

Supporting Information

Synthesis of $[(\pi\text{-Pcyano-nacnac})\text{Cp}]$ and $[(\pi\text{-cyanoP-nacnac})\text{Cp}]$ zirconium Complexes, and their Remote Activation for Ethylene Polymerization

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Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from *Aldrich* unless otherwise specified. Ethylene was purchased from *Matheson Tri-Gas* (research grade, 99.99 % pure). Toluene, THF, ether and pentane were distilled from benzophenone ketyl. All polymerization reactions were carried out in a Parr autoclave reactor as described below. Toluene for polymerization was distilled from sodium benzophenone. The following instruments were used for the physical characterization of the compounds. NMR: *Varian Inova* 500 (^1H : 500 MHz, ^{13}C : 126 MHz, ^{19}F : 470 MHz, ^{11}B : 160 MHz), *Bruker Unity Plus* 600 (^1H : 600 MHz, ^{31}C : 151 MHz, ^{19}F : 564 MHz, ^{11}B : 64 MHz) and *Bruker Advance* 400. Most NMR assignments were supported by additional 2D experiments. FT-IR spectra were recorded on a Bruker Vector-22 Spectrophotometer using KBr pellets, and in solution using C_6D_6 as solvent. X-ray crystal structure analyses: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, 276, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski & W. Minor, *Acta Cryst.* **2003**, A59, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, A46, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122), graphics XP (BrukerAXS, 2000). Graphics show the thermal ellipsoids with 50 % probability, R values are given for the observed reflections, wR^2 values for all reflections.

Typical Homopolymerization of Ethylene.

Polymerizations were carried out in a Parr autoclave reactor (100 mL), loaded inside a glovebox with an appropriate amount (6.8 μmol) of the pre-catalyst (**3**, **4**, **6** or **7**) and the corresponding MAO with toluene, such that the final volume of the toluene solution was 30 mL. The reactor was sealed inside the glovebox (when is indicated, MAO was put into the addition funnel). The reactor was attached to an ethylene line and the gas was fed continuously into the reactor to the pressures of 12.5 bar. The pressurized reaction mixture was stirred at temperature of 75 °C. After 10 min, the ethylene was vented and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried overnight.

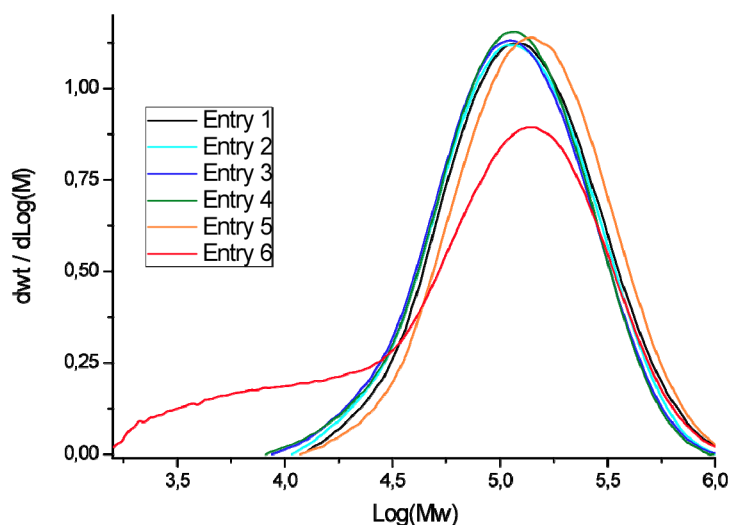
Polymer Characterization.

Polymers were dried overnight under vacuum and the polymerization activities calculated from the mass of product obtained. These values were to within 5% of the calculated mass determined by measuring the ethylene consumed by use of a mass flow controller.

The polymers were characterized by Gel Permeation Chromatography (GPC). GPC analysis was performed on a Waters Alliance GPC 2000 system equipped with a refractive index detector. Samples were run at 150 °C in spectrophotometric grade 1,2,4-trichlorobenzene (TCB), stabilized with BHT (0.5 g BHT / 4 L solvent). Molecular weights were calculated by using a universal calibration from narrow polystyrene standards in the molecular weight range of 580 to 7.5 million g/mol. Mark-Houwink parameters of $a = 0.7$ and $k = 47.7$ were utilized to correct for polyethylene.

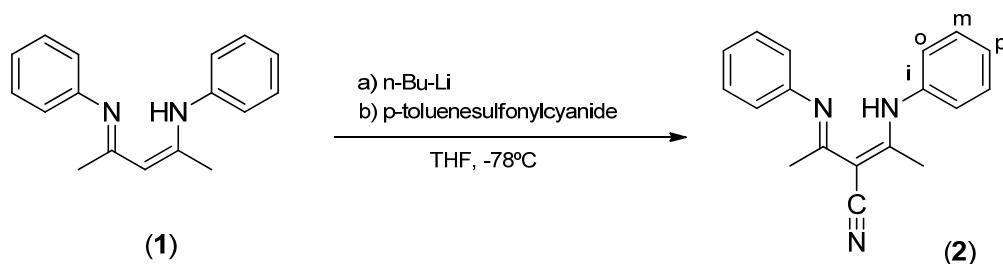
Polymer melting points were measured on a TA Instruments differential scanning calorimeter (model DSC 2920) at a rate of 10 °C/min for two cycles in the temperature range of 25-200 °C.

Figure S-1. GPC traces of polymers produced using complexes **3** and **4**. Additional information related to one included in Table 1 of the manuscript.



Synthesis and Characterization of Compounds.

3-Cyano-2-(phenyl)aminopent-2-en-4-(phenyl)imine (**2**)



n-BuLi (5.7mL, 1.6M, 9.0mmol) was added drop-wise to a stirred solution of 2-(phenyl)aminopent-2-en-4-(phenyl)imine (**1**) [S. G. McGeachin, Canadian Journal of Chemistry (1968), 46(11), 1903-1912] in THF (30 mL) (1.6 g, 6.5 mmol) at -78 °C. The reaction was allowed to warm to room temperature over 2 hours to afford the lithium salt. The resulting yellow suspension was then cooled to -78 °C, and p-toluenesulfonyl cyanide (1.4 g, 7.7 mmol) in THF (20 mL) was added. The reaction mixture was again allowed to warm to room temperature over 24 hours. From this mixture, all volatiles were removed under vacuum, and the residue was dissolved in

CH₂Cl₂ (50 mL). This was washed with Brine (2 × 100 mL), dried over Na₂SO₄ and filtered. The solvent was subsequently removed under vacuum to yield light brown solid. Precipitation from methanol provided light yellow solid of 3-cyano-2-(phenyl)aminopent-2-en-4-(phenyl)imine (**2**) in 70 % yield (1.23g, 4.5mmol).

¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ/ppm = 14.42 (s, 1H, NH), 7.36 (t, 4H, *m*-Ph), 7.18 (t, 2H, *p*-Ph), 6.99 (d, 4H, *o*-Ph), 2.27 (s, 6H, N=CMe^{Ph}).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ/ppm = 165.8 (C=N^{Ph}), 144.1 (*i*-Ph), 129.6 (*m*-Ph), 125.7 (*p*-Ph), 123.9 (*o*-Ph), 122.2 (C≡N), 82.3 (C^{CN}), 19.9 (N=CMe^{Ph}).

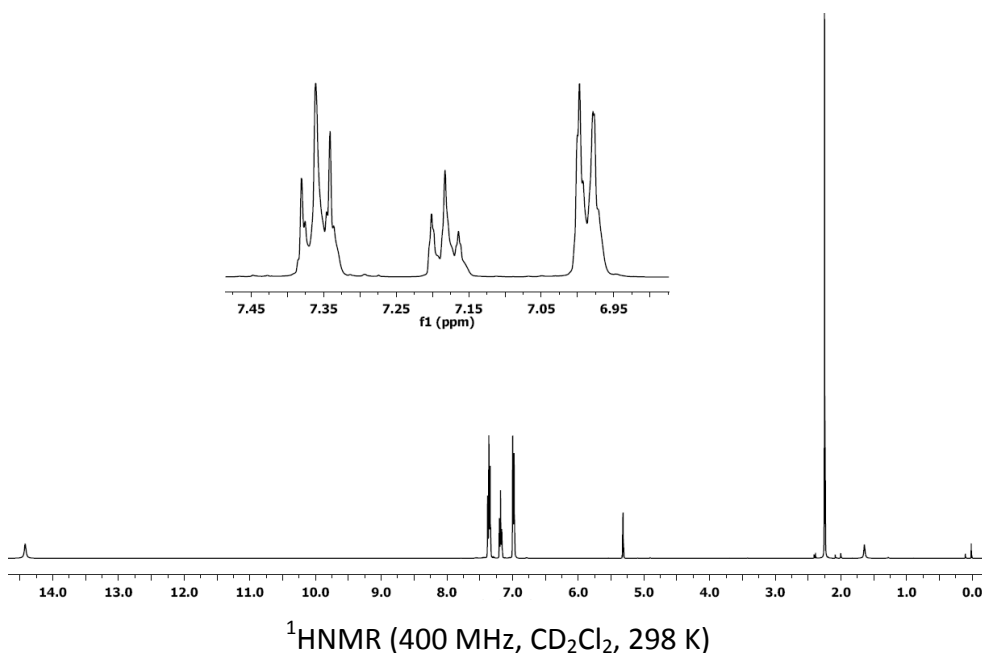
¹H, ¹³C-GHMBC (400 MHz / 100 MHz, CD₂Cl₂, 298 K): δ¹H / δ¹³C = 7.36 / 144.1 (*m*-Ph / *i*-Ph), 2.25 / 165.8, 82.3 (Me^{Ph} / C=N^{Ph}, C^{CN}).

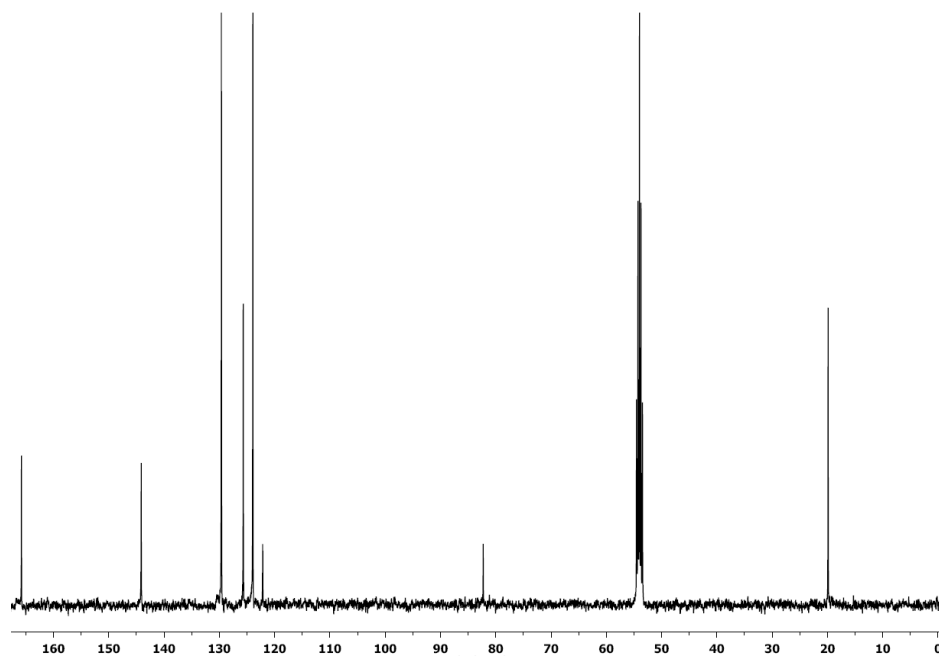
¹H, ¹³C-GHSQC (400 MHz / 100 MHz, CD₂Cl₂, 298 K): δ¹H / δ¹³C = 7.36 / 129.6 (*m*-Ph / *m*-Ph), 7.18 / 125.7 (*p*-Ph / *p*-Ph), 6.99 / 123.9 (*o*-Ph / *o*-Ph), 2.25 / 19.9 (Me^{Ph} / Me^{Ph}).

GCOSY (400 MHz / 400 MHz, CD₂Cl₂, 298 K): δ¹H / δ¹H = 7.36 / 6.99 (*m*-Ph / *o*-Ph), 7.36 / 7.18 (*m*-Ph / *p*-Ph).

IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 3456, 3064, 2965, 2919, 2783, 2190 (ν(C≡N), s), 1613, 1592, 1561, 1490, 1466, 1449, 1429, 1368, 1294, 1224, 1173, 1152, 1072, 1044, 1025, 971, 915, 852, 843, 813, 777, 760, 725, 697, 633, 617, 591, 513.

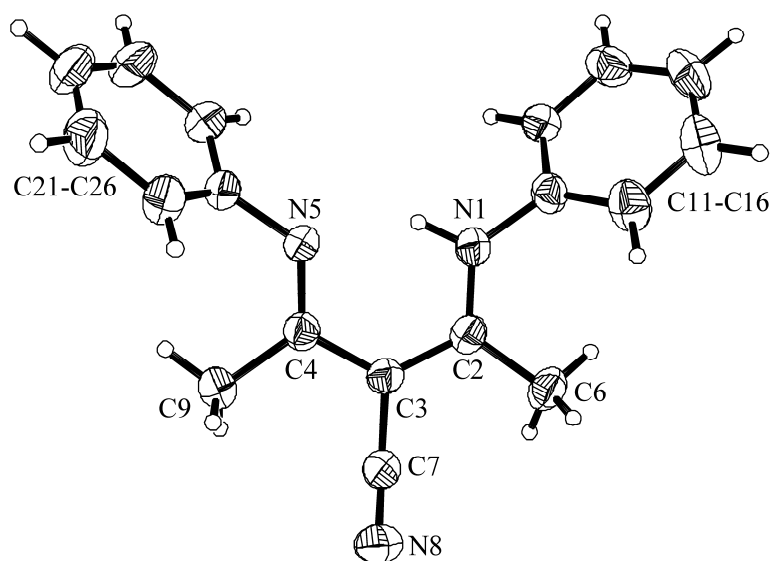
Elemental analysis (%) C₁₈H₁₇N₃ (M = 275.35 g/mol): calculated C 78.52, H 6.22, N 15.26; found C 78.36, H 6.15, N 15.30.



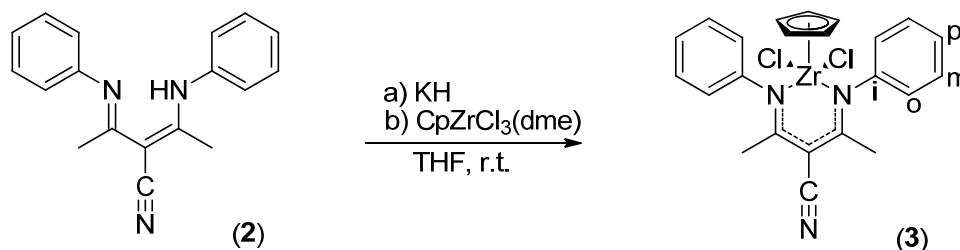


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 298 K)

X-ray crystal structure analysis of **2**: Crystal data for $\text{C}_{18}\text{H}_{17}\text{N}_3$, $M = 275.35$, triclinic, $P1bar$ (No. 2), $a = 11.3372(2)$, $b = 11.4394(2)$, $c = 13.2279(3)$ Å, $\alpha = 90.974(1)$, $\beta = 109.646(1)$, $\gamma = 110.002(1)^\circ$, $V = 1501.23(5)$ Å³, $D_c = 1.218$ g cm⁻³, $\mu = 0.074$ mm⁻¹, $F(000) = 584$, $Z = 4$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, 13598 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å⁻¹, 6933 independent ($R_{\text{int}} = 0.045$), and 5590 observed reflections [$I \geq 2\sigma(I)$], 389 refined parameters, $R = 0.063$, $wR^2 = 0.149$, $\text{GoF} = 1.063$.



[[3-Cyano-2-(phenyl)aminopent-2-en-4-(phenyl)imine]](η^5 -C₅H₅)ZrCl₂ (3**)**



3-Cyano-2-(phenyl)aminopent-2-en-4-(phenyl)imine (**2**) (100 mg, 0.36 mmol) and KH (22 mg, 0.54 mmol) were stirred in THF for 12 hours. The reaction showed rapid gas evolution. The slightly cloudy mixture was filtered through Celite and added dropwise to CpZrCl₃(dme) (116 mg, 0.33 mmol) in THF. The reaction mixture was stirred for 12 hours. The resulting yellow solution was filtered over Celite. The solvent volume was reduced, pentane and ether were added separately to wash the solid. A light brown powder corresponding to compound **3** was isolated in 84 % yield (153 mg, 0.31mmol).

¹H NMR (400 MHz, CD₂Cl₂, 298 K) δ /ppm = 7.51 (m, 4H, *m*-Ph), 7.37 (m, 2H, *p*-Ph), 7.12 (broad, 4H, *o*-Ph), 6.19 (s, 5H, Cp), 2.26 (s, 6H, Me).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ = 168.4 (C=N), 148.8 (*i*-Ph), 130.0 (*m*-Ph), 127.3 (*p*-Ph), 123.8 (*o*-Ph), 118.8 (Cp), n.o. (C \equiv N), 74.3 (C^{CN}), 21.3 (Me).

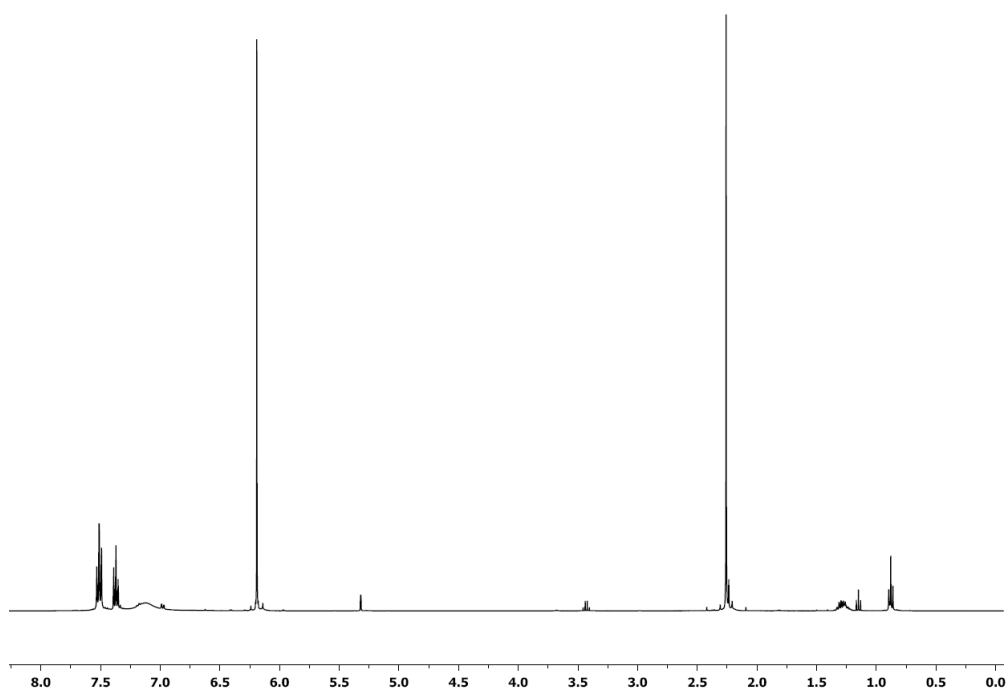
¹H, ¹³C-GHMBC (500 MHz / 126 MHz, CD₂Cl₂, 298 K): $\delta^1\text{H} / \delta^{13}\text{C}$ = 7.51 / 149.0 (*m*-Ph / *i*-Ph), 7.37 / 124.0 (*p*-Ph / *o*-Ph), 2.26 / 168.6, 74.6 (Me^{Ph} / C=N^{Ph}, C^{CN}).

¹H, ¹³C-GHSQC (500 MHz / 126 MHz, CD₂Cl₂, 298 K): $\delta^1\text{H} / \delta^{13}\text{C}$ = 7.51 / 130.2 (*p*-Ph / *p*-Ph), 7.37 / 127.5 (*m*-Ph / *m*-Ph), 7.12 / 124.0 (*o*-Ph / *o*-Ph), 6.19 / 119.0 (Cp / Cp), 2.26 / 21.5 (Me^{Ph} / Me^{Ph}).

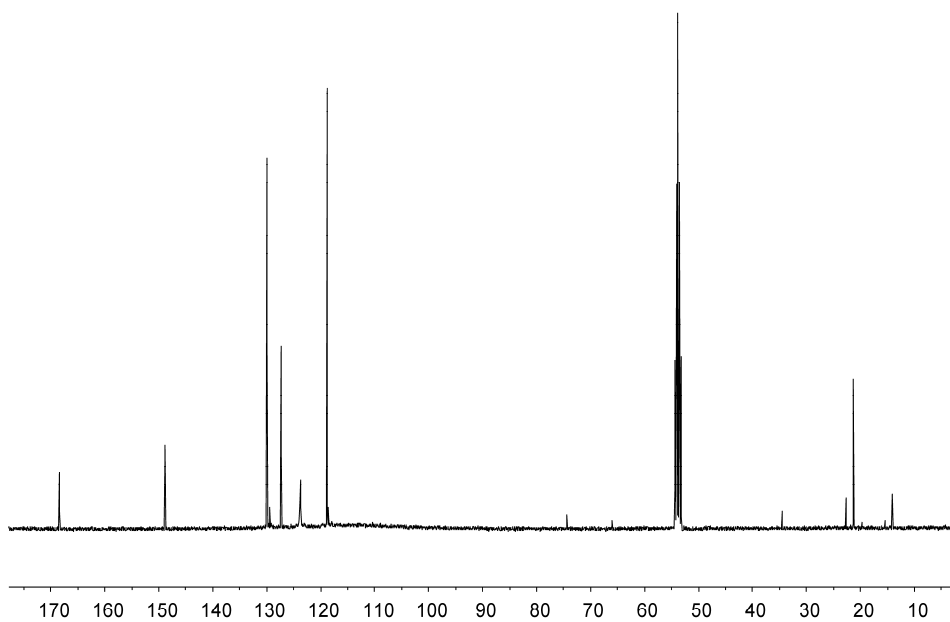
GCOSY (500 MHz / 500 MHz, CD₂Cl₂, 298 K): $\delta^1\text{H} / \delta^1\text{H}$ = 7.51 / 7.37 (*m*-Ph / *p*-Ph), 7.37 / 7.12 (*p*-Ph / *o*-Ph).

IR (KBr): $\tilde{\nu}$ /cm⁻¹ = 3448, 3111, 2921, 2209 (ν (C \equiv N), s), 1567, 1488, 1449, 1423, 1382, 1352, 1244, 1214, 1169, 1156, 1071, 1020, 999, 919, 856, 827, 784, 769, 727, 699, 631, 618, 592, 514.

Elemental analysis (%) C₂₃H₂₁Cl₂N₃Zr (M = 501.56 g/mol): calculated C 55.08, H 4.22, N 8.38; found C 55.03, H 4.36, N 8.05.

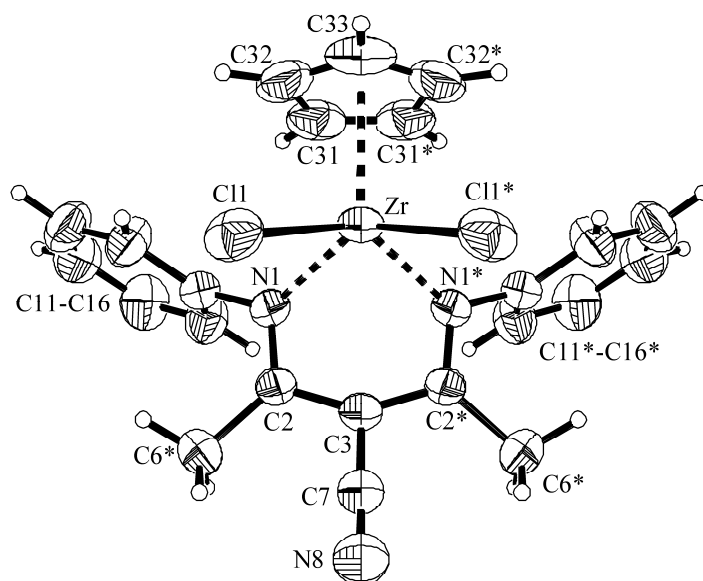


^1H NMR (400 MHz, CD_2Cl_2 , 298 K)



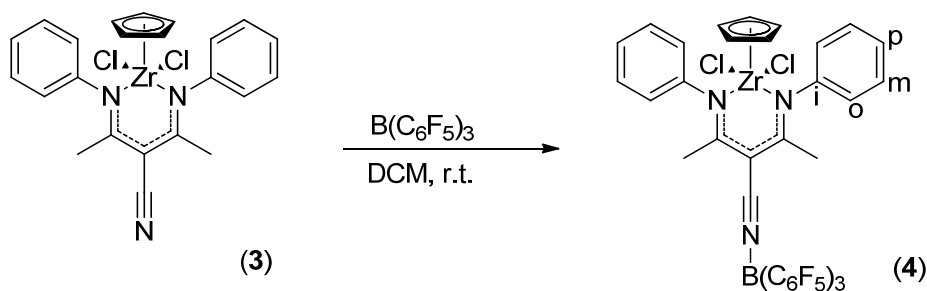
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K)

X-ray crystal structure analysis of **3**: Crystal data for $C_{23}H_{21}Cl_2N_3Zr$, $M = 501.55$, orthorhombic, $Pnma$ (No. 62), $a = 7.6639(1)$, $b = 13.2857(2)$, $c = 25.1922(5)$ Å, $V = 2565.08(7)$ Å³, $D_c = 1.299$ g cm⁻³, $\mu = 0.649$ mm⁻¹, $F(000) = 1016$, $Z = 4$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, 14370 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å⁻¹, 3123 independent ($R_{int} = 0.044$), and 2818 observed reflections [$I \geq 2\sigma(I)$], 140 refined parameters, $R = 0.041$, $wR^2 = 0.119$, $GoF = 1.015$.



[(3-Cyano-2-(phenyl)aminopent-2-en-4-

(phenyl)imine)tris(pentafluorophenyl)borate](η^5 -C₅H₅)ZrCl₂ (4**)**



1 Eq. of tris(pentafluorophenyl)borane (51 mg, 0,099 mmol in 1 mL of DCM) was added to a DCM solution of **3** (50 mg, 0.099 mmol). The reaction mixture was stirred for 1 hour at room temperature, filtered through Celite and the volatiles were removed under vacuum and washed with pentane. Compound **4** was isolated as light yellow solid in 77 % yield (77.8 mg, 0.077 mmol)

¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ/ppm = 7.55 (m, 4H, *m*-Ph), 7.42 (m, 2H, *p*-Ph), 7.14 (broad, 2H, *o*-Ph), 6.19 (s, 5H, Cp), 2.16 (s, 6H, Me).

¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K): δ/ppm = 170.1 (C=N), 148.3 (dm, ¹J_{FC} ~ 241 Hz, C₆F₅), 147.9 (*i*-Ph), 140.6 (dm, ¹J_{FC} ~ 250 Hz, C₆F₅), 137.5 (dm, ¹J_{FC} ~ 250 Hz, C₆F₅), 130.3 (*m*-Ph), 128.0 (*p*-Ph), 123.5 (broad, *o*-Ph), 119.8 (Cp), 116.3 (broad, *i*-C₆F₅), n.o. (C≡N), 69.0 (C^{CN}), 21.7 (Me).

¹H, ¹³C-GHMBC (500 MHz / 126 MHz, CD₂Cl₂, 298 K): δ¹H / δ¹³C = 7.54 / 147.9, 130.3 (*m*-Ph / *i*-Ph, *m*-Ph), 2.15 / 170.3, 69.2 (Me^{Ph} / C=N^{Ph}, C^{CN})

¹H, ¹³C-GHSQC (500 MHz / 126 MHz, CD₂Cl₂, 298 K): δ¹H / δ¹³C = 7.54 / 130.3 (*m*-Ph / *m*-Ph), 7.41 / 128.2 (*p*-Ph / *p*-Ph), 6.17 / 119.9 (Cp / Cp), 2.15 / 21.9 (Me^{Ph} / Me^{Ph}).

GCOSY (500 MHz / 500 MHz, CD₂Cl₂, 298 K): δ¹H / δ¹H = 7.54 / 7.41 (*m*-Ph / *p*-Ph).

¹H{NOE} NMR (500 MHz, CD₂Cl₂, 298 K): δ¹H_{ir} / δ¹H_{res} = 7.54 / 6.17, 2.15 (*m*-Ph / Cp, N^CMe^{Ph}).

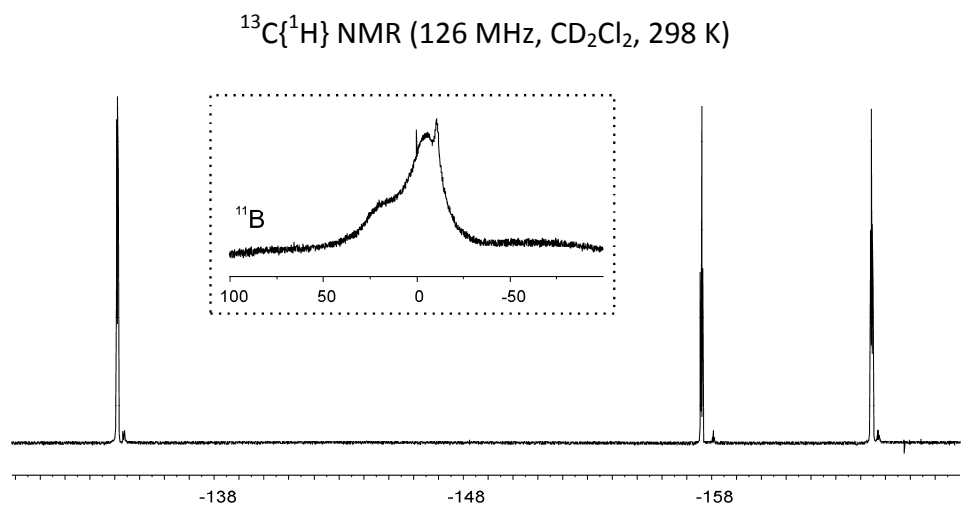
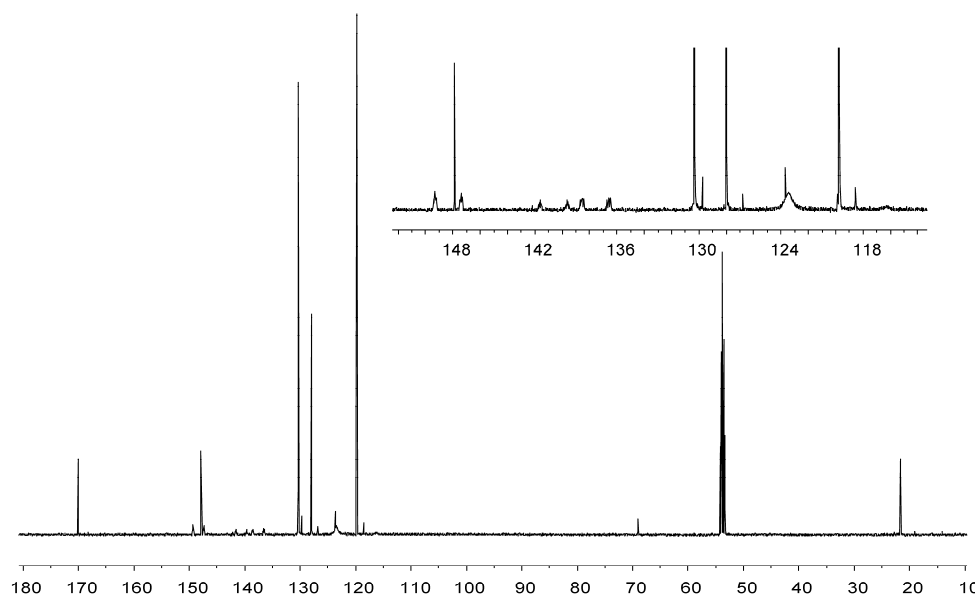
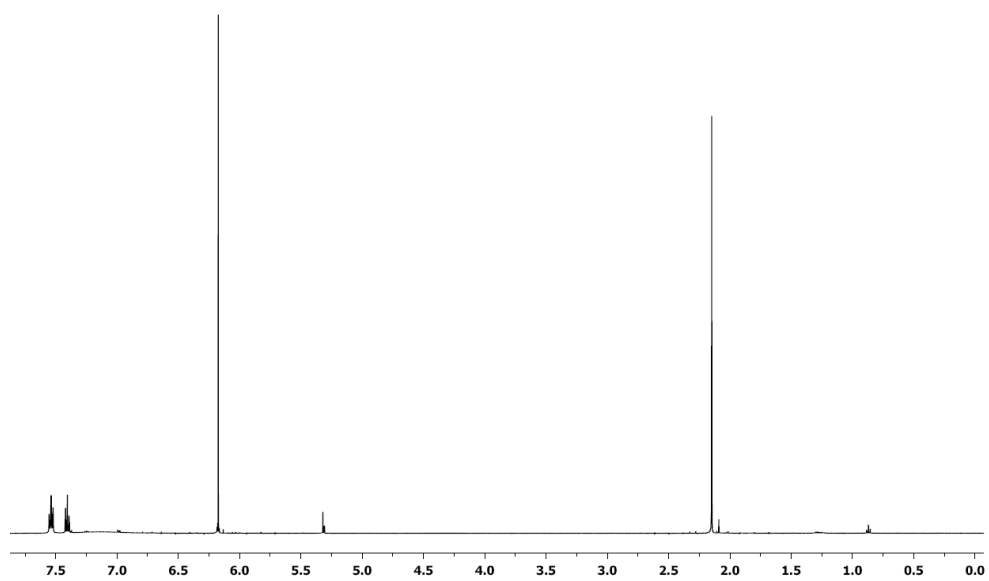
1D TOCSY (500 MHz, CD₂Cl₂, 298 K): δ¹H_{ir} / δ¹H_{res} [ppm] = 7.54 / 7.41, 7.15 (*m*-Ph / *p*-, *o*-Ph), 7.41 / 7.54 (*p*-Ph / *m*-Ph).

¹⁹F NMR (470 MHz, CD₂Cl₂, 298 K): δ/ppm = -134.1 (m, 2F, *o*-C₆F₅), -157.6 (t, ³J_{FF} = 20.3 Hz, 1F, *p*-C₆F₅), -164.4 (m, 2F, *m*-C₆F₅).

¹¹B{¹H} NMR (160 MHz, CD₂Cl₂, 298 K): -10.6 ppm (ν_{1/2} ~ 300 Hz)

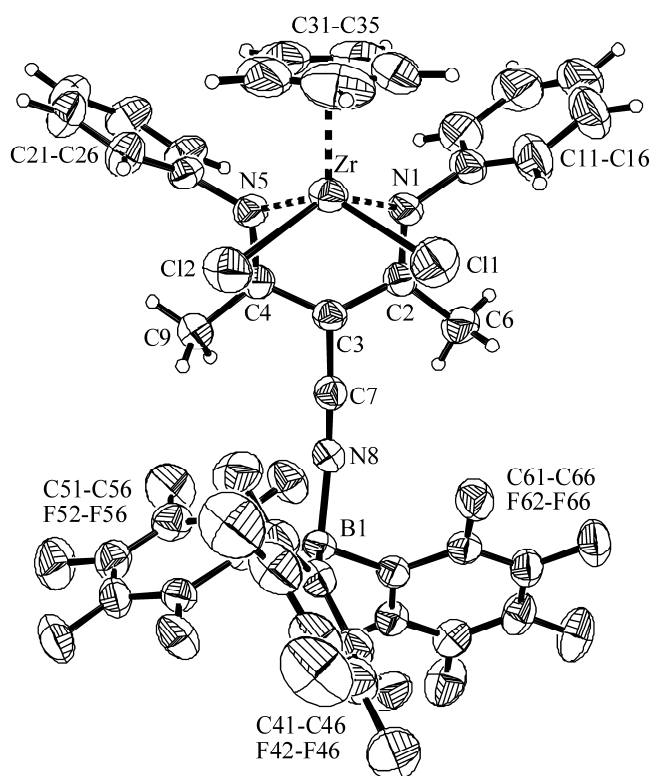
IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 3107, 2927, 2261 (ν(C≡N), s), 1646, 1615, 1573, 1518, 1470, 1383, 1287, 1103, 979, 827, 775, 737, 693.

Elemental analysis (%) C₄₁H₂₁Cl₂F₁₅N₃Zr (M = 1013.54 g/mol): calculated C 48.59, H 2.09, N 4.15; found C 48.73, H 2.18, N 4.03.

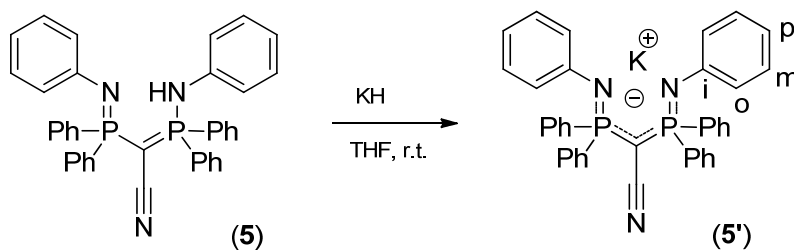


^{19}F NMR (470 MHz, CD_2Cl_2 , 298 K) and $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CD_2Cl_2 , 298 K)

X-ray crystal structure analysis of **4**: Crystal data for $C_{41}H_{21}BCl_2F_{15}N_3Zr \cdot C_5H_{12}$, $M = 1085.68$, triclinic, $P1bar$ (No. 2), $a = 10.7744(2)$, $b = 12.2695(3)$, $c = 18.4381(4)$ Å, $\alpha = 101.946(1)$, $\beta = 99.864(1)$, $\gamma = 91.168(2)^\circ$, $V = 2345.47(9)$ Å³, $D_c = 1.537$ g cm⁻³, $\mu = 0.445$ mm⁻¹, $F(000) = 1088$, $Z = 2$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, 20491 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å⁻¹, 10883 independent ($R_{int} = 0.047$), and 9090 observed reflections [$I \geq 2\sigma(I)$], 615 refined parameters, $R = 0.067$, $wR^2 = 0.175$, GoF = 1.096.



[Bis(N-phenyl-diphenylphosphinimino)acetonitrile] potassium (5')



Preparation of the Potassium Salt 5'. Compound **5** (100 mg, 0.17 mmol) and KH (15 mg, 0.37 mmol) were stirred in THF for 6 h. The reaction showed rapid gas evolution. The slightly cloudy mixture was filtered through Celite and THF was removed under vacuum, washed with pentane and dry under vacuum. A dark yellow powder corresponding to compound **5'**× **1THF** was isolated in 86% yield (102mg, 0.15mmol).

¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ/ppm = 7.74 (m, 4H, *o*-Ph^P), 7.33 (m, 2H, *p*-Ph^P), 7.24 (m, 4H, *m*-Ph^P), 6.87 (m, 2H, *m*-Ph^N), 6.53 (m, 1H, *p*-Ph^N), 6.38 (m, 2H, *o*-Ph^N), 3.66 (m, 6H, THF), 1.81 (m, 6H, THF).

¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K): δ / ppm = 152.6 (broad, *i*-Ph^N), 135.4 (broad m, *i*-Ph^P), 134.6 (Br, *i*-Ph^P), 132.6 (m, *o*-Ph^P), 131.0 (broad, *p*-Ph^P), 129.5 (*m*-Ph^N), 128.4 (m, *m*-Ph^P), 122.9 (broad, *o*-Ph^N), 117.1 (broad, *p*-Ph^N), 68.1 (THF), 25.9 (THF), n.o. (C^{CN}, CN).

GCOSY (500 MHz / 500 MHz, CD₂Cl₂, 298 K): δ¹H / δ¹H = 7.74 / 7.24 (*o*-Ph^P / *m*-Ph^P), 7.33 / 7.24 (*p*-Ph^P / *m*-Ph^P), 6.87 / 6.53, 6.38 (*m*-Ph^N / *o*-Ph^N, *p*-Ph^N).

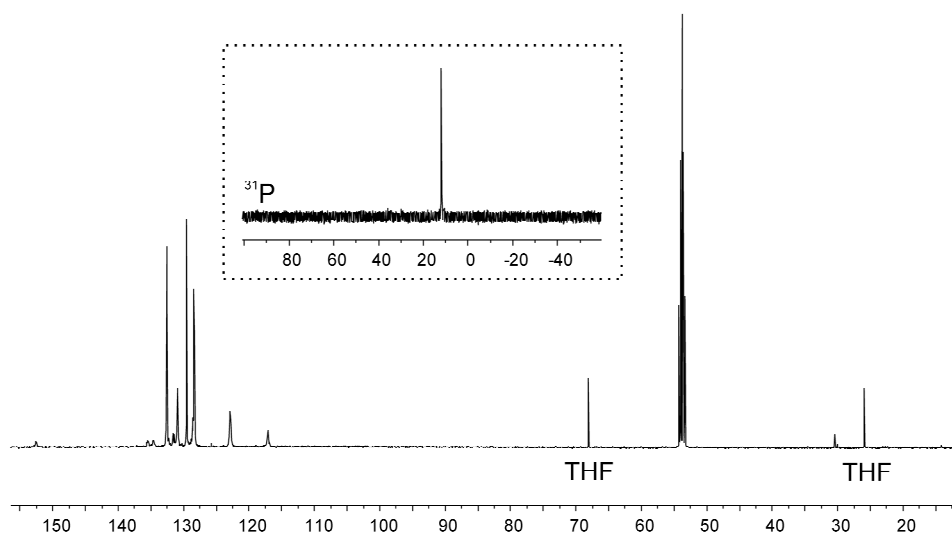
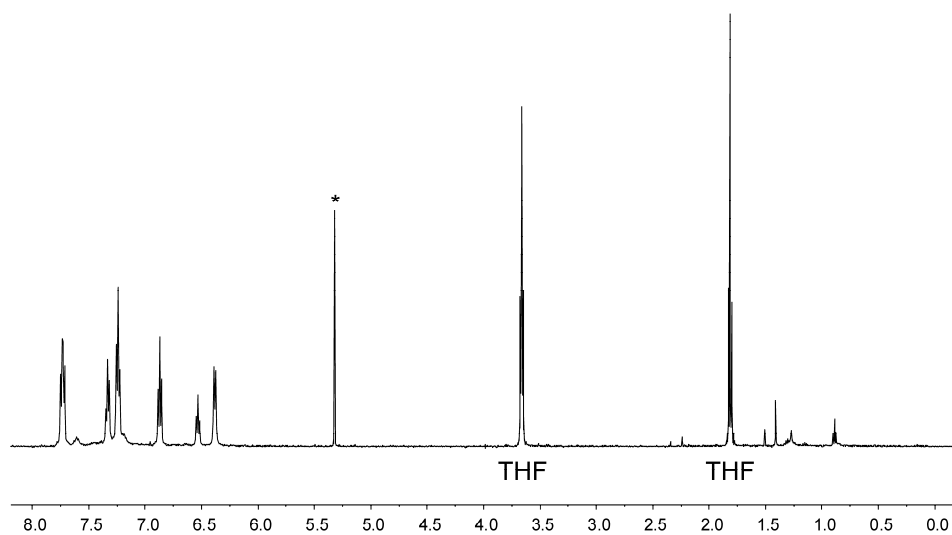
¹H, ¹³C-GHSQC (500 MHz / 126 MHz, CD₂Cl₂, 298 K): δ¹H / δ¹³C = 7.74 / 132.6 (*o*-Ph^P), 7.33 / 130.9 (*p*-Ph^P), 7.24 / 128.4 (*m*-Ph^P), 6.87 / 129.5 (*m*-Ph^N), 6.38 / 122.9 (*o*-Ph^N).

1D-TOCSY (500 MHz, CD₂Cl₂, 298 K): δ¹H_{ir} / δ¹H_{res} = 7.74 / 7.33, 7.24 (*o*-Ph^P / *p*-Ph^P, *m*-Ph^P), 7.33 / 7.74, 7.24 (*p*-Ph^P / *o*-Ph^P, *m*-Ph^P), 7.24 / 7.74, 7.33 (*m*-Ph^P / *o*-Ph^P, *p*-Ph^P), 6.87 / 6.53, 6.38 (*m*-Ph^N / *p*-Ph^N, *o*-Ph^N), 6.53 / 6.38 (*p*-Ph^N / *o*-Ph^N), 6.38 / 6.87, 6.53 (*o*-Ph^N / *m*-Ph^N, *p*-Ph^N).

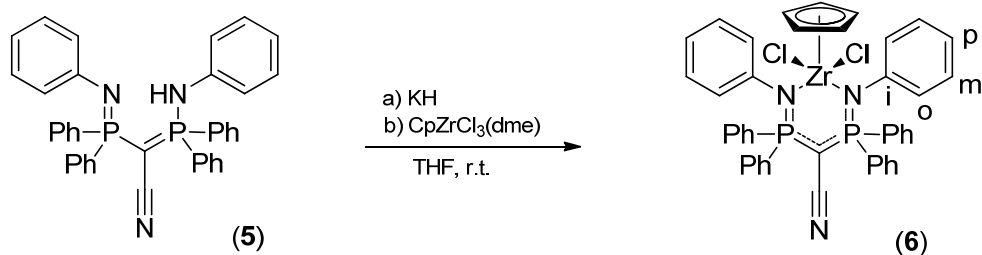
¹H{NOE} NMR (500 MHz, CD₂Cl₂, 298 K) [selected experiments]: δ¹H_{ir} / δ¹H_{res} = 7.74 / 7.24, 6.38 (*o*-Ph^P / *m*-Ph^P, *o*-Ph^N), 7.24 / 7.74 (*m*-Ph^P / *o*-Ph^P), 6.87 / 6.53, 6.38 (*m*-Ph^N / *p*-Ph^N, *o*-Ph^N), 6.53 / 6.87 (*p*-Ph^N / *m*-Ph^N), 6.38 / 7.74, 6.87 (*o*-Ph^N / *o*-Ph^P, *m*-Ph^N).

³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): δ / ppm = 12.0 (ν_{1/2} ~ 30 Hz).

IR (KBr): ν̄/cm⁻¹ = 3051, 2976, 2929, 2868, 2134 (ν(C≡N), s), 1588, 1559, 1480, 1435, 1306, 1263, 1176, 1104, 1038, 1013, 878.



[Bis(N-phenyl-diphenylphosphinimino)acetonitrile](η^5 -C₅H₅)ZrCl₂ (6**)**



Bis(N-phenylphosphinimino)acetonitrile (**5**) [L. Braun, G. Kehr, R. Fröhlich, G. Erker, *Inorg. Chim. Acta*, 2008, 361(6), 1668-1675]. (50 mg, 0.085 mmol) and KH (5 mg, 0.13 mmol) were stirred in CH₂Cl₂ for 12 hours. The reaction showed rapid gas evolution. The slightly cloudy mixture was filtered through Celite and added dropwise to CpZrCl₃(dme) (30 mg, 0.085 mmol) in CH₂Cl₂. The reaction mixture was stirred for 12 hours. The resulting yellow solution was filtered over Celite. The solvent volume was reduced, pentane and ether were added separately to wash the solid. A light yellow solid corresponding to compound **6** was isolated in 85% yield (59 mg, 0.072 mmol).

¹H NMR (600 MHz, CD₂Cl₂, 298 K): δ /ppm[†] = 7.90 (4H, *o*), 7.54 (2H, *p*), 7.35 (4H, *m*) (each broad, PPh), 7.35 (4H, *o*), 7.17 (2H, *p*), 6.97 (4H, *m*) (each broad, PPh'), 7.23 (4H, *m*), 7.12 (4H, *o*), 7.08 (2H, *p*) (each broad, NPh), 5.82 (s, 5H, Cp). Ligand (ca. 30%): 7.74 (4H, *o*), 7.55 (2H, *p*), 7.40 (*m*, 4H) (each broad, PPh), 7.03 (2H, *m*), 6.80 (2H, *o*), n.o. (1H, *p*) (each broad, NPh). [[†] tentative assignment].

¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 298 K): δ /ppm[†] = 137.0 (*o*), 133.4 (*p*), 132.9 (*m*), n.o. (*i*) (each broad, PPh), 132.4 (*p*), 128.7 (*m*, *m*), 127.1 (*o*), n.o. (*i*) (each broad, PPh'), 149.0 (*i*), 129.0 (*m*), 128.7 (*m*, *o*), 124.9 (*p*) (each broad, NPh), 119.5 (Cp), 7.9 (t, ¹J_{PC} = 91.7 Hz, ^PC^P), n.o. (CN). Ligand: 133.2 (*o*), n.o. (*i*, *p*), 129.2 (*m*) (each broad, PPh), 129.3 (*m*), 121.4 (*o*), n.o. (*i*, *p*) (each broad, NPh). [[†] tentative assignment].

¹H, ¹³C-GHMBC (600 MHz / 151 MHz, CD₂Cl₂, 298 K): $\delta^1\text{H} / \delta^{13}\text{C} = 7.55 / 133.0$ (*(o-Ph^P)'* / *i-Ph^P*), 7.17 / 132.8 (*(p-Ph^P)'* / *(m-Ph^P)'*), 7.35 / 127.1 (*(m-Ph^P)'*, *(m-Ph^P)'* / *m-Ph^P*, *(m-Ph^P)'*), 7.08 / 129.0 (*(o-Ph^N)'* / *m-Ph^N*).

GCOSY (600 MHz / 600 MHz, CD₂Cl₂, 298 K): $\delta^1\text{H} / \delta^1\text{H} = 7.90 / 7.35$ (*(o-Ph^P)'* / *m-Ph^P*), 7.55 / 7.35 (*(o-Ph^P)'* / *(m-Ph^P)'*), 7.35 / 7.90, 7.55, 6.97 (*(m-Ph^P)'*, *(m-Ph^P)'* / *(o-Ph^P)'*, *(o-Ph^P)'*,

$p\text{-Ph}^P$), 7.23 / 7.08 ($m\text{-Ph}^N$ / $o\text{-Ph}^N$), 7.17 / 6.97 ($(p\text{-Ph}^P)'$ / $p\text{-Ph}^P$), 6.97 / 7.35, 7.17 ($p\text{-Ph}^P$ / $m\text{-Ph}^P$, $(m\text{-Ph}^P)'$ ($p\text{-Ph}^P)'$).

^1H , $^{13}\text{C}\text{-GHSQC}$ (600 MHz / 151 MHz, CD_2Cl_2 , 298 K): $\delta^1\text{H} / \delta^{13}\text{C} = 7.90 / 136.9$ ($o\text{-Ph}^P$ / $o\text{-Ph}^P$), 7.55 / 133.3 ($(o\text{-Ph}^P)'$ / $(o\text{-Ph}^P)'$), 7.35 / 132.8 ($m\text{-Ph}^P$, $(m\text{-Ph}^P)'$ / $m\text{-Ph}^P$, $(m\text{-Ph}^P)'$), 7.17 / 132.4 ($(p\text{-Ph}^P)'$ / $(p\text{-Ph}^P)'$), 7.23 / 129.0 ($m\text{-Ph}^N$ / $m\text{-Ph}^N$), 6.97 / 128.7 ($p\text{-Ph}^P$ / $p\text{-Ph}^P$), 7.35 / 127.1 ($m\text{-Ph}^P$, $(m\text{-Ph}^P)'$ / $m\text{-Ph}^P$, $(m\text{-Ph}^P)'$), 7.08 / 124.9 ($o\text{-Ph}^N$ / $o\text{-Ph}^N$).

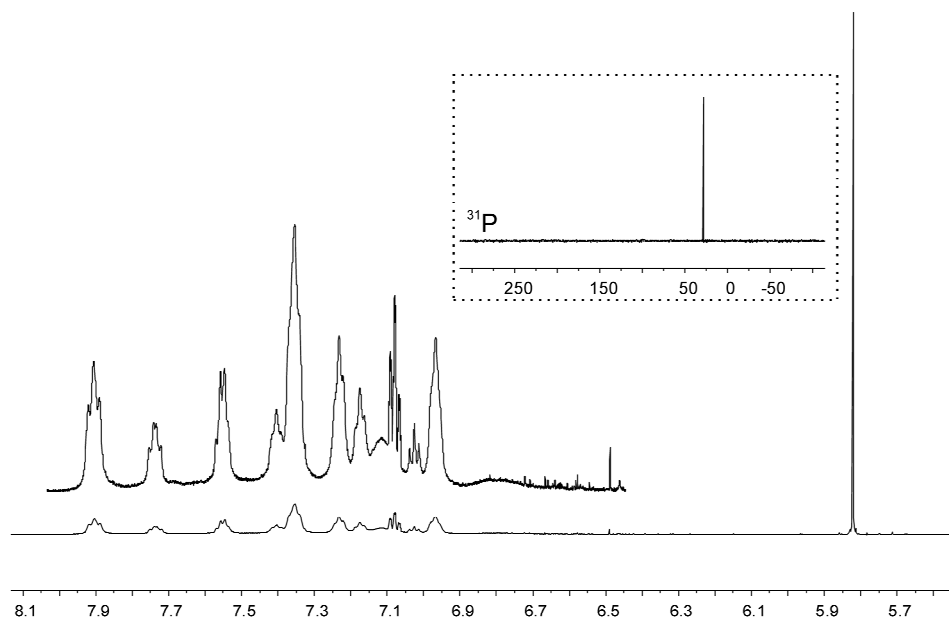
$^1\text{H}\{\text{NOE}\}$ NMR (600 MHz, CD_2Cl_2 , 298 K): $\delta^1\text{H}_{\text{ir}} / \delta^1\text{H}_{\text{res}} = 7.90 / 7.35$ ($o\text{-Ph}^P$ / $m\text{-Ph}^P$, $(m\text{-Ph}^P)'$), 7.55 / 7.17 ($(o\text{-Ph}^P)'$ / $(p\text{-Ph}^P)'$), 7.35 / 7.90, 6.97 ($m\text{-Ph}^P$ / $o\text{-Ph}^P$, $p\text{-Ph}^P$), 7.17 / 7.55 ($p\text{-Ph}^P)'$ / $(o\text{-Ph}^P)'$, 7.08 / 7.23 ($o\text{-Ph}^N$ / $m\text{-Ph}^N$), 6.96 / 7.35 ($p\text{-Ph}^P$ / $m\text{-Ph}^P$).

1D TOCSY (600 MHz, CD_2Cl_2 , 298 K): $\delta^1\text{H}_{\text{ir}} / \delta^1\text{H}_{\text{res}} = 7.90 / 7.35$ ($o\text{-Ph}^P$ / $m\text{-Ph}^P$), 7.55 / 7.35, 7.17 ($(o\text{-Ph}^P)'$ / $(m\text{-Ph}^P)'$, $(p\text{-Ph}^P)'$), 7.35 / 7.90, 6.97 ($m\text{-Ph}^P$ / $o\text{-Ph}^P$, $p\text{-Ph}^P$), 7.17 / 7.55, 7.35 ($(p\text{-Ph}^P)'$ / $(o\text{-Ph}^P)'$, $(m\text{-Ph}^P)'$), 6.97 / 7.35 ($p\text{-Ph}^P$ / $m\text{-Ph}^P$), 7.23 / 7.08 ($m\text{-Ph}^N$ / $o\text{-Ph}^N$).

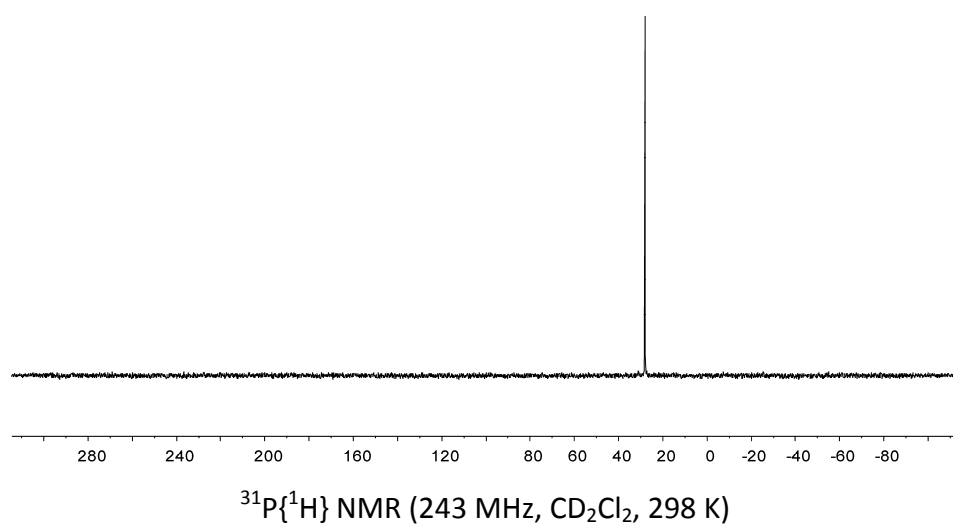
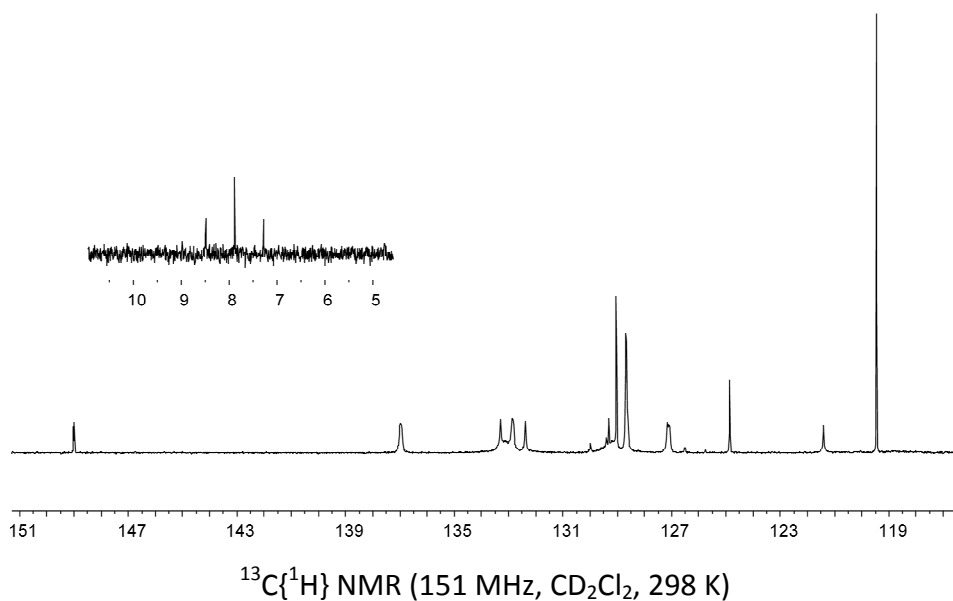
$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2 , 298 K): $\delta / \text{ppm} = 28.1$ ($\nu_{1/2} \sim 2$ Hz).

IR (KBr): $\tilde{\nu}/\text{cm}^{-1} = 3056, 2859, 2177$ ($\nu(\text{C}\equiv\text{N})$, s), 1589, 1559, 1485, 1436, 1306, 1283, 1230, 1151, 1104, 1024, 1008, 980, 963.

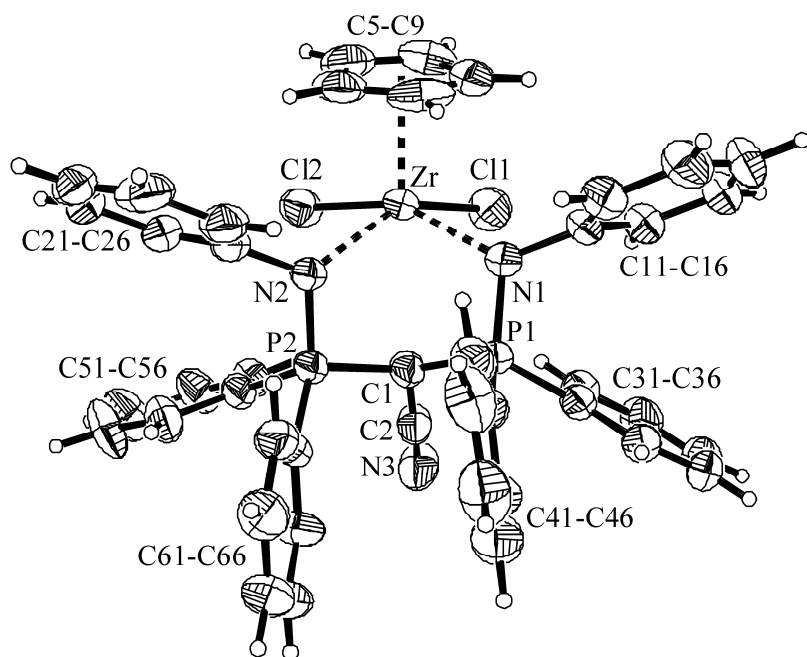
Elemental analysis (%) $\text{C}_{43}\text{H}_{35}\text{Cl}_2\text{N}_3\text{P}_2\text{Zr}$ ($M = 817.84\text{g/mol}$): calculated C 63.15, H 4.31, N 5.11; found C 62.99, H 4.12, N 4.98.



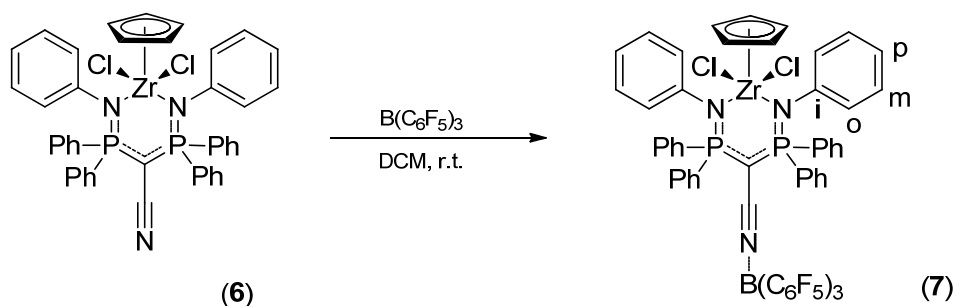
^1H NMR (600 MHz, CD_2Cl_2 , 298 K) and $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2 , 298 K)



X-ray crystal structure analysis of **6**: Crystal data for $\text{C}_{43}\text{H}_{35}\text{Cl}_2\text{N}_3\text{P}_2\text{Zr} \cdot 2 \text{CH}_2\text{Cl}_2$, $M = 987.65$, monoclinic, $P2_1/c$ (No. 14), $a = 10.2317(2)$, $b = 22.4233(4)$, $c = 20.5016(5)$ Å, $\beta = 98.196(1)^\circ$, $V = 4655.61(17)$ Å³, $D_c = 1.409$ g cm⁻³, $\mu = 0.684$ mm⁻¹, $F(000) = 2008$, $Z = 4$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, 26608 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å⁻¹, 10825 independent ($R_{\text{int}} = 0.051$), and 8637 observed reflections [$I \geq 2\sigma(I)$], 514 refined parameters, $R = 0.080$, $wR^2 = 0.199$, GoF = 1.051.



**[[Bis(N-phenyl-diphenylphosphinimino)acetonitrile]-tris(pentafluorophenyl)borate]-
(η⁵-C₅H₅)ZrCl₂ (7)**



1 Eq of tris(pentafluorophenyl)borane (50 mg, 0.098 mmol in 1 mL of DCM) was added to a DCM solution of **6** (80 mg, 0.098 mmol). The reaction mixture was stirred for 1 hour, filtered through Celite and the volatiles were removed under vacuum, washed with pentane. Compound **7** was isolated as light yellow solid in 87 % yield (113mg, 0.085mmol).

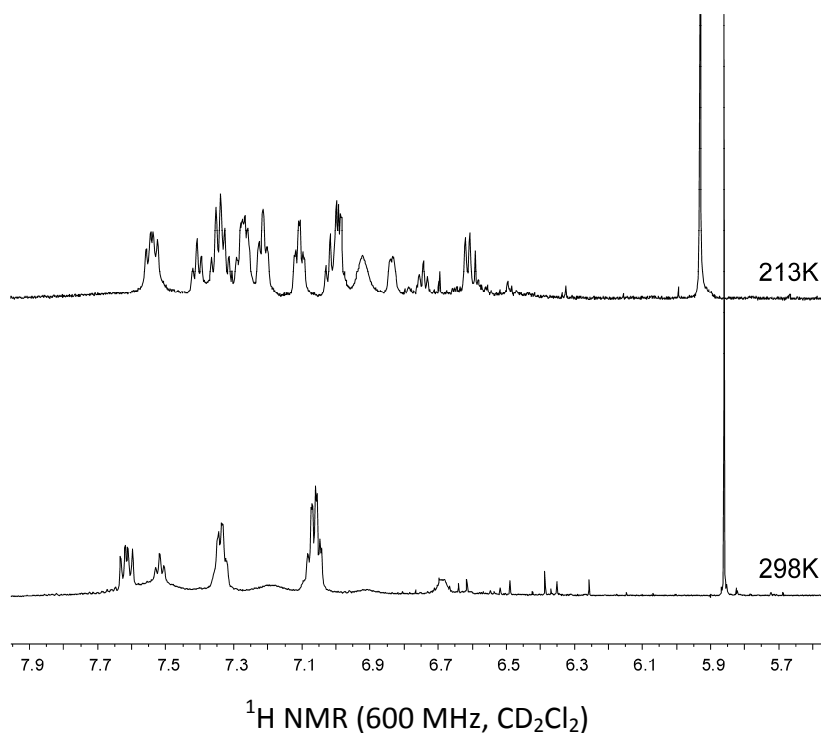
The realization of NMR experiments of compound **7** was difficult due to the poor solubility of **7** in CD₂Cl₂. Additionally, the dynamic behavior of **7** in solution resulted in complex NMR spectra.

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2 , 298 K): δ / ppm = 27.6 ($\nu_{1/2} \sim 2$ Hz).

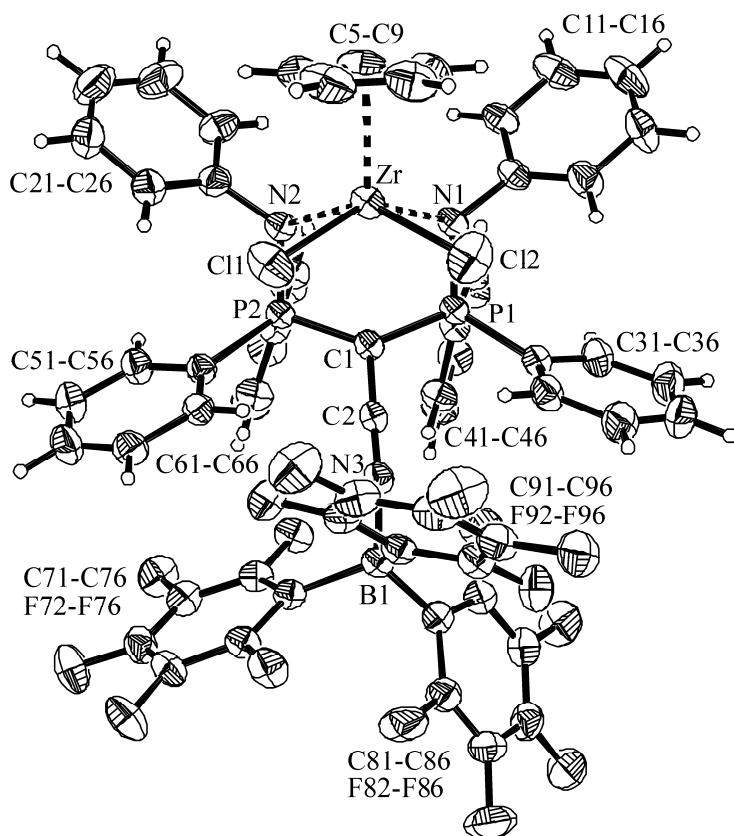
$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, CD_2Cl_2 , 298 K): -12.0 ppm ($\nu_{1/2} \sim 350$ Hz).

IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 3058, 2956, 2861, 2260 ($\nu(\text{C}\equiv\text{N})$, s), 1589, 1518, 1472, 1666, 1437, 1387, 1285, 1219, 1102, 1021, 980, 943, 876, 815, 797, 745, 690.

Elemental analysis (%) $\text{C}_{61}\text{H}_{35}\text{BCl}_2\text{F}_{15}\text{N}_3\text{P}_2\text{Zr}$ ($M = 1329.82\text{g/mol}$): calculated C 55.09, H 2.65, N 3.16; found C 54.96, H 2.73, N 3.36.



X-ray crystal structure analysis of **7**: Crystal data for $\text{C}_{61}\text{H}_{35}\text{BCl}_2\text{F}_{15}\text{N}_3\text{P}_2\text{Zr} \cdot \text{CH}_2\text{Cl}_2$, $M = 1414.72$, triclinic, $P1bar$ (No. 2), $a = 11.2880(1)$, $b = 13.1301(2)$, $c = 20.3011(3)$ Å, $\alpha = 87.214(1)$, $\beta = 81.712(1)$, $\gamma = 78.068(1)^\circ$, $V = 2912.57(7)$ Å³, $D_c = 1.613$ g cm⁻³, $\mu = 0.520$ mm⁻¹, $F(000) = 1416$, $Z = 2$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, 25213 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å⁻¹, 13644 independent ($R_{\text{int}} = 0.048$), and 12320 observed reflections [$I \geq 2\sigma(I)$], 793 refined parameters, $R = 0.055$, $wR^2 = 0.151$, $\text{GoF} = 1.052$.



Crystallography Characterization.

The crystal data and refinement of **2**, **3**, **4**, **6** and **7** are summarized in **Table S-1**.

Selected bond distance (Å) and angle (deg) are shown in **Table S-2** and **S-3**.

Table S-1. Crystal Data and Structure Refinement for Compound **2**, **3**, **4**, **6** and **7**.

	2	3	4	6	7
Empirical formula	C ₁₈ H ₁₇ N ₃	C ₂₃ H ₂₁ Cl ₂ N ₃ Zr	C ₄₁ H ₂₁ B ₂ Cl ₂ F ₁₅ N ₃ Zr* Zr*C ₂ H ₁₂	C ₄₃ H ₃₃ Cl ₂ N ₃ P ₂ Zr* 2CH ₂ Cl ₂	C ₆₁ H ₃₃ BCl ₂ F ₁₅ N ₃ P ₂ Zr* *CH ₂ Cl ₂
Formula weight (g mol ⁻¹)	275.35	501.55	1085.68	987.65	1414.72
Temperature (K)	223(2)	223(2)	223(2)	223(2)	223(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	orthorhombic	triclinic	monoclinic	triclinic
Space group	P-1 (No.2)	Pnma (No.62)	P-1 (No.2)	P2 ₁ /c (No.14)	P-1 (No.2)
Unit cell dimensions (Å, deg)	a = 11.3372(2) α = 90.974(1) b = 11.4394(2) β = 109.646(1) c = 13.2279(3) γ = 110.002(1)	a = 7.6639(1) α = 90.000 b = 13.2857(2) β = 90.000 c = 25.1922(5) γ = 90.000	a = 10.7744(2) α = 101.946(1)° b = 12.2695(3) β = 99.864(1)° c = 18.4381(4) γ = 91.168(2)	a = 10.2317(2) α = 90.000 b = 22.4233(4) β = 98.196(1) c = 20.5016(5) γ = 90.000	a = 11.2880(1) α = 87.214(1) b = 13.1301(2) β = 81.712(1) c = 20.3011(3) γ = 78.068(1)
Volume (Å ³)	1501.23(5)	2565.08(7)	2345.47(9)	4655.61(17)	2912.57(7)
Z	4	4	2	4	2
Density (calculated) Mg/m ³	1.218	1.299	1.537	1.409	1.613
Absorption coefficient (mm ⁻¹)	0.074	0.649	0.445	0.684	0.520
F(000) e	584	1016	1088	2008	1416
Crystal size (mm)	0.32 x 0.19 x 0.17	0.20 x 0.10 x 0.05	0.33 x 0.17 x 0.05	0.20 x 0.13 x 0.07	0.30 x 0.23 x 0.10
Theta range (deg)	4.12 to 27.92	4.19 to 27.89	4.16 to 28.12	4.08 to 27.87	4.17 to 28.10
Index ranges	-14<h<=14, -14<k<=14, -15<l<=17	-10<h<=10, -17<k<=17, -32<l<=33	-14<h<=14, -16<k<=16, -24<l<=23	-13<h<=13, -29<k<=26, -26<l<=26	-14<h<=14, -16<k<=17, -26<l<=26
Reflections collected	13598	14370	20491	26608	25213
Independent reflections	6933 [R(int) = 0.045]	3123 [R(int) = 0.044]	10883 [R(int) = 0.047]	10825 [R(int) = 0.051]	13644 [R(int) = 0.048]
Completeness to Theta = 27.77° (%)	96.4	98.1	94.8	97.5	96.1
Data / restraints / parameters	6933 / 0 / 389	3123 / 0 / 140	10883 / 39 / 615	10825 / 43 / 514	13644 / 0 / 793
Goodness-of-fit on F ²	1.063	1.015	1.096	1.051	1.052
Final R indices [I > 2σ(I)]	R1 = 0.0634, wR ² = 0.1341	R1 = 0.0406, wR ² = 0.1144	R1 = 0.0672, wR ² = 0.1576	R1 = 0.0799, wR ² = 0.1864	R1 = 0.0553, wR ² = 0.1422
R indices (all data)	R1 = 0.0799, wR ² = 0.1492	R1 = 0.0454, wR ² = 0.1190	R1 = 0.0834, wR ² = 0.1754	R1 = 0.0977, wR ² = 0.1991	R1 = 0.0616, wR ² = 0.1512
Largest diff. peak and hole e.Å ⁻³	0.278 and -0.216	0.380 and -0.420	0.490 and -0.838	1.115 and -0.865	1.620 and -1.467
Max. and min. Transmission	0.9876 and 0.9768	0.9683 and 0.8811	0.9781 and 0.8672	0.9537 and 0.8754	0.9498 and 0.8596
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents

Table S-2 Selected structural parameters of the nacnac-CN systems **2**, **3** and **4**.

	2	3	4
Zr–N1	-	2.224(2)	2.250(3)
Zr–C3	-	2.747(3)	2.690(3)
Zr–N5	-	-	2.241(3)
Zr–C2	-	2.796(2)	2.809(4)
Zr–C4	-	-	2.766(4)
Zr–Cl1	-	2.469(1)	2.439(1)
Zr–Cl2	-	-	2.447(1)
C2–N1	1.319(2)	1.309(3)	1.286(5)
C2–C3	1.411(2)	1.438(3)	1.462(5)
C3–C4	1.441(2)	-	1.452(5)
C4–N5	1.306(2)	1.309(3)	1.295(4)
C3–C7	1.426(2)	1.423(5)	1.409(5)
C7–N8	1.146(2)	1.144(5)	1.141(4)
N1–C2–C3	118.7(2)	118.2(2)	116.1(3)
C2–C3–C4	125.5(2)	122.6(3)	123.8(3)
C3–C4–N5	118.9(2)	-	116.9(3)
C3–C7–N8	179.7(2)	179.2(4)	177.4(4)
Cl1–Zr–Cl2	-	89.0(1)	90.3(1)
N1–Zr–N(x)	-	76.5(1)	76.0(1)
C11–N1–Zr	-	135.1(1)	132.2(3)
C2–N1–C11–C12	135.2(2)	-102.0(3)	-89.6(5)
C4–N5–C21–C22	56.2(3)	-	99.7(4)

^a Bond lengths in Å, angles and dihedral angles in deg.

Table S-3 Selected structural parameters of the P-nacnac-CN systems **6** and **7**

	6	7
Zr-CCp	2.492(6)-2.539(6)	2.493(3)-2.535(3)
Zr-N1	2.226(4)	2.268(2)
Zr-P1	3.151(1)	-
Zr-C1	2.793(5)	2.839(2)
Zr-P2	3.182(1)	-
Zr-N2	2.288(4)	2.271(2)
Zr-Cl1	2.501(2)	2.467(1)
Zr-Cl2	2.493(1)	2.465(1)
P1-N1	1.621(4)	1.616(2)
P1-C1	1.785(5)	1.791(2)
C1-P2	1.759(5)	1.791(3)
P2-N2	1.623(4)	1.619(2)
C1-C2	1.431(6)	1.388(3)
C2-N3	1.151(6)	1.148(3)
N3-B1	-	1.567(3)
N1-P1-C1	103.7(2)	101.8(1)
N2-P2-C1	100.8(2)	101.4(1)
P1-C1-P2	119.0(3)	120.9(1)
C2-C1-P1	115.7(3)	115.6(2)
C2-C1-P2	114.3(3)	118.1(2)
C11-N1-Zr	131.8(3)	126.5(2)
C21-N2-Zr	128.8(3)	125.0(2)
C1-C2-N3	178.7(6)	178.8(3)
Cl1-Zr-Cl2	83.4(1)	84.9(1)
N1-Zr-N2	90.1(1)	84.5(1)
B1-N3-C2	-	174.9(2)
P1-N1-C11-C12	78.6(5)	114.7(3)
P2-N2-C21-C32	-69.5(5)	-112.8(3)

^a Bond lengths in Å, angles and dihedral angles in deg.