 6.08 (m, 1 H, C\(_5\)H\(_4\)), 6.48 (m, 1 H, C\(_5\)H\(_4\)), 6.67 (d, \(\text{J}_{\text{PH}} = 12.4\) Hz, 1 H, CH\(_{\text{ylide}}\)), 6.96–6.98 (m, 6 H, pTol\(_3\)P), 7.61–7.65 (m, 6 H, pTol\(_3\)P) ppm.

\(^{13}\)C-NMR (125 MHz, C\(_6\)D\(_6\), 305 K): \(\delta = 21.3\) (CH\(_3\)), 28.5 (Ad CH), 28.6 (Ad CH), 29.5 (Ad CH), 30.0 (Ad CH), 32.4 (Ad CH), 32.5 (2 x Ad CH\(_2\)), 33.5 (Ad CH), 36.1 (Ad CH), 37.5 (Ad CH\(_2\)), 38.5 (Ad CH\(_2\)), 39.1 (Ad CH\(_2\)), 39.2 (Ad CH\(_2\)), 39.4 (Ad CH\(_2\)), 39.4 (Ad CH), 39.5 (Ad CH\(_2\)), 44.2 (Ad CH\(_2\)), 45.1 (Ad CH\(_2\)), 45.1 (CH\(_{\text{exo}}\)), 100.1 (C\(_5\)H\(_4\)), 103.5 (C\(_5\)H\(_4\)), 107.4 (C\(_5\)H\(_4\)), 107.4 (C\(_5\)H\(_4\)), 107.5 (C\(_5\)H\(_4\)), 108.2 (C\(_5\)H\(_4\)), 110.3 (2 x C\(_5\)H\(_4\)), 113.4 (C\(_{\text{exo}}\) Fv), 122.9 (C\(_{\text{ipso}}\) Fv), 123.4 (d, \(\text{J}_{\text{PC}} = 16.4\) Hz, CH\(_{\text{ylide}}\), 123.7 (C\(_{\text{ipso}}\) Cp), 129.0 (d, J = 11.1 Hz, pTol\(_3\)P), 132.3 (d, \(\text{J}_{\text{PC}} = 80\) Hz, pTol\(_3\)P), 133.5 (d, J = 9.3 Hz, pTol\(_3\)P), 140.9 (d, J = 2.7 Hz, pTol\(_3\)P) ppm.

\(^{31}\)P-NMR (202 MHz, C\(_6\)D\(_6\), 305 K): \(\delta = 12.1\) ppm.

IR (ATR, 16 scans): \(\tilde{\nu} = 2960, 2899, 2846, 1600, 1500, 1448, 1399, 1353, 1311, 1260, 1212, 1195, 1096, 1059, 1033, 1019, 930, 883, 801, 753, 729, 710, 688, 676, 646, 628, 609, 579 cm\(^{-1}\).

EA: Anal. calcd. for C\(_{52}\)H\(_{59}\)PTi: C 81.87, H 7.80; found C 71.36, H 7.74.
Synthesis of Ti2e:

(NEt₂)₃PCH₃I (0.517 g, 1.33 mmol) and NaH (0.048 g, 1.99 mmol) were placed in a Schlenk tube, tetrahydrofuran (10 ml) was added and the resulting suspension was refluxed for 4 hours. After cooling to room temperature, the suspension was filtered into a Schlenk tube containing a solution of Ti1b (0.500 g, 0.89 mmol) in 2 ml of tetrahydrofuran. The former blue solution turns brown and was stirred overnight at room temperature. Evaporation of the solvent and drying in vacuo afforded Ti2e in quantitative yield as dark red-brown solid, m.p. 83 °C (dec.).

¹H-NMR (500 MHz, C₆D₆, 305 K): δ = 0.85–0.88 (m, 18 H, CH₃), 2.08 (s, 3 H, CH₃), 2.11 (s, 3 H, CH₃), 2.15 (s, 6 H, CH₃), 2.67–2.75 (m, 6 H, CH₂), 2.82–2.91 (m, 6 H, CH₂), 4.43 (m, 1 H, C₅H₄), 4.76 (m, 1 H, C₅H₄), 4.80 (m, 1 H, C₅H₄), 4.83 (m, 1 H, C₅H₄), 5.12 (s, 1 H, CHexo), 5.56 (m, 1 H, C₅H₄), 6.47 (m, 1 H, C₅H₄), 6.70 (m, 1 H, C₅H₄), 6.82–6.84 (m, 3 H, C₅H₄ + pTol CH), 6.92 (m, 1 H, CH₃(CH₃)), 6.94 (m, 6 H, pTol CH), 7.11 (d, J = 7.6 Hz, 2 H, pTol CH), 7.23 (d, J = 7.7 Hz, 2 H, pTol CH), 7.59 (d, J = 7.8 Hz, 2 H, pTol CH), 7.65 (d, J = 7.6 Hz, 2 H, pTol CH) ppm.

¹³C-NMR (125 MHz, C₆D₆, 305 K): δ = 14.2 (NCH₂CH₃), 14.3 (NCH₂CH₃), 21.0 (CH₃(CH₃)), 40.2 (NCH₂CH₃), 40.2 (NCH₂CH₃), 52.1 (CHexo), 105.1 (C₅H₄), 105.1 (C₅H₄), 106.2 (C₅H₄), 107.5 (C₅H₄), 107.5 (C₅H₄), 108.6 (Fv Cexo), 109.2 (C₅H₄), 110.0 (C₅H₄), 111.4 (C₅H₄), 113.4 (C₅H₄), 123.3 (pTol C), 123.3 (Cipso Cp), 127.1 (pTol CH), 127.5 (pTol CH), 128.6 (pTol CH), 129.0 (pTol CH), 129.0 (pTol CH), 129.2 (pTol CH), 129.5 (pTol CH), 132.4 (pTol C), 132.6 (pTol CH), 133.0 (pTol C), 135.3 (pTol C), 135.6 (pTol C), 142.7 (pTol C), 144.2 (pTol C), 145.2 (pTol C), 147.1 (pTol C), 151.0 (d, ¹³JC = 62.7 Hz, CH₃(CH₃)) ppm.

³¹P-NMR (202 MHz, C₆D₆, 305 K): δ = 56.6 ppm.

IR (ATR, 16 scans): ν = 2969, 2921, 2870, 1508, 1455, 1379, 1295, 1260, 1203, 1172, 1054, 1017, 946, 924, 864, 796, 762, 737, 688, 638, 569 cm⁻¹.
Synthesis of Ti4a and Ti4b.

Ti3 (0.500 g, 1.2 mmol) and Y1 (0.331 g, 1.2 mmol) were placed in a Schlenk tube and n-hexane (10 ml) was added. The former blue suspension turns red and was stirred at room temperature overnight. Subsequently, the mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo only afforded a mixture of two products being subject to a reversible thermodynamic equilibrium. In this, the two compounds Ti4a and Ti4b are present in the ratio of 1:1. Increasing the temperature (353 K), the equilibrium can be influenced in favor of compound Ti4b. Combined data for Ti4a and Ti4b were as follows.

1H-NMR (500 MHz, C6D6, 303 K): δ = 0.93 (s, 3 H, C5Me4), 1.29 (s, 3 H, C5Me4), 1.47–2.47 (Ad), 1.74 (s, 3 H, C5Me4), 2.04 (s, 15 H, C5Me5), 2.12 (s, 3 H, C5Me4), 2.13 (m, 1 H, CH2), 2.65 (d, 2J = 3.5 Hz, 1 H, CH2), 3.19 (s, 1 H, CHexo), 3.27 (s, 1 H, CHexo), 4.77 (m, 1 H, C5H4), 5.08 (m, 1 H, C5H4), 5.14 (m, 1 H, C5H4), 5.19 (m, 1 H, C5H4), 5.72 (m, 1 H, C5H4), 5.95 (m, 2 H, C5H4), 6.48 (m, 1 H, C5H4), 7.02–7.11 (m, 18 H, C6H5), 7.71–7.75 (m, 12 H, C6H5), 9.01 (d, 2JPH = 4.8 Hz, CH) ppm.

13C-NMR (125 MHz, C6D6, 303 K): δ = 10.9 (C5Me4), 11.8 (C5Me4), 13.5 (Cp*), 13.5 (C5Me4), 14.5 (C5Me4), 28.4 (Ad CH), 28.6 (Ad CH), 28.6 (Ad CH), 28.6 (Ad CH), 32.4 (Ad CH2), 32.5 (Ad CH2), 32.8 (Ad CH2), 32.9 (Ad CH2), 33.0 (Ad CH), 33.0 (Ad CH2), 33.1 (Ad CH), 33.2 (Ad CH2), 38.4 (Ad CH2), 38.7 (Ad CH2), 39.0 (Ad CH2), 39.1 (Ad CH2), 39.2 (Ad CH2), 39.3 (Ad CH2), 44.1 (CHexo), 45.9 (CHexo), 75.4 (CH2), 104.9 (C5H4), 106.8 (C5H4), 107.7 (C5H4), 108.4 (C5H4), 19.7 (C5H4), 111.4 (C5H4), 112.5 (C5H4), 118.7 (C5H4), 119.7 (C5H4), 121.2 (C5H4), 126.5 (C5H4), 128.4 (d, J = 12.7 Hz, PPh3), 128.54 (d, J = 11.3 Hz, PPh3), 130.2 (C5Me4), 130.6 (d, J = 2.6 Hz, PPh3), 131.0 (d, J = 2.8 Hz, PPh3), 132.7 (d, J = 9.0 Hz, PPh3), 133.7 (d, J = 9.3 Hz, PPh3), 133.7 (Cipso Cp), 134.3 (d, 1JPC = 80.0 Hz, PPh3), 135.3 (d, 1JPC = 84.1 Hz, PPh3), 135.5 (Cipso Cp), 136.1 (C5Me4), 173.5 (d, 1JPC = 29.1 Hz, CHylide) ppm.
Synthesis of Ti4b:

\[
\begin{align*}
\text{Me}_4 & \quad \text{Cl} \quad \text{Ti} \\
\text{AdH} & \quad \text{CH}_2
\end{align*}
\]

Ti3 (1 g, 2.4 mmol) and Y1 (0.020 g, 0.072 mmol) were placed in a Schlenk tube, 10 ml of \(n\)-hexane was added and the resulting red suspension stored at 60 °C over night. Evaporation of the solvent and drying in vacuo afforded Ti4b in quantitative yield, m.p. 125 °C.

\(^1\)H-NMR (500 MHz, \(\text{C}_6\text{D}_6\), 305 K): \(\delta = 0.92\) (s, 3 H, \(\text{C}_5\text{Me}_4\)), 1.28 (s, 3 H, \(\text{C}_5\text{Me}_4\)), 1.61–2.46 (14 H, Ad), 1.74 (s, 3 H, \(\text{C}_5\text{Me}_4\)), 2.12 (s, 4 H, \(\text{C}_5\text{Me}_4\), \(\text{CH}_2\)), 2.65 (d, \(^2J = 3.4 \text{ Hz}\), 1 H, \(\text{CH}_2\)), 3.19 (s, 1 H, \(\text{CH}_\text{exo}\)), 5.08 (m, 1 H, \(\text{C}_5\text{H}_4\)), 5.14 (m, 1 H, \(\text{C}_5\text{H}_4\)), 5.94 (m, 1 H, \(\text{C}_5\text{H}_4\)), 6.47 (m, 1 H, \(\text{C}_5\text{H}_4\)) ppm.

\(^{13}\)C-NMR (125 MHz, \(\text{C}_6\text{D}_6\), 305 K): \(\delta = 10.9\) (\(\text{C}_5\text{Me}_4\)), 11.8 (\(\text{C}_5\text{Me}_4\)), 13.5 (\(\text{C}_5\text{Me}_4\)), 14.5 (\(\text{C}_5\text{Me}_4\)), 28.4 (Ad CH), 28.6 (Ad CH), 32.5 (Ad CH), 32.8 (Ad CH), 32.9 (Ad CH), 33.1 (Ad CH), 38.4 (Ad CH), 39.0 (Ad CH), 39.1 (Ad CH), 45.3 (\(\text{CH}_\text{exo}\)), 75.4 (CH2), 106.8 (\(\text{C}_5\text{H}_4\)), 109.7 (\(\text{C}_5\text{H}_4\)), 111.4 (\(\text{C}_5\text{H}_4\)), 118.7 (\(\text{C}_5\text{H}_4\)), 121.2 (\(\text{C}_5\text{Me}_4\)), 126.5 (\(\text{C}_5\text{Me}_4\)), 128.6 (\(\text{C}_5\text{Me}_4\)), 130.2 (\(\text{C}_5\text{Me}_4\)), 133.7 (\(\text{C}_\text{ipso}\) Cp), 135.6 (\(\text{C}_5\text{Me}_4\)) ppm.

IR (ATR, 16 scans): \(\tilde{\nu} = 2963, 2902, 2848, 1468, 1449, 1377, 1260, 1089, 1061, 1017, 874, 795, 745, 693, 619, 603, 580 \text{ cm}^{-1}\).
Synthesis of Ti5:

Ti3 (0.500 g, 1.2 mmol) and Y1 (0.331 g, 1.2 mmol) were placed in a Schlenk tube and 10 ml of n-hexane was added. The resulting red suspension was stirred for 8 hours at room temperature and subsequently an excess acetone was added. After storing at 60 °C overnight, the resulting yellow suspension was filtrated to remove triphenylphosphineoxide (0.196 g, 0.7 mmol, 59%). The solvent was evaporated and the resulting yellow solid dried in vacuo, yielding 0.361 g (0.76 mmol, 63%) of Ti5, m.p. 156 °C.

Single crystals suitable for x-ray diffraction could be obtained from a saturated solution of Ti5 in n-hexane at 5 °C.

1H-NMR (500 MHz, C6D6, 305 K): δ = 1.23 (s, 3 H, OC(CH3)2), 1.48 (s, 3 H, OC(CH3)2), 1.50–2.41 (14 H, Ad), 1.53 (s, 3 H, C5Me4), 1.69 (s, 3 H, C5Me4), 1.72 (s, 3 H, C5Me4), 2.33 (d, 3JCH = 13.2 Hz, 1 H, CH2), 2.36 (s, 3 H, C5Me4), 2.70 (d, 3JCH = 13.2 Hz, 1 H, CH2), 3.21 (s, 1 H, CHexo), 5.53 (m, 1 H, C5H4), 5.59 (m, 1 H, C5H4), 5.84 (m, 1 H, C5H4), 6.49 (m, 1 H, C5H4) ppm.

13C-NMR (125 MHz, C6D6, 305 K): δ = 11.5 (C5Me4), 12.8 (C5Me4), 13.1 (C5Me4), 14.2 (C5Me4), 28.5 (2 x Ad CH), 32.0 (OC(CH3)2), 32.0 (Ad CH), 32.6 (Ad CH), 33.0 (Ad CH2), 33.0 (Ad CH2), 34.5 (OC(CH3)2), 38.4 (CH2), 38.7 (CH2), 39.1 (CH2), 39.3 (CH2), 44.1 (CHexo), 108.6 (OC(CH3)2), 109.7 (C5H4), 111.9 (C5H4), 114.9 (C5H4), 115.6 (C5Me4), 116.4 (C5Me4), 121.1 (C5H4), 121.8 (C5Me4), 132.1 (C5Me4), 138.2 (Cipso Cp), 140.8 (C5Me4) ppm.

IR (ATR, 16 scans): ν = 2965, 2902, 2875, 2849, 1488, 1449, 1377, 1359, 1292, 1255, 1194, 1143, 1113, 1100, 1058, 1023, 965, 909, 852, 806, 778, 691, 608, 595, 572 cm⁻¹.

EA: Anal. calcd. for C28H39ClOTi: C 70.81, H 8.28; found C 71.05, H 8.38.
Synthesis of Ti6:

Ti3 (0.250 g, 0.6 mmol) and Y1 (0.166 g, 0.6 mmol) were placed in a Schlenk tube and 7 ml of n-hexane was added. The resulting red suspension was stirred for 8 hours at room temperature and subsequently ferrocenealdehyde (0.128 g, 0.6 mmol) was added. After storing at 60 °C overnight, single crystals suitable for x-ray diffraction could be obtained from the reaction mixture. The mother liquor was decanted and the red crystals dried in vacuo, yielding 0.104 g (0.16 mmol, 27%) of Ti6, m.p. 135 °C.

1H-NMR (500 MHz, C6D6, 305 K): δ = 1.49–2.44 (14 H, Ad), 1.55 (s, 3 H, C5Me4), 1.69 (s, 3 H, C5Me4), 1.72 (s, 3 H, C5Me4), 2.44 (s, 3 H, C5Me4), 2.47 (dd, 2JCH = 12.8, 3JCH = 10.3 Hz, 1 H, CH2), 3.07 (dd, 2JCH = 12.9 Hz, 3JCH = 6.1 Hz, 1 H, CH2), 3.29 (s, 1 H, CHexo), 4.01 (m, 2 H, FcC5H4), 4.11 (s, 5 H, FcC5H5), 4.12 (m, 2 H, FeC5H4), 5.58 (m, 1 H, C5H4), 5.72 (m, 1 H, C5H4), 5.93 (m, 1 H, C5H4), 6.28 (dd, 3JCH = 10.3 Hz, 6.1 Hz, 1 H, FcCHO), 6.47 (m, 1 H, C5H4) ppm.

13C-NMR (125 MHz, C6D6, 305 K): δ = 11.4 (C5Me4), 12.7 (C5Me4), 12.9 (C5Me4), 13.6 (C5Me4), 28.4 (Ad CH), 28.5 (Ad CH), 32.0 (Ad CH), 32.5 (Ad CH), 33.0 (Ad CH2), 33.4 (CH2), 38.4 (Ad CH2), 38.8 (Ad CH2), 39.0 (Ad CH2), 43.7 (CHexo), 66.6 (FcCH), 67.8 (FcCH), 67.9 (FcCH), 68.0 (FcCH), 69.0 (FcCH), 92.9 (FcC), 97.4 (FcCHO), 110.6 (C5H4), 112.7 (C5H4), 115.7 (C5H4), 116.2 (C5Me4), 117.7 (C5Me4), 120.1 (C5H4), 121.3 (C5Me4), 131.5 (C5Me4), 138.5 (Cipso C5Me4), 139.4 (Cipso Cp) ppm.

IR (ATR, 16 scans): ν = 3094, 2902, 2846, 1487, 1467, 1448, 1411, 1378, 1354, 1332, 1293, 1260, 1105, 1058, 1035, 1015, 1002, 972, 955, 933, 883, 850, 827, 806, 781, 721, 690, 685, 646, 632, 604, 586 cm⁻¹.

EA: Anal. calcd. for C36H43ClFeOTi: C 68.54, H 6.87; found C 70.63, H 6.29.
Synthesis of Ti7:

![Diagram of Ti7](image)

Ti3 (0.250 g, 0.6 mmol) and catalytic amounts of Y1 were placed in a Schlenk tube and 7 ml of n-hexane was added. The resulting red suspension was stored at 60 °C overnight, subsequent addition of tritylitrile (0.162 g, 0.6 mmol) and stirring at room temperature overnight results in a turquoise suspension. The mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo afforded 0.304 g (0.35 mmol, 58%) of Ti7 as turquoise solid, m.p. 125 °C (dec.).

$^1$H-NMR (500 MHz, C$_6$D$_6$, 305 K): $\delta = 1.27$–2.47 (14 H, Ad), 1.46 (s, 3 H, C$_5$Me$_4$), 1.60 (s, 3 H, C$_5$Me$_4$), 1.64 (s, 3 H, C$_5$Me$_4$), 2.34 (s, 3 H, C$_5$Me$_4$), 2.89 (d, $^3$$J$$_{CH}$ = 17.5 Hz, 1 H, CH$_2$), 3.15 (s, 1 H, CH$_{exo}$), 3.69 (d, $^3$$J$$_{CH}$ = 17.5 Hz, 1 H, CH$_2$), 5.27 (m, 1 H, C$_5$H$_4$), 5.49 (m, 1 H, C$_5$H$_4$), 5.69 (m, 1 H, C$_5$H$_4$), 6.54 (m, 1 H, C$_5$H$_4$), 7.01 (t, $^3$$J$$_{CH}$ = 7.3 Hz, 3 H, p-C$_6$H$_5$), 7.13–7.14 (m, 6 H, m-C$_6$H$_5$), 7.51 (d, $^3$$J$$_{CH}$ = 7.4 Hz, 6 H, o-C$_6$H$_5$) ppm.

$^{13}$C-NMR (125 MHz, C$_6$D$_6$, 305 K): $\delta = 12.1$ (C$_5$Me$_4$), 12.2 (C$_5$Me$_4$), 12.3 (C$_5$Me$_4$), 13.4 (C$_5$Me$_4$), 28.3 (Ad CH), 28.6 (Ad CH), 31.4 (Ad CH), 32.7 (Ad CH), 32.8 (Ad CH$_2$), 33.2 (Ad CH$_2$), 38.3 (CH$_2$), 38.4 (CH$_2$), 38.5 (CH$_2$), 43.3 (CH$_{exo}$), 71.1 (CPh$_3$), 108.8 (C$_5$H$_4$), 112.0 (C$_5$H$_4$), 113.7 (C$_5$H$_4$), 118.5 (C$_5$Me$_4$), 119.3 (C$_5$Me$_4$), 121.6 (C$_5$Me$_4$), 123.6 (C$_5$H$_4$), 126.5 (p-C$_6$H$_5$), 127.9 (m-C$_6$H$_5$), 130.0 (C$_5$Me$_4$), 131.3 (o-C$_6$H$_5$), 136.5 (C$_5$Me$_4$), 139.4 (C$_{ipso}$ Cp), 146.1 (C$_{ipso}$ C$_6$H$_5$), 196.0 (C=N) ppm.

$^{15}$N-NMR (51 MHz, C$_6$D$_6$, 305 K): $\delta = 123.0$ ppm.

IR (ATR, 16 scans): $\tilde{\nu}$ = 3063, 3019, 2928, 2895, 2846, 1606, 1594, 1489, 1447, 1263, 1099, 1050, 1030, 876, 828, 804, 781, 768, 740, 701, 648, 632, 600, 556 cm$^{-1}$.

EA: Anal. calcd. for C$_{45}$H$_{48}$ClNTi: C 78.77, H 7.05, N 2.04; found C 75.86, H 6.95, N 2.05.
Synthesis of Ti7a:

By heating a solution of Ti7 in n-hexane, a color change from turquoise to red can be observed, affording Ti7a in quantitative yield, m.p. 165 °C.

Single crystals suitable for x-ray diffraction could be obtained from a saturated solution of Ti7a in n-hexane at 5 °C.

$^{1}H$-NMR (500 MHz, C$_6$D$_6$, 305 K): $\delta = 1.29$–2.60 (14 H, Ad), 1.43 (s, 3 H, C$_5$Me$_4$), 1.65 (s, 3 H, C$_5$Me$_4$), 1.72 (s, 3 H, C$_5$Me$_4$), 2.50 (s, 3 H, C$_5$Me$_4$), 3.03 (s, 1 H, CH$_{exo}$), 5.04 (m, 1 H, C$_5$H$_4$), 5.20 (m, 2 H, C$_5$H$_4$), 5.37 (s, 1 H, C$_5$Me$_4$CH), 6.51 (m, 1 H, C$_5$H$_4$), 7.04 (t, $^3J_{CH} = 7.3$ Hz, 3 H, p-$C_6H_5$), 7.16–7.18 (m, 6 H, m-$C_6H_5$), 7.49 (d, $^3J_{CH} = 7.5$ Hz, 6 H, o-$C_6H_5$), 8.79 (s, 1 H, NH) ppm.

$^{13}C$-NMR (125 MHz, C$_6$D$_6$, 305 K): $\delta = 11.5$ (C$_5$Me$_4$), 12.0 (C$_5$Me$_4$), 12.3 (C$_5$Me$_4$), 14.0 (C$_5$Me$_4$), 28.2 (Ad CH), 28.3 (Ad CH), 31.9 (Ad CH), 32.1 (Ad CH$_2$), 32.2 (Ad CH), 38.3 (Ad CH$_2$), 38.7 (Ad CH$_2$), 38.8 (Ad CH$_2$), 43.5 (CH$_{exo}$), 66.2 (CPh$_3$), 105.1 (C$_5$H$_4$), 105.7 (C$_5$Me$_4$CH), 107.4 (C$_5$H$_4$), 113.6 (C$_5$H$_4$), 119.5 (C$_5$Me$_4$), 119.7 (C$_5$Me$_4$), 125.6 (C$_5$Me$_4$), 126.8 (p-$C_6H_5$), 127.1 (C$_5$H$_4$), 128.1 (m-$C_6H_5$), 131.3 (o-$C_6H_5$), 141.1 (C$_{ipso}$ Cp), 144.1 (C$_5$Me$_4$), 144.9 (C$_5$Me$_4$), 145.6 (C$_{ipso}$ C$_6$H$_5$), 174.1 (CNH) ppm.

$^{15}N$-NMR (51 MHz, C$_6$D$_6$, 305 K): $\delta = 289.9$ ppm.

IR (ATR, 16 scans): $\tilde{\nu} = 3354$, 3057, 2963, 2904, 2849, 1595, 1492, 1448, 1318, 1260, 1152, 1088, 1016, 866, 795, 753, 743, 724, 699, 644, 622, 584, 568 cm$^{-1}$. 
Synthesis of Ti8:

Ti3 (0.250 g, 0.6 mmol) and catalytic amounts of Y1 were placed in a Schlenk tube and 7 ml of n-hexane was added. The resulting red suspension was stored at 60 °C overnight and subsequently ferrocenenitrile (0.127 g, 0.6 mmol) was added. After stirring the suspension at room temperature overnight, the mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo afforded 0.204 g (0.32 mmol, 54%) of Ti8 as red-brown solid, m.p. 183 °C.

Single crystals suitable crystals for x-ray diffraction could be obtained by slowly cooling a hot saturated solution of Ti8 in n-hexane.

$^1$H-NMR (500 MHz, C$_6$D$_6$, 305 K): δ = 1.53–2.60 (14 H, Ad), 1.57 (s, 3 H, C$_5$Me$_4$), 1.75 (s, 3 H, C$_5$Me$_4$), 1.76 (s, 3 H, C$_5$Me$_4$), 2.45 (s, 3 H, C$_5$Me$_4$), 3.45 (s, 1 H, CHexo), 4.08 (s, 2 H, FcC$_5$H$_4$), 4.23 (s, 5 H, FcC$_5$H$_4$), 4.29 (s, 1 H, FcC$_5$H$_4$), 4.45 (s, 1 H, FcC$_5$H$_4$), 5.26 (m, 1 H, C$_5$H$_4$), 5.37 (s, 1 H, C$_5$Me$_4$CH), 5.63 (m, 1 H, C$_5$H$_4$), 5.68 (m, 1 H, C$_5$H$_4$), 6.46 (m, 1 H, C$_5$H$_4$), 9.25 (s, 1 H, NH) ppm.

$^{13}$C-NMR (125 MHz, C$_6$D$_6$, 305 K): δ = 11.5 (C$_5$Me$_4$), 12.1 (C$_5$Me$_4$), 12.5 (C$_5$Me$_4$), 13.9 (C$_5$Me$_4$), 28.3 (Ad CH), 28.3 (Ad CH), 32.4 (Ad CH), 32.4 (Ad CH), 32.6 (Ad CH), 33.5 (Ad CH), 38.3 (Ad CH), 38.9 (Ad CH), 39.1 (Ad CH), 44.4 (CHexo), 65.3 (FcC$_5$H$_4$), 66.5 (FcC$_5$H$_4$), 68.7 (FcC$_5$H$_4$), 69.3 (FcC$_5$H$_4$), 69.9 (FcC$_5$H$_4$), 81.8 (FcC), 97.1 (C$_5$Me$_4$CH), 107.9 (C$_5$H$_4$), 110.3 (C$_5$H$_4$), 112.1 (C$_5$H$_4$), 119.7 (C$_5$Me$_4$), 120.0 (C$_5$Me$_4$), 123.1 (C$_5$H$_4$), 126.9 (C$_5$Me$_4$), 130.8 (C$_{ipso}$ Cp), 144.13 (C$_5$Me$_4$), 147.0 (C$_{ipso}$ C$_5$Me$_4$), 167.2 (FcCCH) ppm.

$^{15}$N-NMR (51 MHz, C$_6$D$_6$, 305 K): δ = 277.6 ppm.

IR (ATR, 16 scans): ν = 3379, 2900, 2846, 1660, 1600, 1487, 1467, 1448, 1375, 1338, 1314, 1261, 1100, 1057, 1030, 926, 889, 827, 810, 732, 691, 662, 645, 621, 595 cm$^{-1}$.

EA: Anal. calcd. for C$_{36}$H$_{42}$ClFeNTi: C 68.86, H 6.74, N 2.23; found C 67.01, H 6.58, N 2.29.
Synthesis of Ti9:

Ti3 (0.250 g, 0.6 mmol) and catalytic amounts of Y1 were placed in a Schlenk tube and 7 ml of n-hexane was added. The resulting red suspension was stored at 60 °C overnight and subsequently p-chlorobenzonitrile (0.083 g, 0.6 mmol) was added. After stirring the suspension at room temperature overnight, the mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo afforded 0.215 g (0.39 mmol, 65%) of Ti9 as red solid, m.p. 160 °C.

Single crystals suitable crystals for x-ray diffraction could be obtained by slowly cooling a hot saturated solution of Ti9 in n-hexane.

1H-NMR (500 MHz, C6D6, 305 K): δ = 1.45–2.38 (14 H, Ad), 1.57 (s, 3 H, C5Me4), 1.76 (s, 3 H, C5Me4), 1.78 (s, 3 H, C5Me4), 2.42 (s, 3 H, C5Me4), 3.26 (s, 1 H, CHexo), 5.26 (m, 1 H, C5H4), 5.36 (s, 1 H, C5Me4CH), 5.51 (m, 1 H, C5H4), 5.74 (m, 1 H, C5H4), 6.34 (m, 1 H, C5H4), 7.16 (m, C6D6 + 2 H C6H4), 7.18 (m, 2 H, C6H4), 9.00 (s, 1 H, NH) ppm.

13C-NMR (125 MHz, C6D6, 305 K): δ = 11.5 (C5Me4), 12.1 (C5Me4), 12.5 (C5Me4), 13.7 (C5Me4), 28.2 (Ad CH), 28.2 (Ad CH), 32.3 (2 x Ad CH2), 32.5 (Ad CH), 33.2 (Ad CH), 38.2 (Ad CH2), 38.7 (Ad CH2), 38.8 (Ad CH2), 44.2 (CHexo), 99.3 (C5Me4CH), 108.4 (C5H4), 111.8.4 (C5H4), 112.2 (C3H4), 119.9 (C5Me4), 120.8 (C5Me4), 121.3 (C3H4), 126.9 (C6H4), 126.9 (C5Me4), 128.9 (C6H4), 132.6 (Cipso Cp), 134.1 (C6H4), 136.9 (C6H4), 144.3 (C5Me4), 146.6 (C5Me4), 167.6 (CNH) ppm.

15N-NMR (51 MHz, C6D6, 305 K): δ = 267.9 ppm.

IR (ATR, 16 scans): ν = 2904, 2847, 1601, 1586, 1566, 1486, 1447, 1397, 1381, 1328, 1292, 1262, 1212, 1168, 1087, 1061, 1012, 982, 953, 873, 852, 824, 802, 732, 694, 661, 644, 623, 604, 590, 567 cm\(^{-1}\).

EA: Anal. calcd. for C32H37Cl2NTi: C 69.32, H 6.73, N 2.53; found C 69.26, H 6.91, N 2.44.
Synthesis of Ti10:

Ti3 (0.250 g, 0.6 mmol) and catalytic amounts of Y1 were placed in a Schlenk tube and 7 ml of n-hexane was added. The resulting red suspension was stored at 60 °C overnight and subsequently acetonitrile (0.53 ml, 0.60 mmol, 1.14 M in toluene) was added dropwise. After storing at 60 °C over night a red suspension has been formed, which was decanted and the red solid dried in vacuo. NMR experiments indicate a complex mixture of multiple compounds. However, few single crystals suitable for X-ray diffraction could be obtained from a hot saturated solution of the reaction product in n-hexane at 60 °C.
**Synthesis of Zr2a:**

Zr1a (0.110 g, 0.24 mmol) and Y1 (0.066 g, 0.24 mmol) were placed in a Schlenk tube and 7 ml of n-hexane was added. The former red solution turns into a yellow suspension and was stirred at room temperature overnight. The mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo afforded 0.077 g (0.11 mmol, 46%) of Zr2a as yellow solid, m.p. 145 °C (dec.).

**$^1$H-NMR** (500 MHz, C$_6$D$_6$, 305 K): $\delta$ = 1.45–2.31 (14 H, Ad), 2.07 (s, 15 H, C$_5$Me$_5$), 3.31 (s, 1 H, CH$_{exo}$), 5.06 (m, 1 H, C$_5$H$_4$), 5.08 (d, $^2$J$_{PH}$ = 11.3 Hz, 1 H, CH$_{ylide}$), 5.47 (m, 2 H, C$_5$H$_4$), 5.92 (m, 1 H, C$_5$H$_4$), 7.10 (m, 9 H, PPh$_3$), 7.10 (m, 6 H, PPh$_3$) ppm.

**$^{13}$C-NMR** (125 MHz, C$_6$D$_6$, 305 K): $\delta$ = 12.8 (C$_5$Me$_5$), 28.5 (Ad CH), 32.0 (Ad CH), 32.6 (Ad CH$_2$), 33.3 (Ad CH), 38.6 (Ad CH$_2$), 39.2 (Ad CH$_2$), 43.8 (CH$_{exo}$), 104.4 (C$_5$H$_4$), 104.5 (d, $^1$J$_{PC}$ = 34.5 Hz, CH$_{ylide}$), 107.4 (C$_5$H$_4$), 110.0 (C$_5$H$_4$), 110.8 (C$_5$H$_4$), 118.1 (C$_5$Me$_5$), 128.4 (d, $J = 11.3$ Hz, PPh$_3$), 130.7 (d, $J = 2.7$ Hz, PPh$_3$), 133.5 (d, $J = 9.2$ Hz, PPh$_3$), 133.8 (C$_{ipso}$ Cp), 135.6 (d, $^1$J$_{PC}$ = 81 Hz, PPh$_3$) ppm.

**$^{31}$P-NMR** (202 MHz, C$_6$D$_6$, 305 K): $\delta$ = 16.6 ($^1$J$_{PC}$ = 81 Hz) ppm.

**IR** (ATR, 16 scans): $\tilde{\nu}$ = 3058, 2907, 2848, 1482, 1435, 1261, 1185, 1095, 1062, 1044, 1023, 998, 852, 813, 748, 706, 692, 595 cm$^{-1}$.

**EA:** Anal. calcd. for C$_{44}$H$_{49}$ClPZr: C 71.85, H 6.72; found C 68.80, H 6.91.
Synthesis of Zr2b:

Zr1b (0.250 g, 0.48 mmol) and Y1 (0.133 g, 0.48 mmol) were placed in a Schlenk tube and 7 ml of n-hexane was added. The former red solution turns into a yellow suspension and was stirred at room temperature overnight. The mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo afforded 0.248 g (0.31 mmol, 65%) of Zr2b as yellow solid, m.p. 153 °C (dec.). Single crystals suitable for x-ray diffraction were obtained from a saturated solution of Zr2b-benzo in n-hexane at 5 °C.

^1H-NMR (500 MHz, C₆D₆, 305 K): δ = 1.97 (s, 15 H, C₅Me₅), 2.05 (s, 3 H, CH₃), 2.10 (s, 3 H, CH₃), 4.79 (m, 1 H, C₅H₄), 5.04 (m, 1 H, C₅H₄), 5.20 (d, ^2JPH = 12.5 Hz, 1 H, CHylide), 5.41 (m, 1 H, C₅H₄), 5.96 (s, 1 H, CHexo), 6.27 (m, 1 H, C₅H₄), 6.86 (d, J = 7.9 Hz, 2 H, pTol CH), 7.00–7.06 (m, 11 H, pTol CH + PPh₃), 7.20 (d, J = 8.0 Hz, 2 H, pTol CH), 7.50 (d, J = 8.0 Hz, 2 H, pTol CH), 7.68–7.72 (m, 6 H, PPh₃) ppm.

^13C-NMR (125 MHz, C₆D₆, 305 K): δ = 12.8 (C₅Me₅), 21.0 (pTol CH₃), 21.1 (pTol CH₃), 51.6 (CHexo), 103.0 (C₅H₄), 105.7 (d, ^1JPC = 33.1 Hz, CHylide), 109.7 (C₅H₄), 110.8 (C₅H₄), 111.9 (C₅H₄), 118.3 (C₅Me₅), 129.0 (pTol CH), 129.2 (pTol CH), 129.6 (pTol CH), 130.4 (pTol CH), 130.7 (d, J = 2.7 Hz, PPh₃), 133.4 (d, J = 9.1 Hz, PPh₃), 134.8 (Cipso Cp), 134.8 (pTol C), 135.1 (d, ^1JPC = 81 Hz, PPh₃), 135.5 (pTol C), 142.6 (pTol C), 144.4 (pTol C) ppm.

^31P-NMR (202 MHz, C₆D₆, 305 K): δ = 16.5 (^1JPC = 81 Hz) ppm.

IR (ATR, 16 scans): ̅v = 3074, 2962, 2899, 2860, 1510, 1481, 1437, 1377, 1262, 1186, 1102, 1069, 1040, 1024, 999, 950, 951, 804, 785, 762, 750, 705, 694, 577 cm⁻¹.

EA: Anal. calcd. for C₄₉H₅₀ClPZr: C 73.88, H 6.33; found C 72.86, H 6.62.
Synthesis of Zr2a-benzo:

Zr1a-benzo (0.250 g, 0.44 mmol) and Y2 (0.121 g, 0.44 mmol) were placed in a Schlenk tube and 7 ml of n-hexane was added. The former red solution turns into a yellow suspension and was stirred at room temperature overnight. The mother liquor was decanted and the solid washed with n-hexane (3 x 5 ml). Drying in vacuo afforded 0.273 g (0.34 mmol, 69%) of Zr2a-benzo as yellow solid, m.p. 99 °C (dec.).

Single crystals suitable for x-ray diffraction were obtained from a saturated solution of Zr2a-benzo in n-hexane at room temperature.

Due to the poor solubility of Zr2a-benzo in common deuterated NMR solvents, NMR experiments could not be performed.

IR (ATR, 16 scans): ṽ = 3052, 3018, 2954, 2907, 2859, 1588, 1509, 1483, 1437, 1376, 1346, 1262, 1184, 1099, 1022, 999, 962, 938, 857, 806, 776, 757, 745, 710, 693, 639, 595, 575 cm⁻¹.

EA: Anal. calcd. for C₄₈H₇₀ClPZr: C 71.64, H 8.77; found C 63.76, H 8.04.
Synthesis of Zr2b-benzo:

Zr1b-benzo (0.250 g, 0.44 mmol) and Y1 (0.121 g, 0.44 mmol) were placed in a Schlenk tube and 7 ml of n-hexane was added. The former red solution turns into a yellow suspension and was stirred at room temperature overnight. The mother liquor was decanted and the solid washed with n-hexane (3 x 5 ml). Drying in vacuo afforded 0.305 g (0.36 mmol, 82%) of Zr2b-benzo as yellow solid, m.p. 115 °C (dec.). Single crystals suitable for x-ray diffraction were obtained from a saturated solution of Zr2b-benzo in n-hexane at 5 °C.

1H-NMR (500 MHz, C6D6, 305 K): δ = 1.74 (s, 15 H, C5Me5), 2.01 (s, 3 H, CH3), 2.16 (s, 3 H, CH3), 2.72 (d, 2JPH = 22.1 Hz, 1 H, CHylide), 5.86 (d, J = 2.8 Hz, 1 H, C5H2), 5.92 (d, 1 H, J = 2.8 Hz, C5H2), 6.25 (m, 1 H, C5H4), 6.42 (m, 1 H, C6H4), 6.57 (s, 1 H, CHexo), 6.83 (m, 2 H, pTol CH), 7.08 (m, 11 H, PPh3 + pTol CH), 7.18 (m, 2 H, pTol CH), 7.28 (m, 1 H, C6H4), 7.38 (m, 1 H, C6H4), 7.60 (m, 6 H, PPh3), 7.77 (m, 2 H, pTol CH) ppm.

13C-NMR (126 MHz, C6D6, 305 K): δ = 12.6 (C5Me5), 21.0 (CH3), 21.1 (CH3), 51.3 (CHexo), 91.3 (C5H2), 103.9 (d, 2JPC = 40.2 Hz, CHylide), 114.4 (C5H2), 119.0 (C5Me5), 123.0 (C6H4), 124.8 (C6H4), 124.9 (C6H4), 125.0 (C6H4), 126.3 (C6H4), 128.1 (d, JPC = 11.3 Hz, CHylide), 129.1 (pTol CH), 129.27 (pTol CH), 129.31 (pTol CH), 130.6 (d, J = 2.7 Hz, PPh3), 131.0 (pTol CH), 132.7 (Cp Cipso), 133.0 (C6H4), 133.6 (d, J = 9.3 Hz, PPh3), 135.0 (pTol C), 135.2 (d, 1JPC = 82.1 Hz, PPh3), 135.4 (pTol C), 141.8 (pTol C), 143.6 (pTol C) ppm.

31P-NMR (202 MHz, C6D6, 305 K): δ = 5.92 (1JPC = 82.0 Hz) ppm.

IR (ATR, 16 scans): ν = 3058, 3025, 2959, 2903, 2858, 1587, 1492, 1482, 1451, 1435, 1377, 1296, 1262, 1153, 1098, 1075, 1028, 999, 951, 880, 801, 772, 750, 740, 695, 624, 601 cm⁻¹.

EA: Anal. calcd. for C53H52ClPZr: C 75.19, H 6.19; found C 73.70, H 6.62.
Synthesis of Zr2c:

Zr1b (0.250 g, 0.48 mmol) and Y2 (0.142 g, 0.48 mmol) were placed in a Schlenk tube and 7 ml of n-hexane was added. The former red solution turns into a yellow suspension and was stirred at room temperature overnight. The mother liquor was decanted and the solid washed with n-hexane (2 x 3 ml). Drying in vacuo afforded 0.282 g (0.35 mmol, 72%) of Zr2c as yellow solid, m.p. 193 °C (dec.).

$^1$H-NMR (500 MHz, C$_6$D$_6$, 305 K): $\delta$ = 1.0–1.91 (30 H, PCy$_3$), 1.97 (s, 15 H, C$_5$Me$_5$), 2.07 (s, 3 H, CH$_3$), 2.12 (s, 3 H, CH$_3$), 5.71 (d, $^2$J$_{PH}$ = 17.2 Hz, 1 H, CH$_2$ylide), 5.13 (m, 1 H, C$_5$H$_4$), 5.48 (m, 1 H, C$_5$H$_4$), 6.06 (m, 1 H, C$_5$H$_4$), 6.10 (s, 1 H, CH$_3$exo), 6.89 (m, 1 H, C$_5$H$_4$), 6.98 (d, $^2$J$_{PH}$ = 7.9 Hz, 2 H, pTol CH), 7.04 (d, $^2$J$_{PH}$ = 7.8 Hz, 2 H, pTol CH), 7.43 (d, $^2$J$_{PH}$ = 8.0 Hz, 2 H, pTol CH), 7.61 (d, $^2$J$_{PH}$ = 8.0 Hz, 2 H, pTol CH) ppm.

$^{13}$C-NMR (125 MHz, C$_6$D$_6$, 305 K): $\delta$ = 12.8 (C$_5$Me$_5$), 21.0 (pTol CH$_3$), 21.1 (pTol CH$_3$), 26.7 (CH$_2$), 27.7 (CH$_2$), 28.0 (CH$_2$), 36.8 (d, $^1$J$_{PC}$ = 47.0 Hz, Cy CH), 51.6 (CH$_3$exo), 102.5 (C$_5$H$_4$), 107.5 (C$_5$H$_4$), 109.5 (C$_5$H$_4$), 109.7 (C$_5$H$_4$), 111.1 (d, $^1$J$_{PC}$ = 23.7 Hz, CH$_2$ylide), 117.5 (C$_5$Me$_5$), 129.2 (pTol CH), 129.2 (pTol CH), 129.8 (pTol CH), 130.4 (pTol CH), 135.0 (Cp C$_{ps}$), 135.1 (pTol C), 135.5 (pTol C), 142.5 (pTol C), 144.8 (pTol C) ppm.

$^{31}$P-NMR (202 MHz, C$_6$D$_6$, 305 K): $\delta$ = 26.7 ($^1$J$_{PC}$ = 46.4 Hz) ppm.

IR (ATR, 16 scans): $\tilde{\nu}$ = 3021, 2929, 2854, 1627, 1510, 1447, 1376, 1313, 1260, 1181, 1110, 1022, 1007, 929, 909, 851, 807, 763, 690, 593, 576 cm$^{-1}$.
Crystallographic Data

Single crystals of the corresponding compounds were selected and measured on a 'Bruker APEX-II CCD' diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystals were cooled during data collection. Using Olex2,[10] the structure was solved with the ShelXS[11] structure solution program using Direct Methods and refined with the ShelXL[12] refinement package using Least Squares minimization.

Table 1. Crystal Structure Data for Zr2a-benzo, Zr2b, Zr2b-benzo and Ti2b including CCDC deposition numbers.

|             | Zr2a-benzo | Zr2b  | Zr2b-benzo | Ti2b  |
|-------------|------------|-------|------------|-------|
| CCDC        | 1878081    | 1878085| 1878082    | 1878079|
| empirical formula | C₄₈H₇₀ClPZr | C₄₈H₅₀ClPZr | C₄₈H₆₆ClPZr | C₄₈H₇₁PTi |
| formula mass | 804.68     | 796.53 | 932.75     | 738.92 |
| cryst. dimens. mm | 0.2 x 0.1 x 0.5 | 0.24 x 0.1 x 0.03 | 0.20 x 0.08 x 0.06 | 0.24 x 0.12 x 0.04 |
| color, habit | yellow, plate | yellow, plate | yellow, rod | red-orange, plate |
| cryst. system | monoclinic | monoclinic | triclinic | triclinic |
| spacegroup | P2₁/n | P2₁/c | P-1 | P-1 |
| a, Å | 10.3211(4) | 17.3161(8) | 17.3059(14) | 20.1468(12) |
| b, Å | 26.2388(10) | 13.4216(6) | 18.1032(14) | 16.6236(10) |
| c, Å | 15.7335(6) | 17.4479(8) | 18.4382(14) | 20.1468(12) |
| α, deg | 90 | 90 | 117.188(2) | 86.699(2) |
| β, deg | 94.6720(11) | 93.7551(15) | 101.145(2) | 87.586(2) |
| γ, deg | 90 | 90 | 91.753(2) | 77.804(2) |
| V, Å³ | 4246.7(3) | 4046.4(3) | 4994.4(7) | 4049.7(4) |
| Z | 4 | 4 | 4 | 4 |
| D_calcd., g cm⁻³ | 1.259 | 1.308 | 1.240 | 1.212 |
| µ, mm⁻¹ | 0.391 | 0.411 | 0.343 | 0.284 |
| F(000) | 1720 | 1664 | 1968 | 1608 |
| T, K | 100(2) | 100(2) | 100(2) | 100(2) |
| θ range, deg | 1.513, 30.032 | 1.916, 25.026 | 2.19, 22.31 | 1.573, 28.699 |
| no. of rflns collected | 96310 | 95370 | 102058 | 130358 |
| no. of independ. rflns (R(int)) | 12421 (0.0668) | 7138 (0.0945) | 14343 (0.0873) | 20923 (0.0870) |
| no. of rflns with I > 2σ(I) | 9593 | 5300 | 9104 | 14272 |
| abs. cor. | multi-scan | numerical | multi-scan | semi-empirical |
| max., min. transmission | 1.0000, 0.9532 | 0.9963, 0.9244 | 1.0000, 0.8859 | 1.0000, 0.9360 |
| no. of data / restraints / param. | 12421 / 0 / 469 | 7138 / 0 / 480 | 14343 / 0 / 1170 | 20923 / 0 / 927 |
| R indices (all data) | R1 = 0.0567 | 0.0645 | 0.1032 | 0.0863 |
| | wR2 = 0.808 | wR2 = 0.087 | wR2 = 0.1231 | wR2 = 0.1066 |
| final R indices [I > 2σ(I)] | R1 = 0.0350 | 0.0379 | 0.0503 | 0.0457 |
| | wR2 = 0.0724 | wR2 = 0.0778 | wR2 = 0.1021 | wR2 = 0.0913 |
| GoF on F² | 1.024 | 1.027 | 1.012 | 1.004 |
| larg. diff. peak/hole, e Å⁻³ | 0.603, -0.451 | 0.398, -0.337 | 0.626, -0.639 | 0.374, -0.409 |
Table 2. Crystal Structure Data for Ti4, Ti5, Ti6 and Ti7a including CCDC deposition numbers.

|                | Ti4a         | Ti5         | Ti6          | Ti7a         |
|----------------|--------------|-------------|--------------|--------------|
| CCDC           | 1878078      | 1878080     | 1878087      | 1878083      |
| empirical formula | C₄₄H₅₀ClPTi | C₂₈H₃₉ClOTi | C₃₈H₴₃ClFeOTi | C₄₈H₵₅ClNTi |
| formula mass   | 693.16       | 474.94      | 630.90       | 729.28       |
| cryst. dimens. mm | 0.5 x 0.1 x 0.04 | 0.25 x 0.2 x 0.1 | 0.5 x 0.35 x 0.2 | 0.25 x 0.2 x 0.1 |
| color, habit    | red, plate   | yellow, block | gold, block | red, plate |
| cryst. system   | monoclinic   | monoclinic  | monoclinic  | monoclinic  |
| spacegroup      | P2₁/n        | P2₁/c       | P2₁/n        | P2₁/c        |
| a, Å            | 11.1056(7)   | 15.3372(6)  | 24.5582(8)   | 19.3414(12)  |
| b, Å            | 23.4726(15)  | 10.9430(4)  | 12.4675(4)   | 14.1248(8)   |
| c, Å            | 15.0706(9)   | 16.0438(6)  | 29.5762(10)  | 14.6035(9)   |
| α, deg          | 90           | 90          | 90           | 90           |
| β, deg          | 111.418(4)   | 117.7388(16)| 97.9499(15)  | 95.2913(19)  |
| γ, deg          | 90           | 90          | 90           | 90           |
| V, Å³           | 3657.3(4)    | 2383.26(16) | 8968.6(5)    | 3972.6(4)    |
| Z               | 4            | 4           | 12           | 4            |
| Dcalcd., g cm⁻³ | 1.259        | 1.324       | 1.402        | 1.219        |
| µ, mm⁻¹         | 0.381        | 0.490       | 0.870        | 0.317        |
| F(000)          | 1472         | 1016        | 3984         | 1556         |
| T, K            | 100(2)       | 100(2)      | 100(2)       | 250(2)       |
| θ range, deg    | 1.691, 27.103| 1.500, 36.313| 1.390, 33.728| 1.788, 30.033|
| no. of rflns collected | 41847   | 190670      | 325667       | 138193       |
| no. of indep. rflns (R(int)) | 7931 (0.1125) | 11567 (0.0300) | 35811 (0.0311) | 11627 (0.0454) |
| no. of rflns with I > 2σ(I) | 4979   | 10348       | 29650        | 8768         |
| abs. cor.       | semi-empirical | numerical  | numerical   | semi-empirical |
| max., min. transmission | 1.0000, 0.7850 | 0.9461, 0.8754 | 0.8591, 0.6897 | 1.0000, 0.9728 |
| no. of data / restraints / param. | 7931 / 0 / 433 | 11567 / 0 / 286 | 35811 / 0 / 1154 | 11627 / 0 / 469 |
| R indices (all data) | R₁ = 0.1071, R₂ = 0.1257 | R₁ = 0.333, R₂ = 0.0815 | R₁ = 0.0535, R₂ = 0.1031 | R₁ = 0.0621, R₂ = 0.1173 |
| final R indices [I > 2σ(I)] | R₁ = 0.0521, R₂ = 0.1054 | R₁ = 0.0282, R₂ = 0.0783 | R₁ = 0.0407, R₂ = 0.0972 | R₁ = 0.0413, R₂ = 0.1034 |
| GoF on F²      | 0.994        | 1.054       | 1.114        | 1.034        |
| largest diff. peak / hole, e Å⁻³ | 0.461, -0.512 | 0.625, -0.352 | 0.649, -0.453 | 0.641, -0.435 |
Table 3. Crystal Structure Data for Ti8, Ti9 and Ti10 including CCDC deposition numbers.

|                | Ti8            | Ti9            | Ti10           |
|----------------|----------------|----------------|----------------|
| CCDC           | 1878086        | 1878084        | 1878088        |
| empirical formula | C₃₆H₄₂ClFeNTi | C₃₂H₃₇Cl₂NTi  | C₅₄H₇₂Cl₂N₂Ti₂ |
| formula mass   | 627.90         | 554.42         | 915.83         |
| cryst. dimens. mm | 0.28 x 0.14 x 0.1 | 0.25 x 0.2 x 0.1 | 0.2 x 0.16 x 0.06 |
| color, habit   | dark red, block | red, block     | red, plate     |
| cryst. system  | triclinic      | triclinic      | monoclinic     |
| spacegroup     | P-1            | P-1            | P2₁/c          |
| a, Å           | 12.7436(6)     | 8.5146(8)      | 19.1941(19)    |
| b, Å           | 14.4570(6)     | 9.1320(8)      | 13.7102(14)    |
| c, Å           | 17.8069(8)     | 18.4129(16)    | 17.3682(17)    |
| α, deg         | 78.073(2)      | 96.864(2)      | 90             |
| β, deg         | 76.896(2)      | 103.334(2)     | 92.125(3)      |
| γ, deg         | 72.7816(19)    | 99.262(2)      | 90             |
| V, Å³          | 3017.5(2)      | 1356.5(2)      | 4567.4(8)      |
| Z              | 4              | 2              | 4              |
| \(D_{calcd.}\), g cm⁻³ | 1.382          | 1.357          | 1.332          |
| \(\mu\), mm⁻¹ | 0.860          | 0.535          | 0.506          |
| F(000)         | 1320           | 584            | 1952           |
| T, K           | 100(2)         | 100(2)         | 100(2)         |
| \(\theta\) range, deg | 1.492, 32.031  | 2.290, 32.031  | 1.826, 30.032  |
| no. of rflns collected | 96449          | 58216          | 136093         |
| no. of indep. rflns (R(int)) | 20997 (0.0498) | 9443 (0.0355)  | 13367 (0.0670) |
| no. of rflns with \(I > 2\sigma(I)\) | 16611          | 7866           | 9853           |
| abs. cor.      | semi-empirical | semi-empirical | semi-empirical |
| max., min. transmission | 1.0000, 0.9193 | 1.0000, 0.8859 | 1.0000, 0.9340 |
| no. of data / restraints / param. | 20997 / 0 / 737 | 9443 / 0 / 333 | 13367 / 0 / 558 |
| R indices (all data) | R₁ = 0.0716 | R₁ = 0.0456 | R₁ = 0.0655 |
|                | wR₂ = 0.1501   | wR₂ = 0.0888   | wR₂ = 0.1091   |
| final R indices \([I > 2\sigma(I)]\) | R₁ = 0.0546 | R₁ = 0.0340 | R₁ = 0.041 |
|                | wR₂ = 0.1382   | wR₂ = 0.0825   | wR₂ = 0.0961   |
| GoF on \(F^2\) | 1.015          | 1.076          | 1.033          |
| largest diff. peak / hole, e Å⁻³ | 3.186, -1.473 | 0.606, -0.470 | 0.718, -0.481 |
**Figure S1.** Molecular structure of Zr2a-benzo.

**Figure S2.** Molecular structure of Zr2b.

**Figure S3.** Molecular structure of Zr2b-benzo.

**Figure S4.** Molecular structure of Ti2b.

**Figure S5.** Molecular structure of Ti4a.

**Figure S6.** Molecular structure of Ti5.
Figure S7. Molecular structure of Ti6.

Figure S8. Molecular structure of Ti7a.

Figure S9. Molecular structure of Ti8.

Figure S10. Molecular structure of Ti9.

Figure S11. Molecular structure of Ti10.
NMR Spectra of Compounds:

**Figure S12.** $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P{$^1$H}-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Ti2a; 0.89, 1.24 ppm: $n$-hexane.

**Figure S13.** $^{13}$C{$^1$H}-NMR spectrum of Ti2a (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: $n$-hexane.
Figure S14. $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P($^1$H)-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Ti2b; 0.89, 1.24 ppm: $n$-hexane.

Figure S15. $^{13}$C($^1$H)-NMR spectrum of Ti2b (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: $n$-hexane.
Figure S16. $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P($^1$H)-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Ti2c; 0.89, 1.24 ppm: $n$-hexane.

Figure S17. $^{13}$C($^1$H)-NMR spectrum of Ti2c (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: $n$-hexane.
Figure S18. $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P($^1$H)-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Ti$_2$d; 0.89, 1.24 ppm: $n$-hexane.

Figure S19. $^{13}$C($^1$H)-NMR spectrum of Ti$_2$d (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: $n$-hexane.
Figure S20. $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P{$^1$H}-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Ti2e; 0.89, 1.24 ppm: $n$-hexane.

Figure S21. $^{13}$C{$^1$H}-NMR spectrum of Ti2e (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: $n$-hexane.
Figure S22. $^{15}$N/$^1$H-HMBC-NMR spectrum of Ti2e (51 MHz, C$_6$D$_6$, rt).
Figure S23. $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P($^1$H)-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Zr$_2$a; 0.89, 1.24 ppm: n-hexane.

Figure S24. $^{13}$C($^1$H)-NMR spectrum of Zr$_2$a (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: n-hexane.
Figure S25. $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P{$^1$H}-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Zr$_2$b; 0.89, 1.24 ppm: n-hexane.

Figure S26. $^{13}$C{$^1$H}-NMR spectrum of Zr$_2$b (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: n-hexane.
Figure S27. $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P($^1$H)-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Zr2b-benzo; 0.89, 1.24 ppm: n-hexane.

Figure S28. $^{13}$C($^1$H)-NMR spectrum of Zr2b-benzo (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: n-hexane.
Figure S29. $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P($^1$H)-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Zr$_2$c; 0.89, 1.24 ppm: n-hexane.

Figure S30. $^{13}$C($^1$H)-NMR spectrum of Zr$_2$c (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: n-hexane.
Figure S31. $^1$H-NMR (500 MHz, C$_6$D$_6$, rt) and $^{31}$P($^1$H)-NMR spectrum (202 MHz, C$_6$D$_6$, rt) of Ti4a with Ti4b; #: Ti4b.

Figure S32. $^{13}$C($^1$H)-NMR spectrum of Ti4a with Ti4b (125 MHz, C$_6$D$_6$, rt).
Figure S33. $^1$H-NMR spectrum of Ti4b (500 MHz, C₆D₆, rt).

Figure S34. $^{13}$C($^1$H)-NMR spectrum of Ti4b (125 MHz, C₆D₆, rt); 14.3, 23.0, 32.0 ppm: $n$-hexane.
Figure S35. $^1$H-NMR spectrum of Ti5 (500 MHz, C$_6$D$_6$, rt).

Figure S36. $^{13}$C($^1$H)-NMR spectrum of Ti5 (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: n-hexane.
Figure S37. $^1$H-NMR spectrum of Ti6 (500 MHz, C$_6$D$_6$, rt): 0.89, 1.24 ppm: $n$-hexane.

Figure S38. $^{13}$C($^1$H)-NMR spectrum of Ti6 (125 MHz, C$_6$D$_6$, rt): 14.3, 23.0, 32.0 ppm: $n$-hexane.
Figure S39. $^1$H-NMR spectrum of Ti7 (500 MHz, C$_6$D$_6$, rt): 0.89, 1.24 ppm: n-hexane.

Figure S40. $^{13}$C($^1$H)-NMR spectrum of Ti7 (125 MHz, C$_6$D$_6$, rt).
Figure S41. $^{15}$N/$^1$H-HMBC-NMR spectrum of Ti7 (51 MHz, C$_6$D$_6$, rt).
Figure S42. $^1$H-NMR spectrum of Ti7a (500 MHz, C$_6$D$_6$, rt): 0.89, 1.24 ppm: n-hexane.

Figure S43. $^{13}$C($^1$H)-NMR spectrum of Ti7a (125 MHz, C$_6$D$_6$, rt).
Figure S44. $^{15}$N/$^1$H-HMQC-NMR spectrum of Ti7a (51 MHz, C₆D₆, rt).

Figure S45. $^{15}$N/$^1$H-HMBC-NMR spectrum of Ti7a (51 MHz, C₆D₆, rt).
Figure S46. $^1$H-NMR spectrum of Ti8 (500 MHz, C$_6$D$_6$, rt): 0.89, 1.24 ppm: n-hexane.

Figure S47. $^{13}$C($^1$H)-NMR spectrum of Ti7a (125 MHz, C$_6$D$_6$, rt); 14.3, 23.0, 32.0 ppm: n-hexane.
Figure S48. $^{15}$N/$^1$H-HMQC-NMR spectrum of Ti8 (51 MHz, C$_6$D$_6$, rt).
Figure S49. $^1$H-NMR spectrum of Ti9 (500 MHz, C$_6$D$_6$, rt): 0.89, 1.24 ppm: $n$-hexane.

Figure S50. $^{13}$C($^1$H)-NMR spectrum of Ti9 (125 MHz, C$_6$D$_6$, rt): 14.3, 23.0, 32.0 ppm: $n$-hexane.
Figure S51. $^{15}$N/$^{1}$H-HMQC-NMR spectrum of Ti9 (51 MHz, C$_{6}$D$_{6}$, rt).

Figure S52. $^{15}$N/$^{1}$H-HMBC-NMR spectrum of Ti9 (51 MHz, C$_{6}$D$_{6}$, rt).
Temperature-dependent NMR Spectra of Ti4a and Ti4b

Figure S53. Temperature-dependent $^1$H-NMR spectrum of Ti4a (red) with Ti4b (blue) (500 MHz, toluene-d$_8$).

Figure S54. Temperature-dependent $^{31}$P{$^1$H} NMR spectrum of Ti4a (red) with Ti4b (blue) (202 MHz, toluene-d$_8$).
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