Supporting Information

A general benzylic C-H activation and C-C coupling reaction at zirconocenes mediated by C-N bond cleavage in *tert*butylisocyanide – unusual formation of iminoacyl complexes

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1. Experimental Details

1.1. General

All manipulations were carried out in an oxygen- and moisture-free argon atmosphere using standard Schlenk and drybox techniques. The solvents were purified with the Grubbs-type column system "Pure Solv MD-5" and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. *rac*-[1,2-bis-(4,5,6,7-tetra-hydro-inden-1-yl)ethan]zirconium(IV) dichloride ([*rac*-(ebthi)ZrCl₂]) was obtained from MCAT and transferred in Schlenk Tubes stored under argon and used as received. *rac*-(ebthi)Zr(η^2 -Me₃SiC₂SiMe₃) (1) was synthesised as previously described in literature.¹ Commercially available *t*-BuNC (Sigma Aldrich) was dried over molecular sieves and degassed prior to use.

NMR spectra were determined on Bruker AV300 and AV400 spectrometers. ¹H and ¹³C chemical shifts were referenced to the solvent signal: [D₆]benzene ($\delta_{\rm H}$ 7.16, $\delta_{\rm C}$ 128.06²). Raman spectra were recorded on a LabRAM HR 800 Raman Horiba spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by different laser sources: 633 nm (17 mW, air cooled), 784 nm Laser diode (100 mW, air-cooled) or 473 nm Ar+ Laser (20 mW, air-cooled). All measurements were carried out at ambient temperature. IR spectra were recorded on a Bruker Alpha FT-IR, ATR Spectrometer, spectra are not corrected. MS analysis was done using a Finnigan MAT 95-XP instrument (Thermo-Electron) in Cl⁺/Cl⁻ mode (isobutene) and for the air stable compounds in EI mode. CHN analysis was done using a Leco Tru Spec elemental analyser. Melting points are uncorrected and were determined in sealed capillaries under Ar atmosphere using a Mettler-Toledo MP 70. X-Ray diffraction data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS-97)³ and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014).⁴ For the compound **2** contributions of co-crystallised solvent molecules were removed from the diffraction data with PLATON/SQUEEZE.⁵ XP (Bruker AXS) and Diamond⁶ were used for graphical representations. All DFT calculations were carried out with the Gaussian 09 package of molecular orbital programs.⁷

1. 2. Synthesis of complex 2



To a solution of *rac*-(ebthi)Zr(η^2 -Me₃SiC₂SiMe₃) (**1**) (0.284 g, 0.50 mmol) in benzene (10 mL) *t*-BuNC (0.058 mL, 0.51 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 20 min at ambient temperature all volatiles were removed in vacuum resulting in an orange solid of complex **2.** Yield: 0.238 g (73 %).

M.p.: 116 °C (decomp. under Ar). ¹**H NMR** (300 MHz, [D₆]benzene, 297 K): δ = 0.41, 0.58 (s, each 9H, SiMe₃), 1.14 (s, 9H, t-Bu), 4.71 (d, ³J = 2.8 Hz, 1H, CH=CH ebthi), 5.20 (d, ³J = 2.8 Hz, 1H, CH=CH ebthi), 5.36 (d, ³J = 3.1 Hz, 1H, CH=CH ebthi), 5.74 (d, ³J = 3.1 Hz, 1H, CH=CH, ebthi) ppm (CH₂ resonances of the ebthi ligand appear as broad multiplet between 1.32 and 2.48 ppm, 20 H). (1.40 and 3.58 (m, each 1H, CH₂ THF). ¹³C NMR (75 MHz, [D₆]benzene, 297 K): δ = 2.2, 3.7 (SiMe₃), 23.27, 23.36, 23.39, 23.6, 23.8, 24.0, 24.01, 24.2, 26.8, 27.9 (CH₂ *ebthi*), 30.2 (CH₃ *t*-Bu), 56.4 (*Cq t*-Bu), 96.2, 96.6, 97.9, 106.6, (CH=CH ebthi), 112.1, 113.6, 113.7, 118.1, 118.9, 120.8, (Cq ebthi), 180.2, 182.5, 191.9 (*C*=C resp. *C*=N) ppm (25.8 and 67.8 CH₂ THF). **IR** (ATR, cm⁻¹): ν = 2111 (m, *C*=N-*t*Bu), 1612(s, Me₃Si-*C*=*C*-SiMe₃). MS: *m*/*z* (CI): 528 [M⁺⁻ *t*-Bu], 171 [Me₃SiC₂SiMe₃]⁺, 84 [(CH₃)₃C)NC. **Elemental analysis** calcd (%) for C₃₃H₅₁NSi₂Zr · 0.25 THF (C₃₄H₅₃NSi₂Zr 621.28 g·mol⁻¹): C 65.53, H 8.57, N 2.25; found: C 64,89 H 8.48, N 2.03.

1. 3. Synthesis of complex 3a



To a solution of rac-(ebthi)Zr(η^2 -Me₃SiC₂SiMe₃) (1) (0.263 g, 0.50 mmol) in toluene (15 mL) *t*-BuNC (0.054 ml, 0.5 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 2 h at room temperature further *t*-BuNC (0.1 mL, 1.0 mmol) was added. After heating the reaction mixture 12 days at 80 °C, all volatiles were removed in vacuum and the remaining oil was washed twice with 2 mL of *n*-hexane. The formed pale yellow powder was dissolved in diethyl ether, filtered and the solution was kept at -78 °C, which resulted in the formation of small pale yellow crystals of **3a**. These were isolated by decanting of the mother liquor and drying in vacuum. Yield: 0.115 g (41 %).

Mp.: 162-164 °C (decomp. under Ar). ¹**H NMR** (300 MHz, [D₆]benzene, 297 K): δ = 1.41 (s, 9H, t-Bu), 3.88 (d, ²J = 15.2 Hz, 1H, *CH*₂-Ph), 4.22 (d, ²J = 15.2 Hz, 1H, *CH*₂-Ph), 4.41 (d, ³J = 2.8 Hz, 1H, CH=CH), 4.91 (d, ³J = 2.8 Hz, 1H, CH=CH), 5.71 (d, ³J = 2.9 Hz, 1H, CH=CH), 5.94 (d, ³J = 2.9 Hz, 1H, CH=CH), 7.13 (m, 4H, Ph), 7.17 (m, 1H, Ph) ppm (CH₂ resonances of the ebthi ligand appear as broad multiplet between 1.94 and 3.14 ppm, 20 H). ¹³**C NMR** (75 MHz, [D₆]benzene, 297 K): δ = 22.7, 23.0, 23.2, 23.3, 23.60, 23.69, 23.72, 24.7, 27.3, 27.6 (*C*H₂ ebthi), 30.3 (*C*H₃ *t*-Bu), 42.5 (*C*H₂ Ph), 62.0 (*Cq t*-Bu), 98.1, 104.8 105.8, 106.5 (*C*H=*C*H, ebthi), 117.2, 120.7, 122.6, 123.8, 123.9, 126.7 (*Cq* ebthi), 127.3, 128.4, 129.0, 130.4 (*C*H-Ph), 138.0 (*Cq*-Ph), 157.4 (*C*≡N), 231.1 (*C*=N) ppm. **IR** (ATR, cm⁻¹): *ν* = 2119 (w, *C*=*N*-*t*Bu), 1620 (w, RCH₂-*C*=*N*-*t*Bu). **MS**: *m*/*z* (CI): 555 [M], 528 [M⁺ - C≡N]⁺, 174 [Me₃C-NC-CH₂-Ph]⁺. **Elemental analysis** calcd (%) for C₃₃H₄₀N₂Zr (555 g·mol⁻¹): C 71.30, H 7.25, N 5.04; found: C 71.32, H 7.37, N 4.86.

1.4. Synthesis of complex 3b



To a solution of rac-(ebthi)Zr(η^2 -Me₃SiC₂SiMe₃) (**1**) (0.263 g, 0.50 mmol) in benzene (10 mL) *t*-BuNC (0.057 mL, 0.5 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 2 h at room temperature further *t*-BuNC (0.114 mL, 1.0. mmol) and an excess (1 mL, 8.5 mmol) of *p*-xylene were added. After heating the reaction mixture 12 days at 80 °C, all volatiles were removed in vacuum and the remaining deep brown oil was washed with three 1 mL portions of cold *n*-hexane. The obtained yellow-brown sticky solid was dissolved in diethyl ether, which was subsequently removed in vacuum. After addition of 1 mL of benzene light brown yellow crystals were obtained after one week at room temperature. These were isolated by filtration, washed twice with cold pentane and dried in vacuum. Yield: 0.125 g of a mixture of **3b** + **4** (1:0.25). Several crystallisation steps from benzene or diethyl ether yielded only a small amount of crystals of **3b** free of **4**. Single crystals of **3b** suitable for X-ray analysis were not obtained.

¹**H NMR** (300 MHz, [D₆]benzene, 297 K): δ = 1.45 (s, 9H, *t*-Bu), 2.15 (s, 3H, *Me*-xylene), 3.93 (d, ²*J* = 15.2 Hz, 1H, *CH*₂-xylene), 4.50 (d, ³*J* = 2.8 Hz, 1H, CH=CH ebthi), 5.01 (d, ³*J* = 2.8 Hz, 1H, CH=CH ebthi), 5.75 (d, ³*J* = 2.9 Hz, 1H, CH=CH ebthi), 5.98 (d, ³*J* = 2.9 Hz, 1H, CH=CH ebthi), 7.05, 7.07, 7.13, 7.15 (br., 4H, CH xylene) ppm (CH₂ resonances of the ebthi ligand appear as broad multiplet between 1.90 and 2.98 ppm, 20 H). ¹³**C NMR** (100 MHz, [D₆]benzene, 297 K): δ = 21.1 (*Me*-Ph) 22.8, 23.06, 23.22, 23.4, 23.6, 23.70, 23.73, 24.7, 27.3, 27.6 (*CH*₂ ebthi), 30.3 (*Me*-t-Bu), 42.0 (*CH*₂-Ph), 62.0 (*Cq*-t-Bu), 98.2, 104.7 105.8, 106.5 (*CH*=*CH*, ebthi), 117.2, 120.6, 122.5, 123.82, 123.86, 126.7 (*Cq*-ebthi), 127.3, p 129.3, (*CH*-Ph), 134.9, 136.8 (*Cq*-Ph), 157.4 (*C*=N), 231.3 (*C*=N) ppm. **IR** (ATR, cm⁻¹): ν = 2110 (w, *C*=*N*-tBu), 1623 (w, RCH₂-*C*=*N*-tBu). **MS**: *m*/*z* (CI): 569 [M]⁺, 542 [M⁺- C=N]⁺, 188 [Me₃C-NC-CH₂-xylene]⁺.

1. 5. Synthesis of complex 3d



To a solution of *rac*-(ebthi)Zr(η^2 -Me₃SiC₂SiMe₃) (1) (0.263 g, 0.50 mmol) in benzene (10 mL) *t*-BuNC (0.057 mL, 0.5 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 2 h at room temperature further *t*-BuNC (0.115 mL, 1.0. mmol) and an excess (1 mL, 8.30 mmol) of *o*-xylene were added. After heating the reaction 12 days at 80 °C, all volatiles were removed in vacuum and the remaining dark oil was washed twice with 1 mL of *n*-hexane. The obtained orange-red sticky solid was dissolved in diethyl ether, which was subsequently removed in vacuum. After adding a mixture of ether/*n*-hexane (1:1), filtration from the insoluble oily precipitate and standing for three weeks at -78 °C, orange-red crystals had formed, which were isolated and identified as a 1:1 mixture of **3d** and **4** by NMR spectroscopy. When pure diethyl ether is used for crystallisation a 1:4 (**3d**:**4**) mixture was obtained.

¹**H NMR** (400 MHz, [D₆]benzene, 297 K): δ = 1.49 (s, 9H, *t*-Bu, **3d**), 2.08 (s, 3H, *Me*-Ph, **3d**), 3.14 – 0.9 (m, 40H, CH₂-ebthi, **3d** + **4**), 3.89 (d, ²*J* = 15.5 Hz, 1H, CH₂-Ph, **3d**), 4.44 (d, ²*J* = 15.5 Hz, 1H, CH₂-Ph, **3d**), 4.56 (m, 2H, ebthi, **3d** + **4**), 4.75 (d, *J* = 2.9 Hz, 1H, **4**), 4.90 (d, ³*J* = 2.9 Hz, 1H, ebthi, **3d**), 5.31 (d, ³*J* = 2.9 Hz, 1H, **4**), 5.56 (d, ³*J* = 2.9 Hz, 1H, **4**), 5.79 (d, ³*J* = 2.9 Hz, 1H, ebthi, **3d**), 5.90 (d, ³*J* = 2.9 Hz, 1H, CH-ebthi, **3d**), 7.01 – 7.13 (m, 3H, Ph, **3d**), 7.35 (dd, *J* = 7.5, 1.5 Hz, 1H Ph, **3d**) ppm. ¹³**C NMR** (75 MHz, [D₆]benzene, 297 K): δ = 21.4 (*Me*-Ph, **3d**), 22.7, 22.8, 23.2, 23.5, 23.6, 23.72, 23.73, 23.8, 23.9, 24.5, 24.6, 25.5, 24.8, 25.5, 26.0, 29.4, 30.3, 32.0 (*CH*₂-ebthi, **3d** + **4**), 30.0 (*Me*-t-Bu, **3d**), 39.5 (*CH*₂-Ph, **3d**), 62.8 (*Cq*-t-Bu, **3d**), 96.6, 98.4, 100.3, 100.6 (*CH*-ebthi, **4**), 98.5, 105.0, 105.6, 106.1 (*CH*-ebthi, **3d**), 113.3, 116.0, 126.0, 127.5, 129.6 (*Cq*-ebthi, **4**), 117.0, 121.3, 122.7, 122.8, 123.7, 126.1 (*Cq*-ebthi, **3d**), 131.1, 130.4, 127.48, 126.7 (*CH*-Ph, **3d**), 136.71, 136.72 (*Cq*-Ph, **3d**), 157.5 (*C*=N, **3d**), 213.6 (*C*=N, **4**), 230.0 (*C*=N, **3d**) ppm. **IR** (ATR, cm⁻¹): *ν* = 2118 (w, *C*=*N*-tBu), 1618 (w, RCH₂-*C*=*N*-tBu) **MS**: *m/z* (CI): 760 [M]⁺ (**4**) 569 [M]⁺ (**3d**), 542 [M⁺- C=N]⁺, 188 [Me_{3d}-NC-CH₂-C₆H₄Me]⁺

1. 6. Synthesis of complex 3e



Synthesis of complex 3e: To a solution of *rac*-(ebthi)Zr(η^2 -Me₃SiC₂SiMe₃) (**1**) (0.263 g, 0.50 mmol) in benzene (10 mL) *t*-BuNC (0.057 mL, 0.5 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 2 h at room temperature further *t*-BuNC (0.115 mL, 1.0. mmol) and an excess (1 mL, 7.25 mmol) of mesitylene were added. After heating the reaction mixture 12 days at 80 °C, all volatiles were removed in vacuum and the remaining dark oil was washed several times with 1 mL of *n*-hexane. The formed orange sticky solid was dissolved in diethyl ether, which was subsequently removed in vacuum. After adding a mixture of ether/*n*-hexane (1:1), filtration and standing one week at -78 °C, light orange crystals had formed which were isolated and identified as a 2:1 mixture of **3e** and **4** by NMR spectroscopy.

¹**H NMR** (300 MHz, [D₆]benzene, 297 K): δ = 1.47 (s, 9H, *t*-Bu, **3e**), 2.22 (m, 6H, *Me*-Ph, **3e**), 3.14 – 0.9 (m, 30H, CH₂-ebthi, **3e + 4**), 3.96 (d, ²J = 15.5 Hz, 1H, CH₂-Ph, **3e**), 4.20 (d, ²J = 15.5 Hz, 1H, CH₂-Ph, **3e**), 4.56 (d, J = 2.9 Hz, 0.5H, ebthi, **4**), 4.61 (d, ³J = 2.8 Hz, 1H, ebthi, **3e**), 4.75 (d, J = 2.9 Hz, 0.5H, ebthi, 4), 4.99 (d, ³J = 2.8 Hz, 1H, ebthi, 3e), 5.31 (d, J = 2.9 Hz, 0.5H, 4), 5.56 (d, J = 2.9 Hz, 0.5H, 4), 5.75 (d, ³J = 2.9 Hz, 1H, ebthi, **3e**), 5.99 (d, ³J = 2.9 Hz, 1H, CH-ebthi, **3e**),), 6.80 (s, 1H, Ph, **3e**), 6.92 (s, 2H, H-Ph, **3e**); (6.72 and 2.17 (m, traces free mesitylene)) ppm.^{13d} ¹³C NMR (100 MHz, [D₆]benzene, 297 K): δ = 21.4 (*Me*-Ph, **3e**), 22.8, 22.91, 22.95, 23.21, 23.62, 23.72, 23.73, 24.7, 27.4, 27.5 (*CH*₂ebthi, 3e), 22.7, 23.20, 23.6, 23.7, 24.5, 24.8, 25.5, 26.0, 29.4, 30.3 (CH2-ebthi, 4), 30.2 (Me-t-Bu, 3e), 42.4 (CH2-Ph, 3e), 62.0 (Cq-t-Bu, 3e), 96.6, 98.4, 100.3, 100.6 (CH-ebthi, 4), 98.2, 104.8 105.7, 106.4 (CH-ebthi, **3e**), 113.3, 116.0, 126.0, 127.5, 129.6 (Cq-ebthi, **4**), 117.2, 120.8, 122.6, 123.8, 123.9, 126.7 (Cq-ebthi, 3e), 128.4, 128.8 (CH-Ph, 3e), 137.9, 138.3 (Cq-Ph, 3e), 157.5 (C=N, 3e), 213.6 (C=N, **4**), 231.7 (*C*=N, **3e**) ppm. **MS**: *m/z* (CI): 760 [M]⁺ (**4**), 583 [M]⁺ (**3e**), 556 [M⁺- C≡N]⁺, 201 [Me_{3d}-NC-CH₂- $C_6H_4Me_2$ ⁺. The *n*-hexane fractions were combined and the volume reduced in vacuum – after 1 week at -78 °C a grey perticipate could be isolated, which gave after crystallisation from benzene less crystals of pure **3e** which were suitable for X-ray crystallography, NMR and Raman spectroscopy. **3e**: ¹**H NMR** (300 MHz, [D₆] benzene, 297 K): δ = 1.47 (s, 9H, *t*-Bu), 2.22 (m, 6H, *Me*-Ph), 3.14 – 0.9 (m, 20H, CH₂-ebthi), 3.96 (d, ${}^{2}J$ = 15.5 Hz, 1H, CH₂-Ph), 4.20 (d, ${}^{2}J$ = 15.5 Hz, 1H, CH₂-Ph), 4.61 (d, ${}^{3}J$ = 2.8 Hz, 1H, ebthi), 4.99 (d, ³J = 2.8 Hz, 1H, ebthi), 5.75 (d, ³J = 2.9 Hz, 1H, ebthi), 5.99 (d, ³J = 2.9 Hz, 1H, CH-ebthi),), 6.80 (s, 1H, Ph), 6.92 (s, 2H, Ph), (6.72 and 2.17 (m, traces free mesitylene) ppm. ¹³C **NMR** (75 MHz, [D₆]benzene, 297 K): δ = 21.4 (*Me*-Ph), 22.8, 22.91, 22.95, 23.2, 23.6, 23.72, 23.73, 24.7, 27.4, 27.5 (CH2-ebthi), 30.2 (Me-t-Bu), 42.4 (CH2-Ph), 62.0 (Cq-t-Bu), 98.2, 104.8 105.7, 106.4 (CH-ebthi), 117.2, 120.8, 122.6, 123.8, 123.9, 126.7 (Cq-ebthi), 128.4, 128.8 (CH-Ph), 137.9, 138.3 (CqPh), 157.5 (*C*≡N), 231.7 (*C*=N), (21.3, 127.4, 137.6 free mesitylene) ppm. **Raman** (633 nm, 10 sec, 20 acc, cm⁻¹): *ν* = 2121 (w, *C*=*N*-*t*Bu), 1625 (w, RCH₂-*C*=*N*-*t*Bu)

1.7. Reaction Monitoring by ¹H-NMR spectroscopy

The following chapter summarizes a series of ¹H NMR *in situ* experiments performed to gain a better understanding of the reaction processes. We combined 2 (20 mg, 0.03 mmol), excess of Ar-CH₃ species (0.5 mmol) and stoichiometric amount of tert-butylisocyanide (0.03 mmol, 3,5 µL), dissolved them in C_6D_6 (0.6 mL), sealed the NMR young tubes in an Ar atmosphere and heated them to 80 °C.To monitor the reactions we measured a series of ¹H NMR at 25°C, the reported time correspond to the time of heating the samples (see Figure S6 - Figure S15). For a simple kinetic consideration, we have classified the solvent C₆D₆ as inert and have related all integrals to this signal to obtain a rough statement about the concentrations of all present compounds. On the basis of this evaluation, it was initially shown that in all reactions a supposedly paramagnetic species first develops, since the total intensities of all Me₃Si, t-Bu and EBTHI signals of complex 2 decreases dramatically. In addition, no products can be identified whose integrals are growing at the same rate as those of component 2 diminish. These observations are collected for 3d derivative exemplary in Figure S1 - Figure S3. During this study we were able to identify in all reactions a parallel isocyanide -nitrile conversion that appears to be catalytic (see below) in the presence of the hitherto unknown paramagnetic species. Furthermore, the studies show that the complex 4 develops only after consumption of the tertbutylisocyanide; this is accompanied by a color change of the reaction solutions from orange to black-greenish. In addition, it could be shown that during the course of the reaction both t-BuH and isobutene are formed, which additionally indicates a radical mechanism. These species were identified via 1D ¹H-TOCSY experiments of enriched samples (Figure S4 and Figure S5).



Figure S1. Plot of the exemplary integral analysis of the *insitu* measurement for the reaction to complex **3d**. Plot of all relative integrates of the main reaction partners in the high field range.



Figure S2. Plot of the exemplary integral analysis of the *insitu* measurement for the reaction to complex **3d**. Plot of all relative integrates of the main reaction partners in the low field range as well as their sum (blue).



Figure S3. Plot of the percentage integral "loss" in relation to the start value (t = 0 h).



Figure S4. The representation of the 1D 1H-TOCSY experiment shows the identified correlation signals for isobutene.



Figure S5. The representation of the 1D 1H-TOCSY experiment shows the identified correlation signals for t-butane.



Figure S6. Representation of the high field region of the ¹H NMR reaction monitoring during for the formation of **3a** and **4**. Assignment: Red star = **3a**, blue square = **2**, blue triangle = *t*-BuNC, yellow triangle = *t*-BuH, red triangle = *t*-BuCN, red square = free Me₃SiC₂SiMe₃.



Figure S7. Representation of the low field region of the ¹H NMR reaction monitoring during for the formation of **3a** and **4**. Assignment: Red star = **3a**, blue square = **2**, green square = **4**, green triangle = isobutene.



Figure S8. Representation of the high field region of the ¹H NMR reaction monitoring during for the formation of **3b** and **4**. Assignment: Red star = **3b**, blue square = **2**, blue triangle = *t*-BuNC, yellow triangle = *t*-BuH, red triangle = *t*-BuCN, red square = free Me₃SiC₂SiMe₃.



Figure S9. Representation of the low field region of the ¹H NMR reaction monitoring during for the formation of **3b** and **4**. Assignment: Red star = **3b**, blue square = **2**, green square = **4**, green triangle = isobutene.



Figure S10. Representation of the high field region of the ¹H NMR reaction monitoring during for the formation of **3c** and **4**. Assignment: Red star = **3c**, blue square = **2**, blue triangle = *t*-BuNC, yellow triangle = *t*-BuH, red triangle = *t*-BuCN, red square = free Me₃SiC₂SiMe₃.



Figure S11. Representation of the low field region of the ¹H NMR reaction monitoring during for the formation of **3c** and **4**. Assignment: Red star = **3c**, blue square = **2**, green square = **4**, green triangle = isobutene.



Figure S12. Representation of the high field region of the ¹H NMR reaction monitoring during for the formation of **3d** and **4**. Assignment: Red star = **3d**, blue square = **2**, blue triangle = *t*-BuNC, yellow triangle = *t*-BuH, red triangle = *t*-BuCN, red square = free Me₃SiC₂SiMe₃.



Figure S13. Representation of the low field region of the ¹H NMR reaction monitoring during for the formation of **3d** and **4**. Assignment: Red star = **3d**, blue square = **2**, green square = **4**, green triangle = isobutene.



Figure S14. Representation of the high field region of the ¹H NMR reaction monitoring during for the formation of **3e** and **4**. Assignment: Red star = **3e**, blue square = **2**, blue triangle = *t*-BuNC, yellow triangle = *t*-BuH, red triangle = *t*-BuCN, red square = free Me₃SiC₂SiMe₃.



Figure S15. Representation of the low field region of the ¹H NMR reaction monitoring during for the formation of **3e** and **4**. Assignment: Red star = **3e**, blue square = **2**, green square = **4**, green triangle = isobutene.

1.8. Addition of further *t*-BuNC to reaction solutions

After the described ¹H-NMR monitoring experiments we added to each of the reaction solutions an exess of further *t*-BuNC and heated the mixtures to 80 °C to test the option of obtaining better yields of complexes 3. All experiments reveal the same reaction behaviour as is shown in Figure S16 exemplarly for the complex 3b. After adding the *t*-BuNC we observed again the isomerization to *t*-BuCN as the major reaction besides a small conversion to further complex **3b** but the long heating period leads to decomposition of the before formed complex **4**.



Figure S16. Representation of the ¹H NMR reaction monitoring before (lower 4 spectra) and after addition of further t-BuNC (upper 3 spectra) to the reaction solution of the synthesis of **3b**. Assignment: Red star = **3b**, green square = **4**, green triangle = isobutene, blue triangle = t-BuNC, blue triangle = t-BuCN, red square = free Me₃SiC₂SiMe₃. For the representation a part of the x-axis was cut out and a different zoom level was used in the low-field region to be able to recognise the signals better.

1.9. Synthesis of 3a in Toluene-[D8] at 110 °C reaction monitoring by ¹H-

NMR spectroscopy



Figure S17. Representation of the ¹H NMR monitoring of the reaction to **3a** carried out in toluene-[D8] at 110 °C. The reaction was about 35 times faster than at 80 °C, but also shows the formation of a larger amount of **4**. Assignment: Red star = **3a**, yellow triangle = *t*-BuH, red triangle = *t*-BuCN, red square = free Me₃SiC₂SiMe₃, green square = **4**, green triangle =

isobutene. For the representation a part of the x-axis was cut out and a different zoom level was used in the low-field region to be able to recognise the signals better.



Figure S18. The direct comparison of the NMR reactions carried out in toluene-[D8] at 110 °C (top) as well as in benzene-[D6] in the presence of toluene at 80 °C (bottom) clearly shows the origin of the CH₂-Ar group in **3b** due to the absence of their signals in the upper case. Furthermore, it shows the formation of a larger amount of **4** at 110 °C. Assignment: Red star = **3a**, yellow triangle = *t*-BuH, red triangle = *t*-BuCN, red square = free Me₃SiC₂SiMe₃, green square = **4**, green triangle = isobutene. For the representation a part of the x-axis was cut out and a different zoom level was used in the low-field region to be able to recognise the signals better.

1. 10. Catalytic isomerisation of t-BuNC into tBuCN via complex 2 as precatalyst



To a solution of *rac*-(ebthi)Zr(CN*t*Bu)(η^2 -Me₃SiC₂SiMe₃) (**2**) (0.02 g, 0.03 mmol, 1,7 mol%) in benzene-[D6] (0.6 mL) the *t*-BuNC (0.147 g, 1.77 mmol) was added. The NMR young tube was sealed and the resulting mixture was heated to 110 °C for 15 hours. The catalytic isomerisation of *t*-BuNC into *t*-BuCN using complex **2** as precatalyst was investigated with the help of ¹H and ¹³C-NMR spectroscopy (see below) and show 98 % conversion.



Figure S19. Representation of the ¹H-NMR spectrum (400.13 MHz, 25 °C, C_6D_6) after catalytic isomerisation of *t*-BuNC into *t*-BuCN. Assignment: blue triangle = *t*-BuNC, red triangle = *t*-BuCN.



Figure S20. The shown ¹³-C NMR spectrum (106.3 MHz, 25 °C, C_6D_6) unambiguously identified the product of the isomerization as the *t*-BuCN. Assignment: red triangle = *t*-BuCN.

1. 11. Proof of thermal stability of complex 2 in solution at 80 °C



A solution of *rac*-(ebthi)Zr(CN*t*Bu)(η^2 -Me₃SiC₂SiMe₃) (**2**) (0.02 g, 0.03 mmol) in benzene-[D6] (0.6 mL) was sealed in a NMR young tube and heated to 80 °C for 9.5 days. The thermal stability was proofed by monitoring the reaction via ¹H-NMR spectroscopy (see below). During the thermal treatment the formation of complex **4** can be seen but after the given time only 8 % of the initial *rac*-(ebthi)Zr signal intensity and 28 % of the original Me₃Si intensity are present. This suggests the formation of previously unidentified paramagnetic species.



Figure S21. Representation of the ¹H NMR reaction monitoring during for thermal treatment of complex **2** without further *t*-BuNC and Ar-CH₃ species. Assignment: Blue square = **2**, green square = **4**, green triangle = isobutene, yellow triangle = *t*-BuH, red square = free Me₃SiC₂SiMe₃. For the representation a part of the x-axis was cut out and a different zoom level was used in the low-field region to be able to recognise the signals better.

1. 12. Proof of thermal stability of mixture of 3/4 in solution at 80 °C

A solution of isolated compound mixtures of **3b/4** as well as **3e/4** in benzene-[D6] (0.6 mL) was sealed in a NMR young tube and heated to 80 °C for 22 days. The thermal stability was proofed by monitoring the reaction via ¹H-NMR spectroscopy (see below). During the thermal treatment the slow decomposition of complex **4** can be seen.



Figure S22. Representation of the low field region of the ¹H NMR reaction monitoring during for the thermal treatment of a mixture of **3b** and **4**. Assignment: Red star = **3b**, green square = **4**.



Figure S23. Representation of the low field region of the ¹H NMR reaction monitoring during for the thermal treatment of a mixture of **3e** and **4**. Assignment: Red star = **3e**, green square = **4**.

2. Crystallographic details

Table S1. Crystallographic details of 2, 3a and 3d/4.

	2	3a	3d/4	
Chem. Formula	$C_{33}H_{51}NSi_2Zr$	$C_{33}H_{40}N_2Zr$	$C_{82}H_{96}N_4Zr_3$	
Form. Wght [g mol ⁻¹]	609.15	555.89	1411.28	
Colour	red	yellow	red	
Cryst. system	monoclinic	monoclinic	triclinic	
Space group	C2/c	P2 ₁ /n	PĪ	
a [Å]	30.5599(5)	11.5367(6)	10.7718(6)	
b [Å]	11.0773(2)	15.1627(7)	15.6210(9)	
c [Å]	21.3300(4)	15.5805(7)	20.8511(12)	
α [°]	90	90	103.768(2)	
β[°]	105.4728(6)	96.2381(8)	101.7318(19)	
γ [°]	90	90	91.398(2)	
V [ų]	6959.0(2)	2709.3(2)	3326.8(3)	
Z	8	4	2	
ρ _{calc.} [g cm ⁻³]	1.163	1.363	1.409	
μ [mm ⁻¹]	0.405	0.430	0.510	
Т [К]	150(2)	150(2)	150(2)	
radiation type	ΜοΚα	ΜοΚα	ΜοΚα	
reflections measured	43491	28486	123844	
independent	7587	6547	16077	
reflections				
observed reflections	6811	5785	14674	
with $1 > 2\sigma(1)$	0.0225	0.0270	0.0262	
	0.0235	0.0276	0.0263	
F(000)	2592	1168	1472	
$R_1 (l > 2\sigma(l))$	0.0245	0.0264	0.0369	
wR ₂ (all data)	0.0670	0.0662	0.0869	
GOF on F ²	1.069	1.030	1.024	
Parameters	343	328	900	
CCDC number	CCDC 1940866	CCDC 1940867	CCDC 1940868	

Table S2. Crystallographic details of 3e.

	Зе
Chem. Formula	$C_{35}H_{44}N_2Zr$
Form. Wght [g mol ⁻¹]	583.94
Colour	colourless
Cryst. system	triclinic
Space group	PĪ
a [Å]	9.3286(10)
b [Å]	10.6590(11)
c [Å]	14.8127(16)
α [°]	87.887(3)
β[°]	83.265(3)
γ [°]	85.072(3)
V [ų]	1456.8(3)
Z	2
ρ _{calc.} [g cm ⁻³]	1.331
μ [mm ⁻¹]	0.404
Т [К]	150(2)
radiation type	ΜοΚα
reflections measured	55886
independent	7036
reflections	/030
observed reflections	6666
with $l > 2\sigma(l)$	
R _{int.}	0.0245
F(000)	616
$R_1 (l > 2\sigma(l))$	0.0243
wR ₂ (all data)	0.0629
GOF on F ²	1.045
Parameters	386
CCDC number	CCDC 1940869

2.1. Compound 2



Figure S24. Numbering scheme of 2. H atoms are omitted for clarity.

C1–Zr1	2.2937(13)	C2–Zr1–C1	33.29(5)
C2–Zr1	2.2583(14)	C2–C1–Si1	144.38(11)
C9–Zr1	2.2799(13)	C1–C2–Si2	135.18(11)
C1–C2	1.3044(19)	N1–C9–Zr1	175.45(11)
C9–N1	1.1572(18)	Si1–C1–C2–Si2	17.8(3)
C1–Si1	1.8323(14)	C9-N1-C10	175.75(14)
C2–Si2	1.8497(14)		
C10-N1	1.4598(17)		

 Table S3. Selected bond lengths (Å), angles and torsion angles (°) of 2.

2.2. Compound 3a



Figure S25. Numbering scheme of 3a. H atoms are omitted for clarity.

C1–Zr1	2.2396(15)	N1–Zr1–C1	32.91(5)
N1–Zr1	2.2275(12)	N1–Zr1–C13	82.80(5)
C13–Zr1	2.3241(15)	N2–C13–Zr1	178.07(14)
C1-N1	1.2655(19)	C2-C1-N1-C9	0.8(3)
C1–C2	1.514(2)		
C2–C3	1.507(2)		
C9–N1	1.4934(19)		
C13–N2	1.143(2)		

Table S4. Selected bond lengths (Å), angles and torsion angles (°) of 3a.

2.3. Compound 3d/4



Figure S26. Ball and stick representation of 3d/4. H atoms are omitted for clarity. Lower occupancy sites are depicted with white coloured bonds.

C1–Zr1	2.229(2)	N1–Zr1–C1	33.15(7)
N1–Zr1	2.2254(17)	N1–Zr1–C14	84.42(7)
C14–Zr1	2.331(2)	N2-C14-Zr1	174.0(2)
C1-N1	1.271(3)	C2-C1-N1-C9	1.4(4)
C1–C2	1.512(3)		
C2–C3	1.520(3)		
C9-N1	1.494(3)		
C14–N2	1.143(3)		

Table S5. Selected bond lengths (Å), angles and torsion angles (°) of 3d in 3d/4.

Table S6. Selected bond lengths (Å), angles and torsion angles (°) of 4 in 3d/4.

Zr2 C35A	2.473(5)	Zr2 N3A	2.384(3)
Zr2 C35B	2.044(11)	Zr2 N4B	2.527(8)
Zr2 C36A	2.174(4)	Zr3 N3B	2.521(7)
Zr2 C36B	2.548(13)	Zr3 N4A	2.394(3)
Zr3 C35A	2.166(4)	C35A N3A	1.182(5)
Zr3 C35B	2.552(13)	C36A N4A	1.176(5)
Zr3 C36A	2.496(5)	C35B N3B	1.198(13)
Zr3 C36B	2.045(11)	C36B N4B	1.192(13)

Comparison of structural features with DFT BP86/TZVP/Lanl2DZ optimised structure.

Zr2 C35A	2.473(5)	Zr2 N3A	2.384(3)
DFT	2.482	DFT	2.356
Zr2 C36A	2.174(4)	Zr3 N4A	2.394(3)
DFT	2.230	DFT	2.358
Zr3 C35A	2.166(4)	C35A N3A	1.182(5)
DFT	2.227	DFT	1.208
Zr3 C36A	2.496(5)	C36A N4A	1.176(5)
DFT	2.488	DFT	1.208
Zr2-Zr3	3.550		
DFT	3.647		

2.4. Compound 3e



Figure S27. Numbering scheme of 3e. H atoms are omitted for clarity. Lower occupancy sites are depicted with white coloured bonds.

Table S7. Selected bond	lengths (Å), angles ar	nd torsion angles (°) of 3e .
-------------------------	------------------------	--------------------------------------

C1–Zr1	2.2318(13)	N1–Zr1–C1	32.97(4)
N1–Zr1	2.2351(11)	N1–Zr1–C15	83.51(4)
C15–Zr1	2.3198(13)	N2–C15–Zr1	178.91(12)
C1-N1	1.2676(17)	C2-C1-N1-C11	-2.2(3)
C1–C2	1.5157(18)		
C2–C3	1.5149(19)		
C11-N1	1.4886(17)		
C15–N2	1.1452(18)		

3. Details of NMR spectroscopy

3.1. ¹H and ¹³C NMR spectra of 2



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3.2. ¹H and ¹³C NMR spectra of 3a



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 δ (ppm)

Figure S31. $^{13}\text{C}\{^{1}\text{H}\}$ NMR spectrum of 3a (25 °C, [D₆]benzene, 75.47 MHz).

3.3. ¹H and ¹³C NMR spectra of 3b



o (ppm) **Figure S33.**¹³C{¹H} NMR spectrum of **3b** (25 °C, [D₆]benzene, 100.61 MHz). The signals of compound **4** were not labeled.

3.4. ¹H and ¹³C NMR spectra of 3d



Figure S35. ¹³C{¹H} NMR spectrum of 3d (25 °C, [D₆]benzene, 75.47 MHz) The signals undoubtedly assigned to compound 4 were not labeled.

3.5. ¹H and ¹³C NMR spectra of 3e



Figure S37. ¹³C{¹H} NMR spectrum of **3e** (25 °C, [D₆]benzene, 100.61 MHz).

4. Details of vibrational spectroscopy

4.1. Assignment of the most important vibrations

In this chapter the experimental IR and Raman spectra (black) with their respective calculated uncorrected vibration spectra (red) are presented. For complex **2** we calculated the vibrational spectrum with two different methods and compared the calculated and experimental spectra. From this comparison the frequency analysis with BP86/LANL2DZ/TZVP level of theory turned out to be more accurate besides a shorter time required for calculation (compared to M062x/def2tzvp). This level of theory was used for all further calculations and interpretation of vibrational spectroscopy.

Compound	C≡N	C≡N	RCH ₂ - C1=N - <i>t</i> Bu	RCH ₂ - C1=N - <i>t</i> Bu	
Compound	vib. calc.	vib. exp.	vib. calc.	vib. exp.	
За	2131 cm ⁻¹	2119 cm ⁻¹	1635 cm ⁻¹	1620 cm ⁻¹	
3b	2131 cm ⁻¹	[c]	1638 cm ⁻¹	1623 cm ⁻¹	
Зc	2131 cm ⁻¹	-	1632 cm ⁻¹	-	
3d	2132 cm ⁻¹	2118 cm ⁻¹	1631 cm ⁻¹	1618 cm ⁻¹	
Зе	2131 cm ⁻¹	2121 cm ⁻¹	1635 cm ⁻¹	1625 cm ⁻¹	
4	1889 cm ^{-1 [a]}	1892 cm ⁻¹	-	-	
	1843 cm ^{-1 [b]}				
4b ^[d]	1834 cm ^{-1 [a]}				
	1779 cm ^{-1 [b]}				

Table S8. Assignment of the most important vibrations of compound 3a, 3b, 3d, 3e and 4.

[a] in-phase vibration mode, [b] out-of phase vibration mode, [c] Unfortunately, no satisfactory Raman spectrum could be recorded from this compound, [d] **4b** shows the same structure as **4**, with N and C atoms of the cyanide units exchanged.

4.2. Experimental and calculated vibrational spectra



Figure S38. Experimental (ATR, red) and calculated IR spectra (BP86, black) of 2.



Figure S39. Experimental (ATR, red) and calculated IR spectra (M062x, black) of 2.





Figure S41. Experimental IR-ATR spectrum of **3b** co-crystallised with **4** (red), calculated (BP86) spectrum of **3b** (blue) and calculated (BP86) spectrum of complex **4** (black).



Wavenumber (cm-1)

Figure S42. Experimental IR-ATR spectrum of 3d co-crystallised with 4 (red), calculated (BP86) spectrum of 3d (blue) and calculated (BP86) spectrum of complex 4 (black).



Figure S43. Experimental IR-ATR spectrum of 3e co-crystallised with 4 (red), calculated (BP86) spectrum of 3e (blue) and calculated (BP86) spectrum of complex 4 (black).



Figure S44. Experimental (red) and calculated (BP86, black) Raman spectra of 3a.



Figure S45. Experimental Raman spectrum of 3d co-crystallised with 4 (red), calculated (BP86) spectrum of 3d (blue) and calculated (BP86) spectrum of complex 4 (black).



Figure S46. Experimental (red) and calculated (BP86, black) Raman spectra of 3e.

5. Computational details

All calculations were carried out with the Gaussian 09 package of molecular orbital programs.⁷ For the whole investigations we used real-size molecules and performed our calculations with the pure density functional method BP86⁸ in combination with the basis set combination TZVP(C,H,N,Si)⁹/LANL 2DZ(Zr)¹⁰ based on our good experience with this approach. Therefore, if not further mentioned the energies and discussed results were obtained with this procedure. Vibrational frequencies were also computed, to include zero-point vibrational energies in thermodynamic parameters and to characterise all structures as minima on the potential energy surface. In addition, we used these results to assign the experimental IR and RAMAN spectra and to superimpose the experimental and calculated vibration spectra (see above). NBO analyses were performed using NBO 6.0.¹¹ All optimised structures are provided in xyz format in a separate file.

5.1. Thermochemistry

For basic thermochemistry, molecular structures were optimised using the pure density functional (DF) BP86 in combination with the LANL2DZ basis set and corresponding ECP at Zr and the TZVP basis set on all other atoms (notation BP86/LANL2DZ/TZVP). All optimised structures were confirmed as minima by frequency analyses.





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5.2. Bond dissociation energies (BDE) for isocyanides and their complexes 2

In order to gain a better understanding of the experimentally observed fundamentally different reactivities of the two isocyanides *t*-BuNC and XyNC we calculated the bond dissoziation energies (BDE) on the UBP86/TZVP level of theory as well as the BDEs for the investigated zirconocene complexes (UBP86/LANL2DZ/TZVP).

	BDE		BDE	
Products	Δ_{R} H [kJ/mol]	Δ_{R} G [kJ/mol]	Δ_{R} H [kcal/mol]	Δ_{R} G [kcal/mol]
t-Bu radical + cyanide radical	378.5	323.9	90.5	77.4
Xyl radical + cyanide radical	460.0	405.0	109.9	96.8
EBTHIZrCNbtmsa rad + tBu rad	84.7	25.1	20.2	6.0
EBTHIZrCNbtmsa rad + Xyl rad	163.5	98.1	39.1	23.4
Cp2ZrCNbtmsa rad + tBu rad	103.6	44.8	24.8	10.7

Table S 9. Summary of the calculated hemolytic bond splitting (BDE).

Compound	Nimag	HF	ZPE [kcal/mol]	H _{tot} [a.u.]	G _{tot} [a.u.]
hydrogen	0	-1.1775859	6.17472	-1.164441	-1.179255
CN anion	0	-92.8866719	2.94384	-92.878675	-92.901033
isobutene	0	-157.2718059	65.53193	-157.160979	-157.194157
t-butyl cation	0	-157.5940012	70.81439	-157.473667	-157.511479
Xylene cation	0	-310.0034049	85.21022	-309.857646	-309.901972
CN radical	0	-92.7480952	2.98949	-92.740026	-92.763026
t-butyl radical	0	-157.8414821	70.84747	-157.7212	-157.757013
Xylene radical	0	-310.2856691	86.45389	-310.138611	-310.182273
Me3SiCCSiMe3	0	-894.8660333	141.899520	-894.620897	-894.684702
t-butane	0	-158.5009759	79.974950	-158.366730	-158.400241
t-butylisocyanide	0	-250.7395886	78.850460	-250.605387	-250.643397
t-butylnitrile	0	-250.7721707	79.166870	-250.637567	-250.675432
toluene	0	-271.6438151	77.660310	-271.512732	-271.550467
benzyl radical	0	-270.9928333	69.63896	-270.875004	-270.911681
o-xylene	0	-310.9708986	94.564230	-310.811409	-310.851957
m-xylene	0	-310.9713097	94.242310	-310.811858	-310.855321
p-xylene	0	-310.9712048	94.284260	-310.811790	-310.853425
mesitylene	0	-350.2987628	110.870810	-350.110938	-350.159092
xyleneisonitrile	0	-403.2132988	93.236590	-403.053842	-403.099553
ebthiZr(Me3SiCCSiMe3)	0	-1718.393524	379.834590	-1717.749584	-1717.855751
ebthiZr(Me3SiCCSiMe3)CNtBu	0	-1969.167459	459.923480	-1968.387060	-1968.512619
ebthiZr(Me3SiCCSiMe3)CNXy	0	-2121.640285	474.357300	-2120.834486	-2120.965664
ebthiZr(benzyl)CN	0	-1187.459398	313.714290	-1186.929945	-1187.018225
ebthiZr(XylCNTol)CN	0	-1590.719423	410.441110	-1590.025871	-1590.134878
ebthiZr(tBuCNTol)CN	0	-1438.247649	396.313210	-1437.579303	-1437.683571
ebthiZr(tBuCNoXy)CN	0	-1477.573297	413.509180	-1476.876196	-1476.980127
ebthiZr(tBuCNmXy)CN	0	-1477.575332	412.788050	-1476.878764	-1476.987701
ebthiZr(tBuCNpXy)CN	0	-1477.575768	413.235460	-1476.878767	-1476.985083
ebthiZr(tBuCNMes)CN	0	-1516.903159	429.545640	-1516.178078	-1516.291168
EBTHIZRCNtBu3btmsa	0	-2470.695039	622.88381	-2469.639775	-2469.796317
EBTHIZRCNXy3btmsa	0	-2928.124449	665.54562	-2926.993502	-2927.168559
(EBTHIZrCN)2	0	-1832.908684	487.05594	-1832.089082	-1832.201947
(EBTHIZrNC)2	0	-1832.880935	486.48154	-1832.062016	-1832.175195
EBTHIZrCNbtmsa anion	0	-1811.362728	383.6003	-1810.710042	-1810.821558
EBTHIZrCNbtmsa radical	0	-1811.288608	384.96606	-1810.6336	-1810.746027
Cp2ZrCNbtmsa anion	0	-1421.729132	248.14603	-1421.30097	-1421.395467
Cp2ZrCNbtmsa radical	0	-1421.651611	249.19044	-1421.22148	-1421.318705
Cp2ZrCNtBubtmsa	0	-1579.537404	323.88877	-1578.982147	-1579.092784
Me2SiCp2ZrTMSCCTMSCNtBu	0	-1947.744539	356.77025	-1947.131869	-1947.252995

Table S10. Summary of thermodynamic parameters.

5.3. Bond Analysis

Analysis of the Natural Localised Molecular Orbitals (NLMO) of iminoacycl complex 3a

GaussView5.0 Software^[12] was used for NLMO representations. To gain a better understanding of the bonding situation of these complexes we first performed a single point calculation for **3a** with the experimentally determined molecular structure, followed by the same NBO/NLMO analysis based on optimised molecular structure (BP86/TZVP/LANL2DZ). Both values are reported in the table below, their values as well as representations differ only slightly from each other (< 0.5 %) therefore we abstained from a redundant plot.

 Table S11. Representation of the Natural Localized Molecular Orbitals (NLMO) of iminoacycl complex 3a and selected values from the calculations (only values with a contribution larger than 1% are given).

NLMO 40: LP(1) N3, iso 0.04	NLMO 43: LP(1) N25, iso 0.04
optimised structure	optimised structure
40. (2.00000) 82.3843% LP (1) N 3	43. (2.00000) 97.7175% LP (1) N 25
2.241% C 1 s(3.14%)p30.34(95.24%)d 0.52(1.62%)	1.026% C 9 s(27.37%)p 2.65(72.63%)d 0.00(0.00%)
82.454% N 3 s(20.29%)p 3.93(79.69%)d 0.00(0.03%)	97.718% N 25 s(49.59%)p 1.01(50.32%)d 0.00(0.08%)
11.185% Zr 4 s(7.83%)p 0.02(0.14%)d11.75(92.03%)	
single point calculation	single point calculation
42. (2.00000) 82.7050% LP (1) N 74	43. (2.00000) 97.7452% LP (1) N 75
2.050% C 1 s(3.79%)p24.96(94.53%)d 0.45(1.69%)	1.115% C 29 s(28.30%)p 2.53(71.70%)d 0.00(0.00%)
82.790% N 74 s(21.48%)p 3.65(78.49%)d 0.00(0.03%)	97.745% N 75 s(46.75%)p 1.14(53.15%)d 0.00(0.10%)
11.604% Zr 76 s(7.72%)p 0.01(0.11%)d11.95(92.17%)	
NLMO 45: C1-C2 B(1), iso 0.04	NLMO 46: C1-N3 B(1), iso 0.04

optimised structure	optimised structure
45. (2.00000) 98.2043% BD (1) C 1- C 2	46. (2.00000) 98.3352% BD (1) C 1- N 3
46.037% C 1 s(38.81%)p 1.58(61.14%)d 0.00(0.06%) 52.216% C 2 s(25.96%)p 2.85(73.97%)d 0.00(0.07%)	37.136% C 1 s(30.53%)p 2.27(69.37%)d 0.00(0.09%) 61.291% N 3 s(44.48%)p 1.25(55.39%)d 0.00(0.13%)
	single point calculation
	45. (2.00000) 98.2129% BD (1) C 1- N 74
	37.098% C 1 s(29.98%)p 2.33(69.92%)d 0.00(0.10%)
	61.216% N 74 s(44.08%)p 1.27(55.78%)d 0.00(0.14%)
	1.061% Zr 76 s(4.97%)p 0.56(2.81%)d18.55(92.22%)
NLMO 47: C1-N3 B(2), iso 0.04	NLMO 48:C1-Zr4, iso 0.04
optimised structure	optimised structure
47. (2.00000) 95.4966% BD (2) C 1- N 3	48. (2.00000) 94.3701% BD (1) C 1-Zr 4
32.606% C 1 s(0.02%)p99.99(99.76%)d 9.15(0.22%)	69.103% C 1 s(30.07%)p 2.32(69.91%)d 0.00(0.01%)
2.897% N 3 s(0.02%)p99.99(99.89%)a 4.18(0.09%) 2.760% Zr 4 s(0.01%)p17.04(0.17%)d99.99(99.82%)	1.22U% N 3 st 21.U4%)p 3.65(/6./2%)d U.11(2.25%) 25.378% Zr 4 st 3.54%)p 0.02(0.06%)d27.24(96.40%)
	1.626% C 8 s(28.82%)p 2.47(71.14%)d 0.00(0.04%)

single point calculation	single point calculation
46. (2.00000) 95.4387% BD (2) C 1- N 74	47. (2.00000) 94.5692% BD (1) C 1-Zr 76
32.550% C 1 s(0.35%)p99.99(99.43%)d 0.64(0.22%)	69.713% C 1 s(31.17%)p 2.21(68.81%)d 0.00(0.02%)
62.924% N 74 s(0.29%)p99.99(99.62%)d 0.32(0.09%)	1.627% C 16 s(28.20%)p 2.55(71.77%)d 0.00(0.04%)
2.822% Zr 76 s(0.17%)p 1.52(0.26%)d99.99(99.56%)	1.208% N 74 s(19.84%)p 3.92(77.76%)d 0.12(2.39%)
	25.012% Zr 76 s(3.98%)p 0.02(0.06%)d24.09(95.95%)
NLMO 52: N3-C8, iso 0.04	NLMO 53: Zr4-C9, iso 0.04
optimised structure	optimised structure
52. (2.00000) 98.6610% BD (1) N 3- C 8	53. (2.00000) 98.8061% BD (1)Zr 4- C 9
60.050% N 3 s(33.00%)p 2.03(66.95%)d 0.00(0.05%)	22.718% Zr 4 s(13.27%)p 0.01(0.13%)d 6.53(86.60%)
38.637% C 8 s(22.07%)p 3.53(77.87%)d 0.00(0.07%)	76.177% C 9 s(59.01%)p 0.69(40.99%)d 0.00(0.00%)
	single point calculation
	81. (2.00000) 98.7066% BD (1) C 29-Zr 76
	75.772% C 29 s(57.71%)p 0.73(42.29%)d 0.00(0.00%)
	23.047% Zr 76 s(14.54%)p 0.01(0.12%)d 5.87(85.33%)
NLMO 59: C9-N25 B1, iso 0.04	NLMO 60: C9-N25 B2, iso 0.04

optimised structure	optimised structure
59. (2.00000) 99.7251% BD (1) C 9- N 25	60. (2.00000) 98.8582% BD (2) C 9- N 25
38.295% C 9 s(40.06%)p 1.49(59.84%)d 0.00(0.10%)	41.907% C 9 s(0.00%)p 1.00(99.85%)d 0.00(0.15%)
61.432% N 25 s(50.50%)p 0.97(49.16%)d 0.01(0.35%)	56.953% N 25 s(0.00%)p 1.00(99.77%)d 0.00(0.23%)
single point calculation	single point calculation
78. (2.00000) 99.7553% BD (1) C 29- N 75	79. (2.00000) 98.9699% BD (2) C 29- N 75
38.230% C 29 s(40.37%)p 1.47(59.53%)d 0.00(0.10%)	42.029% C 29 s(0.00%)p 1.00(99.84%)d 0.00(0.16%)
61.529% N 75 s(53.28%)p 0.87(46.34%)d 0.01(0.38%)	56.943% N 75 s(0.01%)p 1.00(99.74%)d 0.00(0.25%)
NLMO 61: C9-N25 B3, iso 0.04	
Antimized structure	
optimised structure	
61. (2.00000) 98.6785% BD (3) C 9- N 25	
41.774% C 9 s(0.02%)p99.99(99.83%)d 9.38(0.15%)	
56.905% N 25 s(0.05%)p99.99(99.72%)d 4.31(0.23%)	
single point calculation	
80. (2.00000) 98.8367% BD (3) C 29- N 75	
42.054% C 29 s(0.01%)p 1.00(99.83%)d 0.00(0.16%)	
56.784% N 75 s(0.02%)p99.99(99.72%)d11.61(0.25%)	

Table S12. Representation of the Natural Localized Molecular	Orbitals (NLMO) of complex 4.				
NLMO 57: LP(1) Zr77, iso 0.04 side view	NLMO 57: LP(1) Zr77, iso 0.04 top view				
Selection of NBO Analysis	Selection of NLMO Analysis				
57. (0.72626) LP (1)Zr 77 s(0.66%)p 0.02(0.01%)d99 99(57. (2.00000) 27.6655% LP (1)Zr 77				
99 33%) List of NAO coefficients	30.188% Zr 77 s(0.36%)p 0.05(0.02%)d99.99(99.63%)				
	30.128% Zr 78 s(0.37%)p 0.05(0.02%)d99.99(99.62%) 10.929% C 91 s(4.23%)p22.62(95.61%)d 0.04(0.16%) 5.595% N 92 s(1.94%)p50.52(98.03%)d 0.01(0.03%) 10.738% C 93 s(4.31%)p22.17(95.53%)d 0.04(0.16%)				
0.0038 0.0000 -0.0087 -0.0004 0.0000					
0.0003 0.0012 -0.1230 0.0031 0.0071					
-0.0049 -0.0701 -0.0249 0.9546 (see below) 0.0492 -0.2306 0.0758	5.463% N 94 s(1.95%)p50.32(98.02%)d 0.01(0.03%)				
NLMO 58: LP(1) N92, iso 0.04	NLMO 59: LP(1) N94, iso 0.04				
NLMO 152: Zr77-C93 BD, iso 0.04	NLMO 153: Zr78-C91 BD, iso 0.04				

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NATURAL POPULATIONS: Natural atomic orbital occupancies

NAC) Atom	No	lang	Туре	e(AO)	Occu	pancy	Energy
925	Zr 77	S	Cor(4s)	1.984	169	-1.8052	0
926	Zr 77	S	Val(5s)	0.200	28	0.05792	2
927	Zr 77	s	Ryd(6s)	0.002	210	13.6575	51
928	Zr 77	рх	Cor	(4p)	1.99	342	-1.088	75
929	Zr 77	рх	Ryd	(5p)	0.00)183	1.760	10
930	Zr 77	рх	Ryd	(6p)	0.00	0088	0.866	46
931	Zr 77	ру	Cor	(4p)	1.99	397	-1.088	94
932	Zr 77	ру	Ryd	(5p)	0.00)229	1.316	34
933	Zr 77	ру	Ryd	(6p)	0.00	0097	0.333	54
934	Zr 77	pz	Cor	(4p)	1.99	602	-1.100	77
935	Zr 77	pz	Ryd	(5p)	0.00)148	1.169	24
936	Zr 77	pz	Ryd	(6p)	0.00	0084	0.266	88
937	Zr 77	dxy	Val	(4d)	0.50	0621	-0.052	14
938	Zr 77	dxy	Ryd	d(5d)	0.0	1380	0.386	53
939	Zr 77	dxz	Val	(4d)	0.44	108	-0.082	82
940	Zr 77	dxz	Ryc	d(5d)	0.0	1452	0.472	56
941	Zr 77	dyz	Val	(4d)	0.48	3026	-0.043	88
942	Zr 77	dyz	Ryc	d(5d)	0.0	1083	0.422	.93
943	Zr 77	dx2	y2 V	al(4d) 0.	73203	-0.03	644
944	Zr 77	dx2	y2 R	yd(50	d) 0.	01768	0.43	3923
945	Zr 77	dz2	Val	(4d)	0.52	L219	-0.085	04
946	Zr 77	dz2	Ryo	d(5d)	0.0	2068	0.505	511

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5.4. Biradical character of complex 4

In case of compound **4**, we carried out CAS(2,2) as well as CAS(4,4) calculations. As the latter gives no better results than the CAS(2,2) calculation, only the results from this calculation (Basis set: def2svp¹³) are discussed here. The calculations show that the contributions to the multi-determinant wave function are the two determinants placing two electrons either in the formal HOMO (ϕ_1) or LUMO (ϕ_2 , $\beta = 13$ %).



Figure S47. Schematic depiction of the active orbitals of the CAS(2,2) calculation. The orbital localisation scheme indicates that the radical of each zirconium is partly delocalised over the ZrCN unit.

ϕ_1 HOMO side view	ϕ_1 HOMO top view
ϕ_2 LUMO side view	ϕ_2 LUMO top view

Table S13. Surface Plot of the active orbitals of the CAS(2,2) calculation. H-atoms are omitted for clarity, surfaces were generated with Avogadro and rendered with POV-Ray.^[14]

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